Reassessment of the formation volume of vacancies in gold

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Possible causes of disagreement between various values of vacancy-formation volumes in gold are discussed, with special emphasis on quenching experiments. The effect of pressure on vacancy loss during quenches as a function of quench rate is calculated for single vacancies migrating to several geometries of sinks. Experiments are performed on gold specimens both in high-pressure argon and in helium gas above the liquid in a cryostat. The results are in good agreement. A formation volume is derived from the pressure measurements. The relationship between present and previous formation-volume values and the temperature scale used is discussed. The remaining uncertainties are outlined.

I. INTRODUCTION

In recent years there have been many attempts to determine experimentally the lattice relaxation around a vacancy in gold. At least three methods have been used. In one, the effect of pressure on vacancy concentration (as determined by quenched-in electrical resistance) is interpreted thermodynamically as the single-vacancy formation volume ΔV_f. In another, the change in x-ray lattice parameter or specimen length as vacancies anneal from the lattice is used to determine the lattice relaxation. In a third, the effect of pressure on the thermal emf of vacancies is used to derive a ΔV_f.

Two recent articles[1,2] have pointed out inconsistencies in results obtained by the various methods in general and have questioned the quenching method in particular. The theoretical and experimental backgrounds of the methods have been extensively reviewed[3,4,5] and will not be repeated here. We begin by outlining the relevant features of the three methods. Previous experimental results are tabulated, and difficulties with each method are outlined. Model calculations of the effect of pressure on vacancy loss during quenching as well as new experimental results are presented. The results are then discussed in terms of choosing an appropriate formation volume.

II. THE FORMATION VOLUME IN GOLD

A. Experimental methods—quenching

The quenching method[2,6-8] does not require a knowledge of the absolute vacancy concentration in order to determine the formation volume. It is sufficient to know the dependence of the relative equilibrium vacancy concentration on temperature and pressure.

Precise temperature determination is essential here because the effect of temperature on vacancy concentration is much greater than that of pressure (in terms of the ease with which these parameters can be changed experimentally). For example, for gold in the vicinity of 640 °C, a 6-kbar pressure change reduces the equilibrium vacancy concentration the same amount as a temperature decrease of only 30 °C or so. Errors of a few degrees in temperature can thus have a very large effect on the inferred value of ΔV_f.

B. Dimensional changes

On the other hand, a knowledge of the quench temperature is not even required in the length and lattice parameter methods.[9-11] One makes a precise measurement of the dimensional change and at the same time a measurement of the electrical resistivity change. To convert these values to a volume requires the knowledge of the specific resistivity of a vacancy, usually expressed as the resistivity per unit concentration of vacancies. Determination of the latter requires that the absolute vacancy concentration be known in a sample whose excess resistivity has also been determined. Whereas the dimensional measurements can be made quite accurately, determination of the absolute vacancy concentration is quite different.

C. Thermal emf of vacancies

In the experiment by Bourassa, Lazarus, and Blackburn[12] (subsequently referred to as BLB) a junction at nearly atmospheric pressure is maintained at the same temperature as one at elevated pressure. The pressure of the one junction is varied at constant temperature, and the difference in emf between the two junctions is measured differentially. Pressure changes not only the vacancy concentration but also the Fermi level (through lattice parameter changes), the electron-phonon interaction, and the phonon distribution. BLB attempted to subtract the latter effects by using the low-temperature results, where the

vacancy concentration is negligible, as a base. Uncertainties in subtracting the background are a source of error in this method. Although the pressure medium was argon, small amounts of helium were added for leak-detection purposes, so that variations in gas solubility with pressure could also introduce errors. In this experiment the pressure coefficient of resistance up to 1000 °C was also measured. Since the entire vessel was at the elevated temperature, atmospheric-pressure temperature measurements with a platinum resistance thermometer could be made with good accuracy.

III. PREVIOUS ANALYSES

A. Self-consistency

Ball[1] has recently questioned a self-consistent analysis[13] of vacancy parameters in gold because it used a specific resistivity of 1.5 $\mu\Omega$m/u.c. (where u.c. is unit concentration) without question. Ball argues that a value of 1.7 $\mu\Omega$m/u.c. is more consistent with the ΔV_f values determined by dimensional changes and Lengeler's[14] results. Ball's Fig. 7 summarizes the relationship between ΔV_f determined by length change[9,10] and by lattice parameter[11] versus specific resistivity. Lengeler's[14] specific-resistivity value is consistent with these, whereas the Emrick and McArdle[8] (referred to subsequently as EM) ΔV_f is not. Consistency would be most simply attained if ΔV_f were lower.

Ball concludes that the EM value is in error because of the relatively low quench rates and the extrapolation required and because their extrapolated zero-pressure excess resistivity is 25% less than Lengeler's value at the same quench temperature.

B. Other pressure measurements

In Table I we summarize previous determinations of ΔV_f by the methods so far described. In addition, pressure diffusion measurements also yield an activation volume for self-diffusion through the relation $\Delta V_{act} = \Delta V_f + \Delta V_m$. Emrick[15] has found ΔV_m to be 0.15 Ω.

