Pressure Effect on Defect Migration in Aluminum†*

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The effect of hydrostatic pressure up to 9.5 kbar on the annealing rate of the excess resistivity in quenched aluminum was measured in two annealing regions. One was at −65°C following quenches from 580°C and the other at 0°C following quenches from 331°C. Effective activation volumes for motion were determined to be $(3.0\pm0.3)\times10^{-24}$ cm³ and $(2.8\pm0.3)\times10^{-24}$ cm³, respectively. These results were interpreted in terms of vacancy and divacancy motion. The −65°C anneal value represents the motion of divacancies. The 0°C anneal value cannot unambiguously be assigend to a single type of defect. However, assignment of a single-vacancy motional volume close to the 0°C anneal value is consistent with these and diffusion results if it is assumed that there is a divacancy contribution to self-diffusion in aluminum, or that the motional volume is temperature-dependent.

I. INTRODUCTION

LARGE nonequilibrium concentrations of vacancies and vacancy multiples are produced by rapidly quenching an fcc metal from high temperatures. The vacancies and divacancies are mobile in appropriate temperature ranges and can migrate through the lattice until they reach a sink and are absorbed.[1] The application of hydrostatic pressure changes the amount of energy necessary for an atom neighboring a vacant site to jump into it. The change in energy is equal to the external pressure times the motional volume or lattice dilatation as the jumping atom goes from a filled site to the saddle point between vacant sites.[2] The motional volume associated with the annealing mechanism can be determined from a measurement of the effect of pressure on the decay rate of excess resistivity caused by the defect concentrations. Since the mechanism usually involves more than one atomic process, association of the derived motional volume with a particular atomic process is difficult.

Pressure studies of the defect properties of aluminum to date have determined the activation volume of self-diffusion ΔV_{sd} and the formation volumes of vacancies ΔV_f^v and of divacancies ΔV_f^{vv}. When self-diffusion occurs by the vacancy mechanism, diffusion theory[3] shows that ΔV_{sd} is the sum of ΔV_f^v and ΔV_m^v, the motional activation volume for vacancies. Butcher, Hutto, and Ruoff[4] found that in aluminum $\Delta V_{sd}=1.35V_a$ by a high-temperature creep experiment. The radioactive-tracer diffusion technique was used by Beyeler and Adda,[5] who found $\Delta V_{sd}=1.29V_a$. Norris[6] measured the effect of pressure on the annealing of prismatic dislocation loops in quenched aluminum and concluded that ΔV_{sd} fell between $0.44V_a$ and $0.87V_a$. The atomic volume V_a of aluminum at 20°C and atmospheric pressure is 16.6×10^{-24} cm³.

Emrick and McArdle[7] quenched aluminum wires at high pressure and found $\Delta V_f^v=0.64V_a$. Bourassa, Lazarus, and Blackburn[8] (BLB) measured the effect of pressure on the thermoelectric power and the electrical resistance of aluminum. The thermoelectric power experiment yielded a value for ΔV_f^v of $0.54V_a$ and a divacancy formation volume ΔV_f^{vv} of $0.96V_a$. The pressure effect on the electrical resistance yielded values for ΔV_f^v of $0.60V_a$ and $\Delta V_f^{vv}<1.45V_a$.

If we subtract the quenching and BLB values of ΔV_f^v from the diffusion values of ΔV_{sd} and assume the single-vacancy diffusion mechanism, a value of ΔV_m^v of about $0.7V_a$ is obtained. Although no calculations or measurements of ΔV_m^v have been made for aluminum, this value is much larger than might be expected on the basis of calculations for other materials and on the only other ΔV_m measurement to data. The latter was a value of $0.15V_a$ in gold.[9] In the case of gold this value of ΔV_m plus ΔV_f^v [7,8] is just within experimental error of ΔV_{sd} determined by pressure diffusion experiments.[2,5,10] On the basis of existing data for aluminum, one can conclude that ΔV_m^v is indeed very large, that large errors exist in the ΔV_{sd} or ΔV_f^v measurements, or that single vacancies alone are not responsible for self-diffusion. The agreement between the two ΔV_{sd} measurements and between the ΔV_f^v measurements by different techniques reduces the likelihood of such large experimental errors. A measurement of the effect of

