where n is the number of conduction electrons per atom, $|\psi(0)|^2$ is the probability density of a conduction electron at the nucleus, μ is the Bohr magneton, and p is the polarization of the conduction electrons. It would appear that $n|\psi(0)|^2$ is roughly the same in the two alloys, since they show about the same isomer shift[9] (see Figs. 1 and 3).[9a] If, on the other hand, the polarization of conduction electrons (produced by the adjacent magnetic electrons) increases with saturation magnetization, then the polarization and so also H_c is greater numerically in Mn_2Sn than in Mn_4Sn. The simplest explanation of the large positive field in Mn_2Sn is that H_c is a *positive* field.

As for the pure transition elements,[3,10,11] it is necessary to postulate, in addition to H_c, the presence of a negative field, presumably associated with polarization of the core electrons of tin. In Mn_4Sn this field predominates. That this field is smaller, if different at all, in Mn_2Sn is consistent with the fact that the Weiss field is smaller, since the Curie temperature is lower and the magnetization larger in Mn_2Sn than in Mn_4Sn.

These effects observed in the manganese-tin alloys are somewhat analogous to those obtained by Boyle *et al.*[12] in dilute solutions of tin in the ferromagnetic transition elements. It is gratifying that essentially the same mechanisms[12] can be invoked to explain qualitatively the observations on all these tin alloys.

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[9] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[9a] *Note added in proof.* We are indebted to V. Jaccarino for pointing out that equality of the isomer shifts does not necessarily insure the above argument, since the polarization effect is localized at the top of the conduction band.

[10] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[11] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960).

[12] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960).

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Pressure Effect on Vacancy Migration Rate in Gold*†

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The effect of hydrostatic pressures up to 10 000 kg/cm² on the annealing rate of vacancies quenched in gold is studied. High-purity gold wires are quenched from 700°C, trapping in the equilibrium concentration of vacancies at that temperature. The vacancies are then observed to anneal out in the vicinity of room temperature at various pressures by observing the decay of the quench-induced residual resistance increase. A simple relation for the temperature dependence of the annealing rate is derived, assuming a random distribution of vacancies and vacancy sinks. By applying thermodynamic relations to the expression for the vacancy annealing rate, a volume of motion is derived in terms of the experimentally determined pressure effect on the annealing rate. For gold, the motional volume is found to be 1.50±0.14 cm³/mole compared with the atomic volume of 10.2 cm³/mole. A hard-spheres model for the jump process predicts about a one atomic volume increase of the lattice for the saddle-point configuration as well as a one atomic volume increase when a vacancy is formed. Many theoretical calculations of the lattice distortion around a vacancy and indirect experimental measurements of the volume change of the lattice on forming a vacancy indicate that there is considerable relaxation of the neighboring atoms about a vacancy. These results are used to explain the small value of the motional volume. Activation volumes derived from measurements of the effect of pressure on the rate of self-diffusion are seen to be consistent with the present experimental vlue.

I. INTRODUCTION

THE annealing of lattice vacancies quenched in a close-packed metal is closely related to the self-diffusion process. In the quenching technique, a supersaturation of vacancies is trapped in the lattice by rapidly cooling it from elevated temperatures and then is allowed to reach equilibrium at lower temperatures. The presence of these quenched-in vacancies is determined by the increase in the residual resistance of the lattice which they produce. Thus, the formation and motion of the vacancies can be observed separately. The sum of the energies of formation and of motion of vacancies quenched in various metals is generally in good agreement with self-diffusion activation energies measured for these metals by the radioactive tracer technique. Since most theories of diffusion treat the formation and motion of the defect separately, the quenching technique permits a more direct comparison of experiment with theory than is possible with tracer measurements.

The jump of an atom into a neighboring vacant site cannot be accomplished by a simple shear of the barrier atoms. Some dilatation of the lattice must occur to permit the interchange. The purpose of the present experiment is to determine the volume change of the

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TABLE I. Activation volumes for various materials.

Material	Structure	Diffusion mechanism[a]	Activation volume (cm^3)	Molar volume (cm^3)	Experimental method[b]
White phosphorus[c]			30.0	68.2	*sd*
Sodium[d]	bcc	*v*	12.4	24	*sd*
Lead[e]	fcc	*v*	13.0	18.2	*sd*
Silver-zinc[f]	fcc	*v*	5.36	10.0	*ar*
Oxygen-vanadium[g]	bcc	*i*	1.7		*ar*
Nitrogen-vanadium[g]	bcc	*i*	1.2		*ar*

[a] *v*—vacancy mechanism; *i*—interstitial mechanism.
[b] *sd*—self-diffusion; *ar*—anelastic relaxation.
[c] N. H. Nachtrieb and A. W. Lawson, J. Chem. Phys. **23**, 1193 (1955).
[d] See reference 26.
[e] N. H. Nachtrieb, H. A. Riesing, and S. A. Rice, J. Chem. Phys. **31**, 135 (1959).
[f] See reference 11.
[g] See reference 27.

lattice when such a diffusive jump occurs. Because of this volume change, an increase in pressure on the lattice is expected to change the energy required for the jump and thus to alter the annealing rate. To be sure, even if no volume change occurred, pressure would influence the diffusion rate by changing the interatomic spacing and the normal mode spectrum of the lattice. In order to separate these effects, the interpretation of the effect of pressure on the annealing rate in terms of a volume change of the lattice must be based on a specific model for the atomic jump.

By the simple picture of forming a vacancy by moving a lattice atom to the surface of the crystal an additional atomic volume is added to the volume of the lattice, if the atoms are considered to be hard spheres. The hard-spheres model predicts an additional increase in lattice volume of about one atomic volume when a diffusing atom is midway between adjacent lattice sites. The sum of the formation volume and motion volume is called the total activation volume for diffusion.

The total activation volume has been determined for a number of substances by radioactive tracer and anelastic relaxation techniques (Table I). It would be highly desirable to compare the sum of the volumes of formation and of motion as measured separately by quenching techniques with the total activation volume measured by the tracer techniques. To determine the volume of formation, it is necessary to quench the specimen at high pressure. Tomizuka[1] has shown the feasibility of quenching at pressure in a gas pressure system. However, for the present experiment, no gas system was available, and no satisfactory method for quenching the specimen in the liquid system was devised. The possibility of pulse heating the specimen has not been abandoned and will be investigated in the future. In this experiment, therefore, only the volume of motion is determined.

The specimens, in the form of gold wires, are quenched from about 700°C at atmospheric pressure and then placed in a pressure vessel which is held at constant temperature. The isothermal annealing rate can then be measured as a function of hydrostatic pressure. Gold is chosen for the specimen material for several reasons. First, negligible contamination results from heating the wires in air and then dropping them into a bath of water. Secondly, the quenched-in vacancies anneal out in a temperature range which is easily maintained in the high pressure vessel. Finally, the availability of atmospheric pressure quench data for gold[2,3] provides a check for the high-pressure data.

II. THEORETICAL BACKGROUND

In the present experiment it is not necessary to know the absolute concentration of the vacancies quenched into the lattice. It is not even essential that the entire equilibrium concentration at the quench temperature be trapped in. Only the annealing behavior of the vacancies in excess of the equilibirum concentration at the annealing temperature is required. However, the degree of association of the vacancies into divacancies or higher-order clusters and the distribution of these defects throughout the lattice has a direct bearing on the nature of the annealing kinetics. Koehler, Seitz, and Bauerle[4] have shown that as the quench temperature and the vacancy concentration increase, the concentration of divacancies becomes appreciable. The divacancies have a slightly lower energy of motion than single vacancies, so that as the divacancy concentration increases, the annealing kinetics become more complex. However, for quench temperatures less than 750°C, the divacancy concentration is apparently negligible.

In addition to divacancy formation, complicated dislocation loops may be quenched in from temperatures near the melting point.[5,6] These loops are presumed to result from the collapse of large aggregations of vacancies in the form of plates. Since dislocations are active sinks for vacancies, the vacancy concentration rapidly becomes that of the thermal equilibrium value in the vicinity of dislocation. For large dislocation densities, this effect results in a nonuniform vacancy distribution in bulk of the lattice after a quench. In the light of these considerations, quenches were made from 700°C in order to make the annealing behavior as simple as possible.

Koehler, Seitz, and Bauerle[4] derive the following expression for the concentration of the quenched-in va-

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[1] C. T. Tomizuka, Bull. Am. Phys. Soc. **4**, 181 (1960).

[2] J. W. Kauffman and J. S. Koehler, Phys. Rev. **88**, 149 (1952); Phys. Rev. **97**, 555 (1955).

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

[4] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

[5] A. H. Cottrell, Institute of Metals Monograph and Report Ser. No. 23, (unpublished), p. 1.

