

Measurement of the Equilibrium Concentration of Lattice Vacancies in Silver near the Melting Point*

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Relative changes in macroscopic length, $\Delta L/L$, and x-ray lattice parameter, $\Delta a/a$, of a 99.999% silver bar have been measured from 14 to 956°C, using a rigid parallel pair of filar micrometer microscopes and a rotating single-crystal x-ray method. The expansions agree within experimental precision (about $1:10^5$) at the lower temperatures. At the higher temperatures ($\Delta L/L - \Delta a/a$) progressively increases, showing that atomic sites are added, corresponding to the thermal generation of vacancy-type defects. The concentration of added sites, $\Delta N/N = 3(\Delta L/L - \Delta a/a)$, at the melting point (obtained by a 4° extrapolation) is $(1.7 \pm 0.5) \times 10^{-4}$. This value is only 1/5.5 of the corresponding value previously found for aluminum by the same technique. For reasonable values of the binding energies of vacancy aggregates, it is concluded that more than 90% of these extra sites are present as single vacancies. For an entropy of formation of $(1.5 \pm 0.5)k$ an energy of formation for monovacancies of 1.09 ± 0.10 ev is obtained. This formation energy is slightly larger than half the activation energy for self-diffusion, as similar measurements have shown for aluminum, and as quenching experiments have indicated for gold.

I. INTRODUCTION

THE writers have recently identified the thermally generated lattice defects in aluminum at elevated temperatures as vacancy type and measured their equilibrium concentration by means of precision x-ray lattice parameter and macroscopic length measurements.¹ In this method measurements of the length expansion $\Delta L/L$ and the lattice parameter expansion $\Delta a/a$ are taken as a specimen is reversibly heated and cooled between a low temperature where the defect concentration is negligible and an elevated temperature near its melting point. When vacancy-type defects are thermally generated, extra substitutional atomic sites are added to the specimen and $\Delta L/L$ becomes larger than $\Delta a/a$ according to the simple relation¹⁻³

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

where $\Delta N/N$ is the fractional increase in the total number of substitutional sites.

This method of investigating point defects has the advantage that the measurements are made at temperature with the specimen in thermal equilibrium. Also, the concentration of additional defect sites is obtained absolutely, since Eq. (1) is independent of the detailed nature of the defects and of secondary changes of the host lattice. For example, the degree of lattice relaxation around the defects, the degree of association between defects and changes in the elastic properties of the lattice do not affect the result. The measurements can be arranged so that the constant macroscopic and microscopic defects present in actual metal crystals have a negligible influence. Further, the nature of the pre-

dominant point defect is indicated directly by the sign of $\Delta N/N$ (positive for vacancies; negative for interstitials).

One difficulty associated with such an experiment is the extreme accuracy required in the measurement of $\Delta L/L$ and $\Delta a/a$. In many crystals the atomic fraction of equilibrium point defects is in the range 10^{-3} to 10^{-4} near the melting point. The best precision that can be obtained in the measurement of $\Delta a/a$ by present x-ray measurements is about $1:10^5$. Therefore, $\Delta N/N$ can only be measured in these crystals with reasonable accuracy at temperatures fairly close to the melting point. Also, the technique measures only the net fractional change in the number of sites. For example, if equal numbers of vacancies and interstitials are present no effect occurs. However, this problem is presumably of small importance during equilibrium in the close-packed metal crystals under investigation since interstitial concentrations are almost certainly negligible compared to vacancy concentrations.⁴

In the case of aluminum the fraction of additional sites at the melting point was large enough to be measured with fair precision by this method and $\Delta N/N$ was given by $[\exp(2.4)][\exp(-0.76 \text{ ev}/kT)]$.¹ This result corresponds to a concentration at the melting point (660°C) of $(9.4 \pm 0.4) \times 10^{-4}$. For reasonable values of the binding energies of various vacancy aggregates, it was concluded¹ that these extra sites were present mainly as single vacancies. Additional measurements of the high temperature electrical resistivity of aluminum⁵ also allowed a comparison of the high temperature equilibrium concentrations with extrapolated concentrations obtained from lower temperature data derived from resistivity measurements on quenched samples.⁶ Agreement within a factor of about two was obtained.