As Charles *et al.*[2] pointed out, one must strike a balance in pressure-quenching experiments. The minimum quench temperature is limited by the smallest resistance increase which one can accurately measure. Higher quench temperatures result in greater vacancy losses during quench. These losses can be reduced by increasing the quenching rate. Helium gives the fastest quench but is soluble in the specimen, so it can lead to vacancy-impurity binding as well as to an extra contribution to the quenched-in resistance. Furthermore, cooling rates are pressure dependent, leading to pressure-dependent losses.

C. Quenching strategies

Heubener and Homan's[6] approach to the problem was to use various pressure gases (e.g., He, Ar, N) so that the cooling rate was the same at all of the pressures used. They assumed that at their relatively low (680 °C) quench temperature, losses during quench would be small and, because of the fixed quenching rate, independent of pressure. They did not consider the effects of the differences in the solubility of the various gases. In their experiment the specimen was removed from the pressure vessel after each quench and the resistance measured at liquid-nitrogen temperature.

Grimes[7] attempted to minimize vacancy loss by quenching from only 600 °C. His pressure vessel

TABLE I. Previous determinations of ΔV_f by the following methods: *P*, high-pressure quenching; X, x-ray lattice parameter change; *Q*, calorimetry (heat evolved on anneal/energy per vacancy); *PD*, high-pressure diffusions; *L*, length change; *S*, thermoelectric power. T_Q is the quench temperature; $\dot{T}_{max}$ is the maximum quenching rate in °C/sec.

ΔV_f (Ω) [a]	Method	T_Q	T_{meas}	Environ	$\dot{T}_{max}$	Reference
0.53 ± 0.04	*P*	680 °C	77 K	He, N, Ar	$>2\times10^4$	6
0.52 ± 0.07	*P*	600 °C	−38 °C	Ar	$(1-5)\times10^4$	7
0.65 ± 0.04	*P*	640, 720 °C	23 °C	Ar, Ar + 5%O_2	10^4	8
0.52	*P*	700, 850 °C	77 K	He	8.5×10^4	2
0.53 ± 0.03	*PD*		860–960 °C	Ar		32
0.54	*PD*		700–990 °C	Ar		33
0.44 ± 0.02	X	?	4.2 K	liq. He	10^4	11
0.45 ± 0.10	*L*		50–1050 °C	N_2		34
0.57 ± 0.05	*Q*	820–920 °C	45–60 °C	vacuum	10^4	35
0.62 ± 0.06	*S*		25–1000 °C	Ar		12

[a] $\Omega = 10.5$ cm^3/mole @ 600 °C was used.

had a cold finger so that resistance measurements could be made *in situ* at −38 °C.

In order to gain sensitivity, EM quenched from 720 °C as well as 640 °C. Cooling rates were varied from 200 °C/sec to $\approx 10^4$ °C/sec, the maximum permitted by the pressure gas (argon or argon +5% O_2), by an electronic controller, and the results were extrapolated to infinite rate. They were also the first to use the high-pressure, high-temperature resistivity data of BLB which show that the failure to make a correction results in temperatures over 8 °C too high at 6 kbar. (Bridgman's[16] low-temperature data implied a negligible correction.)

Charles *et al.*[2] found a large reduction in quenched-in resistance for quenches from 850 °C in helium when the specimen was held at the quench temperature for more than a few seconds. Argon and neon produced smaller effects and no effect was observed in 700 °C quenches for any of the gases. They took precautions to limit heating times to a few seconds even at the lower quench temperatures. (For low dislocation density specimens, this might not be long enough to reach the equilibrium vacancy concentration.) It is also possible that dissolved gases could affect the resistance of the wire, thereby altering the resistance versus temperature scale.

IV. EFFECT OF PRESSURE ON VACANCY LOSS DURING QUENCHING

A. Model

In order to determine how pressure would affect vacancy loss, we used the model of single vacancies migrating to a variety of fixed sinks as described earlier by Emrick.[17,18] The sinks are regular and random arrays of parallel dislocation lines and regular and random arrays of spherical surface sinks, all of which maintain the instantaneous equilibrium vacancy concentration. The spherical surface sinks approximate the well-known dislocation cell structure observed in many metals.

The parameters used here to approximate gold are $E_f = 0.94$ eV, $E_m = 0.90$ eV, and $\nu_0 \exp(\Delta S_f/k) = 3.0 \times 10^{13}$ sec^{-1}. These parameters were used in the original paper[17] to compare the model with results of Seidman and Balluffi[19] which were fitted to specimens with known dislocation densities. Changing E_f to 0.97 eV does not significantly alter the inferred dislocation densities. The effect of a pressure of 6 kbar was simulated by adding a term $p\Delta V = 0.042$ eV to E_f, and 0.01 and 0.02 eV to E_m. These correspond roughly to $\Delta V_f = 0.65\ \Omega$ and $\Delta V_m = 0.15$ and $0.3\ \Omega$.

B. Results

The results of these calculations are shown in Figs. 1 and 2. The formation volume is proportional to $\partial \ln(\Delta R/R_0)/\partial P$. Shown in the figure for a few quenching rates are

$$\ln[(\Delta R/R_0)_{p=0}/(\Delta R/R_0)_{p=6\ \text{kbar}}],$$

the pressure derivative to be used in Eq. (1). This value is 0.5338 for the equilibrium value, i.e., infinite quenching rate. It can be seen that for both models this term varies only slightly.