[6] P. B. Hirsch, J. Silcox, R. E. Smallman, and K. H. Westmacott, Phil. Mag. **3**, 897 (1958).

cancies as a function of time:

$$c=c_0\sum_{n=1}^{\infty}\{A_nJ_0(\alpha_nr)-B_nN_0(\alpha_nr)\}\exp(-D\alpha_n^2t). \qquad (1)$$

A_n, B_n, and α_n are constants determined from the boundary conditions. This expression presumes that the vacancies anneal by diffusion to dislocation lines. For low vacancy concentrations, Eq. (1) reduces to the simple expression which can be derived assuming a random distribution of vacancies migrating to a random distribution of sinks.

For Eq. (1) to be of value, we must have an expression for D, the diffusion coefficient. The most widely accepted theory for the temperature dependence of the diffusion coefficient is that based on absolute reaction rate theory. One form of this theory[7] results in the following expression for the diffusion coefficient:

$$D=\alpha a^2fk_tp_d\nu_0\exp(-\Delta G_m/kT), \qquad (2)$$

where α= a constant determined by the lattice, ν_0= a weighted mean frequency, a= the atomic spacing, k_t= the transmission coefficient, f= the correlation factor, p_d= the probability a vacant site is present, and ΔG_m= the change in Gibbs free energy when an atom is in the saddle configuration leaving out the degree of freedom associated with the direction of motion.

Equation (2) can be rewritten by noting that p_d, the probability that a vacancy is adjacent to a diffusing atom, is n_v/n, the concentration of vacancies. The concentration n_v/n can readily be shown to be $\exp(-\Delta G_f/kT)$, where ΔG_f is the free energy required to form a vacancy. Then Eq. (2) becomes

$$D=\alpha a^2fk_t\nu_0\exp(-\Delta G_f+\Delta G_m/kT). \qquad (3)$$

The model used to derive this result is called the equilibrium model, since it presumes that the diffusing atom is in thermal equilibrium with the lattice at all times during a jump. This assumption is necessary in that the lifetime of the excited state must be sufficiently long to ascribe thermodynamic parameters to the saddle point configuration. Irreversibility of the jump is introduced by *fiat* and requires the assumption that a temperature-independent process exists whereby the lattice can absorb the excitation energy of the jumping atom. Other assumptions are also required and are noted in a review paper by Lazarus[7] along with references to the detailed calculations.

Rice[8] has recently proposed a different approach to the diffusion problem. This approach avoids many of the assumptions encountered in the equilibrium theory. In this dynamical theory, the diffusing atom attains sufficient amplitude to permit it to move from one lattice site to another from fluctuations of energy in the subvolume in which it is contained. The bulk of the crystal is replaced by a reservoir assumed to be in thermal contact with every lattice point on the surface of the subvolume. To complete a jump, it is also necessary that the neighboring atoms which tend to obstruct the jump have a correlated out-of-phase motion of sufficient amplitude for the diffusing atom to pass between them. The results of this calculation indicate a dependence principally on the potential energy of the interaction between neighboring atoms rather than on the free energy of the crystal. However, when irreversibility of the diffusion process is taken into account,[9] there is some indication that this theory, too, may result in a dependence on free energies. It will be assumed in this paper that the dependence is on free energies, with a dependence of the form indicated in Eq. (2).

Regardless of the detailed nature of the sink, the annealing rate is determined by the jump frequency of the vacancies, as long as there is no long-range interaction between a vacancy and the sink. For the present analysis, we shall use the simplest model of a random distribution of vacancies migrating to a random distribution of sinks. The decrease in excess vacancy concentration with time can then be written as

$$(dn_v/dt)=-n_v\Gamma_m, \qquad (4)$$

where Γ_m is the probability per unit time that a vacancy will reach a sink. Γ_m is related to the jump frequency of a vacancy, ν_j, by

$$\Gamma_m=N\nu_j, \qquad (5)$$

where N is the average number of jumps required for a vacancy to reach a sink. (N has been estimated by Bauerle[3] to be of the order of 10^6 for gold when annealing rates are comparable to those in the present experiment.) The jump frequency is related to the vacancy diffusion coefficient as

$$\nu_j=D_v/a^2. \qquad (6)$$

Combining Eqs. (4)–(6), we obtain

$$(dn_v/dt)=-n_vND_v/a^2. \qquad (7)$$

The temperature dependence of D_v ,the vacancy diffusion coefficient, may be written in terms of Eq. (2). Since attention is focused on vacancies already present in the lattice, p_d in Eq. (2) is unity. The correlation factor for a vacancy is also unity. Thus, D_v becomes

$$D_v=\alpha a^2k_t\nu_0\exp(-\Delta G_m/kT). \qquad (8)$$

Equation (7) can then be written as

$$(dn_v/dt)=-n_vN\alpha k_t\nu_0\exp(-\Delta G_m/kT). \qquad (9)$$

or in the logarithmic form

$$d\ln n_v/dt=-N\alpha k_t\nu_0\exp(-\Delta G_m/kT). \qquad (10)$$

Let Σ_m be the slope, $(d\ln\Delta\rho/dt)$, of the experimental resistance annealing curve, $\ln\Delta\rho$ vs t. It is apparent from

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[7] For a review of diffusion theories and a list of references, see D. Lazarus, *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10, p. 71.

[8] S. A. Rice, Phys. Rev. **112**, 804 (1958).

[9] S. A. Rice and H. L. Frisch, J. Chem. Phys. **32**, 1026 (1960).

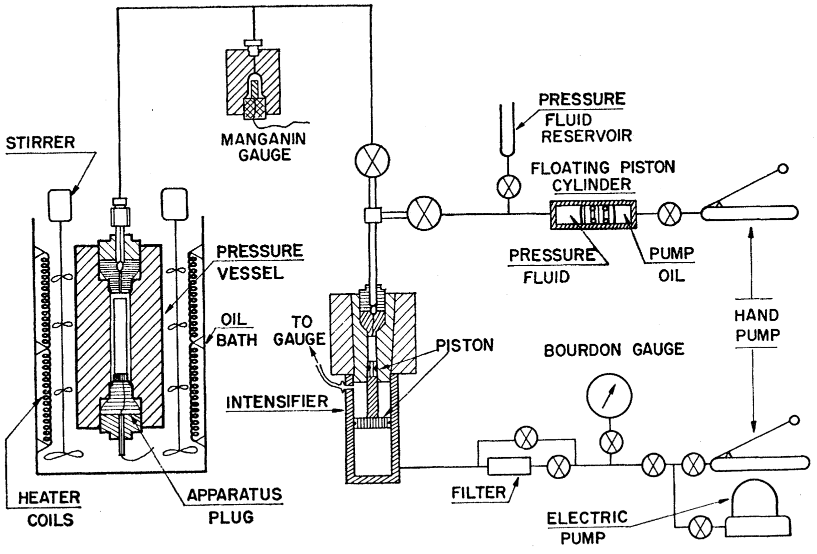

FIG. 1. Schematic diagram of the high-pressure system.

the vacancy model for the quenched-in resistance that $-\Sigma_m = \Gamma_m$. (The explicit sign of Σ_m has been included.) From Eq. (4) it can be seen that Σ_m is the logarithmic derivative of n_v with respect to time. Thus,

$$\Sigma_m = \alpha k_t N \nu_0 \exp(-\Delta G_m/kT). \qquad (11)$$

From the definition of the Gibb's function, $\Delta G_m = \Delta H_m - T\Delta S_m$, so that Eq. (11) becomes

$$\Sigma_m(T) = \alpha k_t N \nu_0 \exp(\Delta S_m/k) \exp(-\Delta H_m/kT). \qquad (12)$$

The energy of motion can be determined from the ratio of anneal rates at two different temperatures:

$$[\Sigma_m(T_1)/\Sigma_m(T_2)] = \exp[-(\Delta H_m/k)(1/T_1 - 1/T_2)]. \qquad (13)$$

This expression has presumed first-order kinetics. Deviations of the experimental annealing data from first order will be discussed later.

It can be shown from thermodynamic relations that $dG = VdP - SdT$. It is apparent that for an isothermal process, the volume change of the system is related to the Gibbs free energy by the expression $V = (\partial G/\partial P)_T$. If differences in the Gibbs energy are considered,

$$\Delta V = (\partial \Delta G/\partial P)_T. \qquad (14)$$

The total activation volume for diffusion, using Eq. (3), is seen to be

$$\Delta V = -kT[\partial \ln D/(\alpha a^2 f k_t \nu_0)/\partial P]_T.$$

It is this expression which is used to determine the activation volume from the experimentally determined pressure effects on tracer diffusion (see Table I).

