

## Measurement of Equilibrium Concentrations of Vacancies in Copper\*

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The net added fraction of thermally-generated atomic sites,  $\Delta N/N$ , has been measured, during equilibrium heating to near the melting point, in a coarse-grained copper bar of 99.999% purity. The linear thermal expansion,  $\Delta L/L$ , and the x-ray lattice expansion,  $\Delta a/a$ , as measured simultaneously, agree within the measurement error of  $\pm 1 \times 10^{-6}$  throughout the temperature interval between 56 and 850°C. At 1000 and at 1075°C,  $\Delta N/N = 3(\Delta L/L - \Delta a/a)$  is  $(0.9 \pm 0.5) \times 10^{-4}$  and  $(1.9 \pm 0.5) \times 10^{-4}$ , respectively. Using expected limits for the binding energies of vacancy clusters, it is concluded that  $\Delta N/N$  consists almost entirely of monovacancies. An assumed value of  $(1.5 \pm 0.5)k$  for the formation entropy, combined with these concentrations, yields a monovacancy formation energy of  $(1.17 \pm 0.11)$  eV. The ratio of this formation energy to the activation energy for self-diffusion is therefore about 0.57, near the ratios found for the other noble metals. The results imply a monovacancy migration energy of  $(0.88 \pm 0.13)$  eV. The present results are compared with the results of a wide variety of other investigations of defects in copper which include: (1) theoretical calculations, (2) quenching and annealing, (3) thermal diffusion, (4) annealing after irradiation, and (5) annealing after cold work. In certain cases apparent disagreement is found. However, it is concluded that in no case is there a sufficiently firm body of experimental data available either to confirm or to contradict the present monovacancy data. The need for further definitive experiments in these areas is emphasized.

### I. INTRODUCTION

QUANTITATIVE information about vacancy defects in a number of pure face-centered cubic metals has now been obtained from: (1) direct measurements of defect concentrations under equilibrium conditions at elevated temperatures, and (2) experiments in which the defects are quenched in and studied at lower temperatures. Equilibrium-type experiments performed with aluminum,<sup>1</sup> silver,<sup>2</sup> and gold<sup>3</sup> have yielded the defect formation energies, and have shown unequivocally that vacant atomic sites are the predominant thermally generated defects in close-packed metals and that self-diffusion in these metals proceeds via a vacancy mechanism. Quenching experiments with the same metals<sup>4-8</sup> have determined the vacancy mobilities more precisely and have been useful in obtaining several other vacancy properties.

The results of equilibrium and of quenching experiments with aluminum, silver, and gold are in rather good agreement and promise to be of help in the interpretation of more complicated phenomena such as radiation damage<sup>9</sup> and cold work.<sup>10</sup> Theoretical

estimates of defect properties, primarily calculated for models of copper, have played an important role in possible interpretations of these phenomena. At present it appears, however, that only a few of the many possible point-defect mechanisms which may be of importance in thermal annealing have been positively identified. Before the present work was undertaken, neither direct equilibrium measurements nor unambiguous quenching experiments had yet been carried out with copper.

The present work on copper: (1) obtains the equilibrium defect concentrations; (2) provides a basis for estimating the formation energy  $E_{1v}^f$  of the monovacancy for comparison with theory; (3) provides a value for the monovacancy migration energy from the relation  $E_{1v}^m = Q - E_{1v}^f$ , where  $Q$  is the self-diffusion activation energy; (4) provides information useful in the atomic interpretation of the annealing of irradiated and of cold-worked copper; and (5) yields data useful for the eventual evaluation, both for monovacancies and for interstitial atoms, of such properties as the defect lattice dilatation, energy, and electrical resistivity.

In the present method, coordinated measurements of relative macroscopic expansion,  $\Delta L/L$ , and of x-ray lattice expansion,  $\Delta a/a$ , at elevated temperatures yield the net added concentrations of substitutional atomic sites,  $\Delta N/N$ , according to the relation

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

This result is independent of the state of aggregation of the thermally generated defects, and also of any detailed model of the lattice dilatation produced by them. Vacancy-type defects are undoubtedly the only point defects present in thermal equilibrium in significant concentrations, and, therefore,  $\Delta N/N$  consists of contri-

and *Recrystallization of Metals*, edited by L. Himmel [Interscience Publishers, Inc., New York, 1963 (to be published)].

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

<sup>2</sup> R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).

<sup>3</sup> R. O. Simmons and R. W. Balluffi, Phys. Rev. **125**, 862 (1962).

<sup>4</sup> F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 570 (1957);

C. Panseri and T. Federighi, Phil. Mag. **3**, 1223 (1958); W. DeSorbo and D. Turnbull, Acta Met. **7**, 83 (1959); Phys. Rev. **115**, 560 (1959).

<sup>5</sup> M. Doyama and J. S. Koehler, Phys. Rev. **119**, 939 (1960); Phys. Rev. **127**, 21 (1962).

<sup>6</sup> L. J. Cuddy and E. S. Machlin, Phil. Mag. **7**, 745 (1962).

<sup>7</sup> F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 370 (1957).

<sup>8</sup> J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957); J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

<sup>9</sup> R. O. Simmons, J. S. Koehler, and R. W. Balluffi, in *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962), Vol. 1, p. 155.

<sup>10</sup> R. W. Balluffi, J. S. Koehler, and R. O. Simmons, in *Recovery*

butions from monovacancies, divacancies, trivacancies, etc. From a knowledge of the magnitude of  $\Delta N/N$  and from estimates of the binding energies of the various vacancy aggregates it is possible to estimate the relative concentrations of the various vacancy aggregates in the equilibrium defect population. In all of the close-packed metals studied to date,<sup>1-3</sup> we have concluded that the monovacancy is the predominant equilibrium defect present. The present method, therefore, investigates the monovacancy almost exclusively.

## II. EXPERIMENTAL METHOD

Accurate determination of the small quantity  $(\Delta L/L - \Delta a/a) \lesssim 10^{-4}$  at different temperatures requires that temperature uncertainties in  $\Delta L/L$  and  $\Delta a/a$  be minimized. Our method<sup>1-3</sup> uses a single massive specimen for simultaneous measurements of  $\Delta L/L$  and  $\Delta a/a$  which are, therefore, referred to a common temperature scale.

### A. Specimen and Furnace

The starting material was American Smelting and Refining Company grade A-58 copper, of nominal 99.999+ % purity. According to the supplier, this shows no impurities by spectrographic analysis with the following known limits of sensitivity (in parts per million by weight): Si < 0.1, Cr < 0.5, Fe < 0.7, Ni < 1, As < 2, Ag < 0.3, Sn < 1, Sb < 1, Te < 2, Pb < 1, and Bi < 0.1. In addition, by chemical analysis it contains S < 1, Se < 1 and by gas analysis 0 < 2 parts per million. Reanalysis after specimen preparation, using methods identical to those originally employed by the supplier, showed no detectable change in the spectrographic and chemical analyses and a moderate increase in the oxygen content to seven parts per million.

Four bar-shaped specimens of dimensions  $1.27 \times 1.27 \times 60$  cm were prepared by melting and controlled directional solidification in order to produce a mean grain size larger than 1 cm. An enclosed spectrographically pure graphite crucible was used in a prepurified nitrogen atmosphere. The bar selected for use was trimmed to 53-cm length having a large crystal of correct orientation at the center. The reference marks required at the ends of the specimen for length measurement were pyramidal Tukon indentations of base width  $30\mu$  produced after the specimen ends were smoothed by mechanical polishing.

The general arrangement of the 3-m-long gas-tight Inconel furnace was the same as for the previous measurements.<sup>1-3</sup> A gas atmosphere was required to suppress evaporation of the specimen during extended periods of time at high temperature. In order to prevent oxidation and surface discoloration of the copper specimen, an atmosphere of composition 2/3 prepurified nitrogen and 1/3 dry carbon monoxide was employed. The effectiveness of this atmosphere in producing a low oxygen concentration in the specimen during the

experiment was demonstrated in a special test (described in detail in Sec. III B) where an oxygen concentration  $\lesssim 2$  parts per million by weight was found after equilibration at 1040°C. We note that this concentration is appreciably lower than the concentration of seven parts per million measured directly after specimen preparation by melting in prepurified nitrogen (see above).