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[1] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1963), p. 77.
[2] L. A. Girifalco, in *Metallurgy at High Pressures and High Temperatures*, edited by K. A. Geschneider, M. T. Hepworth, and N. A. D. Parlee (Gordon and Breach, New York, 1964), p. 260.
[3] N. L. Peterson, Solid State Phys. **22**, 409 (1968).
[4] B. M. Butcher, H. Hutto, and A. L. Ruoff, Appl. Phys. Letters **7**, 34 (1965).
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[6] D. I. R. Norris, Acta Met. **14**, 291 (1966).
[7] R. M. Emrick and P. B. McArdle, Phys. Rev. **188**, 1156 (1969).
[8] R. R. Bourassa, D. Lazarus, and D. A. Blackburn, Phys. Rev. **165**, 853 (1968).
[9] R. M. Emrick, Phys. Rev. **122**, 1720 (1961).
[10] R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, Phys. Rev. **137**, A613 (1965).

pressure on the annealing rate of defects quenched into aluminum would help resolve the problem. We chose to measure the pressure effect on annealing under two widely separated sets of conditions. Ideally, one would like to observe the motion of single vacancies and divacancies separately.

To decide the appropriate temperature ranges, we must consider earlier quench data. Doyama and Koehler[11] did extensive annealing studies of quenched zone-refined aluminum. They attributed the value of ΔV_m derived from -50 and -60°C anneals after 538°C quenches to divacancies. They argued that immediately after the quench one should have only single vacancies and divacancies, since there was not enough time for large clusters to form. Because the jump rate of the vacancy is three orders of magnitude smaller than that of the divacancy, the annealing process is dominated by divacancies. If the divacancies are then annihilated at dislocations, the motional energy derived for the process is $E_m{}^{vv}$. Their value of $E_m{}^{vv}$ of 0.50 ± 0.04 eV along with the value $E_m{}^{v}=0.68$ eV is consistent with the postulated jump rates at -60°C. They point out, however, that for cluster formation, such a simple model would not be adequate. Nonetheless, they base their value of $E_m{}^{vv}$ on the consistency of the arguments of divacancies annealing to dislocations. Desorbo and Turnbull[12] found a motional energy of 0.65 ± 0.06 eV for aluminum quenched from below 300°C. This energy can be attributed to single-vacancy motion if one assumes that the defect concentration is so low that few singles have the chance to combine before reaching a sink. Doyama and Koehler[11] found $E_m{}^{\text{eff}}=0.61$ eV in a specimen quenched from 301°C. As will be discussed in Sec. II, our lowest practical quench temperature was 331°C. The implication of quench results for such a temperature will be considered in the Discussion.

Let us assume that the anneal proceeds by a single mechanism. The migration rate of the mobile defect is proportional to its jump frequency. Statistical rate calculations[13,14] show that the jump frequency is given by

$$\Gamma=\nu e^{-\Delta G_m/kT}, \tag{1}$$

where ν is an effective frequency and ΔG_m is the change in the Gibbs free energy of the crystal as the defect goes from an equilibrium position to a saddle point. The motional volume is defined by the thermodynamic relation

$$\Delta V_m=\left(\frac{\partial\Delta G_m}{\partial P}\right)_T. \tag{2}$$

When the decay of excess resistivity $\Delta\rho$ is controlled by the migration of one type of defect, the decay rate of $\ln(\Delta\rho)$ is given by

$$\frac{1}{\Delta\rho}\frac{d\Delta\rho}{dt}=-f(\Delta\rho)\Gamma, \tag{3}$$

where the functional form of $f(\Delta\rho)$ depends on the vacancy-loss mechanism. We have assumed that the defect concentration is directly proportional to $\Delta\rho$. For convenience, let $-\Sigma(\Delta\rho)$ be defined as the slope of the resistance decay curve $(1/\Delta\rho)(d\Delta\rho/dt)$. By combining Eqs. (1)–(3), we can write the motional volume of the defect as

$$\Delta V_m=-kT\left[\left(\frac{\partial}{\partial P}\ln\Sigma\right)_T-\left(\frac{\partial}{\partial P}\ln\nu\right)_T-\left(\frac{\partial}{\partial P}\ln f(\Delta\rho)\right)_T\right]. \tag{4}$$

The first term is determined experimentally. The last term depends on the nature of the defect sinks in the metal and on the kinetics of the anneal. The pressure dependence of the frequency term can be written as

$$\left(\frac{\partial\ln\nu}{\partial P}\right)_T=\gamma_G\kappa_T, \tag{5}$$

where γ_G is Grüneisen's constant and κ_T is the isothermal compressibility. The last two terms in Eq. (4) are usually small. Our procedure, then, is to measure $\partial\ln\Sigma/\partial P$ experimentally for two extreme quench temperatures and to determine the effective ΔV_m for each temperature by the use of Eq. (4).