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¹ R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 52 (1960).

² R. O. Simmons and R. W. Balluffi, J. Appl. Phys. **30**, 1249 (1959).

³ R. W. Balluffi and R. O. Simmons (to be published).

⁴ See review papers in: *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955); *Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958).

⁵ R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 62 (1960).

⁶ W. DeSorbo and D. Turnbull, Acta Met. **7**, 83 (1959).

In the present paper we present similar measurements of the extra number of thermally generated defect sites in high-purity silver at elevated temperatures. Silver was chosen since it is a monovalent metal of intrinsic interest with a close-packed cubic structure. Also, precise measurements of the activation energy for self-diffusion are available,⁷ and electrical resistivity measurements on the imperfections in quenched wires are in progress.⁸

II. EXPERIMENTAL METHOD

The same experimental apparatus used in the previous aluminum work¹ was used again with only minor modifications. A description of the equipment, together with a discussion of possible sources of error, is given in reference 1.

A. Specimen and Furnace

Simultaneous measurements of $\Delta L/L$ and $\Delta a/a$ at a given temperature are made on a bar-shaped specimen 50 cm long by 1.27 cm by 1.27 cm. The specimen is supported in a smooth horizontal well machined along the axis of a cylindrical graphite core which in turn is located along the axis of a long resistance-heated furnace. A gas-tight jacket allows various atmospheres to be used. Suitable ports are available allowing access for the $\Delta L/L$ and $\Delta a/a$ measurements. Temperatures along the specimen are measured with a butt-welded Pt versus Pt-10% Rh thermocouple⁹ which can be moved along the specimen in order to ascertain the temperature at any point along its length. Temperature variations along the specimen length and during the time of measurement may be maintained at less than $\pm 0.2^\circ\text{C}$. These arrangements essentially eliminate temperature measuring errors in the measurement of the difference ($\Delta L/L - \Delta a/a$).

The silver specimen was prepared from material of initial purity greater than 99.999%.¹⁰ Standard spectrographic and gas analyses of the as-received silver gave the following results: Sb, Tl, Mn, Pb, Sn, Cr, Ni, Bi, Al, Ca, In, Cd, and Zn were not detected; 0.0001 weight percent Fe present; less than 0.0001 weight percent Mg, Si, and Cu present; less than 0.0003 weight percent oxygen present. The bar-shaped specimen was prepared by a melting and controlled solidification procedure, where the silver was melted and cast horizontally in a spectrographically pure graphite mold by rapid cooling from one end in a prepurified nitrogen atmosphere.¹¹

⁷ C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1182 (1956).

⁸ M. Doyama, research in progress, University of Illinois.

⁹ The thermocouple material was obtained from S. Cohn and Company, Mt. Vernon, New York, and the temperatures reported here are believed accurate to -0.0 , $+1^\circ\text{C}$. This accuracy is of importance only in determining the absolute accuracy of the total expansions; it is unimportant in determining the difference, ($\Delta L/L - \Delta a/a$).

¹⁰ Supplied by American Smelting and Refining Company.

¹¹ Properties of the gas as listed by the supplier are: purity greater than 99.996%, oxygen 0.0008%, dew point -68°C . Pub-

The cooling rate was adjusted so that a polycrystal with an average grain size of about 1.5 cm was obtained. The cooling from one end ensured directional solidification and a sound nonporous structure. One large grain near the center of the bar had an orientation suitable for the $\Delta a/a$ measurement and was located at the x-ray port in the final furnace assembly. The prepurified nitrogen atmosphere was used during all measurements.

