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# Nuclear-Magnetic-Resonance Determination of the Activation Volume for Self-Diffusion in Aluminum†

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The spin-echo technique of NMR has been used to measure the activation volume for self-diffusion in aluminum metal in the temperature range 400–450 °C. Measurements were made of the inverse linewidth time $T_2$ at hydrostatic pressure up to 3000 atm at selected isotherms in the above temperature range, the upper temperature being determined by the strength characteristics of the stainless-steel pressure vessel and the lower temperature by the minimum value of $T_2$ that could be measured with confidence. The specimens used were 325 mesh filings from 99.99% pure aluminum rod and single crystal. After subtraction of a temperature-independent contribution, the dipolar contribution to $T_2$, $(T_2')_d$, was found to depend on temperature according to $[\ln(T_2')_d]^{-1} \propto T^{-}$ in accordance with theory, yielding an activation enthalpy for self-diffusion of 1.3 ± 0.2 eV, in good agreement with previous determinations. The pressure dependence of $(T_2')_d$, deduced from ten independent experimental runs, yielded an activation volume for self-diffusion of 0.71 ± 0.13 in units of the atomic volume of aluminum, with no discernible systemmatic dependence on the temperature (cited uncertainty is the standard deviation). Nine of the ten determinations fall within the range 0.71 ± 0.20. The result is consistent with expectations based on monovacancy diffusion in aluminum.

## I. INTRODUCTION

For the elementary metals, the vacancy mechnism has been favored over other models of self-diffusion because it has led to best agreement of calculated and experimental values of the activation enthalpy (energy) $\Delta H_a$.[1] In addition to temperature-dependence studies of self-diffusion, which yield $\Delta H_a$, pressure-dependence measurements furnish an estimate of the activation volume $\Delta V_a$. In the customary interpretation of diffusion as an activated process with a Gibbs free energy of activation $\Delta G_a$, the activation volume, defined as the pressure derivative of $\Delta G_a$, has been interpreted as a real physical volume. On the basis of 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 contributes one atomic volume in the case of close-packed structures, e.g., fcc, but in the bcc case the motional contribution is zero.

The primary objective of the research reported here was to determine the activation volume for self-diffusion of aluminum by the NMR method. This method is not concerned with actual macroscopic mass flow, but with the rapidity of individual atom jumps. The NMR, in contrast with the more conventional radioactive-tracer technique, should suffer very little by the higher rates of diffusion which occur along grain boundaries, surfaces, and other avenues of high mass flow since relatively few atoms take part in this type of flow.[1]

Pulsed-NMR methods were first employed in the study of self-diffusion in metals by Holcomb and Norberg[2] who determined the activation energies for self-diffusion in lithium, sodium, and rubidium. These methods were subsequently combined with high-pressure techniques by Barnes, Engardt, and Hultsch[3,4] to measure the activation volume for self-diffusion in lithium and sodium.

Seymour[5] employed NMR methods (steady state) to study the temperature dependence of diffusion in aluminum. His data were reinterpreted by Spokas[6] and by Spokas and Slichter[7] after they investigated the relaxation times $T_1$ and $T_2$ as functions of the temperature using pulsed NMR. They found it necessary to introduce an unknown interaction, independent of temperature, to interpret their data and determine an activation energy. This assumption has been confirmed by the more recent NMR measurements of Fradin and Rowland[8] of the temperature dependence of diffusion in aluminum.