After completion of the length and lattice-expansion measurements, the furnace was raised to the melting temperature of copper in order to calibrate the Pt vs Pt 10% Rh thermocouple in the arrangement identical to that used in the experiment. The thermocouple calibration was found to lie within the  $\pm 0.1\%$  limits predicted by the supplier. Temperatures reported here conform to a calibration taking 1083.0°C as the copper melting point.

### B. Length-Expansion Measurement

The specimen gauge length was measured with an accuracy of 1:50 000 using a Wild Heerbrugg cathetometer. Changes in length during the experiment were then determined with higher accuracy by means of a rigidly mounted parallel pair of  $50\times$  filar micrometer microscopes equipped with relay lenses and internal-vertical illumination. The length-change measurements reported here were made after the specimen was annealed on its final, flat, horizontal, graphite support for 3 h above 1000°C.

A very slight greenish-yellow film of unknown origin was observed on only one extreme end of the sample during the first-cooling and second-heating runs during which measurements were made. This superficial film appeared to melt at a temperature of about 1076°C at the end of the second-heating run. The underlying metal appeared to be unaffected, however. The film was sufficiently thin so that the essential geometry of the  $30\mu$  wide reference indentations was not altered by this phenomenon, and no difficulty was experienced in using the reference marks for measurements during the second-cooling run.

### C. Lattice-Expansion Measurement

For copper, the present rotating-crystal method employed Ni  $K\alpha_1$  radiation ( $\lambda = 1.65784 \text{ \AA}$ ) and (311) planes, which gave Bragg angles between  $87\frac{1}{3}^\circ$  and  $78^\circ$  for temperatures between 60 and 1075°C. The angle between the diffracting planes and the specimen surface was less than  $4^\circ$ . Changes in Bragg angle,  $\theta$ , were measured on film with an average accuracy 10 to 15 sec of arc. As described in previous papers<sup>1-3</sup> a value for the Bragg angle itself is chosen at a reference temperature of 20°C, in order to produce agreement between computed  $\Delta a/a$  values and measured  $\Delta L/L$  values for the same specimen over a broad temperature range in which vacancy concentrations are negligible. For copper the range adopted was below 650°C. The

value chosen for  $\theta$  (20°C) corresponds to  $a(20^\circ\text{C}) = 3.61473 \text{ \AA}$ , a value in excellent agreement with the determination of Frohnmeyer and Glocker<sup>11</sup> yielding  $a(20^\circ\text{C}) = 3.61472 \text{ \AA}$ . The value  $a(20^\circ\text{C}) = 3.6147 \text{ \AA}$  is given as the "best value" in Pearson's compilation.<sup>12</sup>

### III. EXPERIMENTAL RESULTS

#### A. Expansion Measurements

Ninety-nine measurements of  $\Delta a/a$  were made in the temperature interval 56–1075°C during two heating runs and two cooling runs. Eighty-five measurements of  $\Delta L/L$  were made in the interval 14–1076°C during the second-heating run and two cooling runs. The relative expansions were plotted vs temperature on a 2.3×5.4 m graph, and best smooth curves were drawn through the data points. The mean absolute deviations of the experimental points from the smooth curves were  $7 \times 10^{-6}$  for the  $\Delta a/a$  data and  $8 \times 10^{-6}$  for the  $\Delta L/L$  data. The maximum deviations were  $32 \times 10^{-6}$  and  $35 \times 10^{-6}$ , respectively. As explained in Sec. II C, the curves coincided within experimental error in the temperature interval 56–650°C, in which a total of ninety-four  $\Delta a/a$  and  $\Delta L/L$  data points showed a mean absolute deviation of  $7 \times 10^{-6}$  from a common curve.

No evidence was obtained of any systematic lack of reversibility in  $\Delta L/L$  during heating or cooling, once the specimen shape was stabilized during the first heating as described in Sec. II B. The measurements of  $\Delta a/a$  were also reversible through the two heating and

TABLE I. Macroscopic linear thermal expansion of copper.

T (°C)	Present work	10 <sup>6</sup> [ $\Delta L/L(20^\circ\text{C})$ ]	
		(a)	(b)
50	0.50	0.51	0.50
100	1.35	1.37	1.36
150	2.22	2.21	2.24
200	3.11	3.10	3.12
250	4.02	3.97	4.03
300	4.95	4.93	4.95
350	5.90	5.89	5.88
400	6.86	6.84	6.84
450	7.84	7.83	7.81
500	8.84	8.82	8.80
550	9.87	...	9.81
600	10.91	...	10.85
650	11.98	...	11.90
700	13.07	...	12.98
750	14.19	...	14.08
800	15.34	...	15.20
850	16.51	...	16.34
900	17.70	...	17.51
950	18.93	...	18.71
1000	20.21	...	19.93
1050	21.54	...	...
1083	(22.44)	...	...

<sup>a</sup> See reference 13.  
<sup>b</sup> See reference 14.

<sup>11</sup> G. Frohnmeyer and R. Glocker, *Acta. Cryst.* **6**, 19 (1953).

<sup>12</sup> W. B. Pearson, *Lattice Spacing and Structure of Metals and Alloys* (Pergamon Press, New York, 1958).

TABLE II. Lattice-parameter thermal expansion of copper.

T (°C)	Present work	10 <sup>6</sup> [ $\Delta a/a(20^\circ\text{C})$ ]	
		(a)	(b)
50	0.50	...	...
100	1.35	...	1.6
150	2.22	...	...
200	3.11	...	3.4
250	4.02	...	...
300	4.95	5.11	5.4
350	5.90	...	...
400	6.86	...	7.4
450	7.84	...	...
500	8.84	8.95	9.5
550	9.87	...	...
600	10.91	...	11.7
650	11.98	...	...
671	12.44	12.50	...
700	13.07	...	13.8
750	14.19	...	...
771	14.67	14.67	...
800	15.33	...	16.0
850	16.50	...	...
871	16.99	16.85	...
900	17.69	...	18.5
950	18.91	...	...
1000	20.18	...	21.0
1050	21.49	...	...
1083	(22.37)	...	...

<sup>a</sup> See reference 15.  
<sup>b</sup> See reference 16.

two cooling runs. In particular, at the end of the experiment the lattice parameter returned to its original value within the experimental error of  $\pm 7 \times 10^{-6}$ , indicating that negligible cumulative surface contamination of the specimen had occurred. We consider the problem of possible surface contamination and the significance of the experimentally observed reversibility in detail in Sec. III B.

Our smoothed thermal expansion values for copper are given in Tables I and II, where they are compared to some results of previous investigators.<sup>13–17</sup> All of the relative expansions have been referred to 20°C using a value of  $16.6 \times 10^{-6}$  per degree C for the linear expansion coefficient near room temperature. The excellent agreement between the various macroscopic expansion measurements below 500°C is somewhat fortuitous. More typical of precision thermal expansion data are the 1% agreement above 500°C between the present  $\Delta L/L$  measurements and the results of Esser and Eusterbrock<sup>14</sup> and the 2% agreement over the entire range between the present  $\Delta a/a$  values and the results of Hume-Rothery and Andrews.<sup>15</sup>

<sup>13</sup> F. C. Nix and D. MacNair, *Phys. Rev.* **60**, 597 (1941). References to earlier work are given in this paper.

<sup>14</sup> H. Esser and H. Eusterbrock, *Arch. Eisenhüttenw.* **14**, 341 (1941).

<sup>15</sup> W. Hume-Rothery and K. W. Andrews, *J. Inst. Metals* **68**, 19 (1942).

<sup>16</sup> H. Esser, W. Eilender, and K. Bungardt, *Arch. Eisenhüttenw.* **12**, 157 (1938).

<sup>17</sup> Other references to subsequent unpublished measurements on copper are given in *Handbook of Thermophysical Properties of Solid Materials*, edited by A. Goldsmith, T. E. Waterman, and H. J. Hirschhorn (The MacMillan Company, New York, 1961).