B. Length Change Measurement

$\Delta L/L$ was measured very directly by observing changes in the spacing of reference marks (Tukon micro-hardness indentations) located near the specimen ends. No detectable changes in the detailed appearance of these indentations were observed in the course of the experiment. Measurements were made with the two rigidly mounted parallel filar micrometer microscopes. One modification of the previously described measuring technique¹ was made in order to guard against error due to possible changes in the assumed fixed microscope spacing. An Invar bar standard at constant temperature was constructed and located so that its constant length could be measured periodically during the experiment. These measurements indicated that errors arising from this source were negligible.

C. Lattice Expansion Measurement

The back-reflection rotating single-crystal technique¹ for making precision high-angle measurements of the change in lattice parameter was again used without major modification. The (422) Bragg reflection was used with $\text{NiK}_{\alpha 1}$ radiation ($\lambda = 1.65784 \text{ \AA}$). The (422) direction was inclined 5° from the specimen surface normal. θ varied between about $83^\circ 45'$ and $76^\circ 35'$ during the experiment. The Laue-Bragg intensity falls off more rapidly near the melting point in silver than in aluminum and, therefore, the specimen-to-film distance was set at about 50 cm (approximately para-focusing geometry) in order to maintain the exposure time less than 15 minutes near 960°C .

In the present method an accepted value of the lattice parameter a_r at some reference temperature (say 20°C) is used to compute a reference Bragg angle θ_r , using the accepted x-ray wavelength. Angular changes $\Delta\theta$ at other temperatures T are then obtained from the measured shifts of position of the Laue-Bragg line on the flat film Δx and the known geometry of the apparatus. Since $\theta(T) = \theta_r + \Delta\theta$, values of $a(T)$ and $\Delta a/a \equiv [a(T) - a_r]/a_r$ may then be calculated. Actually, there is some small uncertainty in the accepted value of a_r and in the geometrical conversion of Δx to $\Delta\theta$. The following criterion is therefore used in establishing the precise value of θ_r ,

lished values of the solubility of oxygen in silver indicate that the dissolved oxygen content would be negligible in an atmosphere of this partial pressure. Spectrographic and gas analyses of the sample material after melting indicated no detectable decrease in the 99.999% purity level.

for this apparatus: close agreement between the $\Delta a/a$ values and the measured $\Delta L/L$ values must be obtained over the entire temperature interval at lower temperatures where it is certain that the point defect concentrations must be negligible. The final selected value of a_r must, of course, agree with accepted values within the expected uncertainty of such published measurements. Also, the conversion of Δx to $\Delta \theta$ must agree within expected error with the best value obtained from the measured geometry of the apparatus. The absolute sensitivity of the method depends in part on the fact that the linear dispersion at the film, $\Delta x/(\Delta a/a)$, is approximately proportional to $\tan \theta$ (which changes rapidly at high angles) and in part on the fact that the thermal expansion coefficient is appreciably temperature dependent.

In the present case, the temperature interval chosen for fitting the $\Delta a/a$ and $\Delta L/L$ curves extended from 13 to 601°C, corresponding to a relative expansion of 12.59×10^{-3} . Two smooth curves were drawn through thirty-one $\Delta L/L$ points and forty-four $\Delta a/a$ points in this temperature range. The mean absolute deviation per point for each curve was less than 10×10^{-6} . After fitting, the two curves essentially coincided, and the mean deviation per point of all $\Delta L/L$ and $\Delta a/a$ points from a common best curve was 9×10^{-6} . The value of $a_r(20^\circ\text{C})$ producing this fit was 4.07765 kX, which is well within the range of reported values.¹² Other aspects of the agreement between $\Delta L/L$ and $\Delta a/a$ in silver are discussed elsewhere.³