Previous determinations of the activation volume for self-diffusion in aluminum have employed a variety of techniques. Butcher[9] and Butcher, Hutto, and Ruoff[10] measured the effect of pressure on the steady-state creep of aluminum. Beyeler and Adda[11] utilized the radioactive-tracer technique and pressures to 10 kbar. Norris[12] studied the annealing of dislocation loops at pressures to 60 kbar. In another series of experiments, Emrick and McArdle[13] determined the volume of formation of vacancies $\Delta V_f$ in aluminum from measurements of the quenched-in electrical resistivity of wires, and Buescher and Emrick[14] obtained values for the motional activation volume $\Delta V_m$ from measurements of the effect of pressure on the annealing rate of the excess resistivity in quenched wires. Bourassa, Lazarus, and Blackburn[15] also determined the volume of formation of vacancies from the effect of pressure on the thermoelectric power of aluminum wires. The volume of formation $\Delta V_f$ has also been inferred from the data of Detert and Ständer,[16] and on the length changes accompanying quenching, by Tuler.[17] The results of these various experiments have not been altogether consistent, values of $\Delta V_a$ both greater and smaller than the atomic volume having been obtained. An attempt by Tuler to measure $\Delta V_a$ by NMR methods failed to yield a quantitative result.

In the work reported here, the measurements have been restricted to the temperature range 400–450 °C and to hydrostatic pressures less than 3000 bar because of the rather severe limitations imposed by the relaxation times to be measured and by the strength of the pressure vessel which could be fit into the magnet gap.

## II. THEORY

### A. Nuclear Spin Relaxation Times

This section comprises a very brief summary of the procedure of Holcomb and Norberg[2] for separating the relaxation times associated with the different relaxation mechanisms. These relations between the relaxation times have also been discussed in detail by Spokas[6] and by Spokas and Slichter[7] for the specific case of aluminum.

In general, the total relaxation times $T_1$ and $T_2$ are each determined by the sum of the reciprocals of the times for the different mechanisms. Thus, for $T_1$, $T_1^{-1} = \sum_i (T_1)_i^{-1}$, and a similar relation applies to $T_2$. For each relaxation mechanism, we have

$$(T_2)_i^{-1} = (T_2')_i^{-1} + (T_1')_i^{-1} , \tag{1}$$

where $(T_2')_i$ is associated with the line broadening due to static local fields, and $(T_1')_i^{-1} = \alpha (T_1)_i^{-1}$ , in which $\alpha$ is a numerical coefficient of order unity and never greater than unity and the precise value of which depends upon the type of interaction.[18,19]

In the case of aluminum, the contributions to $T_2$ are the nuclear dipolar contribution $(T_2)_d$, the nuclear dipole-conduction electron term $(T_2)_e$, and the $x$-interaction term $(T_2)_x$ introduced by Spokas and attributed to an interaction between the nuclear quadrupole moment and the electric field gradient at the nuclear site.[6] This interaction was assumed to be independent of temperature and will be discussed more completely in Sec. IV. The fact that $T_1 T$ is constant over the full range of temperature from roughly one degree to above the melting temperature[7,20,21] indicates that the only observable contribution to $T_1$ is $(T_1)_e$. Both $(T_1')_d^{-1}$ and $(T_1')_x^{-1}$ may be set equal to zero. The net result is that the quantity of interest in the present investigation $(T_2')_d^{-1}$ is given by

$$(T_2')_d^{-1} = (T_2)^{-1} - (T_2')_x^{-1} - (T_1)^{-1} \tag{2}$$

in the case of aluminum.

### B. Relation of Nuclear Relaxation Times and the Activation Parameters for Diffusion

The nuclear relaxation times associated with the dipole-dipole interaction depend on the diffusion coefficient $D$, as first shown by Bloembergen, Pound, and Purcell[22] for the case of liquids, and by Holcomb and Norberg[2] for the case of the solid alkali metals. In the present instance, we are only interested in the relation of $(T_2')_d$ to $D$, which is[2]

$$(T_2')_d^{-1} = 4\gamma_N^4 \hbar^2 1(1+1) N/5Dd . \tag{3}$$

Here, $\gamma_N$ is the nuclear gyromagnetic ratio, $N$ is the number of nuclei per unit volume, $D$ is the self-diffusion coefficient, and $d$ is the distance of closest approach of two nuclei. Equation (3) applies only when the rigid-lattice linewidth is narrowed by a high diffusion rate. For small diffusion rates, the atoms have essentially fixed positions in the lattice and $(T_2')_d$ becomes a constant characterizing the rigid-lattice dipole-dipole interaction.