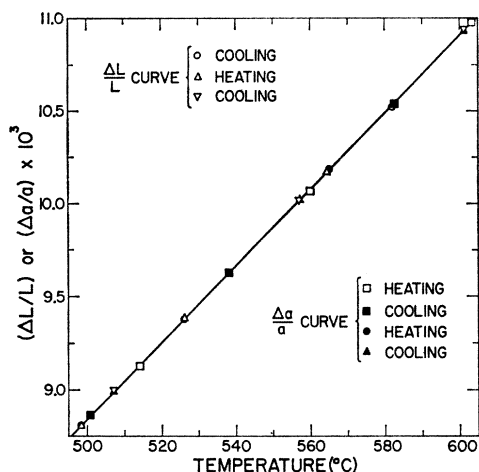


FIG. 1. Measured length expansion  $\Delta L/L$  and lattice parameter expansion  $\Delta a/a$  vs temperature in the interval 498–604°C. The x-ray and length expansions agree within experimental error. Two  $\Delta L/L$  data points, at 500.6 and at 538.6°C, cannot be clearly shown because they essentially coincide with corresponding  $\Delta a/a$  data points.

Comparison of the present smoothed  $\Delta L/L$  and  $\Delta a/a$  values given in Tables I and II shows that the expansions agree within experimental error up to nearly 850°C, a temperature far higher than the upper bound of the fitting interval employed in the lattice-expansion work. The upper bound of the fitting interval was, therefore, conservatively chosen.

The typical detailed agreement between measured  $\Delta L/L$  and  $\Delta a/a$  values in a lower temperature interval

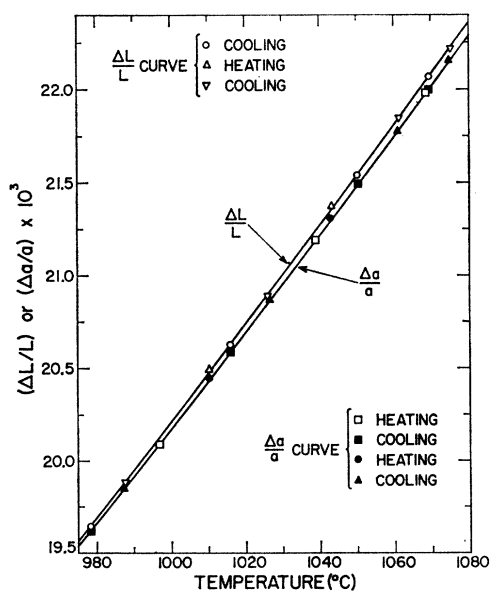


FIG. 2. Measured length expansion  $\Delta L/L$  and lattice parameter expansion  $\Delta a/a$  vs temperature in the interval 977–1076°C.  $\Delta L/L$  becomes larger than  $\Delta a/a$  at these temperatures corresponding to the thermal generation of vacant atomic sites. The melting temperature of copper is 1083°C.

is shown in Fig. 1. Measurements in the highest temperature interval are shown in Fig. 2;  $\Delta L/L$  is larger than  $\Delta a/a$ , which demonstrates that vacancy-type defects are predominant. The reversible nature of the measured divergence between the two types of measurements guarantees that the measured differences correspond to equilibrium values.

An 8°C extrapolation of the smoothed  $\Delta L/L$  and  $\Delta a/a$  curves to the melting temperature (1083°C) yields a difference  $(\Delta L/L - \Delta a/a) = 6.7 \times 10^{-5}$ . An estimated possible error in measuring  $(\Delta L/L - \Delta a/a)$  of  $1.7 \times 10^{-5}$  then corresponds to a possible error in measuring  $\Delta N/N$  of 25%. We will see in Sec. IV that this accuracy is quite sufficient to determine the monovacancy formation energy within about 10% accuracy.

## B. Possible Solute Impurity Effects

Contamination by impurities might affect measurements of the present type by two mechanisms: (1) the addition of impurity atoms may produce lattice dilatation; and (2) the equilibrium vacancy concentration in the contaminated region may be altered if there is a binding energy between impurities and vacancies. The error in the measurement of  $c_v$  which may result from these effects might be appreciable, depending upon the volatility and diffusion rate of the impurity. Two main types of impurities may be distinguished: (a) substitutional impurities with relatively low diffusivities which evaporate onto the specimen via the vapor phase from the furnace walls, etc.; and (b) faster diffusing gaseous impurities which might enter or leave the specimen from the atmosphere.

Consider first the possible effects of impurities of type (a). The mean maximum penetration distance into the specimen is given by  $\bar{x}_{\max} = 2(D_s t)^{1/2}$ , where  $D_s$  is the diffusion coefficient in dilute solution and  $t$  is the total equivalent diffusion time. For example, the average value of  $D_s^{1/2}$  for ten dilute metallic impurities in copper at 1080°C is  $1.2 \times 10^{-4} \text{ cm sec}^{-1/2}$ .<sup>18</sup> Setting  $t \approx 20 \text{ h}$ , we then find  $\bar{x}_{\max} \approx 0.064 \text{ cm}$ . Such impurities will, therefore, be localized near the surface. They will not appreciably affect length measurements on the long bar-shaped specimen used, either through addition of impurity substitutional sites (because such sites are added primarily on the side surfaces) or through possible dilatational stress (because the uncontaminated bulk of the specimen imposes restraints).

Lattice-parameter measurements may be affected, however, by an amount  $\delta a$ . The resulting experimental error in  $c_v$  is then given by  $\delta c_v = -3\delta a/a(20^\circ\text{C})$ . The uncontaminated specimen bulk will not allow any dilatation of the surface region in the plane of the surface. The magnitude of  $\delta a$  will then depend also upon

<sup>18</sup> D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 117.

the degree of relaxation by plastic flow of the internal stresses which tend to develop. If the stresses are completely relaxed,

$$-3k_s c_s + 12(1 - \chi^f/\Omega) c_v c_s \{ \exp[G_{vs}^b/kT] - 1 \} = \delta c_v; \quad (2)$$

and, if no relaxation occurs,

$$-3k_s c_s (1 + 2\nu) + 12(1 - \chi^f/\Omega) (1 + 2\nu) c_v c_s \times \{ \exp[G_{vs}^b/kT] - 1 \} = \delta c_v. \quad (3)$$

Here,  $\chi^f$  is defined as the crystal volume expansion resulting from the creation of a vacancy in an unconstrained crystal containing a fixed number of atoms. The quantity  $\Omega$  is the atomic volume, and  $\nu$  is Poisson's ratio. The parameter  $k_s$  is the constant of proportionality between the fractional impurity concentration  $c_s$  and the change in lattice parameter due to the dilatational field of the impurities. We have also used the relation<sup>19</sup>

$$c_v(\text{impure}) - c_v(\text{pure}) = 12c_v c_s [\exp(G_{vs}^b/kT) - 1] \quad (4)$$

for the difference in equilibrium vacancy concentration in the impure skin and pure interior. The quantity  $G_{vs}^b$  is the free energy of binding between vacancies and impurities.

Now it was observed experimentally that the  $\Delta a/a$  curves were reversible over their entire lengths during two heating and cooling cycles within an experimental error of  $\pm 7 \times 10^{-6}$ . The second term in Eq. (2) was certainly negligible at the lower temperature used, and we therefore conclude that the first term (which is temperature-insensitive) was always negligible. The second term could conceivably have been of significance at elevated temperatures and must be examined more closely. An estimate of the impurity level reached may be made from the observed fact that  $\sum_s 3k_s c_s \leq 7 \times 10^{-6}$ . A survey of values of  $k_s$  for twenty-two conceivable impurities<sup>12</sup> reveals that twenty-one of these values are positive, where  $0.2 \leq k_s \leq 0.3$  for four values,  $0.1 \leq k_s \leq 0.2$  for five values, and  $0 < k_s \leq 0.1$  for twelve values. For nickel,  $k_s = -0.03$ . Barring the extremely unlikely case that positive and negative dilatations canceled, we may conclude that  $\sum_s c_s$  could not have been larger than about  $10^{-4}$  or so. Using this result, it is readily shown that the second term in Eq. (2) must have been small and contributed relatively little error. The fractional error contributed by the second term in Eq. (2) is plotted as a function of binding energy and impurity concentration in Fig. 3 with the reasonable assumption that  $\chi^f/\Omega = 1/2$ .<sup>3</sup> Since it is quite certain that  $G_{vs}^b < 0.4$  eV, the error from this source can be neglected.

It is at least conceivable that type (b) impurities could have reversibly diffused in and out of the specimen during the heating and cooling, producing apparent reversibility while at the same time contributing an appreciable error to the measurement of  $c_v$ . Hydrogen

<sup>19</sup> A. B. Lidiard, *Phil. Mag.* 5, 1171 (1960).