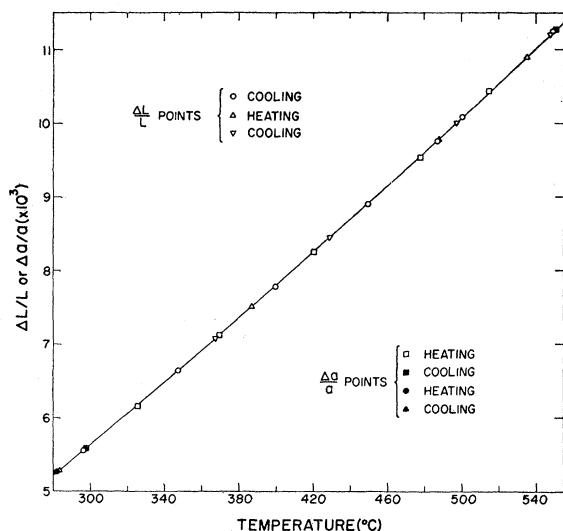


FIG. 1. Measured length expansion $\Delta L/L$ and lattice parameter expansion $\Delta a/a$ versus temperature in the interval 280–552°C. The x-ray and length expansions agree within experimental error. A number of $\Delta a/a$ data points are not shown since they essentially coincided with corresponding $\Delta L/L$ points and could not be clearly shown. The omitted points included: four \blacksquare points at 347.1, 399.4, 449.4 and 500.4°C; four \blacktriangle points at 368.2, 429.1, 497.8, and 549.1°C; two \bullet points at 386.6 and 535.0°C.

¹² W. B. Pearson, *Lattice Spacing and Structure of Metals and Alloys* (Pergamon Press, New York, 1958), p. 259.

III. EXPERIMENTAL RESULTS

Measurements of $\Delta L/L$ and $\Delta a/a$ were made in the temperature range 13–956°C. Seventy-two $\Delta a/a$ measurements were made during two heating runs and two cooling runs while fifty-seven $\Delta L/L$ measurements were made during the second heating run and the two cooling runs. The expansions were plotted versus temperature and best smooth curves were drawn through the data points. The mean absolute deviations of the experimental points from the smooth $\Delta L/L$ and $\Delta a/a$ curves were 7×10^{-6} and 10×10^{-6} , respectively, and the maximum deviations were 18×10^{-6} and 29×10^{-6} , respectively. No evidence was obtained of any systematic lack of reversibility during heating and cooling. As explained in the previous section, the curves coincided within experimental error in the temperature range 13 to 601°C where a total of seventy-five $\Delta L/L$ and $\Delta a/a$ points fell on a common curve with a mean deviation per point of 9×10^{-6} .

Expansion curves are shown in Figs. 1 and 2 for two selected temperature ranges. Figure 1 illustrates the close agreement of $\Delta L/L$ and $\Delta a/a$ in the lower temperature range. Figure 2 shows the divergence of these quantities at higher temperatures due to the thermal generation of vacancy type defects. The high temperature divergence appears quite reversible indicating that the creation and destruction of the point defects upon heating and cooling was isotropic as expected for a cubic metal.^{1–3}

The present thermal expansion values are compared

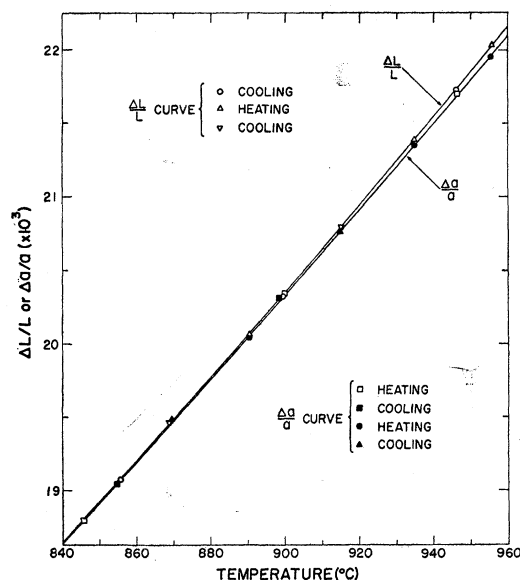


FIG. 2. Measured length expansion $\Delta L/L$ and lattice parameter expansion $\Delta a/a$ versus temperature in the interval 845–960°C. $\Delta L/L$ becomes larger than $\Delta a/a$ at the highest temperatures corresponding to the thermal generation of vacancies.

TABLE I. Macroscopic linear thermal expansion of silver.

