HULT-RA 62-0191

PHYSICAL REVIEW VOLUME 125, NUMBER 6 MARCH 15, 1962

Pressure Dependence of Self-Diffusion in Lithium and Sodium*

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(Received October 23, 1961)

The activation volume ΔV_a for self-diffusion in lithium and sodium has been measured using nuclear magnetic resonance spin-echo techniques. In the region where the resonance line shape is narrowed by diffusion, the nuclear dipole-dipole phase memory time $(T_2')_d$ is proportional to the self-diffusion coefficient D. Measurements of $(T_2')_d$ for lithium as a function of pressure at constant temperature have been made at five temperatures between 35° and 80°C, and at pressures to 7000 atm. The phase memory time has been measured for sodium at three temperatures near −45°C at pressures to 3500 atm. Molar activation volumes of 3.6±0.3 cm³ and 9.6±0.5 cm³ have been obtained for lithium and sodium, respectively. These values are, respectively, 28 and 41% of the molar volumes of lithium and sodium, indicating that there occurs considerable relaxation inward on a vacancy by the nearest- and perhaps next-nearest-neighbor atoms of the vacancy. In addition, the experimental values are found to be in excellent agreement with a dynamical theory of diffusion which predicts that corresponding activation parameters for diffusion and melting are proportional. In both metals, the behavior of $\ln D$ is satisfactorily accounted for in terms of a single variable, the reduced melting temperature T_m/T.

INTRODUCTION

STUDIES of the temperature and pressure dependence of diffusion in solids have contributed to a partial understanding of the mechanisms of atom movement in crystals.[1] For the elementary metals the vacancy mechanism has been favored over other models because it has led to the best agreement of calculated and experimental values of the activation enthalpy ΔH_a. Along with temperature dependence studies, which give ΔH_a, pressure dependence measurements have provided the activation volume ΔV_a for a few of the pure metals.[2–5] Since diffusion has been considered as an activated process with a Gibbs free energy of activation ΔG_a, the activation volume, defined as the pressure derivative of ΔG_a, has been interpreted as a real physical volume. On a hard-sphere vacancy model the activation volume should be the sum of the volume of a vacant lattice site and the volume increase of the lattice when an atom is midway in its jump onto a vacancy. On a molar basis each of these contributions amounts to one atomic volume in the case of close-packed structures (e.g., fcc). In the body-centered cubic case, on the other hand, the motional contribution to this volume is zero. The measured values of ΔV_a for pure metals have varied from about 50% of the atomic volume (sodium)[2] to about 90% (silver).[4] Using quenched resistivity measurements, Emrick[6] has found that the motional volume of a vacancy in gold is only 15% of the atomic volume. Tewordt[7] calculated that the static volume of a vacancy in copper is about 50% of the atomic volume. The conclusion from both theory and experiment is that the hard-sphere model for pure metals should be modified to include considerable relaxation of the atoms onto a vacancy.

In the present work, nuclear-magnetic-resonance spin-echo techniques[8] have been used to obtain the activation volumes for lithium and sodium. The nuclear spin-lattice relaxation time T_1 and the inverse linewidth time T_2 were measured at constant temperature for several pressures up to 7000 atm for lithium and up to 3500 atm for sodium. The temperatures were in the range 35°–80°C for lithium and near −45°C for sodium. Holcomb and Norberg[9] made a thorough study at one atmosphere of the relaxation times in these metals, and showed how their data could be used to obtain the temperature dependence of the diffusion coefficients. Similarly, our data have been used to obtain the pressure dependence of these diffusion coefficients at a few temperatures. The present experiment has been inspired by and greatly dependent upon the work of Holcomb and Norberg.

Rice and Nachtrieb[10] have developed a dynamical theory of the effect of pressure on diffusion. Their theory does not use the assumptions of an activated state, but leads to equations relating the fusion parameters and the diffusion parameters as they are formally defined in the activated state theory. The results of the present experiment for both lithium and sodium and of radioactive tracer experiments on silver[4] and lead[3] are in good agreement with the

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[1] A recent review of diffusion theories and experiments has been presented by D. Lazarus, *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 71.

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

[3] N. H. Nachtrieb, H. A. Resing, and S. A. Rice, J. Chem. Phys. **31**, 135 (1959).

[4] C. T. Tomizuka, *Report of the Lake George Conference on Very High Pressure* (John Wiley & Sons, Inc., New York, 1961).

[5] R. E. Hoffman, J. B. Hudson, J. S. Kouvel, W. H. Meikeljohn-D. S. Rodbell, and R. H. Wilson, U. S. Air Force, Wright-Patterson Air Force Base, Air Research and Development Command, Air Force Research Division, Aeronautical Research Laboratory, ARL Technical Report 60-321, 1960 (unpublished).

[6] R. M. Emrick, Phys. Rev. **122**, 1720 (1961).

[7] L. Tewordt, Phys. Rev. **109**, 61 (1958).

[8] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[9] D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

[10] S. A. Rice and N. H. Nachtrieb, J. Chem. Phys. **31**, 139 (1959).

predictions of the dynamical theory. The value of the activation volume for sodium obtained here appears to be more reliable than the radioactive tracer value[2] which does not fit the equations of the dynamical theory.

A study of the effect of pressure on diffusion has been carried out for zinc,[11] a noncubic metal. The results are difficult to interpret because of the strong dependence of ΔV_a on both pressure and crystal orientation. Experiments on some silver halides[12] and alkali halides[13] have supported the idea that atoms relax about a vacancy, although in ionic materials the relaxation should be away from the vacancy in contrast to the case in metals.

McCall, Douglass, and Anderson[14] have used nuclear magnetic resonance to obtain the activation volume of several liquids. The technique of those experiments is somewhat different from that used here and takes advantage of the thousand-fold greater diffusion rates in liquids compared to the rates in the solids in this experiment.

Finally, we note that the relaxation times measured here depend directly on the rate of atom jumping, in contrast to radioactive tracer experiments in which the net transport effect of diffusion is observed.

THEORY

1. Nuclear Spin Relaxation Times

This section comprises a summary of the procedure of Holcomb and Norberg[9] for separating the relaxation times associated with different mechanisms. Each of the total relaxation times T_1 and T_2 is determined by the sum of the reciprocals of the times for the different mechanisms. For example, for T_1,

$$1/T_1=\sum_i(1/T_1)_i, \tag{1}$$

with a similar equation holding for T_2. A relation between $(T_1)_i$ and $(T_2)_i$ for each mechanism is

$$(1/T_2)_i=(1/T_2')_i+(1/2T_1)_i, \tag{2}$$

where $(T_2')_i$ is associated with the line broadening due to static local fields.

In lithium and sodium relaxation occurs through the interaction of the nuclei with the conduction electrons and by direct nuclear dipole-dipole interaction. It is the dependence of this latter interaction upon the rate of atom movement that makes possible the use of nuclear resonance to study diffusion.