Taking the derivative of the logarithm of both sides of Eq. (11) with respect to pressure at constant temperature, we find

$$\left(\frac{\partial \ln\Sigma_m}{\partial P}\right)_T = \left(\frac{\partial \ln\alpha k_t N}{\partial P}\right)_T + \left(\frac{\partial \ln\nu_0}{\partial P}\right)_T - \frac{1}{kT}\left(\frac{\partial \Delta G_m}{\partial P}\right)_T. \qquad (15)$$

The third term on the right in Eq. (15) is $-\Delta V_m/kT$. If it is assumed that α, k_t, and N are constant with respect to pressure, Eq. (15) can be written as

$$\Delta V_m = -kT(\partial \ln\Sigma_m/\partial P)_T + kT(\partial \ln\nu_0/\partial P)_T. \qquad (16)$$

Although no pressure diffusion experiments have been carried out for gold, a rough estimate of the activation volume for motion can be made using the semiempirical relation proposed by Keyes,[10] $\Delta V = 4\beta\Delta H$, where β is the compressibility. This relation gives agreement within about a factor of two for a large number of results. ΔH_m as determined for gold by Bauerle[3] is 0.82 ev. The compressibility of gold is 5.7×10^{-7} cm^2/kg. Using these values, Keyes' expression predicts an activation volume for motion in gold of about 1.8 cm^3/mole in comparison with the atomic volume of 10.2 cm^3/mole.

Table I lists values of the total activation volume for a number of substances. It is apparent that the experimental ΔV is roughly half the atomic volume for these substances. Tichelaar and Lazarus[11] conclude from their experimental results and from the calculation of ΔV_f by Tewordt[12] that the formation volume comprises most of the activation volume. On the basis of these considerations, the pressure effect on the annealing rate of quenched-in resistivity is expected to be small. As will be

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[10] R. W. Keyes, J. Chem. Phys. **29**, 467 (1958).
[11] G. W. Tichelaar and D. Lazarus, Phys. Rev. **113**, 438 (1959).
[12] L. Tewordt, Phys. Rev. **109**, 61 (1958).

seen, this prediction is borne out by the present experimental results.

III. EXPERIMENTAL RESULTS

A standard intensifier-driven liquid pressure system is used in this experiment. A schematic diagram of the system is shown in Fig. 1. The pressure system is capable of producing hydrostatic pressures of 10 000 kg/cm^2. Both petroleum ether and 1 to 3 centistoke Dow-Corning 200 fluid are used as pressure fluids. The pressure in the system is measured by means of a coil of No. 40 B and S manganin wire in a separate pressure vessel located in a region of fairly constant temperature. After a 5-hr anneal at 140°C in mineral oil, the manganin coil is calibrated by measuring the coil resistance at atmospheric pressure and at the freezing pressure (7640 kg/cm^2) of mercury at 0.00°C. According to Bridgman,[13] the pressure coefficient of manganin is constant within one half percent from 0 kg/cm^2 to 12 000 kg/cm^2.

The pressure vessel is maintained at a uniform temperature by means of a large oil bath which can be raised to completely cover the vessel. The well-stirred temperature bath is controlled by a differential mercury thermoregulator. Observations with a Beckmann differential mercury thermometer show the oil bath temperature regulation to be ±0.02 C° for better than a day. Absolute temperature measurements are made with ASTM thermometers with calibrations certified to ±0.02C°. The absolute temperature of the interior of the pressure vessel is assumed to be the value recorded in the oil bath after thermal equilibrium is reached.

A chromel-alumel thermocouple calibrated against the ASTM thermometers indicates that the fluctuations in the internal temperature of the vessel are smaller than the thermocouple calibration error of about ±0.03C°. Agreement between internal and external temperature readings is also within ±0.03C° after thermal equilibrium is established.

The specimen-dummy arrangement and electrical measuring apparatus are similar to those used by Kauffman and Koehler[2] and by Bauerle and Koehler.[3] A bridge (see Fig. 2) compares the resistance of the quenched specimen with that of an unquenched dummy. In most experiments of this type, the specimen-dummy resistance difference is measured at liquid nitrogen or even liquid helium temperature to reduce the lattice contribution to the resistivity. The large thermal inertia of the pressure system requires that all measurements of quenched-in resistance in this experiment be carried out at the annealing temperature. Thus, a differential resistance measurement is even more important, since the dummy must balance out the thermal resistance of the specimen so that only the excess resistance due to quenched-in vacancies is measured.

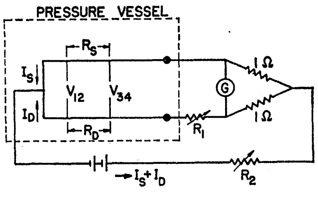

FIG. 2. Schematic diagram of bridge used to compare specimen and dummy resistance.

The specimen-dummy potentials are measured with a Rubicon type 2767 μv potentiometer which can detect potential differences of less than 10^{-8} v. Bridge balance is limited by the accuracy of the standard resistors to one part in 25 000. Since the measuring current is kept at 0.10000 amp, the smallest specimen resistivity change which can be detected is 10^{-11} ohm cm for the specimen used in this experiment. This resistivity corresponds to about 0.1% of the resistivity quenched in from 700°C. The direction of the measuring current is reversed for each measurement and the average of the two voltage readings taken, in order to cancel out thermal emf's. The thermal emf's are found experimentally to be about 0.6 μv out of a total emf of the order of 10 μv. As will be discussed later, fluctuations in specimen-dummy temperature difference rather than bridge sensitivity limit the experimental accuracy in measuring the resistance quenched in.

The specimen and dummy are mounted on the apparatus plug of the pressure vessel as shown in Fig. 3. Electrical leads through the plug are of the standard pipestone cone insulated type. The pipestone cones have a wall thickness of about 0.012 in. and provide a resistance of at least 100 meg between the steel conductor cones and the plug at all temperatures and pressures encountered in the present experiment. Since the resistance of the specimen and dummy is less than 0.1 ohm, the cone resistance would have a negligible effect on the experimental accuracy even if it should decrease by several orders of magnitude.

The insertion of the steel cone in the copper potential lead does not present a serious problem despite a large copper-steel thermal emf, because of the current reversal in the measuring procedure. In addition to the steel cones, a chromel and an alumel cone permit the use of an internal thermocouple when the vessel is closed during the pressure run. The thermocouple junction is placed as close to the center of the specimen wire as possible, but is not in direct contact with it. After being mounted on the apparatus plug, this thermocouple is calibrated aginst the ASTM thermometers by placing the entire apparatus plug in a small oil bath.

The specimens are made from hard drawn 99.999% pure gold wire 0.016 in. in diameter.[14] Residual resistance measurements on well annealed samples confirm the purity quotation. The room temperature resistivity

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[13] P. W. Bridgman, *The Physics of High Pressures* (G. Bell & Sons, Ltd., London, 1952).

[14] Supplied by Sigmund Cohn Corporation, Mount Vernon, New York.

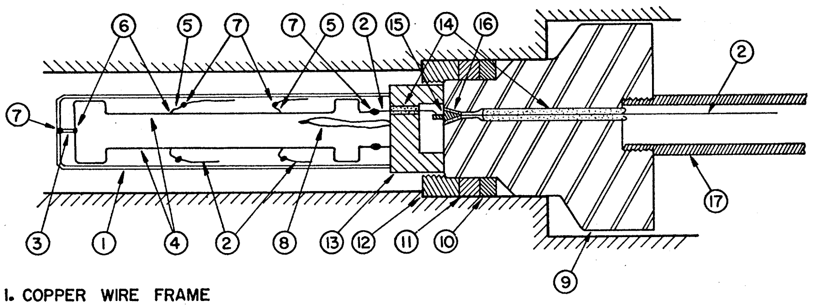

FIG. 3. Cross section of apparatus plug in place in pressure vessel showing arrangement of specimen and dummy, thermocouple location, and pressure seals. For clarity, only one electrical lead through the plug is shown.

1. COPPER WIRE FRAME
2. #22 ENAMELED COPPER WIRE
3. .030″ GOLD WIRE
4. .016″ GOLD WIRE
5. .002″ GOLD WIRE
6. SPOT WELD
7. HARD SOLDER
8. THERMOCOUPLE
9. SAE 4340 STEEL APPARATUS PLUG
10. LEADED STEEL PACKING RING
11. COPPER PACKING RING
12. STEEL EXTRACTOR RING
13. BRASS HOLDER
14. ALUNDUM TUBING
15. COLD-ROLLED STEEL CONE
16. PIPESTONE CONE
17. LEAD-OUT TUBE

of a sample of the wire from which the specimen and dummy used in the pressure runs were taken was 4.99×10^{-6} ohm cm. The liquid helium temperature (4.2°K) resistivity was 7.84×10^{-10} ohm cm, giving a resistivity ratio $[\rho(293°\mathrm{K})/\rho(4.2°\mathrm{K})]$ of 6350. Measurement of the resistivity ratio of a section of the specimen itself after the series of pressure runs had a ratio of better than 1500. Accidental damage to the specimen after the runs prevented a more accurate measurement.