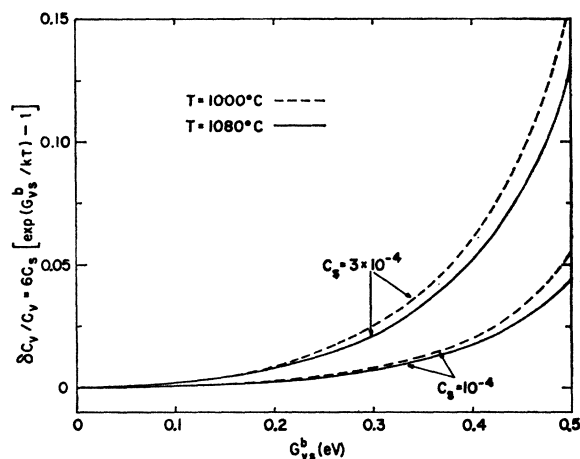


FIG. 3. Calculated fractional error in vacancy concentration measurement,  $\delta c_v/c_v$ , due to the second term in Eq. (2) assuming that  $\chi^f/\Omega = \frac{1}{2}$ . The error is calculated as a function of the vacancy-solute binding free energy,  $G_{vs}^b$ , for two different impurity concentrations,  $c_s$ , at the temperatures 1000 and 1080°C.

and oxygen are two soluble gaseous impurities which may have been present. However, the solubility of hydrogen<sup>20</sup> at a partial pressure as high as 7.6 torr is only  $5.4 \times 10^{-6}$  atom fraction at the melting point, and is, therefore, negligible.

The saturation solubility of oxygen in copper<sup>21</sup> at 1040°C is about  $2.8 \times 10^{-4}$  atom fraction. Also  $D(0 \text{ in Cu}) = 2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  at 1080°C.<sup>22</sup> The oxygen could then diffuse in and out of the specimen at least several mm during each thermal cycle. In order to test for the possible presence of oxygen under these conditions, a special test was carried out. A copper sample was heated to 1040°C for twenty-four hours in the identical nitrogen-carbon monoxide atmosphere used throughout the present work in order to equilibrate the entire sample volume with the atmosphere at an elevated temperature. The sample was then water-quenched, and any possible surface region affected by oxidizing conditions during the quench was removed by a heavy chemical etch. Subsequent gas analysis indicated an oxygen content of the sample of  $\leq 2$  parts per million by weight. This test, therefore, indicates that negligible oxygen was dissolved at the highest temperature of the experiment. A reasonably large estimate for  $k_s$  for oxygen in Eq. (3) would be  $|k_s| = 0.2$ . Therefore, by neglecting relaxation and possible diffusion to the specimen center, the largest possible error which the impurity dilatation could produce would then be  $|\delta c_v| \leq |3k_s c_s (1 + 2\nu)| \approx 8 \times 10^{-6}$ . It is also readily seen from Fig. 3 that the second term in either Eq. (2) or (3) is

<sup>20</sup> C. J. Smithells, *Metals Reference Book* (Interscience Publishers, Inc., New York, 1955), p. 535.

<sup>21</sup> M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 604.

<sup>22</sup> See quotations and references in: J. L. Meijering in *La Diffusion dans les Metaux*, edited by J. D. Fast (Bibliotheque Technique Philips, Eindhoven, 1957), p. 97.

negligible in this case for any reasonable binding energy. We also note that the specimen surface at the x-ray port, which was readily visible during the experiment, appeared clean and shiny at the elevated temperatures. No evidence of any oxide formation was observed.

We conclude that the effects of impurities on the present measurements of  $c_v$  were small and may be neglected in future discussion.

#### IV. CONCENTRATIONS AND PROPERTIES OF VACANCIES

The measured  $\Delta N/N$  values can be analyzed to obtain the equilibrium monovacancy abundance as a function of various multivacancy binding energies. We conclude that monovacancies are the predominant defects in the present equilibrium experiment. Values for the monovacancy formation and migration energy in copper are then obtained.

##### A. Monovacancy Abundance

All thermally-generated point defects, including both vacancy and interstitial type, contribute to the measured difference  $3(\Delta L/L - \Delta a/a) = \Delta N/N$ , and other data are required before the relative contributions of the various species of equilibrium defects to  $\Delta N/N$  can be accurately determined. Enough information is already available, however, to effect a partial reduction of the problem.

The equilibrium interstitial concentrations depend upon the energy of formation  $G_{1i}^f = E_{1i}^f - TS_{1i}^f$ . Measurements have been made of energy release<sup>23</sup> and of lattice-parameter decrease<sup>24</sup> in the interstitial-monovacancy recombination peaks in the annealing of irradiated copper. These give the ratio

$$R = (E_{1v}^f + E_{1i}^f)\Omega / (\chi_{1v}^f + \chi_{1i}^f),$$

provided that the interstitials and vacancies are situated, before annealing, more than a few atomic diameters apart. Here  $\chi_{1v}^f$  and  $\chi_{1i}^f$  are the volume changes during the defect formation. From Table III these lie in the ranges  $\chi_{1i}^f/\Omega = 0.7 \pm 0.5$  and  $\chi_{1v}^f/\Omega = 0.7 \pm 0.2$  for copper. Adopting  $\chi_{1v}^f + \chi_{1i}^f = 1.2\Omega$  and taking the measured ratio,  $R = 4.4$  eV then gives  $E_{1v}^f + E_{1i}^f \approx 3.7$  eV, within about 20%. Clearly, therefore,  $E_{1i}^f$  is about 2 to 4 times larger than the  $E_{1v}^f$  to be determined. Further, the formation entropy,  $S_{1i}^f$ , is probably relatively small. The equilibrium concentration of interstitials is therefore expected to be negligible.

It is probable that only a limited number of multiple-vacancy species need be considered in equilibrium. Direct evidence for this conclusion has not yet been obtained for copper, however. Existing theoretical estimates for copper (see Sec. V A) and fairly straight-

<sup>23</sup> A. V. Granato and T. G. Nilan, Phys. Rev. Letters **6**, 171 (1961).

<sup>24</sup> R. O. Simmons and R. W. Balluffi, Phys. Rev. **109**, 1142 (1958).

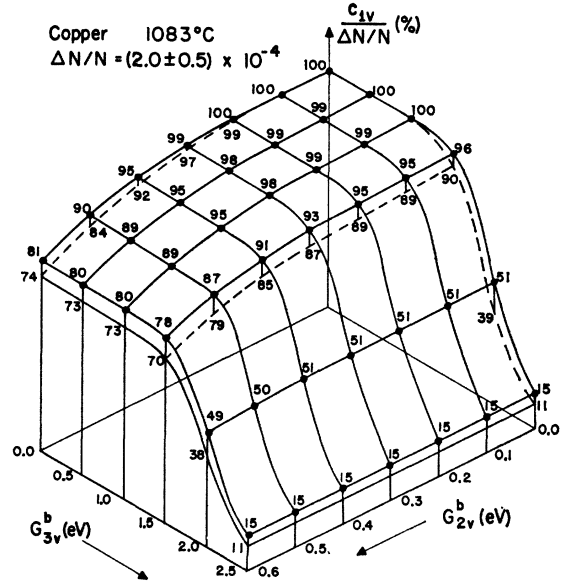


Fig. 4. Relative monovacancy abundance  $c_{1v}/(\Delta N/N)$ , as a function of various divacancy and tetrahedral trivacancy binding energies  $G_{2v}^b$  and  $G_{3v}^b$ , in copper just below the melting temperature. The upper and lower surfaces correspond to the lower and upper limits, respectively, on the measured  $\Delta N/N$  value.

forward interpretation of annealing of gold<sup>8,25</sup> and of silver<sup>5</sup> after quenching (see Table IV) suggest that, with the possible exception of the trivacancy and larger clusters of  $j$  vacancies, no binding energies  $G_{jv}^b$  larger than a few tenths of an electron volt are to be expected.