The quantity whose pressure dependence has been of greatest interest is $(T_2')_d$, where the subscript refers to the dipole-dipole interaction. $(T_2')_d$ is obtained from the measured relaxation times using the following equation derived from (1) and (2) and the fact that $(T_1)_e=(T_2)_e$:

$$(1/T_2')_d=1/T_2-1/T_1+(1/2T_1)_d. \tag{3}$$

The other relaxation time whose pressure dependence was observed, though only qualitatively, is $(T_1)_d$, given by

$$(1/T_1)_d=(1/T_1)-(1/T_1)_e. \tag{4}$$

The conduction electron spin-lattice time $(T_1)_e$ has such a weak pressure dependence relative to the dipole-dipole times that $(T_1)_e$ has been considered to be independent of pressure. The pressure dependence of $(T_1)_e$ may be inferred from the work of Benedek and Kushida[15] on the pressure dependence of the Knight shifts of lithium and sodium.

2. Relation of Nuclear Relaxation Times and Diffusion Coefficient

Bloembergen, Purcell and Pound[16] explained how the nuclear relaxation times associated with the dipole-dipole interaction depend on the diffusion coefficient D in liquids. Holcomb and Norberg[9] used this theory to derive the following relations for solid-state diffusion in the alkali metals[17]:

$$(1/T_2')_d=4\gamma_N{}^4\hbar^2I(I+1)N/5Dd, \tag{5}$$

$$(1/T_1)_d=144\pi\gamma_N{}^4\hbar^2I(I+1)ND/25\omega^2d^5, \quad (\omega^2\tau_c{}^2\gg1) \tag{6}$$

$$(1/T_1)_d=2\pi\gamma_N{}^4\hbar^2I(I+1)N/5Dd, \quad (\omega^2\tau_c{}^2\ll1). \tag{7}$$

Here γ_N is the nuclear gyromagnetic ratio, N is the number of nuclei per unit volume, D is the self-diffusion coefficient, ω is the Larmor precession frequency of the nuclei, and d is the distance of closest approach of two nuclei. τ_c is the correlation time for diffusional motion and can be considered to be an estimate of the average time for which an atom remains on a lattice site between jumps. Equation (5) applies only when the rigid-lattice resonance linewidth is narrowed by a high diffusion rate. For small diffusion rates $(T_2')_d$ becomes a constant characterizing the dipole-dipole interaction when the atoms have fixed positions in the lattice.

3. Diffusion Coefficient and Activation Parameters

The diffusion coefficient can be written as

$$D=\gamma a^2\nu_0\exp(-\Delta G_a/RT), \tag{8}$$

where γ is a constant depending on the crystal structure,

[11] T. Liu and H. Drickamer, J. Chem. Phys. **22**, 312 (1954).
[12] S. W. Kurnick, J. Chem. Phys. **20**, 219 (1952).
[13] C. B. Pierce, Phys. Rev. **123**, 744 (1961).
[14] D. W. McCall, D. C. Douglass, and E. W. Anderson, Phys. Fluids **2**, 87 (1959).
[15] G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **15**, 241 (1958).
[16] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[17] Another derivation of these equations gives the numerical factor in Eq. (6) as 192/25 [R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954)]. This does not affect the use of this equation in the present instance.

a is the lattice constant, ν_0 is the Debye frequency, usually taken to be 10^{13} sec^{-1}, and ΔG_a is the Gibbs free energy of activation. Using $\Delta G_a=\Delta H_a-T\Delta S_a$, where ΔH_a and ΔS_a are the activation enthalpy and entropy, Eq. (8) becomes

$$D=[\gamma a^2\nu_0 \exp(\Delta S_a/R)]\exp(-\Delta H_a/RT). \quad (9)$$

The expression in brackets is practically independent of temperature, and is often treated as a constant, D_0.

Equations (5) and (9) can be combined to give

$$\Delta H_a=-R[\partial \ln(T_2')_d/\partial(1/T)]_P, \quad (10)$$

where the temperature-independent terms are removed by the differentiation.

Nachtrieb[2] defined the activation volume ΔV_a as

$$\Delta V_a=[\partial\Delta G_a/\partial P]_T. \quad (11)$$

To obtain the connection between ΔV_a and $(T_2')_d$ it is convenient to write Eq. (5) as

$$D=\text{const}\times(T_2')_d/a^4, \quad (12)$$

where the constant includes terms that are independent of temperature and pressure. We have used $d\propto a$ and $N\propto N_0/a^3$, where N_0 is the total number of nuclei in the sample. Using Eqs. (8), (11), and (12), we obtain

$$\Delta V_a=-RT\left[\frac{\partial \ln(T_2')_d/a^6\nu_0}{\partial P}\right]_T. \quad (13)$$

This expression can be expanded to give

$$\Delta V_a=-RT\left[\frac{\partial \ln(T_2')_d}{\partial P}-6\frac{\partial \ln a}{\partial P}-\frac{\partial \ln\nu_0}{\partial P}\right]_T. \quad (14)$$

The last two terms on the right can be simplified to a function of the volume compressibility β and the Grüneisen constant γ_G, using $\beta=-3\partial \ln a/\partial P$ and $\gamma_G=-\partial \ln\nu_0/\partial \ln V$. Then we have

$$\Delta V_a=-RT\left[\left(\frac{\partial \ln(T_2')_d}{\partial P}\right)_T+\beta(2-\gamma_G)\right]. \quad (15)$$

Manipulation of Eq. (7) gives the same expression as Eq. (15) for $(T_1)_d$ in the region of relatively high diffusion, $\omega^2\tau_c^2\ll 1$. From Eq. (6) we obtain for $(T_1)_d$ in the region of relatively small diffusion,

$$\Delta V_a=-RT\left[-\left(\frac{\partial \ln(T_1)_d}{\partial P}\right)_T-\beta(2+\gamma_G)\right]. \quad (16)$$

Equation (15) has been used in this experiment to derive values of ΔV_a from measurements of $(T_2')_d$. The relations involving $(T_1)_d$ have been observed qualitatively.

4. Dynamical Theory of the Pressure Dependence of Diffusion

It has been observed that ΔH_a is approximately proportional to either the melting temperature T_m or the heat of fusion ΔH_m. An empirical correlation of ΔH_a and ΔV_a has also been noted. From their dynamical theory of the effect of pressure on diffusion, Rice and Nachtrieb[10] obtained the following relation between fusion and diffusion parameters:

$$\Delta H_a/\Delta V_a=\Delta H_m/\Delta V_m. \quad (17)$$

Here ΔV_m is the change of atomic (molar) volume upon melting. The empirical correlations have been obtained with values of the parameters appropriate to a pressure of one atmosphere, whereas Eq. (17) is expected to hold over the pressure range for which the melting temperature depends linearly on the pressure.

Another relation which had been noted previously and which was supported by the dynamical theory is

$$\ln D\propto T_m/T, \quad (18)$$

again valid in the limit that T_m is linear in the pressure. Equation (18) is a variant of a law of corresponding states since, although $\ln D$ depends on a reduced variable, the proportionality constant should be different for different substances. Equation (18) has also been found to describe diffusion in alloys[18] when T_m depends on the solute concentration.