II. EXPERIMENTAL PROCEDURE

Sample Preparation

The samples consisted of a specimen and a dummy specimen made from 0.014-in.-diam aluminum wire of 99.999% purity supplied by Cominco American, Inc., Spokane, Wash. After the expansion loops were bent into the specimen and dummy wires, the wires were etched in a solution of 73% phosphoric acid, 23% sulfuric acid, and 4% nitric acid. The samples were then mounted in a frame which was fastened to the pressure plug,[9] and potential leads of 0.002-in.-diam, 99.99% purity aluminum wire were spot-welded about 7.5 cm apart on both the specimen and dummy. During the spot welding, care was taken to position the potential leads to reduce the difference in resistance of the gauge lengths of the specimen and dummy to less than 100 $\mu\Omega$. This procedure reduced the effect of temperature fluctuations during the experimental runs to below the resolution of the measuring circuit. The samples were then annealed for $\frac{1}{2}$ h at 550°C, 1 h at 300°C, and $\frac{1}{2}$ h

[11] M. Doyama and J. S. Koehler, Phys. Rev. **134**, A522 (1964).
[12] W. Desorbo and D. Turnbull, Phys. Rev. **115**, 560 (1969).
[13] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).
[14] C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Schockly, J. H. Hollomon, R. Maurer, and F. Seitz (Wiley, New York, 1952), p. 289.

at 100°C to remove any strains due to cold work. This procedure was repeated after each run to remove any strains produced in quenching and to anneal out any remaining quenched-in defects.

General Experimental Techniques and Equipment

The pressure system is a standard liquid system with an intensifier and separate pressure vessel. The pressure fluid used was a mixture of equal volumes of pentane and isopentane, which remains liquid in the pressure range 1 bar to 10 kbar down to −78°C. A manganin gauge calibrated at the freezing point of mercury at 0°C (7574 bar) was used to measure the pressure in the system. A Chromel-Alumel thermocouple was used to monitor the internal temperature of the pressure vessel. Steel or Chromel and Alumel cones insulated by lavite were used to bring the electrical leads out of the vessel. Lead resistance to the vessel was always greater than 1 MΩ.

During the anneals, the pressure vessel was immersed in a bath maintained at constant temperature. The 0°C bath was made by packing wet ice around a bath of kerosene and allowing the vessel and bath to come to equilibrium. The −65°C bath was made by packing dry ice around an insulated container of ethanol. The bath and pressure vessel temperature was maintained by a heating coil in the bath. The bath temperatures were measured by the American Society for Testing Materials (ASTM) thermometers and found to be (0.0±0.1) and (−65.0±0.1)°C. The temperature fluctuations inside the pressure vessel were measured by the internal thermocouple and were found to be less than 0.01°C/h, except for the transient produced by a pressure change. This transient decayed to less than 0.01°C/h in about 1 h.

The quenched-in resistance was measured using the procedure first described by Bauerle and Koehler.[15] The measuring current passed through the specimen and dummy was 0.10000±0.00001 A. The steady thermal emf's in the circuit were cancelled out by measuring with currents in the forward and reverse directions. A Rubicon microvolt potentiometer with a Rubicon photoelectric galvanometer made it possible to determine δR, the specimen minus the dummy resistance, to ±0.05 μΩ. This resistivity sensitivity limited the minimum usable quench temperature T_Q to about 330°C. The resistance quenched in from temperatures less than this could not be measured with sufficient accuracy to give meaningful results.

The base resistance difference δR_0 of the well-annealed specimen and dummy shifted during the 300 and 550°C anneals. Also it was found to shift when the specimen was brought up to the quench temperature of 331°C and then annealed at 100°C for ½ h without quenching. This change in δR_0 was small and in the case of the 580°C quenches the base resistance was taken to be the δR_0 measured before the quench. However, in the analysis of the annealing runs after the 331°C quenches the shift was significant. Consequently, the base resistance difference was taken to be the resistance difference δR_f measured at the end of these runs after an anneal at room temperature for 2½ h.

The room-temperature annealing time was found to be long enough to stabilize the resistance difference δR_f as it did not change with further aging at room temperature. Since Desorbo and Turnbull[16] have found that all of the excess resistance produced by quenching from 270 to 332°C anneals out during isothermal holds at 0 and 27°C using a low-temperature measuring technique, δR_f was assumed to be the base resistance difference.