Thus, this model shows that as long as the quenching rates are the same for all pressures, the inferred formation volume is not affected significantly, unless the motional volume is large. It is also assumed that the sink efficiency is pressure independent. Since the motional volume for gold is small, this model shows that the strategy of Huebener and Homan[6] is appropriate, even when the loss is appreciable.

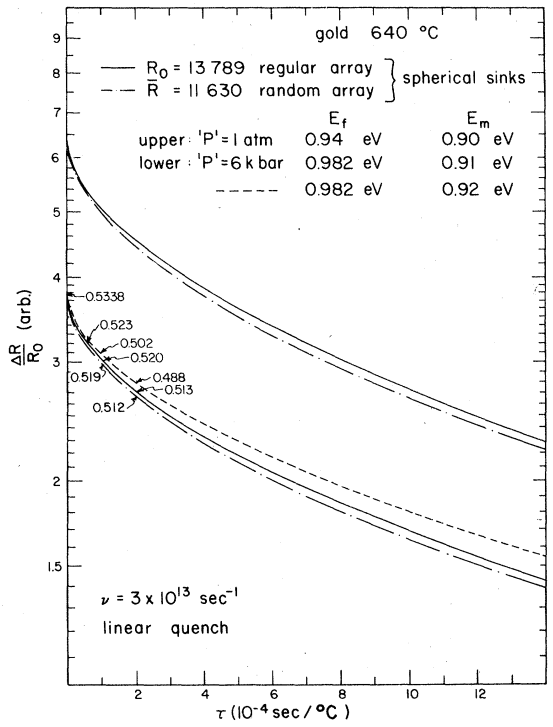

FIG. 1. Resistance remaining after quenches from 640 °C versus (constant) reciprocal quench rate τ for regular and random arrays of spherical sinks which maintain the instantaneous thermal-equilibrium vacancy concentration. The values marked on the lower (6 kbar) curves are the natural logarithms of the ratio of the value on the upper curve to the value on the lower for that particular quench rate. These indicate a decrease in inferred ΔV_f of only 4% at losses of 25% for the smaller ΔV_m.

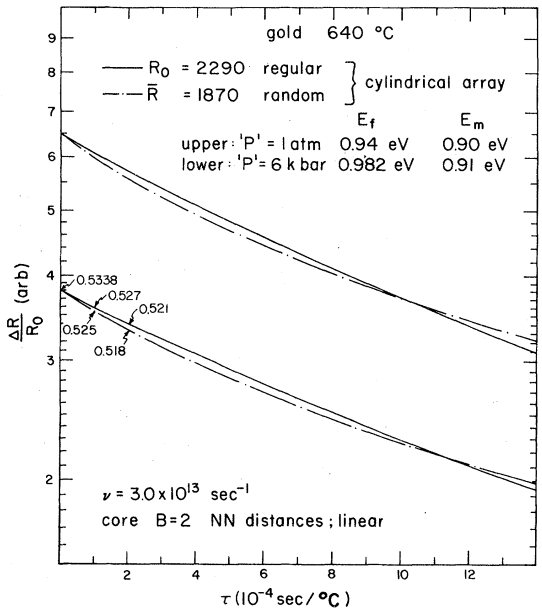

FIG. 2. Resistance remaining after quenches from 640 °C versus (constant) reciprocal quench rate τ for regular and random arrays of cylindrical sinks. Comments in Fig. 1 also apply.

V. EXTRAPOLATION METHODS

A. Loss estimates

The value of $\Delta R/R_0$ extrapolated to infinite quench rate by EM is 25% below the value observed by Lengeler. Before seeking an explanation for the difference, we should ask which value is more typical of previous results. Table II is a compilation of $\Delta R/R_0$ for a representative number of experiments conducted over the last two decades. The Lengeler values are always the highest, whereas those of EM are in the mid-to-low portion of the range.

Before any conclusions are drawn, some comments on Table II are in order, as some degree of uncertainty exists in its construction. First of all, many authors fail to quote their resistance versus temperature calibration. When mentioned, those of Northrup[20] and Meechan and Eggleston[21] were almost universal. The resistance quenched-in is frequently reported as $\Delta R/R_t$ (as in Table II). Usually t is given, but sometimes it is not. Since $R_{20\,°C}/R_{0\,°C} = 1.08$, such information is essential for accurate comparisons. Some authors prefer to quote the resistivity quenched-in, $\Delta\rho$. Rarely is the reference resistivity quoted, however, so there is an uncertainty in converting $\Delta\rho$ to $\Delta R/R_0$. When the author quotes no value, we have used Lengeler's value of $\rho_0 = 20.60$ nΩm. (In the EM paper, the gold captions are incorrect. The gold values are actually $\Delta R/R_0$.)

Measurements of quenched-in electrical resistance are typically made at 4.2 K, 77 K, or room temperature. Conte and Dural[22] have reported a fourfold increase in vacancy resistivity between 4.2 K and room temperature in the case of gold. The consistency of the results in Table II support Zetts's[23] conclusion that there are no such large deviations from Matthiessen's rule.