The results of the present experiment and of a radioactive tracer experiment[3] on lead are described very well by Eqs. (17) and (18). One inference from these experiments is that, to a good approximation in the limit of low pressures,

$$\Delta H_a=\Delta H_0+P\Delta V_a, \quad (19)$$

where ΔV_a is independent of pressure. Using Eq. (17) we can write Eq. (9) as

$$D=D_0\exp[-(\Delta H_0+P\Delta V_a)/RT]. \quad (20)$$

The pressure dependence of the melting temperature can be described by a linear function $T_m=T_0+KP$, where T_0 is the melting temperature at zero pressure (one atmosphere) and

$$K=[dT_m/dP]_{p=0}=T_0\Delta V_m/\Delta H_m, \quad (21)$$

by the Clausius-Clapeyron relation. If these equations are used to express the pressure P as a function of the melting temperature, and Eq. (19) is used, Eq. (20) can be written

$$D=D_0\exp\left(-\frac{\Delta H_0}{RT_0}\frac{T_m}{T}\right). \quad (22)$$

From Eq. (22) we obtain

$$\partial \ln D/\partial(T_m/T)=-\Delta H_0/RT_0, \quad (23)$$

in which the term on the right is the proportionality constant for Eq. (18).

Equating the arguments of the exponential functions

[18] N. H. Nachtrieb, J. Petit, and J. Wehrenberg, J. Chem. Phys. 26, 106 (1957).

of Eqs. (9) and (22) yields

$$\Delta H_a = (\Delta H_0/T_0)T_m. \quad (24)$$

This is a form of the historic correlation of activation enthalpy and melting temperature. Equation (24) applies to the different states of a single substance, rather than to different substances. The experimental evidence is that $\Delta H_0/T_0$ does not have the same value for all substances.

EXPERIMENTAL DETAILS

1. Spin-Echo Apparatus

The measurements of T_2 were made by applying a 90°–180° pulse sequence and observing the decrease of the nuclear spin-echo amplitude as the pulse separation was increased. When the resonance line shape is determined by the diffusion rate, the echo amplitude envelope is a simple exponential with time constant T_2. A 90°–90° pulse pair was used to measure T_1 by observing the increase of the free induction decay amplitude at a fixed time after the second pulse as the pulse separation was increased. This amplitude increase was an exponential function with time constant T_1.

The apparatus for producing high-power rf pulses and detecting the transient nuclear signals was constructed according to the description of Buchta, Gutowsky, and Woessner.[19] This apparatus was designed for use over a wide range of frequencies, but all of our data were obtained at one frequency, 10 Mc/sec. The only significant change made in the system was to use a simpler rf amplifier for the nuclear signals. A 12-in. Varian Associates electromagnet was used having either cylindrical pole caps with a 2-in. gap or tapered pole caps with a 3-in. gap. The data were obtained visually from oscilloscopic display of the detected echoes and free decays. Electronic integration was not used.

The detector was a 1N34 diode which had to be calibrated because of its non-linear characteristic. This calibration was performed by comparing undetected and detected proton echoes from water containing $MnCl_2$. The paramagnetic ions reduced T_2 to about 10 msec. The procedure used was to obtain the envelope of the decay of the undetected echoes and then the envelope of the decay of the detected echoes. Because of the nonlinear diode characteristic the latter was not exponential. A calibration curve was then prepared by comparison of the detected and undetected decay envelopes.

2. Pressure Equipment

The high-pressure bomb was made of nonmagnetic Berylco 25 beryllium-copper alloy. Figure 1 shows the dimensions and details of the rf lead into the bomb,

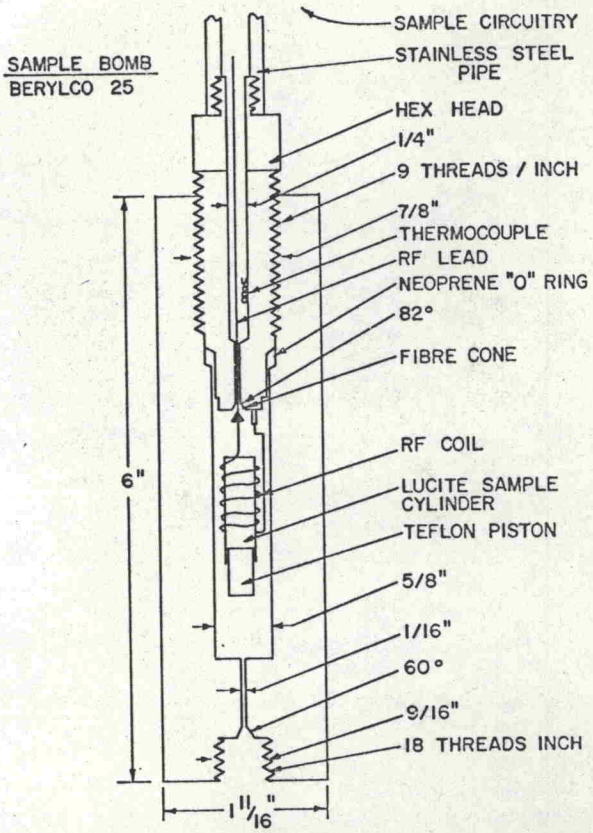


FIG. 1. High-pressure nonmagnetic sample bomb used to 7000 atm. This bomb was constructed following the design of Benedek.[20]

which is essentially a copy of that used by Benedek.[20] The rf sample coil consisted of about 20 turns of No. 26 enameled copper wire and had a diameter of about $\frac{1}{4}$ in. A thin-walled Lucite cylinder about 1 in. long and open at one end served as the sample container. Closely fitted into the open end was a Teflon or Lucite piston.

The pressure-transmitting fluid was a half-and-half mixture of 2-methyl butane and Stanoil Industrial Oil No. 35. During the sodium experiments near −50°C, this mixture froze at about 50 000 psi. The high pressures were produced with a Blackhawk Model P228 hand pump having a capacity of 40 000 psi, followed by a Harwood intensifier which increased the pressure by a factor of about 15. A manganin resistance gauge was used for the pressure measurements with a Heise Bourdon gauge serving as the pressure standard. The Bourdon gauge was used to calibrate the manganin gauge to 50 000 psi, and the calibration was then linearly extrapolated to 100 000 psi. Changes in the resistance of the manganin element were measured with a bridge whose sensitivity permitted measurement of pressure to ±200 psi.

[19] J. C. Buchta, H. S. Gutowsky, and D. E. Woessner, Rev. Sci. Instr. 29, 55 (1958).

[20] G. B. Benedek and E. M. Purcell, J. Chem. Phys. 22, 2003 (1954).

