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

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

I. INTRODUCTION

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

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

Another important measurement by BLB[7] was the pressure coefficient of resistivity of aluminum and gold at high temperatures. The earlier data of Bridgman[8] did not extend much above room temperature. Although these coefficients are pressure-independent, they do depend on temperature. The quench temperatures in the previous ΔV_f measurements were determined from the room-temperature coefficients, thereby introducing a pressure-dependent error in the quench temperature. The quenching experiments also assumed either no vacancy loss during quench or a pressure-independent loss. Flynn, Bass, and Lazarus[9] (FBL), and Kino and Koehler[10] have constructed theories for vacancy loss for constant quenching rates. A recently developed temperature controller[11] permits linear quenches at any rate up to the limit imposed by the specimen environment. We therefore have remeasured ΔV_f for gold and measured ΔV_f for aluminum taking into account these new results. The pressure dependence of the vacancy loss also permits a test of some of the models for the loss during quench.

II. THEORY

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

$$c(T)=c_0e^{-\Delta G_f/kT}, \tag{1}$$

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

$$\Delta V_f=(\partial\Delta G_f/\partial P)_T. \tag{2}$$

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

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

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[1] See, for example, the reviews in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic Press Inc., New York, 1965).
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A measurement of $\Delta R/R_0$ for infinite quench rate from a fixed temperature as a function of pressure can then be interpreted in terms of the formation volume of the defect.

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

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

III. EXPERIMENTAL

A. Gold Specimens

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

B. Aluminum Specimens

The aluminum specimens were made from 0.004-in.-diam wire of nominal 99.999% purity supplied by the Sigmund Cohn Corp. The wires were etched in a phosphoric- and chromic-acid mixture and rinsed in distilled water. Potential leads were also the 0.0006-in.-diam 99.99% gold, since small diameter aluminum leads could never be spot-welded successfully. The initial anneals were 30 min at 550°C and 45 min each at 300 and 100°C. The last two were subsequently reduced to 20 min each. The resistance baseline shifts were somewhat larger than for gold, but reproducible results were obtained after shifts which varied from 0.6 to 3.0 $\mu\Omega$. Data after shifts in excess of the latter value were excluded. The aluminum temperature scale used was that of Simmons and Balluffi.[15]

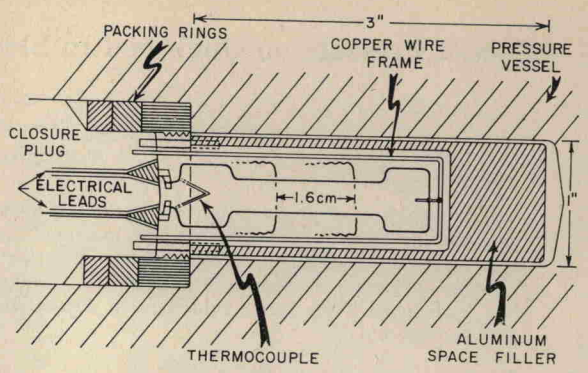

FIG. 1. Schematic diagram of specimen and dummy mounted in pressure vessel. The closure plug has a total of eight electrical leads.

C. Specimen Shape

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

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

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