Potential leads of 0.002-in. diam, 99.999% pure gold wire are spot-welded to the specimen and dummy wires as shown in Fig. 3. A jig holds the specimen and dummy wires parallel while the 0.002-in. leads are held perpendicular to the specimen and dummy and spot welded in place. This procedure keeps the dummy gauge length as nearly equal that of the specimen as possible. The gauge length is about 5 cm. The 0.016-in gold wire is then formed as shown in Fig. 3. The loops at the ends of the specimen and dummy keep thermal gradients away from the gauge length when they are being heated. Observations with an optical pyrometer show uniform temperature to within 2C° along the gauge length at the quench temperature.

After assembling, the specimen and dummy are heat-treated at 950°C for 60 min, 720°C for 5 min, and 500°C for 60 min by passing an electric current from a bank of storage batteries through the wire.

To determine the feasibility of making resistance measurements when the specimen and dummy were maintained at the annealing temperature, a light quench frame patterned after that described by Bauerle and Koehler[3] was constructed. Specimens were quenched by springing the frame into a tank of water. Measurements of the total resistance quenched in were made with the specimen frame in a stirred ice-water bath. Measurements of the annealing rates were made with the frame in a small water bath, controlled by a system similar to that used on the large oil bath.

The experimental procedure for the pressure anneals is somewhat more complicated. The apparatus plug is mounted in a counterweighted cradle as shown in Fig. 4. A Lucite shield over the apparatus protects the heated specimen from drafts. The temperature of the heated specimen is determined by comparing the ratio of the specimen resistance at the elevated temperature to its resistance at 17.3°C, $R(T)/R(17.3°\mathrm{C})$, with the resistivity ratios taken from the data of Northrup[15] and of Meechan and Eggleston.[16]

Before each run, the apparatus plug is placed in the quench cradle and the specimen held at 950°C for 5 to 10 min, at 720°C for 5 to 10 min, and at 500°C for 15 to 20 min. The plug is then placed in a small oil bath which is controlled to within 0.02C° of the large oil bath temperature and the initial specimen-dummy resistance difference is measured. The resistance difference is taken as $\delta R=(\bar{V}_{34}-\bar{V}_{12})/I_m$, where $\bar{V}_{34}$ and $\bar{V}_{12}$ are the averages of the potentials between the two points shown in Fig. 2 for I_m, the measuring current, in the forward and reverse direction. The fact that this resistance difference has a nonzero value indicates that the dummy does not exactly compensate for the specimen in the well-annealed state. It is therefore necessary to measure δR for the well-annealed state as a function of both pressure and temperature. The temperature calibration is taken care of simply by measuring δR_b, the specimen-dummy resistance difference before quench, at the

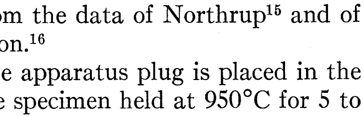

FIG. 4. Sketch of quenching apparatus. Cradle pivots on knife-edge, dropping heated specimen into water.

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[15] E. F. Northrup, J. Franklin Inst. **177**, 287 (1914).

[16] C. J. Meechan and R. N. Eggleston, Acta. Met. **2**, 680 (1954).

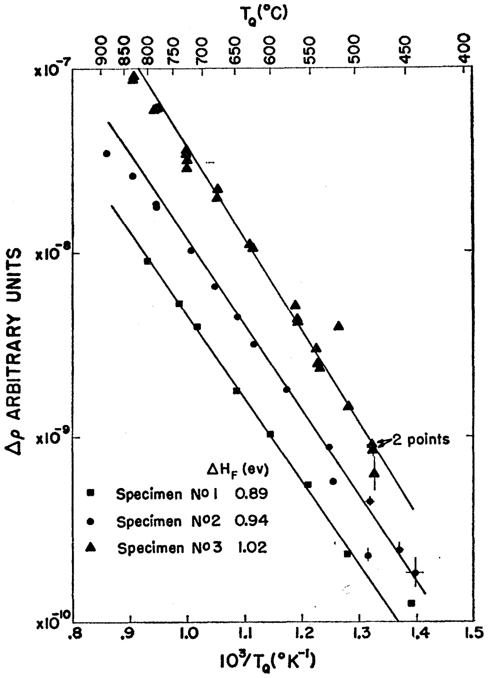

FIG. 5. Semilogarithmic plot of quenched-in resistivity vs reciprocal of the absolute quench temperature. Curves are displaced vertically for the sake of clarity.

annealing temperature, since the anneals are isothermal. The effect of pressure is determined by measuring $\delta R_b(P)$ on a well-annealed specimen held at the annealing temperature. The calibration is rechecked after every third or fourth anneal.

After the measurement of δR_b, the apparatus plug is placed in the quenching cradle and the specimen is heated and quenched. No measurement of the quench rate is made since all quenches are from 700°C±15C°, and the amount quenched in is reproducible and is comparable to the amount quenched in by Bauerle from 700°C. The specimen, dummy, and frame are rinsed with alcohol to remove any water remaining after the quench. A semicylinder of brass is then attached to the apparatus plug to fill the free volume of the vessel and to minimize thermal gradients within the vessel. The apparatus plug is placed in the pressure vessel, the closures tightened, and the oil bath raised about the vessel. Both the oil bath and the pressure vessel are preheated to the annealing temperature to minimize the time required to establish thermal equilibrium. The internal temperature of the pressure vessel is monitored with the internal thermocouple from the time that the pressure fluid is added, so that some correction for the warmup period can be made.

Pressure is applied either immediately after raising the oil bath or after 40 to 50% of the quenched-in resistance has annealed out. The pumping process requires 20 to 30 min. On the runs in which the pressure is applied at the beginning of the anneal, pressure is released after 40 to 50% of the quenched-in resistance has annealed out. The pressure release is made over a period of 5 to 10 min so that there is no danger of deforming the specimen by sudden pressure fluid surges.

Because of the low heat capacity and thermal conductivity of the pressure fluid, convection currents caused by Joule heating of the specimen can easily produce a temperature difference of several hundredths of a degree between the specimen and dummy when the power dissipation by the 0.016-in. wire is as low as 0.01 w. (The resistance of the entire length of the 0.016-in. wire is about 0.08 ohm). A simple calculation shows that a temperature difference of 0.01C° between the specimen and dummy results in a resistance difference corresponding to about 1% of the resistance quenched in from 700°C. It was found experimentally that a current of 0.1 amp is the maximum value consistent with a thermally induced scatter of less than 2% of the total resistance quenched in. It is this scatter which limits the accuracy of the resistance measurements. Further reduction of the measuring current does not result in a commensurate decrease in scatter and therefore leads only to a loss in sensitivity.

A typical set of data shortly after quench for a measuring current of 0.10000 amp is

	V_{12}	V_{34}
forward current	4.968 μv	−8.698 μv
reverse current	4.180 μv	−9.172 μv
average value	4.574 μv	−8.931 μv

The thermal emf's are seen to be about 0.6 μv. The difference between the two readings is $\bar{V}_{34}-\bar{V}_{12}=-13.505$ μv. The sign of the measuring current is negative, so that the resistance difference between the specimen and dummy is 135.05 μohm. Since the resistance difference before quench was 111.11±0.11 μohm, the quenched-in resistance present in the specimen is 23.94 μohm. The error in this reading due to statistical and thermally induced fluctuations is about ±0.3 μohm.

IV. RESULTS

A. Quenched-In Resistance

Before beginning a discussion of the data, a number of frequently used terms will be defined:

R_0 = resistance of the specimen at 0°C;
δR = measured resistance difference between specimen and dummy, $\delta R=[(\bar{V}_{34}-\bar{V}_{12})/I]$;
$\delta R_b = \delta R$ measured before quench;
$\delta R_a = \delta R$ measured after quench;
$\Delta R_0 = \delta R$ immediately after quench $-\delta R_b$ = total resistance quenched into specimen;
$\Delta R = \delta R_a - \delta R_b$;
T_Q = temperature from which specimen is quenched;
T_A = temperature at which specimen is annealed.