Quenching and Annealing Procedure

The specimen was placed horizontally over a quench bath of hexane at −78°C and heated by a dc current to the quench temperature. The quench was performed by allowing the sample and pressure plug to fall into the quench bath just before shutting off the heating current. The quench rate is estimated to have been 10^4 °C/sec by comparing the quenched-in resistivity with the results obtained by Bass.[17]

After the quenches from 331°C, the samples were annealed isobarically at pressures ranging from 1 atm to 9.5 kbar at a temperature of 0°C for about 26 h. Resistance measurements were made during the first 8–12 h of the anneal to determine the rate of decay. The base resistance difference between the specimen and the dummy was measured at the annealing temperature and pressure after an anneal at 25°C for 2½ h. New specimens were used after every two or three runs to avoid possible contamination of the aluminum wire from solder joints or the pressure fluid. Each was given the standard annealing procedure. Bass[17] cites evidence that the sink density does not differ appreciably between specimens so prepared if they are made from the same spool of wire.

The quenches from 580°C produced a large excess resistivity (about 4×10^{-3} μΩ cm) which allowed the use of the slope change method of analysis. The initial anneal was done at various hydrostatic pressures ranging from 1 atm to 9.5 kbar at an annealing temperature of −65°C. After about 5×10^{-4} μΩ cm had annealed out, the pressure was changed to the reference pressure of 1 atm and resistance measurements were continued until an additional 5×10^{-4} μΩ cm annealed out. After an additional anneal of 14 h, the resistance difference between the specimen and dummy was measured at both the initial and reference pressure. By this time, about 60% of the quenched-in resistance had annealed out and the resistance difference δR_f was almost constant, $d\delta R/dt<0.05$ μΩ/h. The remaining excess

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

[16] W. Desorbo and D. Turnbull, Acta Met. **7**, 83 (1959).

[17] J. Bass, Phil. Mag. **15**, 717 (1967).

TABLE I. Influence of pressure on the annealing rate of aluminum after 580°C quenches.

Specimen	Σ_p (h^{-1})	Σ_0 (h^{-1})	(Σ_p/Σ_0)	ΔP (kbar)
A	0.117	0.100	1.17	0.00
A	0.090	0.092	0.98	1.00
B	0.146	0.160	0.91	3.00
B	0.102	0.146	0.70	4.97
B	0.098	0.167	0.54	6.96
B	0.068	0.147	0.46	9.12
B	0.064	0.125	0.51	9.10

resistance was assumed to be due to the stage-II defect concentration[18] and the remaining vacancy concentration.

III. RESULTS

Two resistance-decay curves following quenches from 580°C are shown in Fig. 1. Table I lists the results obtained in the anneals after the high-temperature quenches. Σ_p is the slope of the decay curve measured at high pressure, and Σ_0 is the slope measured at 1 atm. The values of (Σ_p/Σ_0) versus pressure are plotted in Fig. 2. Within the experimental error, the pressure dependence of $\ln(\Sigma_p/\Sigma_0)$ is linear and the value found for the slope using a least-squares fit is

$$\left(\frac{\partial \ln(\Sigma_p/\Sigma_0)}{\partial P}\right)_T = -0.096 \pm 0.009 \text{ kbar}^{-1}. \quad (6)$$

Figure 3 shows resistance-decay curves for three isobars after the quenches from 331°C. Table II lists

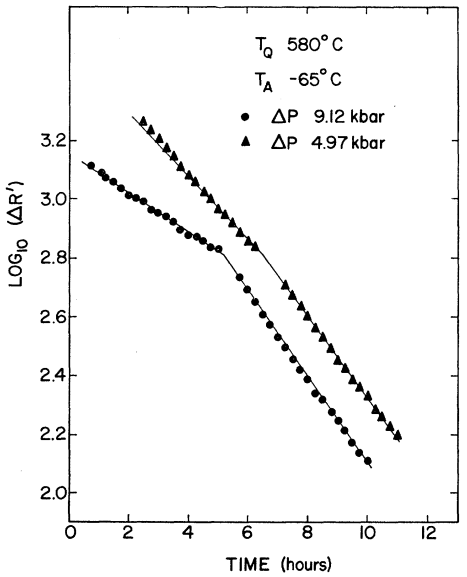

FIG. 1. Influence of pressure on the isothermal annealing rate. Time origins are arbitrarily displaced for clarity.