The relations between the temperature and pressure dependence of $(T_2')d$ and the activation enthalpy $\Delta H_a$ and activation volume $\Delta V_a$ for self-diffusion are derived in Ref. 4. These relations are based on the fact that the diffusion coefficient can be written[23]

$$D = \gamma a^2 \nu_0 e^{-\Delta G_a / RT} , \tag{4}$$

where $\gamma$ is a constant depending on the crystal structure ($\gamma = 1$ in the fcc case), $a$ is the lattice constant, $\nu_0$ is the Debye frequency, and $\Delta G_a$ is the Gibbs free energy of activation. Taking $\Delta G_a = \Delta H_a - T \Delta S_a$, where $\Delta H_a$ and $\Delta S_a$ are the activation enthalpy and entropy, respectively, differentiating with respect to pressure, and defining

$$\Delta V_a = \left( \frac{\partial \Delta G_a}{\partial P} \right)_T \tag{5}$$

leads to the expression[4]

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

Introducing the volume compressibility $\beta$ and the Grüneisen constant $\gamma_G$, and using $\beta = 3 \partial \ln a / \partial P$ and $\gamma_G = - \partial \ln \nu_0 / \partial \ln V$, then yields the final expression for the activation volume,[4]

$$\Delta V_a = - RT \left[ \left( \frac{\partial \ln (T_2')_d}{\partial P} \right)_T + \beta (2 - \gamma_G) \right] . \tag{7}$$

This last expression is used in the present work to obtain values of $\Delta V_a$ from the pressure dependence of ($T_2'$) at constant temperature.

## III. EXPERIMENTAL DETAILS

### A. NMR Equipment

A block diagram of the spin-echo apparatus is shown in Fig. 1. The system was constructed according to previously published designs.[24,25] A crystal-controlled oscillator operating at 5.25 MHz supplies the radio frequency to the rf gate and to the reference. The phase shifter in the reference allows the phase difference between the reference and the nuclear signal to be varied by 360°.

The transmitter develops pulses of 1600 V without a load. When coupled to the sample circuitry and pressure vessel, the pulse voltage at the transmitter output decreases to approximately 400-V peak to peak. Pulse widths of 10–15 $\mu$sec are sufficient to produce a 90° pulse with respect to aluminum. This corresponds to a rotating magnetic field $H_1$ of 25 Oe. With a higher $Q$ tank circuit, such as a high-temperature probe or simply a coax pipe and sample coil connected in the sample circuitry, pulses as short as 2 $\mu$sec yield a 90° pulse for protons at 10.5 MHz. This corresponds to $H_1 = 60$ Oe.

The recovery time of the receiver was originally estimated to be near its nominal value of 20 $\mu$sec, as it took this long after the end of a rf pulse for the detected receiver output to fall from its saturated value to near zero. Attempts to reduce this with switching circuits and balancing networks did not noticeably improve the recovery time.

Later it was found that the true recovery time can only be seen in the presence of a signal, such as the steady reference signal which is normally used to bias the crystal detector. The recovery of normal gain is really the condition of interest. This can most easily be seen by looking at a steady signal at the rf output of the receiver. It was found that after a pulse had been applied to the sample circuitry, the receiver was saturated for 20 $\mu$sec following the pulse and then returned to nearly the amplitude determined by the reference signal but did not fully return to normal amplification until 75 $\mu$sec after the pulse. Accurate amplitude measurements are restricted to echoes which occur 75 $\mu$sec or more after the second pulse, or more than 150 $\mu$sec after the first pulse. This limitation is important if the relaxation time $T_2$ is about this short. A rf output was added ahead of the detector of the amplifier to allow the amplitude of a coherent 10.5-MHz reference signal to be measured relative to the amplitude of the nuclear signal. Knowing the ratio of these signals and the amplitude of the detected nuclear signal one can find the amplitude of the reference signal at the crystal detector. A reference signal of 1.5 V at the detector proved sufficient to bias it into the linear region.