Monovacancy contribution,  $c_{1v}$ , is then given by the following relation, which assumes that contributions to  $\Delta N/N$  from vacancy aggregates larger than four can be neglected:

$$\Delta N/N = c_{1v} + 12c_{1v}^2 \exp(G_{2v}^b/kT) + 6c_{1v}^3 \exp(G_{3v}^b/kT) + 64c_{1v}^4 \exp(G_{4v}^b/kT). \quad (5)$$

Tetrahedral symmetry is assumed for the tri- and quadrivacancies. At the melting point of copper, where  $\Delta N/N = 2.0 \times 10^{-4}$ , with assumed values  $G_{3v}^b \approx 2G_{2v}^b = 0.8$  eV, and  $G_{4v}^b \approx 1.1$  eV, one obtains  $c_{1v} \approx 1.9 \times 10^{-4}$ ,  $2c_{2v} \approx 0.1 \times 10^{-4}$ , and the concentration of the larger vacancy aggregates entirely negligible. Values of  $G_{3v}^b \geq 1.5$  eV and  $G_{4v}^b \geq 2.2$  eV, respectively, are required in order to alter this situation appreciably. At present these values appear unreasonably large, particularly in the case of the quadrivacancy.

Solutions of Eq. (5), without the (negligible) quadrivacancy term, can be presented graphically as the ratio  $c_{1v}/(\Delta N/N)$  vs the energies  $G_{2v}^b$  and  $G_{3v}^b$ .<sup>2</sup> Such results are shown in Figs. 4 and 5. The ratio can be accurately computed using  $\Delta N/N$  data of the accuracy obtained in the present experiment, except for  $G_{3v}^b \lesssim 1.8$  eV, when the accuracy is only about  $\pm 15$  to 25%.

<sup>25</sup> W. Palmer and J. S. Koehler, Bull. Am. Phys. Soc. **3**, 366 (1958).

It is seen that for  $G_{2v}^b < 0.5$  eV and  $G_{3v}^b < 1.5$  eV the monovacancies constitute 90% or more of the equilibrium vacant atomic sites.

We therefore conclude that the monovacancy is the predominant equilibrium defect in copper, and we proceed on this basis.

### B. Monovacancy Formation and Migration Energies

Figures 4 and 5 show that the temperature dependence of  $c_{1v}$  is essentially the same as that of the measured  $\Delta N/N$ , provided that multivacancy binding energies are not exceedingly large. In principle, the formation energy  $E_{1v}^f$  could be derived from the observed temperature dependence of  $\Delta N/N$ . For copper the measured values of  $\Delta N/N$  are small, however, making such a direct determination of limited accuracy. The accuracy can be improved by adopting a value for the formation entropy  $S_{1v}^f$  at a fixed temperature at which  $\Delta N/N$  is known. The value  $S_{1v}^f/k = 1.5 \pm 0.5$  is well justified both by experiment on other fcc metals and by theory.<sup>3</sup>

At 1075°C,  $\Delta N/N = (1.9 \pm 0.5) \times 10^{-4}$ , which gives  $E_{1v}^f = (1.17 \pm 0.11)$  eV. The stated error includes both the estimated error,  $5 \times 10^{-5}$ , in the direct measurement of  $\Delta N/N$  and the uncertainty  $\pm 0.5k$  in the formation entropy, simply added together. We feel that the resulting estimate of possible error is conservative. If the values are treated as independent random errors, for example, the resulting error is reduced to 0.08 eV or about 7%. Furthermore, previous direct equilibrium measurements on silver, gold, and aluminum have

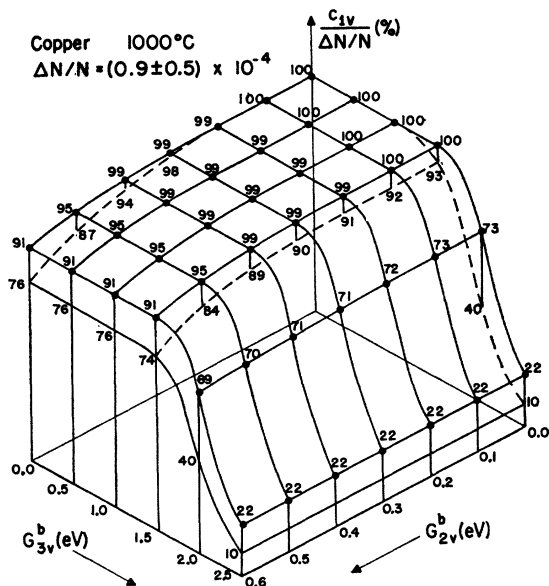


FIG. 5. Relative monovacancy abundance  $c_{1v}/(\Delta N/N)$ , as a function of various divacancy and tetrahedral trivacancy binding energies  $G_{2v}^b$  and  $G_{3v}^b$ , in copper at 1000°C. The upper and lower surfaces correspond to the lower and upper limits, respectively, on the measured  $\Delta N/N$  value.

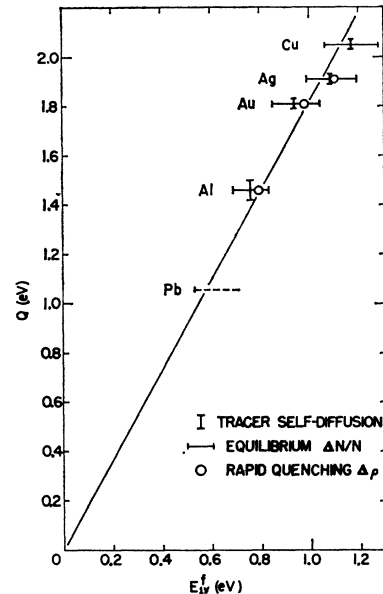


FIG. 6. The activation energy for self-diffusion  $Q_1$  and the monovacancy formation energy  $E_{1v}^f$  are approximately linearly related in those face-centered cubic metals for which equilibrium measurements of  $\Delta N/N$  are available. Stated error limits are shown for the self-diffusion and  $\Delta N/N$  experiments. For the quenching results only "best values" are shown; error estimates derived only from the scatter of data points are usually  $\pm 0.04$  eV. The approximate lower limit on  $E_{1v}^f$  in lead is estimated from an assumed  $S_{1v}^f = 1.5k$  and an upper limit on published vacancy concentrations.

given values of  $E_{1v}^f$  for these metals which differed from values obtained from careful quenching experiments by only 1 to 6%.<sup>9,10</sup> This agreement is illustrated in Fig. 6.

A number of generalizations have been made relating the energy of formation of vacancies to other crystal properties. Empirical correlations have been attempted, for example, between  $E_{1v}^f$  (or  $E_{1v}^m$ ) and the melting temperature<sup>26,27</sup>; these have only qualitative significance.<sup>28</sup> A closer empirical correlation has been noted between  $E_{1v}^f$  and  $Q_1$ ,<sup>2</sup> the activation energy for self-diffusion. The present result for copper is shown in this way in Fig. 6 to be consistent with the previously investigated close-packed metals.

It is interesting to examine explicitly the temperature dependence of  $\Delta N/N$  (that is, essentially, of  $c_{1v}$ ), as given by the present work. Values of  $3(\Delta L/L - \Delta a/a)$  for the present thirteen pairs of measurements in the range 938 to 1075°C are shown in Fig. 7. In each pair, the measurement made at the lower temperature is corrected to the higher temperature of the other measurement by means of an expansion coefficient obtained from the appropriate smooth curve in Fig. 2. These temperature corrections average 0.3 degree, or

<sup>26</sup> A. Sosin and J. A. Brinkman, *Acta Met.* 7, 478 (1959).

<sup>27</sup> M. W. Thompson, *Phil. Mag.* 5, 278 (1960).

<sup>28</sup> R. O. Simmons, in *Proceedings of the 1960 International Summer School in Physics "Enrico Fermi"* (Academic Press Inc., New York, 1963).

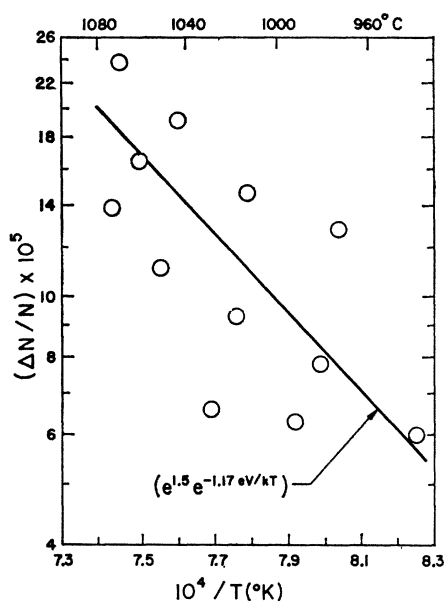


FIG. 7. Fraction of vacant atomic sites  $\Delta N/N$  vs inverse temperature in copper, computed directly from pairs of corresponding length and lattice-parameter expansion measurements. The line shown was obtained by a one-point fit at high temperature using  $S_{1v}^f/k=1/5$ .

less than  $7 \times 10^{-6}$  in relative linear expansion, and introduce negligible error because the  $\Delta L/L$  and  $\Delta a/a$  measurements refer to a common temperature scale. The straight line shown in Fig. 7 uses the adopted value of  $S_{1v}^f$  and the derived value of  $E_{1v}^f$  obtained above. The measured  $\Delta N/N$  values and the postulated line show quite satisfactory consistency.