The dependence of the quenched-in resistivity, Δρ, on quench temperature is shown in Fig. 5, where a semilogarithmic plot of $\Delta\rho$ vs $1/T_Q$ is made for three different specimens. For low quench temperatures, the results are consistent with the simple exponential relationship, $\Delta\rho=A\ \exp(-\Delta H_f/kT)$. It is seen that for quench temperatures above 800°C there is a deviation from linearity. This deviation toward lower resistivities, generally observed in quenching experiments, is attributed to a loss of vacancies during quench. Bauerle[3] obtained an increase in quench rate by using a salt-water quench bath and also by forcibly springing the wire through the quench bath. In the present experiment, all pressure runs are made from quench temperatures near 700°C, so no special attempts are needed to increase the quench rate. It is emphasized that these measurements were made to check the quench apparatus and are not offered as accurately determined values. They serve to show that the present quench techniques result in values of ΔH_f compatible with other experiments.

B. Atmospheric Pressure Anneals

Annealing behavior was studied only for quench temperatures near 700°C, because of the increased complexity of the annealing kinetics for quenches from higher temperatures.[3] Since the light quench frame used in these runs comes to equilibrium with the anneal bath in a few minutes, no warmup correction is necessary. In the anneals where the bath temperature is raised from 40° to 60°C, correction for the temperature shift in δR due to the uncompensated specimen resistance is made by matching the slopes of the anneal curves at the time of the temperature increase.

The data are shown in a semilogarithmic plot of $(\Delta R/\Delta R_0)$ vs t for comparison with Eq. (12). The ΔH_m values are taken from the tangents to the annealing curves at the point of the temperature change using Eq. (13). The use of the tangents is necessary since first-order kinetics are not obtained. Other workers report a constant value of ΔH_m during an anneal, regardless of the annealing kinetics, indicating that ΔH_m is independent of the vacancy concentration. Because of this fact, it is a matter of experimental convenience at which point the temperature is changed. The slope for each anneal temperature is most accurately determined when the temperature is changed after 50% of the quenched-in resistance has annealed out.

The data and the values of ΔH_m derived from the two-temperature anneals are tabulated in Fig. 6. Although the value for the faster anneal is lower than that for the two slower anneals, the three ΔH_m determinations agree within experimental error. The average value for ΔH_m is 0.79±0.10 ev. This result compares well with the values for T_Q less than 750°C determined by Bauerle.[3]

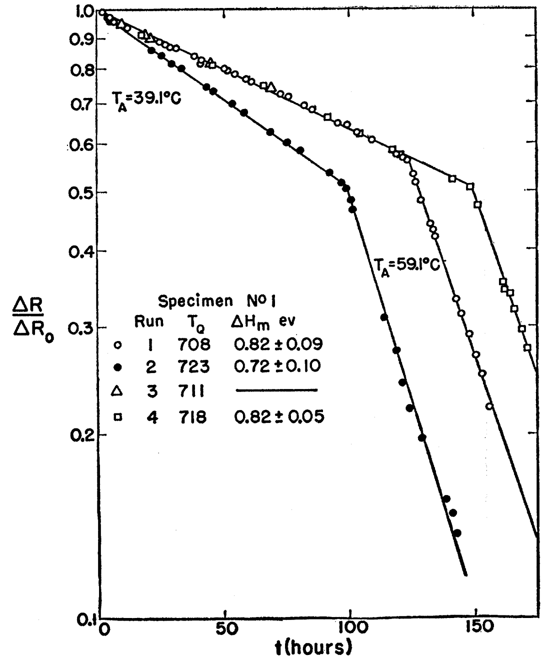

FIG. 6. Energy of motion determination for three quench temperatures near 700°C and anneals at 39.1° and 59.1°C.

C. High-Pressure Anneals

The pressure effect on the anneal rate, in principle, could have been most accurately detected by the change in $\tau_{\frac{1}{2}}$, the time required for one-half of the quenched-in resistance to anneal out at a constant temperature. However, factors other than pressure also have a large effect on $\tau_{\frac{1}{2}}$. In the E_m determinations (see Fig. 6), where quench and anneal temperatures were identical, three anneals had 150-hr half-times, the fourth had only a 100-hr half-time. To cancel the differences caused by other factors, pressure effects in the present experiment were determined by comparing the annealing rate at pressure with that at some reference pressure during the course of a single anneal. Thus, all factors except for pressure were the same during an anneal. In two runs with atmospheric reference pressures, the ΔR values show considerable scatter. A reference pressure of 50 kg/cm² to 100 kg/cm² seems to suppress the scatter, but higher pressures do not decrease the scatter further. Scatter at atmospheric pressure is attributed to vaporization of the volatile pressure fluid, causing currents in the fluid which result in temperature differences between the specimen and dummy.

In treating the data, two corrections must be applied. First, pressure corrections as described in Sec. III are applied to all measurements of ΔR made at pressures above 1000 kg/cm² to account for pressure-induced changes of resistivity in the uncompensated length of the specimen. The correction to ΔR at a pressure of 10 000 kg/cm² is roughly 5 to 10% of the resistance quenched in from 700°C.

Second, the fact that about 2 hr are required for the temperature inside the pressure vessel to come to within 0.03C° of equilibrium requires a temperature correction

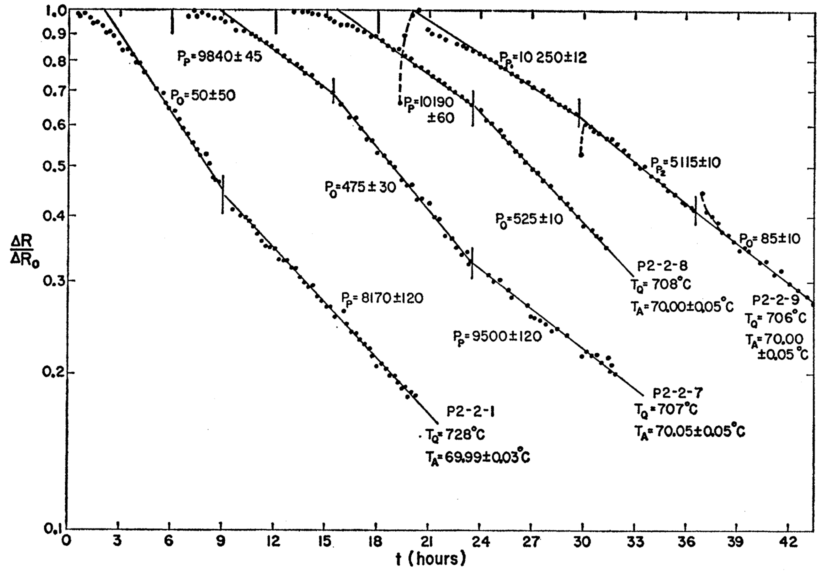

FIG. 7. Influence of pressure on isothermal annealing rate. Curves are displaced horizontally for clarity; time origins are indicated by heavy vertical lines. All pressures are in kg/cm^2.

during the initial portion of the anneal. Three or four strokes of the intensifier piston are made to bring the system to full pressure, causing the temperature to fluctuate over a range of 50C° in a short period. Similar temperature changes occur when the pressure is released during an anneal. The effect of these temperature changes is compensated by shifting the time scale of the anneal. A plot of the internal thermocouple readings as a function of time is approximated by constant-temperature line segments. Using the measured energy of motion, the ratio of annealing rate Σ_1 at the actual temperature to the annealing rate Σ_2 at the equilibrium annealing temperature is determined from Eq. (13). The effective annealing time at the equilibrium temperature can be derived, the effective time origin determined, and the data plotted as in the atmospheric pressure anneals, i.e., a semilogarithmic plot of $(\Delta R/\Delta R_0)$ vs t. The compensated data for some typical pressure runs are shown in Fig. 7.

The slopes of the annealing curves are determined by drawing the best straight lines through the experimental points. The error in the slopes is estimated by drawing the maximum and minimum slopes through the points. Despite the warmup correction, there is some initial curvature before the straight line portion of the annealing curve is reached, resulting in some error in determining the slope. The estimated error limits are unsymmetrical because of the curvature and range from 5 to 10% of the slope value. Except for the few anneals which exhibit little scatter and curvature, the data are also treated by a least-squares analysis. The resulting slope values agree within a few percent with the graphically determined slopes. The calculated standard deviation, which is a measure only of the statistical scatter of the data, is generally 2 to 3% of the slope value. For the least-squares analysis, only those points in the straight-line portion of the curve are used. However, because of the initial curvature, there is some uncertainty in the choice of the number of points to be fitted to a straight line.

The data for the pressure anneals are listed in Table II. P_p is the pressure at which the anneal rate was determined; P_0 is the reference pressure. Σ_p is the slope of the annealing curve at P_p; Σ_0 is the slope at P_0. The errors indicated for the slopes are the standard deviations only. In view of the discussion above, a more accurate estimate of the slope error would be ±5%, resulting in an error in the ratio of slopes of 7 to 8%. The error in the logarithm of the ratio is therefore ±10% to ±12%, since the ratio is between $\frac{1}{2}$ and 1.