T(°C)	$\Delta L/L(20^\circ\text{C}) \times 10^3$		
	Present work	a	b
50	0.57	...	0.59
100	1.54	1.58	1.57
150	2.54	...	2.57
200	3.55	3.61	3.57
250	4.58	...	4.59
300	5.64	5.66	5.62
350	6.71	...	6.66
400	7.81	7.85	7.73
450	8.93	...	8.81
500	10.08	10.05	9.91
550	11.25	...	11.04
600	12.44	...	12.19
650	13.67	...	13.37
700	14.93	...	14.58
750	16.23	...	15.82
800	17.55	...	17.09
850	18.93	...	18.39
900	20.36	...	19.73
950	21.86

^a See reference 13.^b See reference 14.

to those of other investigators¹³⁻¹⁸ in Tables I and II. All values have been referred to 20°C using the expansion data of Nix and MacNair¹⁹ near room temperature. The present $\Delta L/L$ measurements agree rather well with those of Scheel¹³ up to 500°C but are larger than those of Esser and Eusterbrock.¹⁴ The $\Delta a/a$ measurements are in excellent agreement with the widely accepted values of Hume-Rothery and Reynolds¹⁶ but in only fair agreement with references 15, 17, and 18. All of the previous x-ray measurements were made on powdered specimens.

The difference between $\Delta L/L$ and $\Delta a/a$ is of primary interest, and the best measurement of this quantity from Fig. 2 is 56×10^{-6} at 960°C. We estimate the possible error in this value to be about $\pm 17 \times 10^{-6}$ and, therefore,

$$(\Delta N/N)_{960^\circ\text{C}} = 3(\Delta L/L - \Delta a/a)_{960^\circ\text{C}} \\ = (1.7 \pm 0.5) \times 10^{-4}. \quad (2)$$

$\Delta N/N$ decreases rapidly with temperature; and since the probable measuring accuracy at 960°C was no better than about 30%, we have not attempted to derive values at lower temperatures.

¹³ K. Scheel, Z. Physik **5**, 167 (1921).¹⁴ H. Esser and H. Eusterbrock, Arch. Eisenhüttenw. **14**, 341 (1941).¹⁵ H. Esser, W. Eilender, and K. Bungardt, Arch. Eisenhüttenw. **12**, 157 (1938).¹⁶ W. Hume-Rothery and P. W. Reynolds, Proc. Roy. Soc. (London) **A167**, 25 (1938).¹⁷ E. A. Owen and E. W. Roberts, Phil. Mag. **27**, 294 (1939).¹⁸ J. Spreadborough and J. W. Christian, J. Sci. Instr. **36**, 116 (1959).¹⁹ F. C. Nix and D. MacNair, Phys. Rev. **61**, 74 (1942).

TABLE II. Lattice parameter thermal expansion of silver.

T(°C)	$\Delta a/a(20^\circ\text{C}) \times 10^3$				
	Present work	a	b	c	d
50	0.57
97	1.48	1.58	...
100	1.54	1.63±0.15
134	2.22	2.53
150	2.54
185	3.25	3.37	...
200	3.55	3.67±0.15
250	4.58
257	4.73	5.11
299	5.62	5.70	...
300	5.64	5.78±0.15
337.5	6.44	...	6.49
350	6.71
398	7.76	7.81	...
399	7.78	8.00
400	7.81	7.99±0.15
450	8.93
459	9.13	...	9.16
486	9.75	9.75	...
500	10.08	10.14±0.15
550	11.25
552	11.30	11.14
557	11.41	11.29	...
596	12.34	...	12.33
600	12.44	12.50±0.15
650	13.67
700	14.93	15.02±0.15
717	15.37	15.19
724	15.55	...	15.49
750	16.23
800	17.54	17.65±0.15
846	18.80	...	18.80	...	18.77
850	18.92
900	20.34	20.35±0.15
943	21.60	...	21.60
950	21.81

^a Values picked off smooth curve in reference 15.^b See reference 16.^c See reference 17.^d See reference 18.