There is a significant difference between Lengeler's experimental procedure and all of the others quoted here. Lengeler's specimens are 1-mm diameter low-dislocation-density single crystals suspended in a furnace in a helium atmosphere. The specimen temperature before the quench is determined by a Chromel-Alumel thermocouple. In all of the other experiments, the specimen is a polycrystalline wire which is its own resistance thermometer. Dissolved gases and other impurities may result in temperature-scale shifts which could change the absolute amount quenched-in without significantly affecting the values of E_f. Lengeler's values are comparable with those of others when he uses polycrystalline specimens. However, his maximum cooling rate would have been lower by the inverse of the ratio of specimen diameters, so that his polycrystals would have lost a greater fraction of vacancies than the smaller diameter wires.

We can use our model to make some loss estimates to see if it is possible to explain the variations in $\Delta R/R_0$ on vacancy loss alone or if we have to enter the gray area of deciding that the model is inadequate or the temperature scales differ.

B. Reanalysis of earlier data

The extrapolation model used by EM assumed that $\ln\Delta R/R_0$ was proportional to the reciprocal quench rate τ. The model described earlier by Emrick[17,18] shows that for gold quenched under the conditions used by EM, their extrapolation would have been valid only for dislocation densities much lower than actually observed.

The regular and random spherical models give very nearly the same results and both usually give better results than either of the cylindrical models. Since the random spherical model requires roughly 15 times the amount of computer time, we have used only the regular-sphere model here. We chose to fit the 2-kbar data of EM's specimen Γ3 since it had very little scatter. The fitting parameters were the same as in Sec. IV A. The resulting intercept was $\Delta R/R_0 = 6.85\times10^{-4}$ and the sphere radius was 28 200 lattice spacings. The intercept by the EM extrapolation was 6.20×10^{-4} compared with the largest amount actually quenched-in of 6.12×10^{-4} at the maximum quench rate of 1.05

TABLE II. Values of $\Delta R/R_0$ ($\times 10^{-3}$) at various quench temperatures. Medium: W, water; He, N, Ar, pressurized helium, nitrogen, argon; He(T), helium gas at T; a, air.

720 °C	700 °C	640 °C	600 °C	ϕ (mm)	Medium	$\dot{T}_{max}$ ($\times 10^4$ °C/sec)	T_{meas} (K)	
2.6	2.1	0.97	0.58	0.41, 0.76	W	3	77	Bauerle and Koehler, Ref. 9
	2.28/2.08			0.41	W	10/4	4.2	Mori *et al.*, Ref. 10
2.8		0.98		0.10	He, N, Ar	2	77	Huebener and Homan, Ref. 6
2.67		0.93	0.58		synthesis of six experiments			Balluffi *et al.*, Ref. 36
			0.86	0.076	Ar	~2.5	235	Grimes, Ref. 7
2.51/(2.9)		0.95/(0.96)		0.41	W, a	~3/(∞)	4.2	Flynn *et al.*, Ref. 37
2.5/(2.9)		0.89/(1.04)		0.41, 0.25	W	?/(∞)	4.2	Bass, Ref. 38
	1.95 ± 0.1			0.2 (foil)	W	>5	4.2	Siegel, Ref. 39
2.5/2.9			0.68	0.4 (foil)	W	6/10	4.2	Kino and Koehler, Ref. 40
2.77	2.18	0.84	0.54	0.13	He(77 K)	0.72	4.2	Wang *et al.*, Ref. 41
2.02		0.78–0.81		0.10	Ar	1	295	Emrick and McArdle, Ref. 8
	2.80			0.07	He	7	77	Charles and Delaplace, Ref. 42
	2.80			0.07	He, Ar, N	8.5	77	Charles *et al.*, Ref. 2
3.3 ± 0.1	2.67	1.20		1.0	W	3(?)	4.2	Lengeler, Ref. 14
		0.84		0.1	Ar	1	295	Γ3 spherical fit[a]
2.15 ± 0.1		0.9 ± 0.05		0.076	Ar	1	295	Γ6 actual data[a]
2.5 – 2.95		1.0 ± 0.05		0.076	Ar	1	295	Γ6 extrapolated[a]
			0.4/0.55	0.076	He(20 K)	1	4.2	GC1 actual/extrap.[a]
			0.45/0.55	0.076	He(20 K)	1	4.2	GC2 actual/extrap.[a]

[a] Present results.

$\times 10^4$ °C/sec. The intercept converts to a $p=0$ value of 8.4×10^{-4} which is 30% lower than the Lengeler value, although it is within the range of other experimental values. The room-temperature resistance of Γ3 was not remeasured at the end of the experiment, so there exists a possibility that the temperature scale could have shifted.

VI. EXPERIMENTAL

A. Procedure

Rather than simply refitting the remainder of the EM data, we decided to perform new experiments with the same quenching and measuring apparatus on specimens in two different environments. The scatter of the data in a given experiment is generally much less than the scatter between experiments. However, most experiments are done in a single environment. By these experiments we can eliminate differences between measuring systems as a source of systematic error between high pressure and more conventional quenching environments.