Indicated anneal temperature errors are the relative fluctuations. This error figure is important as an indication that the anneal is isothermal. Absolute temperature errors are probably less than 0.2C° and therefore negligible in determining the value of ΔV_m. Absolute pressure errors are less than 1 percent and are also negligible.

The experimental values of $-kT\ln(\Sigma_p/\Sigma_0)$ are plotted as a function of $\Delta P=P_p-P_0$ in Fig. 8. The points are fitted with a least-squares straight line passing through the origin. The resulting value of $-kT(\Delta\ln\Sigma/\Delta P)$ is 2.40×10^{-24} cm^3 with a weighted mean error of $\pm0.23\times10^{-24}$ cm^3.

Systematic errors in T_Q are relatively unimportant in the accuracy of the present experimental results. The simple theory derived in Section II indicates that the annealing kinetics should be independent of T_Q. Bauerle's[3] results show that the annealing kinetics do depend on T_Q, but only in a qualitative way. As long as T_Q is less than 750°C, the annealing kinetics appear to be simple and to be independent of T_Q. In the present experiment, the quench temperatures are reproducible from quench to quench, as are the concentrations

TABLE II. Summary of data for pressure runs. ΔR_0 is the total resistance quenched in from temperature T_Q. Isothermal anneals are made at temperature T_A and the logarithmic slope $\Sigma_P = d(\ln\Delta R)/dt$ is measured at pressure P_p. The slope Σ_0 is measured at the reference pressure P_0.

Run	T_Q (°C)	ΔR_0 (μohm)	T_A (°C)	P_p (kg/cm²)	P_0 (kg/cm²)	$\Sigma_p \times 10^5$ (sec⁻¹)	$\Sigma_0 \times 10^5$ (sec⁻¹)	$-kT \ln(\Sigma_p/\Sigma_0)$ (ev)
1	728	30.5±0.3	69.99±0.03	8170±120	1	−2.209±0.003	−3.186±0.014	0.0109±0.0006
2	722	37.0±0.4	70.10±0.10	8200± 50	1	−4.72 ±0.04	−5.84 ±0.24	0.0062±0.0012
3	713	33.7±1.0	70.06±0.05	8070± 55	930± 20	−3.783±0.038	−4.345±0.08	0.0040±0.0007
4	722	33.1±0.3	70.07±0.07	7290± 25	960± 24	−2.89 ±0.03	−3.64 ±0.08	0.0068±0.0007
5	715	25.5±0.3	70.00±0.13	9940±150	82± 16	−1.760±0.035	−3.034±0.054	0.0161±0.0008
7	707	28.1±0.5	70.05±0.05	9840± 45	475± 30	−1.528±0.016	−2.474±0.040	0.0142±0.0007
				9500±120[a]		−1.55 ±0.05		0.0137±0.0010
8	708	27.7±0.6	70.00±0.05	10190± 60	525± 10	−1.47 ±0.03	−2.26 ±0.03	0.0128±0.0013
10	703	29.8±0.3	70.07±0.07	7085± 15	170± 5	−0.865±0.03	−1.21 ±0.04	0.0100±0.0012
11	700	28.5±0.3	70.15±0.10	5195± 15	85± 10	−0.819±0.04	−1.02 ±0.03	0.0066±0.0011
12	703	27.8±0.3	80.04±0.07	9050±150	100±100	−1.64 ±0.05	−2.93 ±0.85	0.0176±0.0011
13	708	30.7±0.2	79.98±0.05	9400±150	100±100	−1.95 ±0.04	−2.80 ±0.09	0.0111±0.0008
14	707	30.7±0.2	80.01±0.07	9300±150	150±150	−1.620±0.015	−2.939±0.027	0.0182±0.0005
16	704	32.3±0.3	79.95±0.05	7315± 10	110± 10	−1.375±0.015	−1.88 ±0.02	0.0100±0.0005

[a] This run was made with pressure on, off, then on again. Thus, two slope ratios result. See anneal P2-2-7 in Fig. 7.

quenched in. Reproducibility of quench temperature is more important than accuracy in determining the absolute value of T_Q as long as T_Q is less than 750°C. It is unlikely that the absolute T_Q values are in error by more than 10°C.

V. DISCUSSION

A. Atmospheric Pressure Data

Quenches

The quench data are consistent with the vacancy model, in which the equilibrium concentration of vacancies at the quench temperature is trapped in by rapid cooling. Since the quenches in the present experiment were made only to check techniques, sufficient data for an accurate determination of the pertinent parameters were not taken. For a discussion of quench results, attention is called to quenching experiments on gold (see references 3, 4, 17) and on aluminum and platinum (see references 18, 19).

Anneals

The model of a random distribution of vacancies diffusing to a random distribution of sinks has been shown to result in first-order kinetics for the annealing process. While Bauerle[3] reports first-order kinetics for anneals with low initial vacancy concentrations, other workers[17,20,21] report a variety of kinetics other than first order over the entire quench-temperature range. In the present experiment it was observed during the ΔH_m determination anneals that the annealing rate decreased slowly with time. The decrease became quite noticeable after 80% of the quenched-in resistance had annealed out. The data could be arbitrarily fitted to a relation of the form

$$\log(\Delta R - \delta/\Delta R_0) = bt. \tag{17}$$

The resistance change ΔR already contains a term in the form of an additive constant to correct for the temperature effect on the uncompensated portion of the specimen. An error in this term could appear as a departure from first-order kinetics. However, the magni-

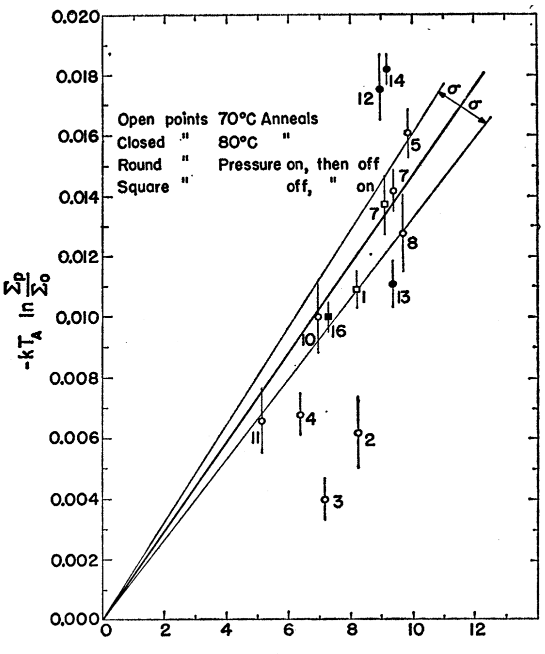

FIG. 8. Experimental values of $-kT\ln(\Sigma_p/\Sigma_0)$ vs ΔP, where ΔP is the difference between the pressures at which the isothermal annealing rates Σ_p and Σ_0 were measured. The heavy line is the least-squares fit of the data, while the lighter lines indicate slopes one standard deviation, σ, from the best slope.

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[17] F. J. Bradshaw and S. Pearson, Phil. Mag. 2, 379 (1957).

[18] F. J. Bradshaw and S. Pearson, Phil. Mag. 1, 812 (1956).

[19] W. DeSorbo and D. Turnbull, Phys. Rev. 115, 560 (1959).

[20] B. G. Lazarev and O. N. Ovcharenko, J. Exptl. Theoret. Phys. (U. S. S. R.) 36, 60 (1959).

[21] M. Meshii, F. Mori, and J. W. Kauffman, Bull. Am. Phys. Soc. 4, 455 (1959).

tude of δ in the above expression was more than half the temperature correction. It is unlikely that such a large error could be made in the correction term.

To remove the uncertainties caused by changing the annealing temperature during the course of an anneal, a series of isothermal anneals were made. Values of specimen-dummy resistance before and after quench were measured in the annealing bath at the annealing temperature so that no temperature correction was required. The results of some of these anneals, shown in Fig. 9, reveal the same slower than exponential annealing rate observed before. Thus, the observed behavior is not due to an error in the temperature correction. Treatment of the data with the relation (17) again resulted in a straight line when a suitable δ was chosen. In most cases, the anneals were stopped when the deviation from first-order kinetics became apparent, so that 15 to 20% of ΔR_0 still remained.