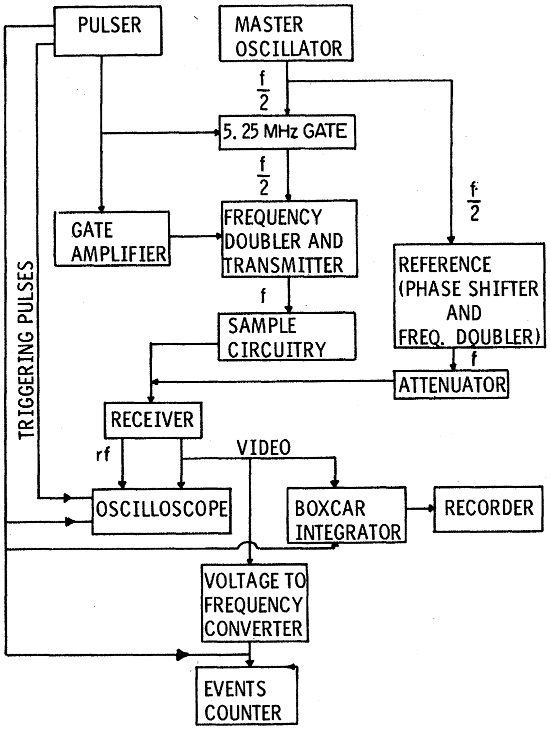

FIG. 1. Block diagram of the spin-echo apparatus.

Values of $T_2$ were obtained from Polaroid multiple-exposure pictures of echo amplitudes for various values of $t = 2\tau$, or from the strip-chart output of a boxcar integrator.[25] The time between rf pulses was adjusted by a step switch and was measured by a Berkeley Universal Counter Model 7360R or a Hewlett Packard Counter Model 524D.

All of the measurements were made in a Harvey Wells 12-in. low-impedance electromagnet, Model L128, with a 3-in. air gap. The associated power supply (Harvey Wells HS-1050) has a current stability of $10^{-5}$ at 5000 Oe. Additional details of the electronic instrumentation are contained in Ref. 26.

### B. Pressure Equipment

The pressure generating equipment is essentially that described in Refs. 4 and 26. Full details are contained in the latter reference.

The design of the pressure vessel itself is rather conventional, and is shown in Fig. 2. The body of the vessel was machined of A286, a precipitation-hardenable stainless steel. This is a nonmagnetic alloy which retains its strength to above 450 °C. The material was obtained from Republic Steel Corp. and hardened to Brinnell No. 321 by following the manufacturer's direction. The plug was machined of another high-temperature nonmagnetic stainless steel 19 – 9$DL$, also obtained from Republic Steel. This material is not hardenable by heat treatment.

The copper sealing rings flowed enough at high temperatures that it was often necessary to tighten the plug a few times with the vessel at about 200 °C before a good seal could be obtained. Part of this difficulty no doubt came from the low viscosity of 3-centistoke silicone oil at temperatures near 450 °C. The pressure fluid first used was Dow-Corning DC200, 200 centistokes. This fluid "crosslinked" at these elevated temperatures and upon disassembly of the pressure vessel was found to contain a puttylike substance composed of many small sticky translucent balls. This substance was probably very fluid at 400 °C, but it would migrate along the pressure line, cool, and plug it. It was found that a simple test for an unplugged line was to increase the pressure at the intensifier and watch the galvanometer connected to the thermocouple imbedded in the vessel. If the temperature dropped within a few seconds it indicated that the pressure fluid was entering the pressure vessel.