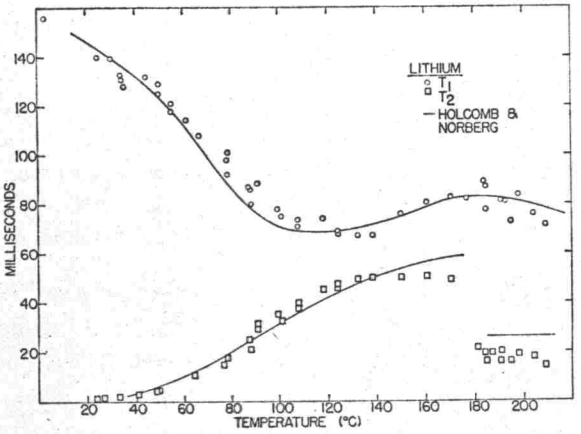


FIG. 2. Experimental values of T_1 and T_2 for lithium at one-atmosphere pressure obtained at a Larmor frequency of 10 Mc/sec. The solid lines represent the measurements of Holcomb and Norberg obtained at a frequency of 9 Mc/sec.[9]

3. Temperature Control

The samples were kept at a constant temperature by immersing the pressure bomb in a regulated temperature bath. For temperatures above room temperature, the liquid used for the bath was Dow Corning 200 fluid of 200 centistoke viscosity at 25°C. The bath was heated by two immersion heaters, with one heater typically almost maintaining the desired temperature, the other being turned on and off by the regulator. Either a Micro-Set mercury thermometer or a thermistor was used as the regulating element. For temperatures below room temperatures, the liquid used for the bath was acetone. The bath was cooled by circulating acetone through coils embedded in the tank, the circulated acetone in turn being cooled by pumping through a dry ice-acetone mixture. Control of the temperature was accomplished by turning the circulating pump on and off. The tank containing the bath was made of thin brass and fitted in the air gap of the magnet with sufficient space for a layer of insulation from the pole caps. Stirring of the bath fluid was achieved by a propeller driven by a motor mounted outside the magnet gap.

Temperature measurements were made with a copper-constantan thermocouple placed near the sample but outside the high-pressure region, as shown in Fig. 1. The thermocouple was forced into contact with the bomb by a Teflon wedge. A dummy run with another thermocouple at the sample site showed that in equilibrium there was an insignificant temperature gradient between the sample site and the thermocouple site outside the pressure region. After each change of pressure the system was allowed about 15 min to come to equilibrium. When the pressure was changed some pressure fluid passed into or out of the bomb, and the waiting time allowed the pressure fluid temperature to equilibrate and the associated slow transient pressure change to die away. It is estimated that the temperature values reported are accurate to at least $\pm\frac{1}{2}°$. In the case of the pressure runs the temperature was maintained constant to within two-tenths of a degree.

4. Samples

Dispersions of lithium and sodium were prepared by vigorously stirring samples of the molten metals in silicon fluid. This was done in a dry box in an argon atmosphere which was not, however, entirely free of water vapor or air. The lithium had less than five millipercent impurity before dispersion, but was probably contaminated to some extent by oxygen and nitrogen after dispersion. Some lithium dispersion produced by the Lithium Corporation of America was also used. Spectroscopic analysis showed this to contain only trace impurities. The commercial dispersion consisted of particles of which 90% had diameter less than 20 μ, adequately smaller than the 60-μ skin depth of lithium at 10 Mc/sec. Measurements of relaxation times in our dispersion and the commercial dispersions showed no sample dependence. The relaxation times for one atmosphere pressure were in agreement with the values of Holcomb and Norberg,[9] within the scatter of our measurements (Fig. 2).

The sodium metal which was dispersed was DuPont Reactor Grade, the only significant impurity being about 100 parts per million of potassium. This sodium was identical to that recently used in an equation of state determination.[21] The skin depth of sodium at 10 Mc/sec is about 30 μ, but the size distribution of the particles in the dispersed metal was not measured. Relaxation times at one atmosphere pressure disagreed somewhat with those given by Holcomb and Norberg[9] (Fig. 3). At the temperatures at which the sodium activation volume was measured, near −50°C, the silicon fluid would freeze, so that hydrostatic pressure could not be transmitted to the metal particles.

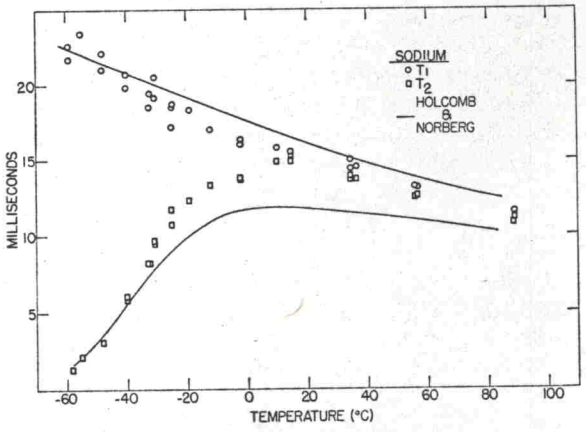


FIG. 3. Experimental values of T_1 and T_2 for sodium at one-atmosphere pressure obtained at a Larmor frequency of 10 Mc/sec. The solid lines represent the measurements of Norberg and and Slichter[22] and of Holcomb and Norberg.[9]

[21] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 18, 329 (1961).

Therefore, the silicone fluid was washed out of the dispersion with ethyl ether, which then became the dispersing fluid. The lithium dispersions were centrifuged after preparation to increase the concentration of metal particles; the sodium particles settled in the ether sufficiently under normal gravity in about a week.

RESULTS

1. Temperature Dependence

The first objective was to measure T_1 and T_2 at several temperatures at one-atmosphere pressure for each metal for comparison with the values of Holcomb and Norberg.[9] These measurements gave us experience with the techniques and verified that our samples were essentially equivalent to those of Holcomb and Norberg. Also, it is necessary to know the temperature dependence of $(T_1)_e$ to obtain $(T_2')_d$ from the measured T_1 and T_2 [Eq. (3)]. Since $(T_1)_e$ is practically independent of pressure, it is sufficient to know the temperature dependence of $(T_1)_e$ at one atmosphere pressure.

Our values of T_1 and T_2 at one atmosphere are shown in Fig. 2 for lithium and in Fig. 3 for sodium. The smooth curves represent the data given by Holcomb and Norberg.[9] Most of the low-temperature data for sodium were obtained by Norberg and Slichter.[22] Our lithium values agree very wlle with the previous work, but the agreement is not as good in the case of sodium. We have not attempted to explain this. At the temperatures near -50°C at which our sodium pressure data were taken, our one-atmosphere values of T_1 and T_2 are approximately the same as those of Norberg and Slichter.[22]

The T_1 temperature dependence for lithium is due to the combination of $(T_1)_e$, which has an inverse temperature dependence, and $(T_1)_d$ which has a minimum near 120°C. These latter two times combine at each temperature according to Eq. (1) to give the total T_1 values of Fig. 2. By graphical interpolation, the curve of $(T_1)_e T = \text{const}$ can be estimated, and the temperature dependence of $(T_1)_e$ obtained. The temperature dependence of $(T_1)_d$ may then also be determined. Not taken into account was the small volume dependence of $(T_1)_e$.[9]

The data of Figs. 2 and 3 were used to derive ΔH_0 for one-atmosphere pressure. Using Eq. (3), $(T_2')_d$ is computed for each temperature at which T_1 and T_2 have been measured. A portion of the plot of $\ln(T_2')_d$ vs $1/T$ can be fitted with a straight line of slope $-\Delta H_0/R$, as given by Eq. (10). For low diffusion rates Eq. (10) is not valid because $(T_2')_d$ becomes the rigid lattice phase memory time when the internuclear distances become constant. Holcomb and Norberg[9] observed for both metals that over a temperature range extending about 100° below the melting point the values of $\ln(T_2')_d$ calculated from Eq. (3) fall below the straight line. This is probably due to the failure of Eq. (3) to give the correct value of $(T_2')_d$ because a third, unknown relaxation mechanism becomes important, rather than to a failure of Eq. (10) to describe the temperature dependence of $(T_2')_d$. It is unlikely that ΔH_0 is changing with temperature. This may be seen by comparing the radioactive tracer[23] and nuclear resonance determinations of the diffusion coefficient of sodium. The radioactive tracer data were obtained at temperatures between 0 and 100°C, whereas the nuclear resonance data used to determine D were obtained in the range -80 to -30°C. The values of both D_0 and ΔH_0 obtained at the lower temperatures agreed with the values obtained at the higher temperatures.