[18] T. Federigi, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic, New York, 1965), p. 217.

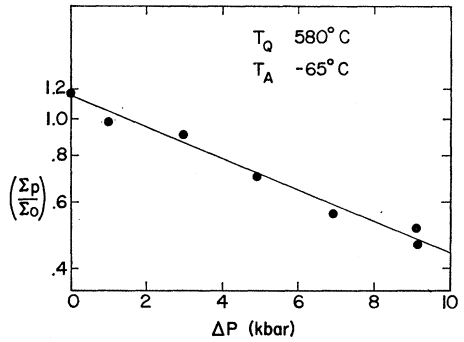

FIG. 2. Semilogarithmic plot of Σ_p/Σ_0 versus ΔP, where ΔP is the difference between the pressures at which the annealing rates Σ_p and Σ_0 were measured.

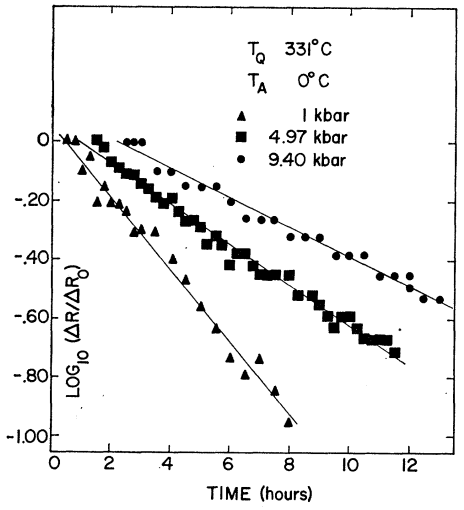

FIG. 3. Isothermal anneals at 3 isobars. Time origins are arbitrarily displaced for clarity.

the values of the slopes of the resistance-decay curves found in this region between the excess resistivity values $\Delta\rho_1$ and $\Delta\rho_2$. Figure 3 is a semilog plot of Σ as a function of pressure. The pressure dependence of $\ln(\Sigma)$

TABLE II. Annealing rate of aluminum quenched from 331°C.

Specimen	$\Delta\rho_1$ (10^{-4} μΩ cm)	$\Delta\rho_2$ (10^{-4} μΩ cm)	Σ (h^{-1})	P (kbar)
C	3.7	2.5	0.043	9.20
C	3.7	2.5	0.055	9.06
D	3.6	1.7	0.089	1.00
E	3.6	2.1	0.064	3.00
E	3.2	1.7	0.064	3.00
F	4.8	2.0	0.082	4.97
F	3.6	1.7	0.070	4.97
G	3.6	1.9	0.070	6.97
G	3.2	1.9	0.058	6.97
H	3.1	1.2	0.121	0.00
H	3.0	1.2	0.094	0.00
I	3.6	2.1	0.049	9.40
I	2.6	1.2	0.122	0.00
J	3.1	1.7	0.075	2.00
J	4.5	2.6	0.050	9.20
J	3.3	1.8	0.112	0.00
K	3.5	2.5	0.043	9.25

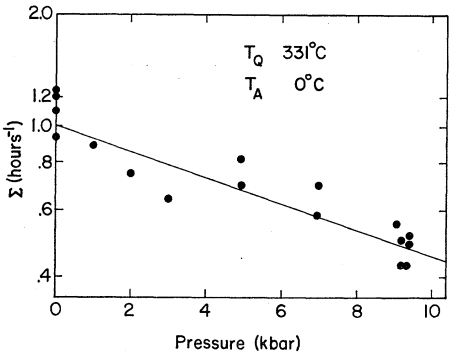

FIG. 4. Semilogarithmic plot of annealing rate versus pressure.

is also linear within the experimental scatter and a least-squares analysis gives

$$\left(\frac{\partial \ln(\Sigma)}{\partial P}\right)_T = -0.080 \pm 0.008 \text{ kbar}^{-1}. \quad (7)$$