IV. INTERPRETATION AND DISCUSSION

Our first objective is to deduce the concentrations of the various possible point defects which may be present from the measured value of $\Delta N/N$. All defects contribute to $\Delta N/N$; and, therefore,

$$\Delta N/N = (c_{v1} + 2c_{v2} + 3c_{v3} + \dots) - (c_{i1} + 2c_{i2} + \dots) \quad (3)$$

where c_{v1} , c_{v2} , and c_{v3} are the fractional concentrations of monovacancies, divacancies, and trivacancies; and c_{i1} and c_{i2} are the corresponding concentrations of interstitial-type defects. The positive sign of $\Delta N/N$ establishes the predominant defects as vacancy-type in agreement with previous expectation.⁴ If we neglect the interstitial concentrations²⁰ and also vacancy aggregates of size larger than three, the concentrations of the vacancy-type defects can be expressed in terms of their

²⁰ Recent measurements of energy release during thermal recovery of low-temperature deuteron-irradiation damage in copper foils [T. Nilan and A. Granato (to be published)] suggest that $(E_{v1} + E_{i1})$ is substantially larger than twice E_{v1} , as expected.

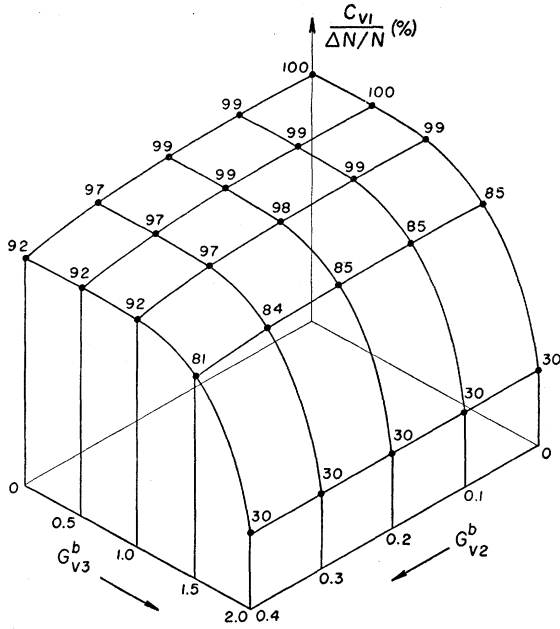


FIG. 3. Relative monovacancy abundance $c_{v1}/(\Delta N/N)$ as a function of divacancy and tetrahedral trivacancy binding energies (G_{v2}^b and G_{v3}^b) in silver at 960°C.

binding energies G_{vj}^b , and $\Delta N/N$ as follows:¹

$$\begin{aligned}
 24 \exp(G_{v3}^b/kT) c_{v1}^3 \\
 + 12 \exp(G_{v2}^b/kT) c_{v1}^2 + c_{v1} &= \Delta N/N \\
 c_{v2} &= 6c_{v1}^2 \exp(G_{v2}^b/kT) \\
 c_{v3} &= g_{v3} c_{v1}^3 \exp(G_{v3}^b/kT).
 \end{aligned} \quad (4)$$

In these relations divacancies are taken to be pairs of nearest neighbor vacancies. The configurational entropy factor g_{v3} in the trivacancy expression depends upon whether the trivacancy exists as a triangular group of nearest neighbor vacancies ($g_{v3}=8$) or as the configuration, recently proposed by Damask et al.²¹ of a quadrivacancy in a tetrahedral configuration with an interstitial in the center ($g_{v3}=2$). Unfortunately, there are no reliable values of the binding energies presently available. Most estimates of G_{v2}^b fall in the range $0.1 < G_{v2}^b < 0.4$ ev.²² However, no acceptable estimates of G_{v3}^b exist. Damask et al.²¹ have concluded on the basis of Morse potential calculations for copper that the tetrahedral trivacancy configuration is stable relative to the triangular one. These workers, however, calculate a tetrahedral trivacancy binding energy which is obviously much too high. This result is not too surprising, considering the approximate nature of the calculation.²³

²¹ A. C. Damask, G. J. Dienes, and V. G. Weizer, Phys. Rev. **113**, 781 (1959).