Using the $\ln(T_2')_d$ vs $1/T$ data which could be fitted with a straight line, values of ΔH_0 were obtained for lithium and sodium of 12.0 and 9.4 kcal/mole, respectively. These should be compared to the values 13.2 kcal/mole for lithium and 10.0 kcal/mole for sodium obtained by Holcomb and Norberg,[9] and to 10.5 kcal/mole for sodium obtained in a radioactive tracer experiment.[23]

The values of ΔH_0 from this work are seen to be systematically smaller than those of Holcomb and Norberg. A second series of T_1 and T_2 measurements on lithium gave a value of ΔH_0 agreeing with our first value above, so that the difference between our value and the value of Holcomb and Norberg may be significant. However, our data were somewhat more scattered than those of Holcomb and Norberg, and the value of ΔH_0 depends very sensitively on the slope of the line fitted to the $\ln(T_2')_d$ vs $1/T$ data. Since Holcomb and Norberg obtained the same value for ΔH_0 for lithium by several independent uses of their data, their value should be more reliable than ours. Similarly, in the case of sodium, the one-atmosphere pressure value of ΔH_0 obtained by Holcomb and Norberg is to be preferred over our value. The data taken in the present pressure-dependence measurements are more precise than the temperature-dependence data, and it will be shown below how these pressure data can be used to give values of ΔH_0 in good agreement with those of Holcomb and Norberg.

2. Pressure Dependence

We have not attempted to throw any light on the unknown relaxation process by studying its pressure dependence. We have been guided by the work of Holcomb and Norberg[9] to make our measurements only at temperatures at which $(T_2')_d$ is correctly given by Eq. (3). For this reason, ΔV_a was not measured above 80°C for lithium nor above -40°C for sodium. The low-temperature limits were determined by the magnitude of T_2, since it is not possible with our

[22] R. E. Norberg and C. P. Slichter, Phys. Rev. 83, 1074 (1951).

[23] N. H. Nachtrieb, E. Catalano, and J. A. Weil, J. Chem. Phys. 20, 1185 (1952).

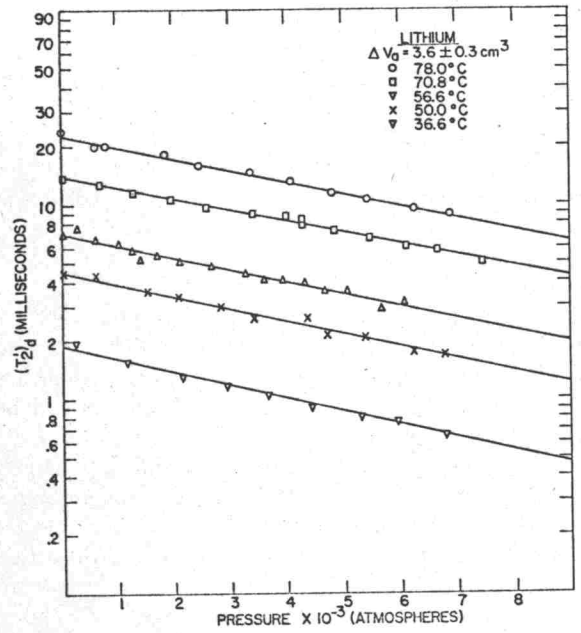


FIG. 4. Experimental values of the dipolar relaxation time $(T_2')_d$ calculated with Eq. (15) for lithium. The measurements were made at constant temperature. The average of the values of the activation volume for the five temperatures is 3.6±0.3 cm³.

apparatus to measure reliably relaxation times less than about 200 μsec. Lithium measurements were not made below 35°C, and sodium measurements were not made below −50°C. Thus, the activation volume could only be measured within a relatively narrow temperature range. In these ranges the effect of $(T_1)_d$ was only about one percent of the calculated value of $(T_2')_d$. The effect of T_1 was less than 10%. In Eq. (15) the term $\beta(2-\gamma_G)$ was less than 5% of the pressure derivative of $\ln(T_2')_d$. It follows that the values of ΔV_a were obtained almost directly from the pressure dependence of T_2.

The effect of pressure in pure metals is to decrease the diffusion coefficient and hence to decrease $(T_2')_d$. For lithium, a pressure of 7000 atm reduced the one atmosphere value of $(T_2')_d$ by a factor of about 3. For sodium, a pressure of 3000 atm reduced $(T_2')_d$ by a factor of about 6.

Figure 4 shows the plots of $\ln(T_2')_d$ vs P for lithium at five temperatures. The data at each temperature were fitted with a straight line by least-squares analysis. The compressibility β and Grüneisen constant γ_G were

TABLE I. Activation volumes for self-diffusion in lithium calculated from the data of Fig. 4 by means of Eq. (15).

Temperature (°C)	Activation volume (cm³)
36.6	3.68
50.0	3.63
56.6	3.61
70.8	3.44
78.0	3.71

TABLE II. Activation volumes for self-diffusion in sodium calculated from the data of Fig. 5 by means of Eq. (15).

Temperature (°C)	Activation volume (cm³)
−42.2	9.57
−45.0	9.86
−50.0	9.26

taken to be $\beta=0.9\times10^{-5}$ atm^{-1} and $\gamma_G=1.0$. With these constants and the slopes of the lines in Fig. 4, ΔV_a was computed for each temperature using Eq. (15). The results are given in Table I. To the accuracy of the measurements there is no temperature dependence of ΔV_a, and the average of the five values, with an estimated error, is ΔV_a(average)$=3.6\pm0.3$ cm³. This is 28% of the atomic volume of lithium.

Figure 5 shows the values of $(T_2')_d$ for sodium for three temperatures and several pressures. Again, the data were fitted with straight lines by least-squares analysis. The values of β and γ_G were taken as $\beta=1.4\times10^{-5}$ atm^{-1} and $\gamma_G=1.3$. Table II shows the values of ΔV_a for sodium calculated with Eq. (15). In this narrow range of temperatures, no temperature dependence of ΔV_a was observed. The average of the three values, with an estimated error, is ΔV_a(average) $=9.6\pm0.5$ cm³, which is 41% of the atomic volume of sodium.