Dow-Corning DC550 silicone fluid was also tried. This lasted longer than DC200, 200 centistokes but it too would crosslink after prolonged time at high temperatures. Finally, Dow-Corning DC200, 3 centistokes was used successfully as a pressure fluid. The only disadvantage of this fluid was that it was difficult to contain. Although kept for several days at high temperatures, it never crosslinked or gelled. The only indication that it had been subjected to such treatment was a slight discoloration.

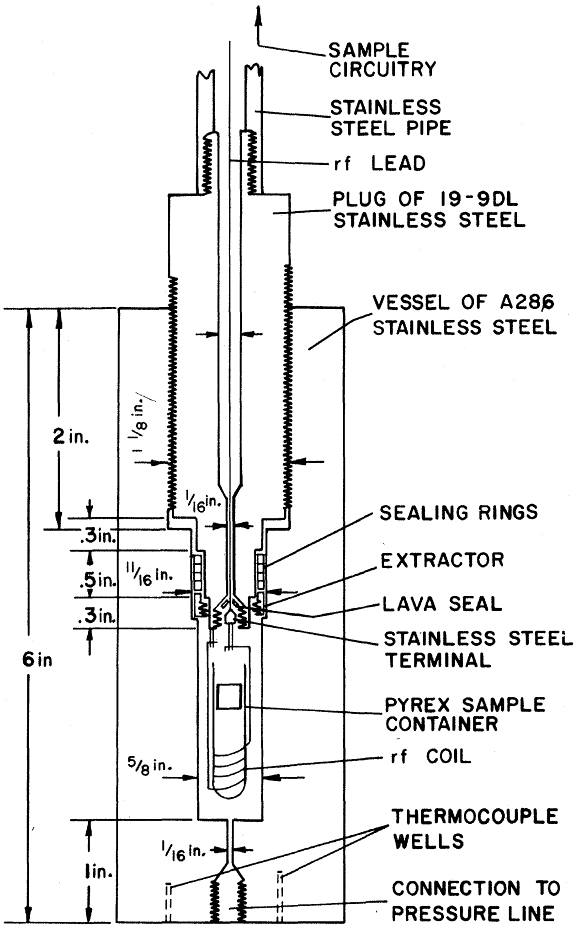

FIG. 2. Stainless-steel pressure vessel used for spin-echo measurements. Outside diameter of the vessel is $2\frac{1}{8}$ in.

The entire pressure vessel was contained in a cylindrical oven which was insulated with asbestos on the outside to prevent heating of the magnet pole pieces. The noninductive heater of this oven was dc powered. Under the usual operating conditions, temperatures remained constant to ± 1 °C without control, however, for some runs a conventional proportioning type controller circuit was used, employing the signal from one of the thermocouples embedded in the pressure vessel (see Fig. 2).

### C. Sample Preparation

Two sources of 99.99% aluminum were used. One source was a single-crystal rod of aluminum purchased from the Monocrystals Co. The rf penetration depth in aluminum is 28 $\mu$ at 10.5 MHz and room temperature, and increases as the temperature is increased. To ensure reasonably uniform penetration the samples used in the pressure dependence study consisted of filings less than 325 mesh (44 $\mu$) obtained from this crystal bar. Ferromagnetic particles were removed from the sample by repeatedly passing a test tube containing small amounts of loosely packed sample through a 5000-G magnetron magnet. These aluminum filings were put in a Pyrex glass tube, 9 mm o.d. and about 3 cm in length, and mixed with Dow-Corning 550 silicone fluid. A loose fitting glass piston was placed in the tube on top of the filings. One sample in which the filings were mixed with Dow-Corning DC200, 3 centistokes silicone fluid sintered at high temperature and pressure.

The other source of samples was a piece of aluminum from an ingot which was part of the Ames Laboratory pure metals stock. This piece was filed, and the filings were sieved and cleaned of ferromagnetic particles. Samples from this source were used only in a temperature dependence study.