The monovacancy migration energy  $E_{1v}^m$  is of considerable interest, because of the expectation that monovacancy migration might play an important role in the annealing of quenched, of irradiated, and of cold-worked metals. One can obtain this energy from the present work and the relation

$$Q = E_{1v}^f + E_{1v}^m, \quad (6)$$

provided that self-diffusion in copper occurs primarily by a monovacancy mechanism.

The ratio of radioactive tracer diffusivities for mono- and divacancies is given by<sup>1</sup>

$$D_{1v}^*/D_{2v}^* \approx 3(c_{1v}/2c_{2v})(\nu_1/\nu_2) \exp[(S_{1v}^m - S_{2v}^m)/k] \times \exp[-(E_{1v}^m - E_{2v}^m)/kT]. \quad (7)$$

The frequency factors  $\nu$  are taken to include any correlation factors. One can evaluate this ratio for silver and for gold using from Table IV the measured values of  $E_{1v}^m$  and  $E_{2v}^m$ , the derived values of  $c_{1v}$  and  $2c_{2v}$  from the binding energies, and the assumptions  $\nu_1 = 2\nu_2$  and  $S_{1v}^m = 2S_{2v}^m = 4k$  for silver and  $2k$  for gold. At the melting point for gold,  $D_{1v}^*/D_{2v}^* \approx 170$  while for silver  $D_{1v}^*/D_{2v}^* \approx 50$ . It is reasonable to assume that in copper a similar result applies. For copper,  $Q = (2.05$

$\pm 0.02)$  eV.<sup>29</sup> Therefore,  $E_{1v}^m = (0.88 \pm 0.13)$  eV. The error limit is again obtained by simple summation; the true value is expected to lie well within the specified range.

## V. COMPARISON WITH OTHER STUDIES

In this section we compare the present results with results of the many other studies which might be expected to yield information about monovacancies in copper. These include (1) theoretical calculations, (2) quenching and annealing, (3) thermal diffusion, (4) annealing after irradiation, and (5) annealing after cold work. It will be found that in no case is there a sufficiently firm body of experimental data available either to confirm or to contradict the present monovacancy data for copper. The need for further definitive experiments in these areas is emphasized.

### A. Theoretical Estimates

Calculations of the properties of models for atomic defects in metals have generally used copper as the prototype. Following Huntington and Seitz,<sup>30</sup> models for the metal typically consist of ions having nearest neighbor Born-Mayer repulsion and a cohesion supplied either by an elastic matrix or by springs external to the finite imperfect crystallite. Zero-point and thermal motion of the ions are neglected or else are taken to enter implicitly in the empirical evaluation of the repulsive parameters required. Some estimates have been made of the importance of electron redistribution due to the defect. On the other hand, some calculations have employed a Morse potential. The literature is voluminous; citations of earlier work may be found elsewhere,<sup>31</sup> while citations of most subsequent investigations are given by Seeger<sup>32</sup> and by Johnson and Brown,<sup>33</sup> and in reference 9.

The qualitative features expected of a number of models for the simplest defects are now clear. However, detailed quantitative comparison between the results obtained from different models has so far proven rather difficult. The precise origin and significance of existing differences between the results of different calculations is uncertain in many cases.

In Table III we collect results<sup>9,31-33</sup> for selected properties of several defects in copper. The ranges given are the ranges of results of different investigators employing different models or techniques of calculation. We will place special reliance upon a selected few of these values in Sec. VI. The values for the monovacancy formation and migration energies obtained in the present

<sup>29</sup> A. Kuper, H. Letaw, L. Slifkin, E. Sonder, and C. T. Tomizuka, Phys. Rev. **96**, 1224 (1954).

<sup>30</sup> H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

<sup>31</sup> *Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958).

<sup>32</sup> A. Seeger, Physica Status Solidi **1**, 669 (1961).

<sup>33</sup> R. A. Johnson and E. Brown, Phys. Rev. **127**, 446 (1962).



TABLE III. Calculated properties of point defects in copper from work cited elsewhere.\*

Defect	Formation energy $E^f$ (eV)	Formation entropy $S^f/k$	Migration energy $E^m$ (eV)	Binding energy $E^b$ (eV)	Volume change $\chi'/\Omega$	Electrical resistivity $\rho$ ( $\mu\text{ohm cm/at. } \%$ )
Vacancy	0.8 to 1.8	1 to 2	0.5 to 1.4	...	0.5 to 0.9	0.4 to 1.7
Divacancy	...	...	0.2 to 1.0	0.06 to 0.6	$\sim 1.0$	0 to 10% less than $2\rho_{1v}$
Trivacancy	...	...	$\sim 1.9$	0.5 to 2.9	...	...
Interstitial	2.4 to 5	$\leq 0.8$	0.05 to 0.6	...	0.2 to 1.2	0.1 to 10

\* See references 9, 31, 32, and 33.

work lie near the middle of the respective ranges, and the assumed formation entropy is consistent with the estimated value.

### B. Quenching and Annealing

Although a number of attempts to quench pure copper have been made in various laboratories, few accounts of the results have been published. In two cases, however, at least partial success has been claimed.<sup>34,35</sup>

It is to be expected that formidable experimental difficulties might be encountered in obtaining reliable results from such work. Both copper and its oxide can dissolve oxygen, copper oxide is relatively stable, and oxygen can combine readily with the common trace impurities in copper. Also, it is difficult to remove dissolved oxygen in the absence of a reducing atmosphere.<sup>36</sup> Further, the present direct measurements show that the equilibrium vacancy concentrations are small. Below 600°C, for example, it appears that they are less than one part per million, which is an order of magnitude below the impurity concentrations in typical highest-purity specimens. Finally, if the divacancy binding energy is appreciable, as it appears to be in silver,<sup>5</sup> then the combination of a small defect concentration plus divacancy formation during quenching would make unambiguous quenching experiments exceedingly difficult.

In the following we review briefly the different quenching results of which the writers are aware. The most complete published experiments have been those described in a note by Airoldi and co-workers.<sup>34</sup> In this work 0.04-mm-diam wires of nominal 99.999% purity were quenched in gaseous argon at an initial rate  $5 \times 10^8$  deg/sec yielding a resistivity increment

$$\Delta\rho = [(11 \pm 3) \times 10^{-4} \text{ ohm-cm}] \exp(-1.0 \text{ eV}/kT_q)$$

for quenching temperatures,  $T_q$ , in the range 600 to 800°C. This becomes about 0.2  $\mu\text{ohm-cm}$  upon extrapolation to the melting point, 1083°C. If it is assumed that this increment is the contribution due to equilib-

rium vacancies, then combination of this value with the directly measured concentrations yields  $\Delta\rho \sim 10 \mu\text{ohm-cm}$  per atomic percent vacancies, a value more than twice the upper limit given by irradiation studies, which are discussed in Sec. VI, and about seven times the values inferred for the other noble metals.<sup>3</sup> Isothermal annealing studies of resistivity<sup>34</sup> in the range 350 to 470°C showed activation energies 1.3 eV or higher. It is conceivable that this value is larger than the monovacancy migration energy  $E_{1v}^m = (0.88 \pm 0.13)$  eV obtained in the present work because of solute atom-vacancy binding effects. We also note that a very large binding energy is required in Eq. (4) in order to harmonize the usually large  $\Delta\rho$  of Airoldi *et al.*,<sup>34</sup> with the present equilibrium concentrations, unless the quenched defect has an unusually large resistivity.

Schüle and co-workers<sup>35</sup> have measured the annealing kinetics of quenched-in resistivity and obtained an activation energy of 1.08 eV. However, these workers were unsuccessful in initially quenching in reproducible defect concentrations,<sup>37</sup> and it is, therefore, difficult to judge the significance of these annealing experiments.