Nachtrieb *et al.*[2] observed a decrease of ΔV_a for sodium with increasing pressure. Their measurements

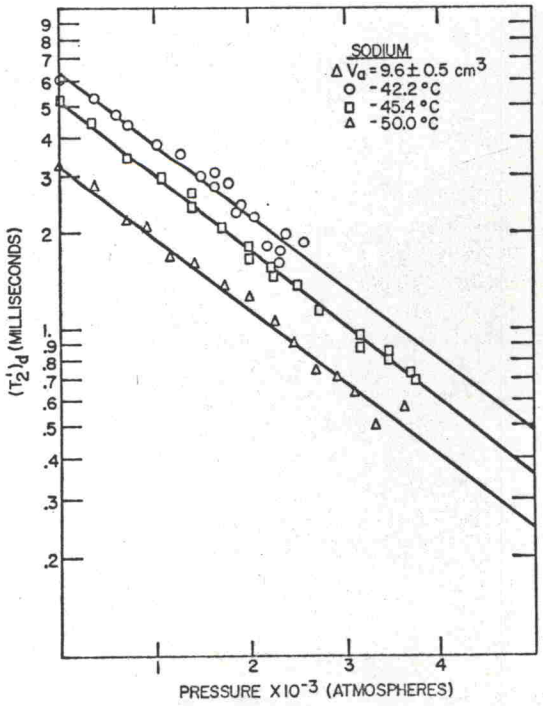


FIG. 5. Experimental values of the dipolar relaxation time $(T_2')_d$ calculated with Eq. (15) for sodium. The measurements were made at constant temperature. The average value of the activation volume for the three temperatures is 9.6±0.5 cm³.

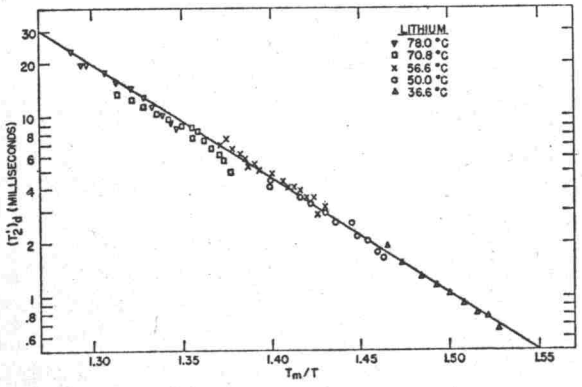


FIG. 6. Experimental values of the dipolar relaxation time $(T_2')_d$ for lithium plotted as a function of the reduced melting temperature T_m/T. The slope of the solid line is -14.5.

were made up to a pressure of 8000 atm. As Fig. 5 shows, we did not obtain a variation of ΔV_a with pressure up to 3000 atm. It may be that measurements of $(T_2')_d$ cannot be carried to sufficiently high pressures to observe the diffusion-dependent curvature of $[\partial \ln(T_2')_d/\partial P]_T$. This is because high pressure will reduce $(T_2')_d$ until Eq. (5) no longer applies, and measurements of $(T_2')_d$ no longer give information about D. For sodium, Eq. (5) is valid for about a thirty-fold decrease of $(T_2')_d$. Since 3000-atm pressure decreases $(T_2')_d$ by a factor of about 6, then if $\ln(T_2')_d$ remains proportional to pressure, diffusion can be studied with these techniques in sodium only up to about 6000 atm.

3. Correlations with Fusion Parameters

Equation (17) can be used to predict values of ΔV_a, Table III lists the one-atmosphere values of ΔH_m. ΔV_m, ΔH_{01}, and ΔH_{02} for lithium and sodium. The last two quantities are, respectively, the activation enthalpies at one atmosphere as determined by Holcomb and Norberg[9] and by the present work. The values of ΔV_a calculated with Eq. (17) are compared with the experimental results in Table IV. For both metals the agreement of experiment with either of the predicted values is satisfactory. With the value of ΔH_0 based on radioactive tracer experiments[23] on sodium, 10.5 kcal/mole, Eq. (17) predicts an activation volume of 9.6 cm³.

TABLE III. Fusion parameters and activation enthalpies for lithium and sodium.

Metal	ΔH_m (kcal/mole)	ΔV_m [a] (cm³/mole)	ΔH_{01} (kcal/mole)	ΔH_{02} (kcal/mole)
Lithium	0.715[b]	0.21	13.2	12.0
Sodium	0.624[c]	0.59	10.0	9.4

[a] O. Kubaschewski, Trans. Faraday Soc. 45, 931 (1949).
[b] T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955).
[c] D. C. Ginnings, T. B. Douglas, and A. F. Ball, J. Research Natl. Bur. Standards 45, 23 (1950).

TABLE IV. Comparison of predicted and experimental values of the activation volume for self-diffusion in lithium and sodium. The predicted values are based on Eq. (17) and the data of Table III.

Metal	$\Delta V_m \Delta H_{01}/\Delta H_m$ (all units are cm³/mole)	$\Delta V_m \Delta H_{02}/\Delta H_m$	ΔV_a(exp)
Lithium	3.9	3.5	3.6±0.3
Sodium	9.4	8.9	9.6±0.5

The value of ΔV_a for sodium from radioactive tracer experiments[2] at 90°C is, in the low-pressure limit, $\Delta V_a(\text{tracer}) = 12.4$ cm³, in poorer agreement with the above prediction than the spin-echo value. Rice and Nachtrieb[10] recognized this poor agreement and suggested that the large pressure dependence of the compressibility of sodium was responsible for the discrepancy. The evidence from the present research is that Eq. (17) is adequate to predict ΔV_a for sodium without additional justification, and that the spin-echo value is more reliable than the radioactive tracer value.

The other relation from the dynamical theory, Eq. (18) or Eq. (23), can also be tested with the present data. In doing this we have also used Eq. (12) and have neglected changes of the lattice constant. A plot of $\ln(T_2')_d$ vs T_m/T includes the data for all pressures and temperatures (except the T_1 and T_2 data of Figs. 2 and 3) obtained for one metal, and yields a single number, the slope of the best straight-line fit to the data. Figure 6 shows a plot of these data for lithium, and Fig. 7 the same for sodium. Values of $T_m(P)$ were obtained from the melting curves of Bridgman.[24] Table V gives the values of the slopes of

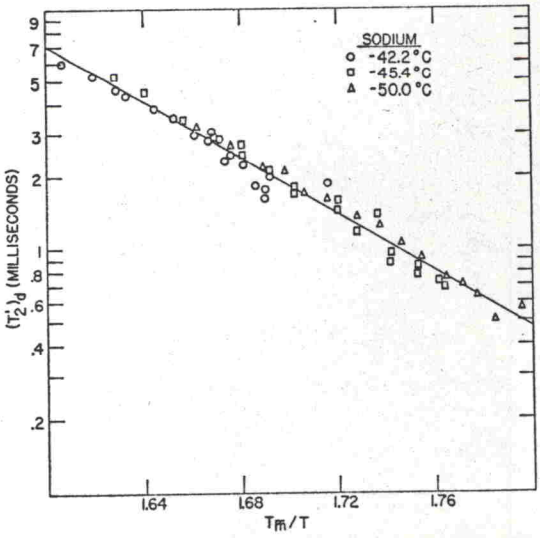


FIG. 7. Experimental values of the dipolar relaxation time $(T_2')_d$ for sodium plotted as a function of the reduced melting temperature T_m/T. The slope of the solid line is -13.5.