A few very long anneals were made to see if Eq. (17) was valid at low vacancy concentrations. In one instance, run P1-1-1 Fig. 9, the temperature was raised to 100°C for 24 hr after 60% of ΔR_0 had annealed out and then returned to the initial annealing temperature. The remaining resistance, ΔR, was found to be less than 4% of ΔR_0. Since the scatter of the data at the very small ΔR values is large, a more reasonable estimate of the residue is $2\% \pm 2\%$ of ΔR_0. Other long anneals showed similar low resistance residues. It is therefore concluded that any residue, if present, is small and that the relation expressed by Eq. (17) is an approximation for only a limited portion of the anneal.

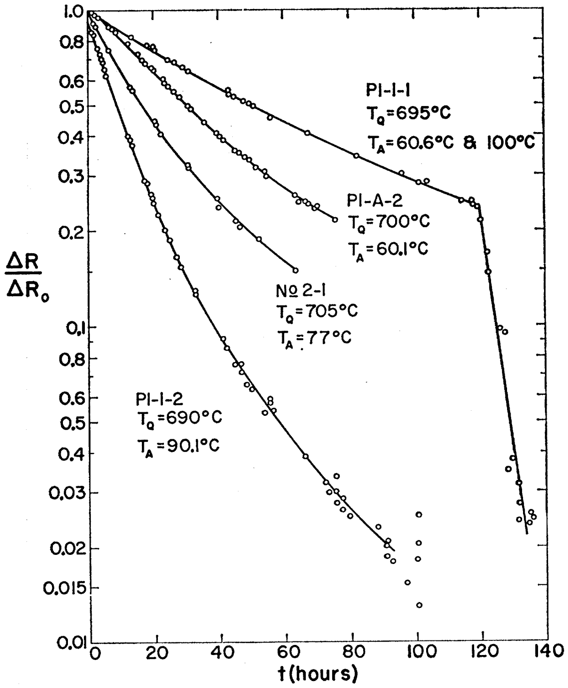

FIG. 9. Semilogarithmic plot of $\Delta R/\Delta R_0$ vs t for isothermal anneals, showing the relative effects of anneal temperature and specimen preparation. Preparation procedures are described in the text.

It is possible that the dislocation density also has an effect on the annealing kinetics. An attempt was made to reduce the dislocation content of the specimen below that resulting from the standard heat treatment to see if any change in annealing kinetics occurred. Heat treatments long enough to permit diffusion over lengths comparable to the specimen dimensions are required to move dislocations out of the crystal. Gold self-diffusion data[22] show that at the standard 950°C heat treatment 10 hr would be required for a diffusion distance of 8 mils, the radius of the wire. In the one-hour heat treatment, the diffusion distance was 2.5 mils. This should have been sufficient to remove a large part of the cold-work in a new specimen.

To determine experimentally the effect of heat treatment on the annealing behavior, a specimen was placed in a furnace and held at more than 1000°C for 12 hr. After removal from the furnace, the specimen was mounted in the quench frame and its temperature raised to 950°C for one hour, 500°C for two hours, and 400°C for one hour to remove the cold-work incurred during mounting. The specimen was then quenched from 700°C and annealed at 60°C. The results are shown in Fig. 9, specimen P1-1-1. The annealing half-time of 50 hr is roughly double that of specimens heat-treated for the standard one hour at 950°C, consistent with previous similar measurements by Bradshaw and Pearson.[17] Because of this increase in $\tau_{\frac{1}{2}}$, it can be assumed that the dislocation density has decreased. However, within the accuracy of the measurements, the annealing kinetics do not differ from those of specimens receiving the standard heat treatment.

It is possible that impurities can cause a departure from the first-order kinetics predicted by the simple model of random vacancies and sinks. An impurity atom can pin a dislocation so that it cannot climb. As vacancies reach jogs in a pinned dislocation, no climb occurs and the dislocation becomes ineffective as a sink. Thus the sink concentration could decrease with time, as dislocations become pinned during climb while the excess vacancies are removed. It is not known if the impurity concentration indicated by residual resistance measurements on the present specimens is compatible with the observed decrease in annealing rate with time. It would be desirable to study the effect of impurity concentration on the annealing behavior.

B. Pressure Anneals

From Eq. (16) it is seen that the value of the activation volume for motion depends not only on the pressure derivative of the annealing rate, but also on the pressure derivative of the frequency factor ν_0. No detailed calculations of ν_0 have been made, since a knowledge of the

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[22] S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) 70, 545 (1957).

vibrational spectrum in the neighborhood of a vacancy is required. However, Lawson, Rice, *et al.*[23] have estimated that in the region of a vacancy the normal mode frequencies may vary by a factor of three, while the factor ν_0 may vary by only 10 to 20%. As a first approximation, therefore, it is reasonable to use the volume properties of the crystal to estimate the pressure effect on ν_0. The natural frequency of vibration of a harmonic system is given by v/λ, where v is the wave velocity in the system and λ the wavelength. For our approximation it is assumed that ν_0 is proportional to the ratio of the velocity of the elastic wave propagation through the crystal to the atomic spacing. The experimental data of Daniels and Smith[24] give the effect of pressure on the velocity of propagation of elastic shear waves in gold. The elastic wave velocity, v, is given by $Y=\mu v^2$, where Y is the elastic constant and μ is the density of the crystal. Taking an average value for the experimental pressure derivatives of the two shear wave velocities,

$$kT(\partial \ln\nu_0/\partial P)_T \simeq kT(\partial \ln v/\partial P)_T = 8\times10^{-26}\ \text{cm}^3,$$

for $T=70$°C. Approximately the same value results when the change in the longitudinal wave velocity is considered. This value is small compared with the logarithmic pressure derivative. It is, in fact, a factor of three smaller than the statistical error in the logarithmic pressure derivative and for this reason has been neglected in determining the value of ΔV_m.

The value for ΔV_m measured in the present experiment is $(2.48\pm0.23)\times10^{-24}$ cm^3. This value is 15% of the atomic volume of gold, 17×10^{-24} cm^3. In terms of molar volumes, $\Delta V_m=1.50\pm0.14$ cm^3/mole and the atomic volume is 10.2 cm^3/mole.

It is interesting to compare this result with a prediction based on the macroscopic elastic constants. Lazarus[25] has estimated the change in the energy of motion of an impurity, ΔH_{mi}, diffusing into an adjacent vacancy relative to that for a solvent atom by considering the changes in the shear modulus of the lattice in the vicinity of the impurity. He shows that for the case of noble metals, the change in energy of motion for the impurity may be related to the change in the small shear modulus by

$$\Delta H_{mi}=\Delta[V\times\tfrac{1}{2}(c_{11}-c_{12})]. \tag{18}$$

where V is the atomic volume. This analysis should be equally valid for pressure-induced shear modulus changes. The data of Daniels and Smith[24] show that at 10 000 kg/cm^2, the change in the elastic modulus $\frac{1}{2}(c_{11}-c_{12})$ is 4.30×10^9 ergs/cm^3. Combining this value with the atomic volume of gold, 17×10^{-24} cm^3, results in a value for ΔE_{mi} of 0.046 ev. In the present experiment, the value of ΔV_m is 2.48×10^{-24} cm^3. Assuming that $\delta\Delta H_m=P\Delta V_m$, the pressure-induced change in energy of motion, $\delta\Delta H_m$, at 10 000 kg/cm^2 is 0.015 ev. Thus, Eq. (18) overestimates the experimentally determined change in energy of motion by a factor of three.

A pressure dependence of ΔV_m is possible, and some pressure diffusion experiments indicate a slight pressure variation of ΔV_m.[26–28] No such effect is found, within limits of error, in the present experiment. It may be desirable to extend the pressure range of the experiment to reduce the fractional errors in the logarithmic slope ratio. Since the absolute errors are relatively constant, the magnitude and pressure dependence of ΔV_m could then be determined with much greater accuracy.

There is no apparent dependence of the pressure derivative of the slope ratio on the order in which the pressure is applied, i.e., in the first or second half of the anneal. Furthermore, no unexpected differences are observed between the 70° and 80°C anneals, despite an increase in the annealing rate at the higher temperature. Thus, to the accuracy of the experiment, the derived ΔV_m appears to be independent of vacancy concentration and of the annealing rate. For the simple model of vacancies diffusing to sinks, no such dependence would be expected.

The data are not sufficiently accurate enough to indicate any temperature dependence of the activation volume. Higher annealing temperatures would result in such short annealing times that the warmup period would occupy the major portion of the measurable anneal. Lower annealing temperatures would result in such long anneals that the pressure could not be maintained long enough to measure the annealing rate accurately. Again, it would be desirable to extend the pressure range so that more accurate slope ratios could be measured and a possible temperature dependence investigated.

In addition to the jump rate of the vacancies, pressure could also affect the effective sink concentration. If such were the case, the observed changes in annealing rate could not be used to derive an activation volume for motion of the vacancies. The possibility of such effects and their influence on the annealing rate will now be considered.