²² See reference 1 for further references and discussion.

²³ Lomer has recently evaluated and criticized various methods of calculating defect properties and concludes that Morse potential calculations may be dangerously inaccurate: W. M. Lomer, *Progress in Metal Physics* (Pergamon Press, New York, 1959), Vol. 8, p. 255.

If we accept the result that the tetrahedral trivacancy is the stable configuration in the noble metals, we may obtain a general picture of the situation by calculating defect concentrations from Eqs. (4) using different divacancy and trivacancy binding energies. Some results are shown in Fig. 3 where the monovacancy abundance at 960°C in silver is plotted as a function of the binding energies. More than 90% of the defect sites are present as monovacancies if $G_{v2}^b < 0.4$ ev and $G_{v3}^b < 1.1$ ev. Since the actual binding energies are probably in this range, we may conclude that the monovacancy is the predominant equilibrium defect and that its concentration at 960°C is $(1.6 \pm 0.6) \times 10^{-4}$. This value was arrived at by subtracting the estimated vacancy aggregate concentrations from the value of $\Delta N/N$ in Eq. (2). Since the relative abundances of the vacancy aggregates decrease with decreasing temperature,¹ the monovacancy should also be the dominant equilibrium point defect at all temperatures.

Our second objective is to obtain a reasonably accurate determination of the monovacancy formation energy E_{v1}^f . One may be made from the present data by assuming a value of the vibrational entropy of formation, S_{v1}^f , in the relation

$$c_{v1} = \exp(S_{v1}^f/k) \cdot \exp(-E_{v1}^f/kT). \quad (5)$$

As Feder and Nowick²⁴ have pointed out, the calculated value of E_{v1}^f is relatively insensitive to the choice of S_{v1}^f which in turn may be estimated within fairly narrow limits. For constant c_{v1} and T we have $\delta E_{v1}^f = T \delta S_{v1}^f$. For example, if the uncertainty in S_{v1}^f is $\pm 0.5k$, then at 960°C the uncertainty in E_{v1}^f is 0.11 ev. S_{v1}^f may be estimated by several means. Huntington et al.²⁵ have calculated $S_{v1}^f \simeq 1.5k$ for copper. Also, Bauerle and Koehler²⁶ have measured length contractions during the annealing out of quenched-in vacancies in gold. A value of $S_{v1}^f = 1.1$ is calculated from these data using a volume relaxation around a vacancy of 0.5 atomic volume.^{27,28} The value of S_{v1}^f measured directly by the writers¹ for aluminum was in the range 2.0 to 2.4k. In view of these results, we shall take $S_{v1}^f = (1.5 \pm 0.5)k$. Using this value and the monovacancy concentration at 960°C of 1.6 ± 0.6 , we obtain $E_{v1}^f = 1.09 \pm 0.1$ ev from Eq. (5).

It is of interest to compare the present results for silver with the previous aluminum measurements.¹ The concentration of defect sites at the melting point in aluminum is about 5.5 times that in silver. Equilibrium vacancy aggregates may therefore be somewhat more important in aluminum than in silver. Calculations were carried out using the same method already described for silver (where it is assumed that $g_{v3}=2$) in

²⁴ R. Feder and A. S. Nowick, Phys. Rev. **109**, 1959 (1958).

²⁵ H. B. Huntington, G. A. Shinn, and E. S. Wajda, Phys. Rev. **99**, 1085 (1955).

²⁶ J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

²⁷ L. Tewordt, Phys. Rev. **109**, 61 (1958).

²⁸ W. DeSorbo, Phys. Rev. **117**, 444 (1960).