Martin<sup>38</sup> has quenched 0.01-cm-diam wire from temperatures up to 800°C into alcohol at  $-78^\circ\text{C}$  with a quenching speed of about  $5 \times 10^8$  deg/sec. He states that this quenching speed was apparently too slow to retain all the defects. The quenched-in resistivity increment never exceeded  $2 \times 10^{-10}$  ohm-cm. The quenched resistivity could be completely annealed out, and about half of it annealed out after 15 min at room temperature. We note that the quenched-in resistivity increment obtained by Martin is smaller than that obtained by Airoldi *et al.*<sup>34</sup> by a factor of more than one hundred even though the quenching rate was at least as rapid.

Lund<sup>39</sup> at the University of Illinois has attempted to quench copper using several techniques. In the first method 0.0051-cm-diam wire was gas-quenched in helium. The system was first evacuated to below  $10^{-7}$  torr, and helium gas was leaked in through a liquid-helium cold trap. Upon heating and quenching, anomalously large and erratic resistivity increments were obtained. In other experiments the technique developed by Doyama and Koehler<sup>5</sup> for quenching

<sup>34</sup> G. Airoldi, G. L. Bachella, and E. Germagnoli, Phys. Rev. Letters 2, 145 (1959).

<sup>35</sup> W. Schüle, A. Seeger, F. Ramsteiner, D. Schumacher, and K. King, Z. Naturforsch. 16a, 323 (1961).

<sup>36</sup> C. E. Ransley, J. Inst. Metals 65, 147 (1939).

<sup>37</sup> W. Schüle (private communication).

<sup>38</sup> D. G. Martin, Phil. Mag. 7, 803 (1962).

<sup>39</sup> C. A. Lund (private communication).

silver was employed without success. Attempts were also made using a technique in which the specimens were deoxidized with a carbon monoxide atmosphere.

R. E. Hoffman<sup>40</sup> at the General Electric Research Laboratory made quenching investigations on copper which yielded inconclusive results. W. Bron and E. S. Machlin<sup>41</sup> at Columbia University are among others who have made quenching studies on copper which have remained unpublished.

The above evidence indicates that the results of presently available quenching experiments with copper are inconclusive and also contradictory in certain cases. We note that the sum of the apparent monovacancy formation energy of Airoldi *et al.*<sup>34</sup> (1.0 eV, later amended to 0.95 eV<sup>42</sup>) and the activation energy of Schüle *et al.*<sup>35</sup> (1.08 eV) is close to the value of the activation energy for self-diffusion,  $Q=2.05$  eV. However, it is clear that this result may be fortuitous. Figure 6, while intended merely to indicate the approximate proportionality of  $E_{1v}^f$  and  $Q$ , with  $E_{1v}^f/Q \approx 0.55$ , does illustrate that a value such as  $E_{1v}^f=0.95$  eV for copper would be surprising in view of the results for the other noble metals. Even more strongly suggestive is the observation that in Fig. 7, a line of slope  $-0.95$  eV drawn through the present  $\Delta N/N$  data yields an entropy factor requiring a *negative* value for  $S_{1v}^f$ . Such a negative value would be very unusual.<sup>42a</sup>

It is hoped that further quenching and annealing experiments will be attempted on pure copper, not only because a comparison with the present equilibrium measurements would be helpful in evaluating several other monovacancy properties but also because such measurements offer the possibility of evaluating some of the multivacancy migration and binding energies in copper.

### C. Thermal Diffusion

Meechan and Lehman<sup>43</sup> have measured mass flow in a large thermal gradient in gold and in copper by means of embedded markers. They found that mass flow occurred in a number of their specimens and obtained the interesting result that the markers in the two metals moved in opposite directions relative to the thermal gradient. By comparing this result with simple theories of the effect they suggest that this differing behavior means that  $E_{1v}^m > E_{1v}^f$  in copper and that  $E_{1v}^f > E_{1v}^m$  in gold. This conclusion is, of course, inconsistent with the present results.

<sup>40</sup> R. E. Hoffman (private communication).

<sup>41</sup> W. Bron and E. S. Machlin (private communication).

<sup>42</sup> Quoted in reference 35.

<sup>42a</sup> Note added in proof. We note that if for copper  $E_{1v}^f$  were indeed 0.95 eV and  $S_{1v}^f/k=1.5$ , then the point defect concentration would be sufficiently dense that self-diffusion would be dominated by a divacancy mechanism. See R. O. Simmons, in *Proceedings of the International Conference on Crystal Lattice Defects*, Kyoto, 1962 (to be published).

<sup>43</sup> C. J. Meechan and G. W. Lehman, *J. Appl. Phys.* **33**, 634 (1962).

Unfortunately, it is difficult at present to judge the meaning or the reliability of this thermal-diffusion experiment. At the present time the physical interpretation of the "heat of transport" is not clear, and it is not firmly established that such an experiment actually measures the difference between  $E_{1v}^f$  and  $E_{1v}^m$ . It is also worth noting that the total marker movements were no larger than the diameter of the markers used and that the marker shifts were sensitive to the soundness of the weld at the marker interface and to the grain boundary structure near the markers. In previous attempts to measure marker shifts in a thermal gradient, negative results have been obtained for zinc,<sup>44</sup> alpha-iron,<sup>45</sup> copper,<sup>46</sup> and silver.<sup>47</sup> In our opinion more work will have to be done on diffusion in solids in a thermal gradient, before it can be decided whether the present results and those of Meechan and Lehman are in disagreement.

### D. Annealing after Irradiation

Monovacancies and interstitial atoms are the primordial atomic defects produced by energetic charged-particle bombardment of metals. It is generally agreed, even though the precise form or forms of the interstitial in copper are as yet unknown, that interstitial migration requires less energy than monovacancy migration. The migration of monovacancies might therefore be expected to be a prominent contribution to the thermal annealing of irradiated copper near room temperature. Such annealing of course may be influenced by the prior history of the sample (for example, by the degree of annealing before irradiation, by the temperature during irradiation, by the irradiation dose, by the method of annealing, etc.) as well as by the nature and concentration of solute impurities.

Published irradiation and thermal-annealing experiments on copper suggest the presence of at least two annealing peaks which may occur near room temperature.<sup>9</sup> The first, in the range 220 to 340°K, has an apparent activation energy of  $0.65 \pm 0.05$  eV in relatively impure copper according to kinetic studies by recognized methods. The second, in the range above 340°K, is supposed to have an associated activation energy near 1.2 eV; it constitutes a very minor proportion of the total electrical resistivity annealing in high-purity material. It appears from the present work, which implies that  $E_{1v}^m \approx 0.9$  eV, that neither of these peaks can be directly identified with simple monovacancy migration.

Electron and pile irradiation at 77°K of spectroscopically pure copper and of dilute binary alloys of copper containing between 0.02 and 1 at. % silver, cadmium,

<sup>44</sup> P. G. Shewmon, *J. Chem. Phys.* **29**, 1032 (1958).

<sup>45</sup> W. G. Brammer, *Acta Met.* **8**, 630 (1960).

<sup>46</sup> W. G. Brammer, *Bull. Am. Phys. Soc.* **2**, 388 (1957).

<sup>47</sup> J. W. Cahn, private communication to W. G. Brammer (see reference 45).

or beryllium has been carried out by Martin.<sup>38,48</sup> In the purest material, electrical resistivity annealing peaks were found at about 130, 200, and 270°K. The peaks, as studied by isochronal annealing methods, were profoundly modified in the alloy samples. While no activation energies are reported in this work, the results clearly indicate that considerable care will be required to arrange a radiation-damage experiment so that the high-temperature annealing is dominated by intrinsic defects.

### E. Annealing after Cold Work

Monovacancies and perhaps interstitials and also various clusters of these defects are expected to be produced by plastic deformation. The migration of monovacancies might therefore be expected to be a prominent contribution to the thermal annealing of cold-worked material. Many investigations on copper have been performed in order to investigate the resulting annealing spectra for the presence of such point-defect migration processes. Such studies are, of course, greatly complicated by the presence of many dislocations.