IV. DISCUSSION

580°C Quenches

After high-temperature quenches, the defect concentration in aluminum consists of vacancies, divacancies, higher-vacancy multiples, and dislocation loops. Doyama[19] calculates the divacancy/single-vacancy concentration ratio after a quench as a function of defect concentration, binding energy, and quench rate. It is strongly dependent on binding energy. For even moderate binding energies, the divacancy concentration can be appreciable. The excess resistance of the quenched specimen is then given by

$$\Delta R = \beta(\rho_v c_v + \rho_{vv} c_{vv} + \Delta\rho_m + \Delta\rho_d), \quad (8)$$

where β depends on the dimensions of the specimen, ρ_v and ρ_{vv} are the vacancy and divacancy resistivities, and c_v and c_{vv} are the vacancy and divacancy concentrations. The terms $\Delta\rho_m$ and $\Delta\rho_d$ are the resistivities of the vacancy multiples or clusters and the dislocation loops. At the annealing temperature -65°C, the cluster and dislocation loops are stable and their concentration remains constant. As discussed in the Introduction, the mobility of divacancies is at least 10^3 times greater than that of singles. (If the $E_m{}^v$ value of Bass[17] is used, the ratio is even greater. The applicability of his value will be discussed shortly.) To describe the motion of divacancies to dislocations, we replace $f(\rho)$ in Eq. (3) by $\alpha\lambda^2$, where α is the sink density and λ is the lattice parameter, and Γ by Γ_{vv}. Since the slope change method is used at this quench temperature, we can rewrite Eq. (4) as

$$\Delta V_m{}^{vv} = -kT\left\{\left[\frac{\partial}{\partial P}\ln\left(\frac{\Sigma_p}{\Sigma_0}\right)\right]_T - \kappa_T\gamma_G - \left[\frac{\partial}{\partial P}\ln(\alpha\lambda^2)\right]_T\right\}. \quad (9)$$

The contribution of the frequency term $\kappa_T\gamma_G$ is less than 2% of the first term and is neglected because of the error involved in determining the pressure dependence of the resistance decay. The pressure dependence of the last term is determined by the nature of the sinks present in the quenched metal.

Electron-microscope studies of quenched aluminum have shown that the vacancy multiple or void concentration is quite high after quenches from 570°C at cooling rates of 10^4 °C/sec.[20,21] Thus the sinks present are the preexisting dislocation lines and the voids formed during the quench. The last term can be written[22] as

$$\left(\frac{\partial}{\partial P}\ln(\alpha\lambda^2)\right)_T = \frac{\partial}{\partial P}\ln\left(2\pi N_d\lambda^2\frac{1}{\ln(r_1/r_0)_d} + 4\pi N_v\lambda^2 r_v\right). \quad (10)$$

In this expression N_d is the number of dislocation lines per cm^2, $(r_1/r_0)_d$ is the ratio of the average distance between dislocations to their capture radius, N_v is the number of voids per cm^2, and r_v is the capture radius of a void. The pressure dependence of the contribution by dislocations to the sink density is small and is assumed to be negligible. $N_d\lambda^2$ has no pressure dependence and since the ratio $(r_1/r_0)_d$ is of the order of 10^6 in a well-annealed metal, $\ln(r_1/r_0)_d$ is insensitive to large variations of the capture radius with pressure.

In the contribution from the void concentration, $N_v\lambda^2$ changes by less than 1% over the pressure range 0–10 kbar. Kiritani[21] has found that the lattice is highly strained in the neighborhood of a void, which makes the pressure dependence of r_v small. This is seen by assuming the voids to be spherical holes in an isotropic solid and the strain field to be caused by a pressure on the external surface. In order to cause an observable compression of the solid in the neighborhood of a void the pressure would have to be >10 kbar. In this case, applying an additional pressure of 10 kbar on the surface would change the capture radius of a void due to its stress field by less than 25%. Since the annealing rate at 10 kbar is observed to be about one-third the annealing rate at 1 atm, the variation of r_v is neglected.

When we substitute our experimental value, Eq. (6), into Eq. (9), we find that the motional volume of

[19] M. Doyama, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic, New York, 1965), p. 167.

[20] M. Kiritani, J. Phys. Soc. Japan 19, 618 (1964).

[21] M. Kiritani, Y. Shimomura, and S. Yoshida, J. Phys. Soc. Japan 19, 1624 (1964).