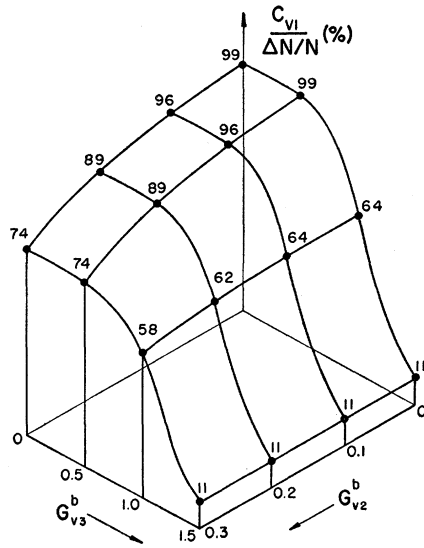


FIG. 4. Relative monovacancy abundance, $c_{v1}/(\Delta N/N)$, as a function of divacancy and tetrahedral trivacancy binding energies (G_{v2}^b and G_{v3}^b) in aluminum at 660°C. Data taken from reference 1.

order to make an effective comparison. The results are given in Fig. 4, and comparison with Fig. 3 shows the expected depression of equilibrium monovacancy concentration at similar binding energies. However, since the monovacancy formation energy is smaller in aluminum than in silver, it appears possible that the binding

energies may also be smaller. At the present time it seems reasonable to conclude that in silver the number of defect sites present as vacancy aggregates near the melting point is quite small ($<10\%$). In the case of aluminum the number may be somewhat larger but is probably still appreciably smaller than the number of monovacancies. Further aspects of this problem have been discussed previously.^{1,5}

It is also of interest to compare presently available monovacancy formation energies in close-packed metals with measured self-diffusion activation energies Q . A list of these energies from different sources^{1,6,7,24,26,28-41} is given in Table III. No values obtained from extrapolation techniques are quoted; such methods may be unreliable because the relative effect of vacancies on high-temperature properties is usually quite small.⁵ The values for Ag, Al, and Au are better established than the Pb, Pt, and Cu values. A number of quenching investigations on Pt have so far failed to converge on energies of formation and migration which add to a constant value Q . The largest such sum is still smaller than the single reported measurement of Q . Further, there is no agreement upon the magnitude of the increase in residual resistance for quenching from a given temperature; this implies different apparent entropies of formation in the different studies. The results in Table III indicate that for these crystals the monovacancy formation energy is generally just about one-half (or slightly larger) than the diffusion activation energy.

V. ACKNOWLEDGMENT

The writers wish to thank Mr. Robert D. Fouchaux for his assistance in the experimental part of this work.

TABLE III. Comparison of presently available vacancy formation and motion energies, E_{v1}^f and E_{v1}^m , and self-diffusion activation energies Q in face-centered cubic metals.

Metal	E_{v1}^f (ev)	E_{v1}^m (ev)	Method of measurement	Q (ev)	E_{v1}^f/Q
Ag	1.09 ^a	...	Present method	1.91 ^a	0.57
Al	0.75 ^b	0.65 ^c	Present method; quenching, resistivity	1.40 ^d	0.54
Au	0.98 ^{d,e}	0.82 ^d	Quenching, resistivity and stored energy	1.81 ^f	0.54
Pb	$\geq 0.53^f$...	Present method	1.05 ^g	≥ 0.50
Pt	1.2 ^g	1.1 ^g	Quenching, resistivity	2.96 ^h	0.44
	1.4 ^h	1.1 ^h	Quenching, resistivity		
	1.2 ⁱ	1.4 ⁱ	Quenching, resistivity		
	1.2 ^j	1.5 ^j	Quenching, resistivity		
	1.4 ^k	...	Quenching, field ion microscope		
Cu	1.0 ^l	...	Quenching, resistivity	2.04 ^m	0.50
	...	1.0 ^m	Ultrasonic experiment		

^a Present work.

^b See reference 1 & 6.

^c See reference 29.

^d See reference 26.

^e See reference 28.

^f See reference 24.

^g See reference 30.

^h See reference 31.

ⁱ See reference 32.

^j See reference 33.

^k See reference 34.

^l See reference 35.

^m See reference 36.

ⁿ See reference 7.

^o See reference 37.

^p See reference 38.

^q See reference 39.

^r See reference 40.

^s See reference 41.

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