## IV. EXPERIMENTAL RESULTS

### A. Previous NMR Work on Aluminum

Spokas[6,7] employed the spin-echo technique to measure the spin-lattice relaxation time $T_1$ and the inverse linewidth relaxation time $T_2$ in 99.99% aluminum foil as a function of temperature from 77 °K to above the melting point. The objective was to obtain the activation energy for self-diffusion from the temperature dependence of $(T_2')_d$ in the motionally narrowed regime. However, $(T_2')_d$ is not measured directly, but must be extracted from the measured quantities $T_1$ and $T_2$.

The difficulties involved and their resolution in the case of aluminum are best seen by considering the temperature dependence of $T_1$ and $T_2$. The spin-lattice relaxation time $T_1$ conforms to the equation $T_1 T = 1.85$ sec deg from a little over 1 °K to above the melting point. This is the dependence expected for an uncomplicated nuclear-spin–conduction-electron-spin interaction (Ref. 19, p. 357). The relaxation time $T_2$ is best studied by considering the decay of the transverse magnetization $M_{xy}$ in three temperature ranges. The first is the low-temperature range extending from the rigid-lattice condition to 360 °C. The intermediate temperature range runs from 360 to 460 °C, in which the decay of $M_{xy}$ is exponential. The high-temperature range extends from 460 °C to the melting temperature 660 °C. In this range, the decay of $M_{xy}$ departs from exponential behavior and gives an indication of the source of an "$x$" interaction which is important to consider in both the intermediate and high-temperature regions.

In the rigid lattice, the decay of $M_{xy}$ is not Gaussian in shape, and hence the motional narrowing theory of Kubo and Tomita,[18] which concerns itself with the transition region wherein the decay shape changes from a Gaussian decay to an exponential decay, is not applicable. Therefore, the data taken in the temperature range 280–360 °C were not amenable to interpretation, although the qualitative change in decay shape was as expected, i.e., a smooth change from the rigid-lattice shape to an exponential decay shape.

In the intermediate-temperature region, the decay shape was exponential. Abragam (Ref. 19, p. 292), for example, shows that in the range of high temperatures and short correlation times, such that the narrowed linewidth is much less than the rigid-lattice width, a single relaxation time $T_2$ exists for a nuclear-dipole–nuclear-dipole interaction between like or unlike spins. If only the nuclear-spin–conduction-electron interaction and the nuclear-dipole–nuclear-dipole interaction were present, the dipolar phase memory time $(T_2')_d$ could be found directly from the measured values of $T_1$ and $T_2$. The temperature independence of $T_1 T$ for aluminum[6] over the entire temperature range 1 to above 660 °K is the expected result if the only relaxation mechanism contributing to $T_1$ is $T_{1e}$. Therefore, $(T_2)^{-1}$ was expected to be given by $(T_2)^{-1} = (T_2')_d^{-1} + (T_1)_e^{-1}$ which is Eq. (2) without the $T_{2x}'$ term. Spokas found that $\ln(T_2')_d^{-1}$ values calculated in this manner were not a linear function of $T^{-1}$ as anticipated. However, by subtracting the constant value of $(T_2')_x^{-1} = 435\ \text{sec}^{-1}$ from the above $(T_2')_d^{-1}$ values, a linear dependence on $T^{-1}$ was obtained.[6,7]