In the first series we quenched 0.10-mm diam Cominco nominally 99.9999% pure gold wires from the same lot used by EM in atmospheric-pressure helium above liquid helium in a cryostat. The cryostat was designed[24] so that the specimen could be raised into a chamber for annealing in air or other gas, then lowered to just above the liquid-helium level for quenching, and finally lowered into liquid helium for resistance measurements at 4.2 K.

In the second series, 0.076-mm diam Cominco 99.999% pure gold wire was quenched in argon, in a pressure vessel at $\frac{1}{2}$, 2, and 4 kbar. (The specimen burned out before a 6-kbar series could be made.) The specimens remained in place in the pressure vessel throughout the entire series of measurements. Resistance measurements were made at room temperature with the specimen-dummy bridge arrangement first described by Kauffman.[25] The smaller wire diameter was chosen to permit greater maximum quenching rates.

In both cases the specimens were initially given a $\frac{1}{2}$-h anneal at 900 °C in air. This was followed by a 10-min anneal at 800 °C, 5 min at 500 °C and 15 min at 300 °C. The latter three steps were also used as cleansing anneals after each quench to return the specimen to a standard condition. They were made in atmospheric-pressure helium in the cryostat and in 1600 psi (gauge) argon in the pressure vessel. The specimen in the cryostat maintained a residual-resistance ratio of 2300 or better throughout the entire series. Residual-resistance–ratio measurements were not made on the specimens in the pressure vessel.

The temperature scale used was a least-squares quadratic fit to the combined data of Northrup[20] and of Meechan and Eggleston.[21] The data were fitted in the vicinity of room temperature and of 640 °C. If T is the Celsius temperature, $R(T)/R_{20\,°C} = \alpha + \beta T + \gamma T^2$. For room temperature we found $\alpha = 0.933\,022$, $\beta = 3.33056\times30^{-3}\,°C^{-1}$, and $\gamma = 9.169\times10^{-7}\,°C^{-2}$ and for high temperatures $\alpha = 1.084\,643$, $\beta = 2.74114\times10^{-3}\,°C^{-1}$, and $\gamma = 1.50741\times10^{-6}\,°C^{-2}$. The correction factors to the $R/R_{20\,°C}$ values according to the high-pressure data of BLB were as follows: $\frac{1}{2}$ kbar, 0.9979; 2 kbar, 0.9919; 4 kbar, 0.9837. The quench rates were held constant by an electronic feedback temperature controller.[26] Such constant cooling rates are assumed in the loss model used to fit the data. Resistance measurements were made with a Rubicon 6-dial potentiometer and related circuitry which has been described elsewhere.[27]

Temperature fluctuations when the specimen in the cryostat was at 640 °C necessitated that quenches be made from 600 °C. This unfortunate situation introduces an extra uncertainty in comparing the 640 °C results with those at 600 °C.

B. Results

The results for GC1 and GC2 are summarized in Fig. 3 and the pertinent parameters listed in

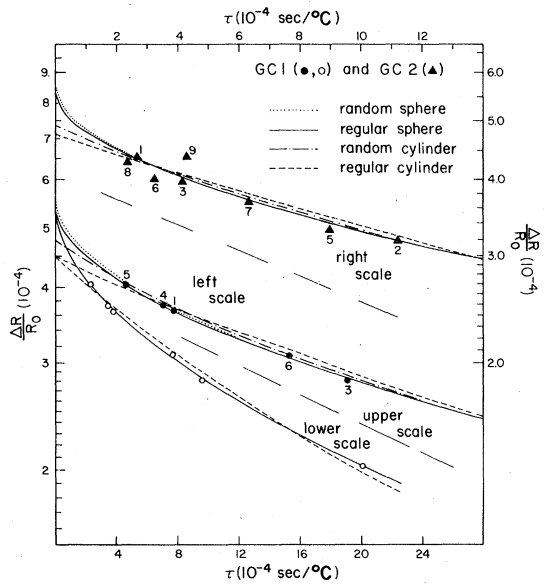

FIG. 3. Resistance quenched-in versus (constant) reciprocal quench rate τ for specimens GC1 and GC2 in helium in a cryostat. (Least-squares computer fits for various models are shown.) Note that upper curve, GC2 uses right-hand scale. The data of GC1 are replotted (lowest curve) to show the fit to the slowest quench. Numbers by the points refer to the sequence in which the points were taken.

TABLE III. Summary of experimental results. Seq. is the ordinal number of the quenches of a given specimen. Fit: *S* denotes regularly distributed spherical sinks; *C* denotes randomly distributed array of parallel dislocations; RS and RC denote random sphere and cylinder, respectively. $\Delta R/R_0|_\infty$ is the value extrapolated to infinite quenching rate. r is the sink radius in nearest-neighbor distances (2.88 Å for gold). Sink size is the sphere radius in microns or dislocation density in cm/cm^3. χ^2 denotes accuracy of fit. Significant only in comparing different models for the same set of data.