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

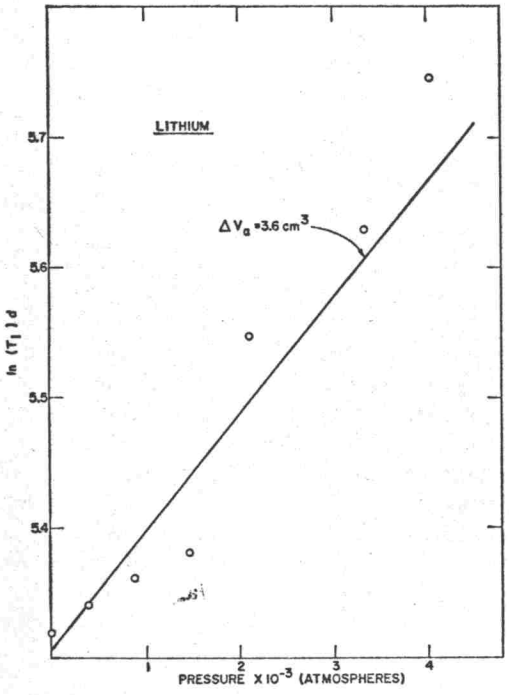


FIG. 8. Plot of the logarithm of the dipolar spin-lattice relaxation time $(T_1)_d$ vs pressure for lithium at 100°C, where $(T_1)_d \propto 1/D$. The slope of the solid line was determined from Eq. (16), assuming an activation volume of 3.6 cm³, and the intercept was chosen to approximate a good fit to the data.

the lines in Figs. 6 and 7 and the calculated values of $\Delta H_0/RT_0$.

The agreement of the experimental slopes and the values of $\Delta H_{01}/RT_0$ is remarkably good for both lithium and sodium. The agreement with the values of $\Delta H_{02}/RT_0$ is satisfactory. We conclude that Eq. (23) is a valid relation, and that $(T_2')_d$ and the diffusion coefficient D, in the limit of low pressure, can be described as functions of the single variable T_m/T. Alternatively, presupposing that Eq. (23) is valid, the data yield values for ΔH_0. These are: $\Delta H_0(\text{Li}) = 13.0$ kcal/mole and $\Delta H_0(\text{Na}) = 9.9$ kcal/mole. It is important to note that the use of Eq. (23) to obtain ΔH_0 requires knowledge of the melting curve so that T_m can be determined for each pressure at which $(T_2')_d$ is measured.

4. Miscellaneous Observations on Lithium

Holcomb and Norberg[9] showed that in the case of lithium $(T_1)_d$ could be obtained as a function of temperature from the $T_1(T)$ measurements. They showed the direct and inverse proportionality of $(T_1)_d$ to the diffusion coefficient in the regions of high and low diffusion, respectively, and were able to measure the activation enthalpy from these dependences. In principle, one can obtain the activation volume from the pressure dependence of $(T_1)_d$. This was attempted in the present work, but the experimental precision was poor. Values of $(T_1)_d$ were

TABLE V. Test of the validity of Eq. (23) with respect to lithium and sodium.

Metal	T_0(°K)	$\Delta H_{01}/RT_0$ (dimensionless quantities)	$\Delta H_{02}/RT_0$	$\partial \ln(T_2')_d/\partial(T_m/T)$
Lithium	453.7[a]	−14.7	−13.4	−14.5
Sodium	371.0[b]	−13.6	−12.8	−13.5

[a] T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955).
[b] D. C. Ginnings, T. B. Douglas, and A. F. Ball, J. Research Nat. Bur. Standards 45, 23 (1950).

obtained from Eq. (4) making use of the fact that $(T_1)_e$ has negligible pressure dependence. Figure 8 shows the plot of $\ln(T_1)_d$ vs P for lithium at 100°C in the region of relatively low diffusion where $(T_1)_d$ is inversely proportional to D. The line in Fig. 8 has been drawn with slope calculated from Eq. (16), assuming an activation volume of 3.6 cm³. Similarly, Fig. 9 shows the plot of $\ln(T_1)_d$ vs P for lithium at 135°C where $(T_1)_d$ is directly proportional to D by Eq. (7). The slope of the line in this case was calculated with Eq. (15). Application of Torrey's detailed theory[25] does not appear warranted in view of the scattering of the $(T_1)_d$ values. Figures 8 and 9 indicate that qualitative verification of the dependence of $(T_1)_d$ on pressure has been obtained.

Although $(T_2')_d$ for lithium cannot be reliably obtained from T_1 and T_2 at temperatures above about 80°C, T_2 was measured at several pressures at 100°C.

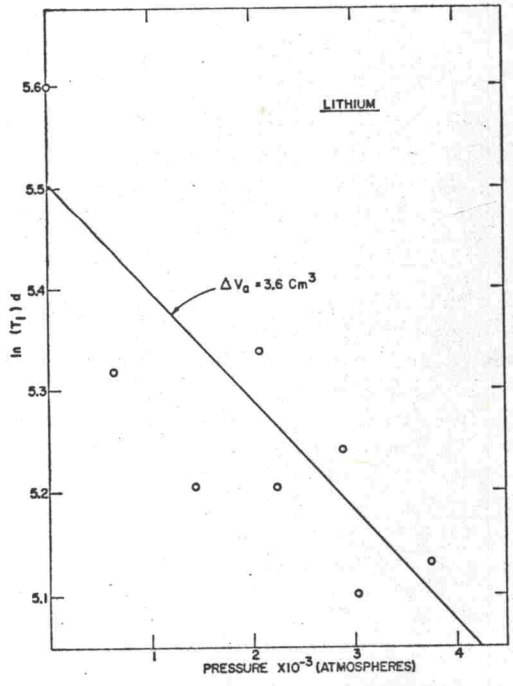


FIG. 9. Plot of the logarithm of the dipolar spin-lattice relaxation time $(T_1)_d$ vs pressure for lithium at 135°C, where $(T_1)_d \propto D$. The slope of the solid line was determined from Eq. (15), assuming an activation volume of 3.6 cm³, and the intercept was chosen to approximate a good fit to the data.

[25] H. C. Torrey, Phys. Rev. 96, 690 (1954).

TABLE VI. Comparison of predicted and experimental values of $\Delta V_a/V$ for various pure metals.

Metal	ΔH_m [a] (kcal/mole)	ΔH_a [b] (kcal/mole)	V (cm³)	$\Delta V_m/V$ [c] (percent)	$\Delta V_a/V$ [percent, from Eq. (17)]	$\Delta V_a/V$ (percent, expt'l)
Lithium	0.715[d]	13.2	13.0	1.65	30	28[e]
Sodium	0.624	10.5	23.7	2.5	42	41[e]
Rubidium	0.52	9.2[f]	5.6	2.5	44	...
Lead	1.14	24.2	18.2	3.5	74	72[g]
Silver	2.70	44.1	10.3	5.0	82	90[h]
Copper	3.11	47.1	7.1	4.15	63	47–55 (theory)[i]
Gold	3.03	41.7	10.2	5.1	70	15 (motion)[j]
Aluminum	2.6	32.3[k]	10.0	6.0	78	...