Although $(T_2')_x$ is constant, its contribution to $T_2^{-1}$ varies in importance as the values of the other terms change with temperature. For example, at 450 °C, $T_2^{-1} = 1430\ \text{sec}^{-1}$ and subtracting $(T_1)_e^{-1}$ and $(T_2')_x^{-1}$ we have $(T_2')_d^{-1} = 603\ \text{sec}^{-1}$. Here the quantity $(T_2')_d^{-1}$ which is sensitive to diffusion contributes less than 50% to the total measured quantity $T_2^{-1}$. If the pressure dependence of the diffusion sensitive $(T_2')_d$ is sought, one should work at lower temperatures where $(T_2')_d$ contributes more substantially to the measured $T_2$. At 400 °C, $(T_2)^{-1} = 3330\ \text{sec}^{-1}$ and $(T_2')_d = 2350\ \text{sec}^{-1}$, which is a much more favorable situation. Spokas's introduction of the "$x$" interaction was justified on the basis that the theory of dipole-dipole narrowing requires $(T_2')_d$ to increase as the diffusion increases.[2,6,22] The simple form of the $x$ interaction is supported by agreement of an activation enthalpy (energy) of 1.4 eV, derived from the slope of $\ln(T_2')_d^{-1}$ vs $T^{-1}$, with that predicted by Nowick,[27] and with that determined by Butcher[9] using steady-state creep measurements. This value is also in agreement with the prediction of a semiempirical formula and the "narrowing temperature" found by Spokas.[6] The source of the "$x$" interaction was attributed to nuclear-quadrupole–electric-field-gradient interaction. The sources of the electric field gradients were more likely due to dislocation lines than to impurities. The supporting arguments are given in Spokas's thesis.[6]

At temperatures above 450 °C, the echo amplitudes, which measure $M_{xy}$, for larger times were observed to fall off more slowly than dictated by the initial variation of echo amplitudes. This was shown theoretically by Spokas[6] to be the expected behavior if the "$x$" interaction was due to a quadrupole interaction. The agreement was qualitative as the precision of the data did not allow quantitative agreement.

An impurity effect was also shown by measuring $T_1$ and $T_2$ as a function of temperature in a 99.5% aluminum-foil sample. Although the data are not as extensive as for the 99.99% aluminum foil, they showed a marked reduction in $T_2$ at temperatures above 360 °C and a slight reduction of $T_1$. Seymour and Flynn[28] conducted a careful study of diffusional narrowing of the NMR in aluminum and copper using steady-state resonance techniques. They found the variation of line shape and width of the $\text{Cu}^{63}$ resonance followed quantitatively the theory of Kubo and Tomita,[18] and found an activation energy for self-diffusion in copper. But, in the case of aluminum, they concluded that the presence of the considerable additional linewidth, of undetermined origin, prevents a precise analysis in terms of the theory of Kubo and Tomita.

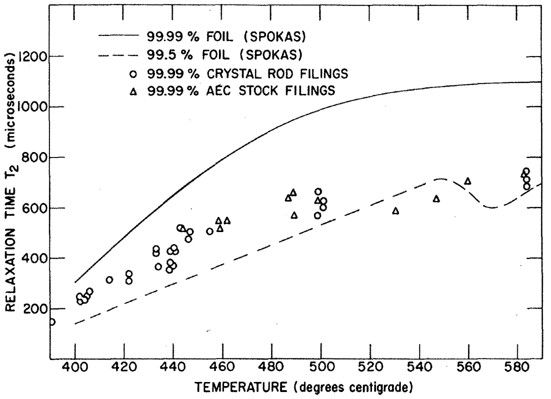

FIG. 3. Temperature dependence of the inverse linewidth relaxation time $T_2$ in aluminum metal.

### B. Present Results

The objective of this work was to measure the pressure dependence of the inverse linewidth relaxation time $T_2$ to determine the activation volume for self-diffusion in aluminum. The diffusion sensitive parameter is the dipolar phase memory time $(T_2')_d$. This parameter, however, cannot be measured directly but must be found from the measured values of $T_1$ and $T_2$, as previously discussed in the review of Spokas's work. As shown by Spokas[6] and others,[28] it is necessary to introduce a temperature-independent "$x$" interaction to explain the temperature dependence of $T_2$. Therefore, the temperature dependence of $T_2$ will be discussed before discussing the pressure dependence.