Spec. No.	T_Q (°C)	P (kbar)	Seq.	Fit	$\frac{\Delta R}{R_0\|_\infty}$ ($\times 10^{-3}$)	r (NN)	Sink size	χ^2
Γ3	640	2	(26–32)	*S*	0.685	28 200		21.6
Γ5	715	$\frac{1}{2}$	(1–12)	*S*	2.83	20 800	6.00 μm	19.8
				C	2.45	2 190	8.0×10^7	22.3
Γ6	720	$\frac{1}{2}$	(1–7)	*S*	2.95	19 100	5.50 μm	131
				C	2.51	2 070	9.0×10^7	163
	640	$\frac{1}{2}$	(8–15)	*S*	1.06	21 100	6.07 μm	166
				C	0.952	2 510	6.1×10^7	179
		$\frac{1}{2}$	(32–40)	*S*	1.00	33 500	9.65 μm	184
				C	0.930	3 430	3.3×10^7	189
		2	(41–47)	*S*	0.885	25 400	7.32 μm	24.1
				C	0.811	2 820	4.8×10^7	29.2
		4	(16–31)	*S*	0.700	25 500	7.34 μm	130
				C	0.638	2 890	4.6×10^7	126
GC1	600	0	(1–6)	*S*	0.547	12 800	3.69 μm	0.84
				RS	0.560	12 900	3.71 μm	0.68
				C	0.448	1 930	1.03×10^8	7.6
				RC	0.477	1 790	1.20×10^8	1.4
GC2	600	0	(1–9)	*S*	0.562	15 700	4.52 μm	72
				RS	0.568	16 200	4.67 μm	72
				C	0.436	2 210	7.9×10^7	73
				RC	0.493	2 140	8.4×10^7	70

Tables II and III. GC2 was the same wire as GC1 but was renumbered because after run 1 it was given a 1-h air anneal at 900 °C followed by the standard post-quench annealing sequence. This anneal reduced R_0 from 0.054 17 Ω to 0.536 68 Ω and increased the residual-resistivity ratio from 2300 to 3000. We note that the decrease in sink density from GC1 to GC2 is consistent with the extra annealing.

The intercepts for both specimens are the same for the spherical fits and nearly the same for the cylindrical. The slight differences in quench temperature would require a difference between intercepts of 9% for $E_f = 0.96$ eV. As has usually been the case where a clear test was possible,[18] the random-sphere model gives a better fit to the data of GC1 than any of the other models. The scatter of the data in GC2 is sufficiently large that all fits are equally good.

The maximum quenching rate in the atmospheric-pressure helium was less than 5000 °C/sec. For the spherical model, the implied vacancy loss at the fastest quench rate for GC1 is just over 25%, a considerable amount at this relatively low quench temperature. Nevertheless, even the cylindrical-model extrapolations are in the same range as other experimental values for quench rates more than an order of magnitude greater than the fastest used here. (Grimes's value[7] is much larger but his base resistance may have been measured at −38 °C instead of 0 °C. If it were, the discrepancy would be much less.)

For comparison with the more numerous 640 °C values, our 600 °C values were scaled by a formation energy of 0.96 ± 0.2 eV. These values, listed in Table II, span all of the other data except Lengeler's. The spherical fits are still 13% lower than Lengeler's value. Given that Lengeler's initial dislocation density was 4 to 5 orders of magnitude smaller and his quench rate nearly an order of magnitude greater, the agreement must be considered quite good.

The results for Γ5 and Γ6 are summarized in Fig. 4 and the pertinent parameters listed in Tables II and III. Because there is not much difference between the results for the random and regular sphere, and since the random cylinder model invariably gives a better fit than the regular, only those two models were used to fit the data. Specimen Γ5 burned out after the 720 °C, $\frac{1}{2}$-kbar

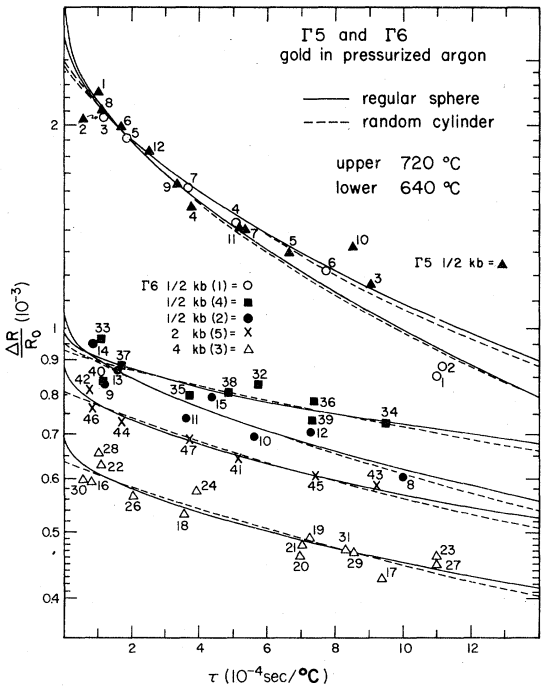

FIG. 4. Resistance quenched-in versus (constant) reciprocal quench rate τ for specimens Γ5 and Γ6 in high-pressure argon. Least-squares computer fits for two models are shown. Numbers by the points indicate sequence in which they were made. Those in parentheses are order in which isobars were made.

series. It has been included to show the consistency in results obtained from different specimens. The results for the 720 °C intercept of the spherical fit are larger than any values other than Lengeler's, which is 10% higher. Similar comments are true for the 640 °C results.