An exhaustive survey of such experiments<sup>10</sup> reveals the following situation. Generally, the annealing spectrum is of an essentially continuous nature. In spite of a great diversity among experiments as to sample properties and physical conditions employed, a few reproducible peaks in the annealing spectra seem to appear in more than one experiment. Existing kinetic studies of these possible annealing peaks are incomplete, however. In no case has a measured peak in electrical-resistivity or in energy-release studies been shown to have a width and time-decay constant characteristic of a uniquely activated process or not to be associated with some possible solute impurity or recrystallization. No positive identification of a migrating point defect with a particular possible annealing peak in cold-worked copper has been made, therefore.

During annealing after plastic strain of a few percent, decrease of the internal friction and increase of the apparent elastic modulus may be attributable to the pinning of dislocations by deformation-produced point defects which diffuse to them. An analysis based on this model of the kinetics observed for copper yields an activation energy of 1.0 eV.<sup>49</sup> Such an experiment may be less prone than resistivity or energy release studies to the difficulty of trapping of migrating defects by solute impurities; the average number of jumps required by the small fraction of mobile defects which produce the modulus and damping effects is only about  $10^2$ .<sup>49</sup>

<sup>48</sup> D. G. Martin, *Phil. Mag.* **6**, 839 (1961).

<sup>49</sup> A. Granato, A. Hikata, and K. Lücke, *Acta Met.* **6**, 470 (1958). The original work used a  $(\text{time})^{2/3}$  strain-aging law; assumption of a  $(\text{time})^{1/2}$  law which actually may be more appropriate for annealing vacancies results in a somewhat lower activation energy (A. V. Granato, private communication).

## VI. POINT-DEFECT PROPERTIES IN THE NOBLE METALS

Enough experiments are now available to frame within rather narrow limits many properties of the simplest point defects in the noble metals. With the aid of the results of the present work, we give the status of this formulation for copper here in order to indicate explicitly the assumptions required in obtaining the known values and to indicate those properties which have not yet been determined. Wherever possible, we also list corresponding values for silver and gold.<sup>50</sup> Both directly measured properties and the properties derived below are collected in Table IV.

Direct information about close interstitial-monovacancy pairs in copper comes from thermal-annealing studies after irradiation near 10°K. During annealing below 60°K,  $\Delta a/a = \Delta L/L$  in deuteron-irradiated copper.<sup>24,51</sup> The result of the annealing is therefore the mutual annihilation of interstitials and monovacancies. A number of annealing peaks are observed in this annealing; measurements of their activation energies agree in 9-MeV deuteron- and in 1.4-MeV electron-irradiated copper.<sup>52,53</sup> In the latter case the damage must consist primarily of single interstitials and monovacancies, because the electron energies are insufficient to produce multiple displacements of atoms during bombardment. Detailed study shows the temperature and width of the annealing peak having the highest activation energy ( $0.11 \pm 0.01$  eV) to be dependent upon the amount of irradiation and upon the presence of defects introduced prior to irradiation.<sup>53</sup> An argument has been given that these data imply a defect which moves in three dimensions.<sup>54</sup> This defect must be some type of interstitial atom, because from the present work  $E_{1v}^m \approx 0.9$  eV. We emphasize that the exact configuration of the interstitial has not yet been determined.

Measurements have been made during annealing below 60°C of the ratios of electrical resistivity change to volume change,<sup>24</sup>

$$\Delta\rho/[3(\Delta a/a)] = (2.3 \pm 0.2) \times 10^{-4} \text{ ohm cm} \equiv A,$$

and of energy release to electrical resistivity change,<sup>23</sup>

$$U/\Delta\rho = (1.9 \pm 0.2) \times 10^4 \text{ eV/ohm cm} \equiv B.$$

If it is assumed that before their mutual annihilation the interstitials and monovacancies are separated widely enough so that their energy, electrical resistivity  $\rho$  (for one atomic percent), and volume expansion,  $\chi$ ,

<sup>50</sup> R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).

<sup>51</sup> R. Vook and C. A. Wert, *Phys. Rev.* **109**, 1529 (1958).

<sup>52</sup> G. D. Magnuson, W. Palmer, and J. S. Koehler, *Phys. Rev.* **109**, 1990 (1958).

<sup>53</sup> J. W. Corbett, R. B. Smith, and R. M. Walker, *Phys. Rev.* **114**, 1452, 1460 (1959).

<sup>54</sup> A. V. Granato and T. G. Nilan, *Bull. Am. Phys. Soc.* **6**, 419 (1961).

TABLE IV. Experimental point-defect properties in copper, silver, and gold.

Property	Method	Cu	Ag	Au
$(\Delta N/N) \times 10^4$ at melting point	equilibrium	$2.0 \pm 0.5^a$	$1.7 \pm 0.5^g$	$7.2 \pm 0.6^j$
$E_{1v}^f$ (eV)	equilibrium	$1.17 \pm 0.11^a$	$1.09 \pm 0.10^g$	$0.94 \pm 0.09^j$
$E_{1i}^f$ (eV)	quenching	See text, Sec. V.B	$1.10 \pm 0.04^{h,i}$	$0.98 \pm 0.03^{k,l}$
$E_{1v}^m$ (eV)	quenching	...	$0.83 \pm 0.05^h$	$0.82 \pm 0.05^{k,l}$
$S_{1v}^f/k$	equilibrium and self-diffusion	$Q - E_{1v}^f = 0.88^{a,b}$	...	...
	equilibrium	...	...	$1.2 \pm 0.3^{j,l}$
	equilibrium and quenching	...	$1.5 \pm 0.5^{g,h,i}$	...
	see ref. c	$1.5 \pm 0.5^c$	...	...
$(\rho_{1v})_1 \%$ ( $\mu\text{ohm-cm}$ )	equilibrium and quenching	...	$1.3 \pm 0.7^{g,h,i}$	$1.5 \pm 0.3^{j,l}$
	see ref. c	$1.5 \pm 0.3^c$	...	...
$(\chi_{1v}^f/\Omega)^p$	equilibrium and quenching	...	...	$0.45 \pm 0.10^{j,l}$
	see ref. c	$0.5 \pm 0.10^c$	...	...
$\chi_{1v}^m/\Omega$	quenching	...	...	$0.15 \pm 0.02^m$
$E_{2v}^f$ (eV)	quenching; $E_{2v}^f \equiv 2E_{1v}^f - G_{2v}^b$	...	$1.80 \pm 0.13^{h,i}$	$1.86 \pm 0.15^{l,n}$
$E_{2v}^m$ (eV)	quenching	...	$0.57 \pm 0.03^{h,i}$	$0.65 \pm 0.05^l$
$E_{1i}^f$ (eV)	theory	$3.5 \pm 1.0$	...	...
$E_{1i}^m$ (eV)	radiation damage	$0.11 \pm 0.01^{d,e}$	$0.08 \pm 0.01^d$	$< 0.67^o$
$(\rho_{1i})_1 \%$ ( $\mu\text{ohm-cm}$ )	see ref. f	$1.2 \pm 0.6^f$	...	...
$\chi_{1i}^f/\Omega$	see ref. f	$0.7 \pm 0.13^f$	...	...

<sup>a</sup> Present work.<sup>b</sup> See reference 29.<sup>c</sup> Assumed value, from other noble metals and from theory.<sup>d</sup> See reference 52.<sup>e</sup> See reference 53.<sup>f</sup> See text, Sec. VI.<sup>g</sup> See reference 2.<sup>h</sup> See reference 5.<sup>i</sup> See reference 6.<sup>j</sup> See reference 3.<sup>k</sup> See reference 7.<sup>l</sup> See reference 8.<sup>m</sup> See reference 50.<sup>n</sup> See reference 25.<sup>o</sup> See reference 9.<sup>p</sup>  $\Omega$  = atomic volume.

are essentially independent then one can write

$$E_{1v}^f + E_{1i}^f = 100B(\rho_{1v} + \rho_{1i}) = AB(\chi_{1v}^f + \chi_{1i}^f)/\Omega. \quad (8)$$

Unfortunately, only  $E_{1v}^f$  has been measured for copper. The two unknowns pertaining to the monovacancy can, however, be estimated with fair accuracy from measurements on the other noble metals (see Table IV). Further, from Table III, theoretical estimates of  $E_{1v}^f$  give the value  $(3.5 \pm 1.0)$  eV, regardless of the precise form of the interstitial atom involved in this annealing. With this assumption, values  $\rho_{1i}$  and  $\chi_{1i}^f$  are then determined.

These are shown in Table IV. The values obtained fall well within the range of theoretical estimates.

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