[22] L. A. Girifalco and H. H. Grimes, NASA Technical Report No. R-38, 1959 (unpublished).

divacancies at $-65°C$ is $(2.76\pm0.28)\times10^{-24}$ cm^3 or $(0.17\pm0.02)V_a$. No previous pressure experiments have been performed on aluminum nor have theoretical calculations been made. The value can be compared with the general strain energy model described by Keyes.[23] From the expression

$$\Delta V=2(\gamma_G-\tfrac{1}{3})\kappa_T\Delta G, \qquad (11)$$

the motional volume of divacancies in aluminum is calculated to be $\Delta V_m{}^{vv}=0.23\ V_a$, in reasonable agreement with the present value. However, theoretical calculations of $\Delta V_m{}^{vv}$ for the noble metals are in poor agreement with this value and with each other. For example, the largest $\Delta V_m{}^{vv}$ Schottky *et al.*[24] calculate is $0.02V_a$ for copper. More recently, Doyama and Cotterill[25] find a value of $0.06V_a$ for copper. The large oscillations in the aluminum potential may result in a larger theoretical $\Delta V_m{}^{vv}$ in aluminum. However, the calculation is yet to be done. BLB[8] found a large relaxation of the lattice about a divacancy in aluminum, i.e., $2V_a-\Delta V_f{}^{vv}>0.55V_a$. This may also be related to the large (relative to theory for noble metals) motional volume.

331° Quenches

If, as is assumed by Desorbo and Turnbull,[12] after a low-temperature quench the decay of excess resistivity is controlled by vacancy migration, we can interpret our low-temperature quenches in terms of a single-vacancy motional volume. $f(\rho)$ in Eq. (3) is $\alpha\lambda^2$ and Γ is Γ_v. An expression analogous to Eq. (9) can be obtained and the same arguments used to neglect the second and third terms. The motional volume which results when we use the result in Eq. (7) is $(3.0\pm0.3)\times10^{-24}$ cm^3 or $(0.18\pm0.02)V_a$.

This effective motional volume cannot be attributed to single vacancies alone. Doyama and Koehler[11] observed a temperature dependence of $E_m{}^{\rm eff}$ in quenched aluminum. As T_Q was lowered below 400°C, $E_m{}^{\rm eff}$ began to increase above 0.50 eV and for a T_Q of 301°C it had risen to 0.61 eV. This value is still below Desorbo and Turnbull's[12] low T_Q value of 0.65 eV. Bass[17] argues that the best value for $E_m{}^v$ is 0.75 ± 0.08 eV. However, his value is for high-temperature ($T>400$°C) rather than room-temperature migration and his analysis assumes that self-diffusion in aluminum is by single vacancies only. The present quench temperature of 331°C is apparently not low enough to assure that only a single-vacancy mechanism is in operation, so that the effective value we measure may not be indicative of any particular atomic process. Johnson[26] has used computer simulated anneals to show that when two or more mechanisms are involved, the effective energy bears no simple relation to the energies of either process.

More recently, in a series of papers Burton and Lazarus[27] have considered a simple single-divacancy annealing mechanism. They show that the slope-change analysis yields an activation energy which is usually between the instantaneous activation energy, characteristic of the actual defect annihilation process, and the effective activation energy, characteristic of the rate controlling process. Thus, if as in the present high-temperature quenches a large divacancy concentration is already present and if the equilibrium concentration is unaffected by the pressure change, divacancy motion is both the rate limiting and rate controlling process.

The Burton and Lazarus analysis is not directly applicable to the present 331°C quenches, since the slope change method was not used. We can, however, estimate the effect of a divacancy (second-order kinetics) contribution. It can be only an estimate, however, since the effect of second-order kinetics cannot be detected within the scatter of the data. By use of the steady-state approximation derived by Damask and Dienes,[1] one finds that the "effective" motional volume is given by

$$\Delta V_m{}^{\rm eff}-\Delta V_m{}^v=-kT\frac{d}{dP}\ln\left(\alpha\nu_1\lambda^2+c_v\frac{168\alpha\nu_2\nu_1\lambda^2e^{-(E_m{}^{vv}+PV_m{}^{vv})/kT}}{14\nu_1e^{-(E_m{}^v+E_b+PV_m{}^v+PV_b)/kT}+2\alpha\nu_2\lambda^2e^{-(E_m{}^{vv}+PV_m{}^{vv})/kT}}\right). \qquad (12)$$