[a] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Sec. 4, p. 130 ff, except for lithium.
[b] See reference 1, p. 116, except for rubidium and aluminum.
[c] O. Kubaschewski, Trans. Faraday Soc. 45, 931 (1949).
[d] T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955).
[e] This work. [f] See reference 9. [g] See reference 10. [h] See reference 4. [i] See reference 7. [j] See reference 6.
[k] J. J. Spokas and C. P. Slichter, Phys. Rev. 113, 1462 (1959).

Using the line drawn in Fig. 8, $(T_1)_d$ was estimated for these pressures and an apparent $(T_2')_d$ was calculated using Eq. (3). $(T_1)_d$ could have been neglected in these calculations since, although pressure dependent, $(T_1)_d$ was always at least three times as large as T_1. Using these values of $(T_2')_d$ at several pressures an activation volume was estimated. The result was $\Delta V_a(100°C) = 2.6$ cm³. This must be considered to be an unreliable value because of the uncertainty in obtaining $(T_2')_d$ at this temperature.

At temperatures above about 150°C, the envelope of the decaying echo amplitude departed from the exponential shape. This is probably due to a factor $\exp(-kl^3)$ multiplying the usual exponential for the envelope. This effect is well understood,[8] and the constant k is proportional to the diffusion coefficient and to the square of the gradient of the magnetic field. Attempts to vary this nonexponential behavior with high pressure were unsuccessful.

DISCUSSION

In Table VI are presented the calculated and experimental values of $\Delta V_a/V$ for several metals. Here V is the atomic (molar) volume. The good agreement of the prediction of Eq. (17) with experiment in the cases of lithium and sodium has been noted above. Rice and Nachtrieb[10] have pointed out that the lead data fit this equation very well. The value of $\Delta V_m/V$ for silver is somewhat uncertain. Two experimenters[26,27] measured 5.0% and another[28] obtained 3.8%. We have used the larger of these in Table VI to calculate a value of ΔV_a in fair agreement with experiment.[4] For copper the prediction of Eq. (17) is compared with the results of Tewordt's[7] calculation of the static volume of a vacancy. For gold, the comparison is with Emrick's[6] measurement of the motional contribution to ΔV_a. No measurements of ΔV_a for rubidium or aluminum are known to us.

As has been noted, the copper and gold experiments and calculations indicate that the static volume of a vacancy is about 50% of the atomic volume, and that the motional volume is about 15–20%. The calculated and measured values of ΔV_a for lead, silver, and aluminum are consistent with these estimates. The alkali metals, however, appear to be in a different class, having total activation volumes which are less than half their atomic volumes. This fact may support some doubts as to the general validity of the concept of the vacancy as a point defect in those metals which are not close-packed structures.

The other equation obtained from the dynamical theory, Eq. (18) or Eq. (23), holds very well for diffusion in lead. The experimental slope of $\ln D$ vs T_m/T was found by Nachtrieb, Resing, and Rice[3] to be -20.7, and the value of $-\Delta H_0/RT_0$ is -20.3. Equation (18) cannot be tested with the data for diffusion in pure silver since the melting curve as a function of pressure is apparently not known. However, Nachtrieb, Petit, and Wehrenberg[18] have shown that silver diffusion in silver-rich Ag-Pd alloys is well described by Eq. (18) up to a 35% increase of T_m, corresponding to about 20 at. % Pd concentration. The slope of $\ln D$ vs T_m/T for these alloys was -17.75, and the value of $-\Delta H_0/RT_0$, using the parameters for pure silver, is -17.9. This supports the expression for the proportionality constant in Eq. (23) although that equation was derived assuming ΔH_a and T_m were linear functions of pressure. It is a straightforward procedure to rederive Eq. (23) assuming that these parameters are linear functions of alloy composition.

Resing and Nachtrieb[29] have measured the diffusion coefficients of lead in lead-thallium alloys. In the lead-rich compositions, T_m is proportional to the Tl atom concentration. These authors found that if they corrected the diffusion coefficients for departures of the lattice constants from Vegard's law, the corrected values of D were in good agreement with the T_m/T relation of Eq. (18). The activation enthalpies

[26] H. Endo, J. Inst. Metals 30, 121 (1923).
[27] L. Losana, Gazz. chim. italal. 68, 836 (1938).
[28] F. Sauerwald, Z. Metallk. 14, 457 (1922).
[29] H. A. Resing and N. H. Nachtrieb, J. Phys. Chem. Solids 21, 40 (1961).

measured at different concentrations were also corrected, giving a rough qualitative indication that ΔH_a is proportional to Tl concentration. However, in the silver-palladium alloys no variation of ΔH_a with composition was noted within experimental error.

The pressure dependence of ΔH_a given by Eq. (19), or implicitly by Eq. (24), is shown only indirectly by measurements of the pressure dependence of $\ln D$ at constant temperature. Determination of ΔH_a from studies of the temperature dependence of $\ln D$ at constant, high pressure has shown directly that ΔH_a increases with pressure. In a radioactive tracer experiment on sodium,[2] ΔH_a at 8000 atm was found to be 12.06 kcal/mole, 15% larger than the zero-pressure (one atmosphere) value of 10.45 kcal/mole. At 8000 atm, T_m for sodium is also 15% greater than the zero-pressure value, in accord with Eq. (24). In the radioactive tracer experiment of Nachtrieb, Resing and Rice with lead[3] too few data were obtained to give a reliable value of ΔH_a at a high pressure, but qualitatively, ΔH_a increased with pressure. In another study of diffusion in lead,[5] pressures up to 40 000 atm were used, and ΔH_a was determined for several isobars. Although T_m increased by about 40% over the range of pressures used, the values of ΔH_a were quite scattered and appeared to increase only about 10%. This is a surprising result, since it disagrees strongly with the prediction of Eq. (24). Other results of this very high pressure work disagreed with the observations of the lower pressure measurements on lead. It appears likely that these differences can only be resolved by further, more precise experiments.

CONCLUSION

The ratios of activation volume to atomic volume for lithium and sodium found here are the smallest values of this quantity yet reported. These results support the equations of the dynamical theory, but cast doubt on the validity of the concept of the vacancy as a point defect. On the usual interpretation of the vacancy model, such small ratios imply that atoms beyond those adjacent to a vacancy are affected by the vacancy. For lithium it is particularly difficult to justify a small motional volume contribution. It would seem that considerable lattice dilatation would be necessary for an atom to jump onto a vacancy having only one-fourth the atomic volume.

This experiment has shown the continuing usefulness of nuclear spin resonance techniques for studying atom movements. Unfortunately, it will probably not prove feasible to use the method described here with heavier metals at high temperatures when the pressure-independent conduction-electron relaxation time becomes comparable to the pressure-dependent nuclear dipole-dipole relaxation time. Extension of this technique to certain other light elements should, however, be possible.

ACKNOWLEDGMENTS

The authors express their appreciation to Dr. W. H. Jones, Jr. for his assistance and council during the early stages of this work, and to R. D. Engardt for aiding with the high-pressure equipment and data-taking throughout the program.