For Γ6 there is a general trend toward lower sink densities for isobars 1 through 4. A $p\Delta V_m$ term was not added to E_m in fitting the data so that the sink densities for the higher pressures should actually be lower. No explanation can be offered for the increase in sink density between isobar 4 ($\frac{1}{2}$ kbar) and isobar 5 (2 kbar). After an increase of 8 $\mu\Omega$ over the first 15 quenches, the base resistance fluctuated ± 1 $\mu\Omega$ for the remaining 32. The resistance quenched-in varied from 10 to 23 $\mu\Omega$ for the 640 °C quenches. It should be mentioned that even smaller baseline shifts occured for GC1 and GC2.

First, as a check of the consistency of the results, we can calculate a formation energy from the 720 °C and 640 °C, $\frac{1}{2}$-kbar intercepts. The random cylinder fit gives E_F = 0.96 eV and the spherical model 1.03 eV. A reduction of the temperature difference between the two isotherms by only 5 °C would reduce the 1.03 eV value to 0.98 eV. Given the small range of temperatures covered, the agreement shows that there are no major inconsistencies in the results.

Second, the intercepts for each type of fit are in excellent agreement with the same type of fit for the cryostat quenches, so that the above comments about the fits for GC1 and GC2 apply here also. The sink densities in these (GC1 and GC2) specimens are slightly larger than in the others, but differences in dislocation densities of a factor of 2 are not particularly great. We have observed earlier[17] that there is somewhat of a tendency for dislocation structures to be more stable the smaller the diameter of the wire. In any event, we find no evidence for errors connected with the different quenching environments. These results further support the adequacy of the spherical sink model in fitting the experimental loss data.

Finally, we are in a position to derive a formation volume from the 640 °C quenches of Γ6. Figure 5 is a semilogarithmic plot of the intercepts of the four isobars versus pressure. The formation volumes corresponding to the slopes of the lines are indicated on the figure. Both models give the same result, as does a linear extrapolation of the data of Fig. 4 after the manner of EM. A line with the slope of the EM value, 6.38 cm³/mole is included in Fig. 5 for comparison. Considering the scatter of the $\frac{1}{2}$-kbar data, the statistical uncertainty in the values is ±0.5 cm³/mole. However, given the rather small pressure range, this is probably an underestimate of the error. Nevertheless, the value is even larger than that of EM, so that doubling the error would barely reconcile the lower limit of this value with the upper limit of the EM value.

There is , however, an important difference between the other pressure ΔV_f values and the

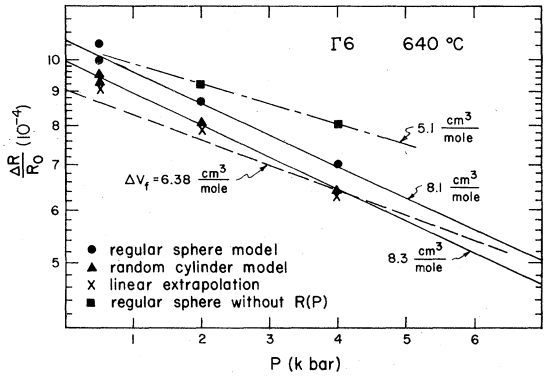

FIG. 5. Intercepts of the Γ5 curves of Fig. 4 for various models versus pressure. Values of formation volume corresponding to the slope of the line are indicated. The EM slope of 6.38 cm³/mole is included for comparison.

present and the EM values. The latter two used the high-pressure temperature correction factor of BLB.[12] These factors were listed earlier. This factor, when applied to our $R(640\,°C)/R(20\,°C)$ ratio of 3.462, gives a ratio of 3.407 at 4 kbar, the value we used in the experiment. A ratio of 3.407 on the $p=0$ temperature scale corresponds to $T=629.4\,°C$. For E_f in the range 0.94–0.97 eV, this would mean a vacancy concentration 15% less than the 640 °C value. Figure 5 also shows the regular-sphere data with the appropriate "correction" for each pressure to remove the effect of the pressure factor. The resulting formation volume is 5.1 cm^3/mole. Taking $\Omega = 10.45$ cm^3/mole, this is $\Delta V_f = 0.49\ \Omega$. A similar value (0.53 Ω) results when the EM data are treated in the same way. Thus all of the pressure-quenching data are in excellent agreement on ΔV_f when the same temperature scale is used.

VII. DISCUSSION AND CONCLUSIONS

It is tempting to accept the agreement between all ΔV_f measurements by rejecting the pressure correction of BLB. Until measurements to the contrary are made, however, we have no reason to do this. It is important to note that ΔV_m and the dimensional measurements are made in the vicinity of room temperature or below, whereas the quenching measurements are performed at 600–700 °C and the diffusion measurements around 900 °C.

Gilder and co-workers[28-30] have interpreted precision high-pressure diffusion experiments in Cd and Zn in terms of an activated vacancy with a thermal-expansion coefficient 15 times that of the lattice. They can explain the curvature of Arrhenius diffusion plots without invoking divacancies or other such mechanisms. Recently Ganne and von Stebut[31] have made measurements of the differential expansion between aluminum with and without a supersaturation of vacancies produced by radiation damage. They deduced a vacancy thermal-expansion coefficient 13 times that of the pure metal.