The effective frequencies ν_1 and ν_2 are assumed to be constant and to have the value 10^{13} sec^{-1}. The vacancy concentration is assumed to be 10^{-6}, which corresponds to an excess resistance of about 1.5 $\mu\Omega$.[25] The term $\alpha\nu\lambda^2$ is assumed to be 2.3×10^7 sec^{-1} as found by Desorbo and Turnbull[12] and the change of volume on the formation of a divacancy from two vacancies ΔV_b is found experimentally[8] to be $0.12V_a$. The migration energies are taken[10] to be $E_m{}^v=0.65$ eV and $E_m{}^{vv}=0.50$ eV. Binding energy values E_b of 0.50, 0.20, and 0.10 eV were used. If the binding energy is large, the difference $\Delta V_m{}^v-\Delta V_m{}^{\rm eff}$ is small. However, this difference depends strongly on E_b, so that for $E_b=0.20$ eV, $\Delta V_m{}^v-\Delta V_m{}^{\rm eff}=0.3\Delta V_m$. As stated earlier the difference between $\Delta V_{\rm sd}$ and $\Delta V_f{}^v$, values which have been determined by at least two independent measurements each, is about $0.7V_a$. If E_b is 0.17 eV, as determined by Doyama and Koehler,[11] $\Delta V_m{}^{\rm eff}$ should be at least three times as large as the present experimental value if we take the $0.7V_a$ value as $\Delta V_m{}^v$. A smaller value

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would be required to reconcile the present ΔV_m^{eff} with a $0.7V_a$ value for ΔV_m^v. There is little, if any, experimental evidence to support a lower value for E_b^{vv}. Admittedly, the frequency factors used in the calculation have not been verified and some of the other measured quantities are uncertain. Nonetheless, such a large single-vacancy ΔV_m should be evident in our low-temperature quench measurements.

The value of ΔV_{sd} for aluminum is larger than for other metals studied to date, whose values range from 0.7 to $0.9V_a$.[3,28] A possible reason for the large ΔV_{sd} in aluminum is that there is a divacancy contribution to self-diffusion. This conclusion is supported by the measured increase of E_{sd} with increasing temperature,[29] although Stoebe and Dawson argue that divacancies alone cannot explain the entire temperature dependence. Another possibility is a temperature dependence of ΔV_m. Both ΔV_{sd} and ΔV_f^v are measured near the melting point, whereas ΔV_m has been measured at room temperature and below. This is also consistent with Stoebe and Dawson's conclusions that there is a temperature dependence of E_m^v. Enough data are not yet available to decide the relative importance of these contributions in the present case.

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V. SUMMARY

The pressure effect on the annealing of electrical resistance quenched into aluminum from two different temperatures was studied. The effective motional volumes were $(0.17\pm0.02)V_a$ for quenches from 580°C and $(0.18\pm0.02)V_a$ for quenches from 331°C. The former is attributed to divacancies. The latter should show evidence of a single-vacancy contribution. It is consistent with these and other pressure data for aluminum that the single-vacancy motional volume is not appreciably different from this value and that the large self-diffusion activation volume in aluminum is the result of a divacancy contribution to diffusion or a temperature dependence of ΔV_m.

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Landau Quantum Oscillations of the Velocity of Sound in Be: The Strain Dependence of the Fermi Surface

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Landau quantum oscillations of the velocity of sound in Be are reported. A general thermodynamic relation between the quantum oscillations of the velocity of sound (elastic moduli) and the strain dependence of the Fermi surface is given and is used to interpret the results. This relation shows that the amplitude of the oscillations is determined by the magnetic susceptibility and the strain dependence of the Fermi-surface extremal areas. An oscillatory as well as a monotonic Alpher-Rubin effect is obtained in this treatment. All major features of this theoretical result are generally verified in the experimental results. The strain dependence of the Fermi surface obtained in this work is in susbtantial agreement with previous hydrostatic pressure studies. At low temperatures, magnetic interaction effects modily the oscillation pattern. These results imply that the (differential) susceptibility at high frequencies is never paramagnetic. This behavior is shown to be consistent with the presence of magnetic domains whose walls are immobile at the sound frequency. Experimental techniques are also presented.

I. INTRODUCTION

IN recent years, Landau quantum oscillations in the velocity of sound have been reported in Bi,[1] Au,[2] and Ga.[3] To date, much of the information provided by these experiments has been limited to determinations, from the measured periods, of the extremal areas of the Fermi surface.[4] Although the conditions normally necessary for the occurrence of Landau quantum oscillations ($\omega_c\tau>1$ and $\hbar\omega_c>kT$) apply as well to the sound velocity behavior, it is apparent on physical grounds that in the latter case the amplitude of the oscillations must also reflect the deformation properties of the Fermi surface. Attempts to calculate the amplitude of this effect[5–7] in terms of all controlling factors are generally compromised by simplifying assumptions in which real metal effects are precluded. There remains,

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