First, the density of dislocations might change with pressure. At the pressures reached in the present experiment, the PV energy available per lattice site is only about 0.01 ev. Thus, very few dislocations could be moved out of the crystal at the annealing temperature during the time of an anneal. As was shown earlier, several hours at 1000°C are necessary to make an appreciable change in the sink concentration.

Second, the pressure-induced change in strain dis-

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[23] A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960).

[24] W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).

[25] D. Lazarus, in *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955), p. 111ff.

[26] N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, J. Chem. Phys. **20**, 1189 (1952).

[27] G. W. Tichelaar, R. V. Coleman, and D. Lazarus, (to be published).

[28] R. V. Coleman (private communication).

tribution about a dislocation could change its cross-section for trapping a vacancy. Such a change would affect the average number of jumps required for a vacancy to reach a sink. It is estimated[29] that the effect of a dislocation is felt over only a few atomic distances. Even changing this number by an order of magnitude would not change appreciably the number of random jumps required for a vacancy to reach a sink. Thus, since it is estimated that 10^6 jumps[3] are required to reach a dislocation,[30] this pressure effect would be negligible.

These estimates indicate that the effect of pressure on the dislocation sink density probably does not change the annealing rate. If any appreciable change in sink concentration does occur because of pressure application, the change is reversible, for in the series of pressure anneals the only change in annealing rate between successive runs was a slow increase in $\tau_{\frac{1}{2}}$. This increase has already been explained in terms of the removal of dislocations by the prequench heat treatment. It is concluded that the observed pressure effects on the annealing rate of the quenched-in resistance are due only to changes in the jump frequency of the vacancies.

C. Comparison of Results with Theory and Experiment

As noted earlier, a hard-spheres atomic model predicts a total activation volume for diffusion of two atomic volumes, while pressure diffusion measurements give a derived value of one-half an atomic volume. The present value for the volume of motion of 15% of the atomic volume is consistent with the low values observed in the diffusion experiments. It has been proposed that relaxation of the atoms neighboring a vacancy will account for the small experimental values of the volumes associated with the diffusion process.

A number of calculations pertinent to this effect have been made of the lattice distortion around a vacancy. Theimer[31] compares calculations of the entropy of formation of a vacancy in NaCl with experimental values and concludes that the relaxation of the atoms surrounding the vacancy is of the order of thermal amplitude. Calculations for crystalline rare gases by Kanzaki[32] for a discrete atomic lattice model using a normal-coordinate expansion of the type used in the dynamical diffusion theory result in nearest-neighbor relaxations of a fraction of a percent of the interatomic spacing. Nardelli and Repanai[33] use an elastic model and a Lennard-Jones 6–12 potential for crystalline rare gases and obtain the same result as Kanzaki. Again, negligible relaxation of the neighboring atoms result from calculations of static lattice energies in metals by Girifalco and Streetman[34] and by Hall.[35] These calculations support the hard spheres model for ΔV_f.

Lawson *et al.*[23] point out that no relaxation is possible for the case in which the restoring force is linear in the displacement, as in the elastic continuum models. It is anharmonic forces which are responsible for relaxation and such forces must be included in the calculations if the relaxation is to be determined. Lawson *et al.* consider a simple cubic crystal with a vacancy and its six nearest-neighbor atoms. The six-atom shell is assumed stable, and its interaction with the surrounding atoms is simulated by adjusting the force constants among the atoms. The calculation indicates a relaxation of about $\frac{1}{3}$ of an atomic volume about a vacancy. Tewordt[12] uses a more refined model in which the discrete nearest-neighbor atoms of a vacancy in an fcc crystal are considered to be nonelastically deformed. These atoms are joined by a set of proper elastic solutions to the bulk of the crystal by an intermediate region of discrete elastically deformed atoms. This calculation indicates a relaxation of as much as $\frac{1}{2}$ an atomic volume about a vacancy in copper.

Experimental evidence for relaxation is indirect. Using a theoretical value for $\Delta\rho$/atom percent of 1.3×10^{-6}, Bauerle[3] uses his values of A in the relation

$$\Delta\rho = A \exp(-\Delta H/kT), \tag{19}$$

and of the volume change vs resistance change to estimate that the volume of a vacancy is 0.4 atomic volume. DeSorbo[36] has measured the energy released on the annealing of vacancies quenched in gold. The concentration of vacancies quenched in was determined from the ratio of the heat evolved on annealing to Bauerle's value of E_f. By combining Bauerle's value of the pre-exponential factor in Eq. (19) with the energy ratio, a value of $\Delta\rho/c$ of about 2.4×10^{-6} ohm cm/atom percent was obtained. Finally, by comparing this value with Bauerle's ratio of resistance change to specimen volume change, DeSorbo concludes that the vacancy volume is about 0.7 atomic volume. Although the experimental uncertainties in these two determinations are large, it is apparent that they are consistent with the anharmonic calculations. It seems quite reasonable to assume that relaxation does occur about a vacancy so that the volume of formation is about one-half an atomic volume. As soon as techniques for quenching at pressure can be developed, it will be most desirable to verify this assumption by direct measurement.

There are few calculations of the activation volume for motion. A hard-spheres model indicates an expansion of the crystal of about one atomic volume for a diffusive

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[29] J. J. Jackson (private communication).

[30] The motional energies and annealing rates for the specimens used in the present experiment agree with those measured by Bauerle within experimental error. Thus, dislocation densities comparable to those found by Bauerle are assumed to be present in the specimens used in the present experiment.

[31] O. Theimer, Phys. Rev. **112**, 1857 (1958).

[32] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).

[33] G. Nardelli and A. Repanai, Physica **24**, *S*182 (1958).

[34] L. Girifalco and J. Streetman, J. Phys. Chem. Solids **4**, 182 (1958).

[35] G. L. Hall, J. Phys. Chem. Solids **3**, 210 (1957).

[36] Warren DeSorbo, Phys. Rev. Letters **1**, 238 (1958).

jump. Huntington and Seitz[37] calculate that the atoms in the shell around a vacancy are displaced by about 10 percent when the diffusing atom is in the saddle configuration. This is roughly twice the value calculated by Fumi.[38]

These results consider only the expansion of the lattice caused when the diffusing atom passes through the shell of atoms surrounding the vacancy. Fumi[38] points out that when the lattice is in the saddle configuration, two partial vacancies are present: One is at the site to which the diffusing atom is jumping, the other is at the site which the diffusing atom has left. If there is relaxation of the neighboring atoms toward these partial vacancies, part of the lattice expansion may be cancelled. For a very rough estimate of the net effect to be expected, Tewordt's calculation of the expansion of the lattice due to an interstitial may be compared with twice his calculation of the relaxation about a vacancy. The calculated ΔV_f of an interstitial is 1.7–2.0 atomic volumes, while twice the volume of formation of a vacancy is 0.9–1.1 atomic volumes. Thus, using these values for the model of an interstitial with two vacancies as an approximation to the saddle configuration, a motional volume of greater than half an atomic volume is obtained. The actual saddle point configuration probably involves much less crowding than would be encountered in creating an interstitial. The hard spheres model predicts only about a one atomic volume increase for the saddle configuration. Relaxation of one-half atomic volume per partial vacancy could just cancel this increase. While neither of these approximations can be expected to give accurate results, they do show that a small motional volume is not inconsistent with the vacancy model, if relaxation effects are considered.

Other models to explain the small motional volume can be constructed. Still consistent with the vacancy model would be the polarization of the diffusing atom. However, from energy considerations, it is unlikely that polarization could account for any great decrease in the displacement of the barrier atoms. Nachtrieb[39] has proposed a defect much less localized than a vacancy, the relaxion, somewhat like a small melted region of the crystal. In such a region containing a hundred atoms or so, one atom would be missing in comparison with the normal lattice arrangement. The vacant site would be distributed over the entire disturbance. Such a defect could move by a process similar to local melting and refeezing. However, it is rather difficult to explain the annihilation of such a defect during anneal.

If we assume that ΔV_f for a vacancy is 0.5 atomic volume as calculated by Tewordt, the present value of ΔV_m gives a total activation volume for diffusion of about 6.5 cm^3/mole. This is somewhat larger than the value of ΔV of 4 cm^3/mole predicted by Keyes' semi-empirical relation between ΔV and ΔH. Recent preliminary results on the pressure effect on self-diffusion in silver by Tomizuka[40] show that the activation volume may be as much as 0.85 atomic volume. Thus, the semi-empirical relation may underestimate ΔV for noble metals. The present value for ΔV_m appears to be consistent with the self-diffusion data and with the theoretical and experimental values for the relaxation about a vacancy.

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[38] F. G. Fumi, Phil. Mag. **7**, 46, 1007 (1955).

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