Since there are no comparable measurements to determine the thermal expansion of vacancies in gold, we unfortunately cannot draw any firm conclusions about the effect of thermal expansion on ΔV_f. At present, the consistency among the greatest number of results argues for ΔV_f in the vicinity of 0.52 Ω, especially at room temperature. Further work will be required to resolve the problems of defect properties at higher temperatures. It would be especially desirable to recheck the high-temperature pressure coefficient of resistance in gold to see if gas solubility gives misleading results. If these high-temperature data are confirmed, all the pressure-quench data will yield a vacancy-formation value close to 0.65 Ω.

The present results show that the model of single vacancies migrating to spherical surface sinks which maintain the instantaneous thermal-equilibrium vacancy concentration is adequate to extrapolate data at finite quenching rates to the equilibrium value. Measurements with the same apparatus made in atmospheric-pressure helium and high-pressure argon are internally consistent and also agree with water-quench results. Variations from one experiment to another are most likely due to systematic variations in temperature-scale determinations.

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[1] C. J. Ball, J. Nucl. Mater. 80, 371 (1979).
[2] M. Charles, C. Mairy, J. Hillairet, and V. Levy, J. Phys. F 6, 979 (1976).
[3] *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic, New York, 1965).
[4] *Vacancies and Interstitials in Metals*, edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970).
[5] Properties of Atomic Defects in Metals, edited by N. L. Peterson and R. W. Siegel [J. Nucl. Mater. 69 & 70 (1978)].
[6] R. P. Huebener and C. G. Homan, Phys. Rev. 129, 1162 (1963).
[7] H. H. Grimes, NASA Technical Report, Lewis Research Center, Cleveland, Ohio (1964).
[8] R. M. Emrick and P. B. McArdle, Phys. Rev. 188, 1156 (1969).
[9] J. E. Bauerle and J. S. Koehler, Phys. Rev. 107, 1493 (1957).
[10] T. Mori, M. Meshii, and J. W. Kauffman, J. Appl. Phys. 33, 2776 (1962).
[11] W. Hertz, W. Waidelich, and H. Peisl, Phys. Lett. 43A, 289 (1973).
[12] R. R. Bourassa, D. Lazarus, and D. Blackburn, Phys. Rev. 165, 853 (1968).
[13] R. P. Sahu, K. C. Jain, and R. W. Siegel, J. Nucl. Mater. 69 & 70, 264 (1978).
[14] B. Lengeler, Philos. Mag. 34, 259 (1976).
[15] R. M. Emrick, Phys. Rev. 122, 1720 (1961).
[16] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 573 (1917).
[17] R. M. Emrick, Philos. Mag. 33, 277 (1976).
[18] R. M. Emrick, Philos. Mag. A37, 355 (1978).

[19]D. N. Seidman and R. W. Balluffi, Phys. Rev. A 139, 1824 (1965).
[20]E. F. Northrup, J. Franklin Inst. 177, 287 (1914).
[21]C. J. Meechan and R. N. Eggleston, Acta Metall. 2, 680 (1954).
[22]R. R. Conte and J. Dural, Phys. Lett. 27A, 368 (1968).
[23]J. S. Zetts, Ph.D. thesis, Michigan State University, 1971 (unpublished).
[24]Similar to that described by D. Schumacher, J. Sci. Instrum. 44, 161 (1967).
[25]J. W. Kauffman and J. S. Koehler, Phys. Rev. 107, 1493 (1957).
[26]R. M. Emrick and D. E. McDonald, Rev. Sci. Instrum. 40, 82 (1969).
[27]R. M. Emrick, USAF OSR Technical Report No. 2581 (unpublished).
[28]H. M. Gilder and L. C. Chhabildas, Phys. Rev. Lett. 26, 1027 (1971).
[29]L. C. Chhabildas and H. M. Gilder, Phys. Rev. B 5, 2135 (1972).
[30]H. M. Gilder and D. Lazarus, Phys. Rev. B 11, 4916 (1975).
[31]J. P. Ganne and J. von Stebut, Phys. Rev. Lett. 43, 634 (1979).
[32]R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, Phys. Rev. 137A, 613 (1965).
[33]M. Beyeler and Y. Adda, J. Phys. (Paris) 29, 345 (1968).
[34]R. O. Simmons and R. W. Balluffi, Phys. Rev. 125, 862 (1962).
[35]W. De Sorbo, Phys. Rev. 117, 444 (1960).
[36]R. W. Balluffi, K. H. Lie, D. N. Seidman, and R. W. Siegel, in *Vacancies and Interstitials in Metals*, edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970), p. 138.
[37]C. P. Flynn, J. Bass, and D. Lazarus, Philos. Mag. 11, 521 (1965).
[38]J. Bass, Phys. Rev. 137, A765 (1965).
[39]R. W. Siegel, Philos. Mag. 13, 359 (1966).
[40]T. Kino and J. S. Koehler, Phys. Rev. 162, 632 (1967).
[41]C. G. Wang, D. N. Seidman, and R. W. Balluffi, Phys. Rev. 169, 553 (1968).
[42]M. Charles and J. Delaplace, Scripta Metall. 6, 1161 (1972).