Two $T_2$-vs-temperature runs were conducted for samples of different origins. Data were taken mainly in the temperature region of interest in this experiment (400–440 °C). The results are shown in Fig. 3. One source of samples was a single-crystal rod of 99.99% aluminum obtained from the Monocrystals Co. This was also the source of the samples used in the pressure study. The other source of samples was a piece of aluminum obtained from an ingot held by the Ames Laboratory as part of its pure metals stock. Its purity was nominally 99.99+%. The samples consisted of filings of less than 325 mesh (44 $\mu$) to ensure reasonably uniform penetration of the rf pulses. As shown, the two temperature runs agreed with each other, but the values of $T_2$ obtained were smaller than those reported by Spokas for 99.99% aluminum foil but greater than his values for 99.5% aluminum foil. For example, at 440 °C the value of $T_2$ obtained in this work was 430 $\mu$sec compared to the values obtained by Spokas of 640 $\mu$sec for 99.99% aluminum foil and 290 $\mu$sec for 99.5% aluminum foil.[6,7]

Although the $T_2$ values were smaller, it was possible, using the procedure outlined in the review of Spokas's work, to find a temperature-independent value of $(T_2')_x^{-1} = 870\ \text{sec}^{-1}$ such that $\ln(T_2')_d$ showed a linear dependence on $T^{-1}$ in the temperature range 400–580 °C. At temperatures above 590 °C, the filed samples sintered and were useless for spin-echo experiments. The activation energy determined by this dependence was $1.3 \pm 0.2$ eV, which is in good agreement with the value of $1.4 \pm 0.1$ eV reported by Spokas.

For temperatures above 450 °C, the "$x$" interaction causes a discernible departure from an exponential decay. The $T_2$ values plotted in Fig. 3 are determined from the "initial" decay rates. Since the data at high temperature often are slightly nonlinear smooth curves of ln (echo amplitude) versus time of echo $2\tau$, the "initial" decay rate is not well defined, and it may be one source of disagreement with Spokas's $T_2$ data at higher temperatures. The pressure dependence of $T_2$ was not determined for temperatures above 450 °C because the strength of the pressure-vessel materials decreases rapidly for temperatures above approximately 450 °C.

It was proposed by Spokas[6] that the "$x$" interaction is a static unnarrowed nuclear-quadrupole–electric-field-gradient interaction, in which the electric field gradients arise mainly from dislocation lines. Furthermore, the linewidth caused by this interaction is approximately given by[6]

$$(T_2')_x^{-1} \simeq \delta\omega_{\text{dis}}(a/l) , \tag{8}$$

where $l$ is the mean distance between the assumed randomly dispersed dislocations, $a$ is the nearest-neighbor distance, and $\delta\omega_{\text{dis}}$ is the interaction strength for nuclei closest to the dislocation. Taking a realistic dislocation density of $10^6$ lines/cm$^2$ necessitates a not unreasonable nearest-neighbor interaction of $\delta\nu_{\text{dis}} = \delta\omega_{\text{dis}}/2\pi = 2\times 10^6$ cps.[6]

To examine the temperature dependence of $(T_2')_x^{-1}$, it is noted that the interaction strength $\delta\omega_{\text{dis}}$ is proportional to the nuclear quadrupole moment and the electric field gradient. Assuming that the electric field gradient produced at a nearest-neighbor site by a dislocation line has the same radial dependence as a line charge, the field gradient and consequently $\delta\omega_{\text{dis}}$ would be proportional to $a^{-2}$. Equation (8) becomes

$$(T_2')_x^{-1} \simeq (A/a^2)(a/l)$$

or

$$(T_2')_x^{-1} \simeq A/al ,$$

where $A$ is a constant. If it is assumed that the total number of dislocations is constant, it follows that the mean distance $l$ between randomly dispersed dislocations is proportional to $a$, and the relationship becomes

$$(T_2')_x^{-1} \simeq B/a^2 ,$$

where $B$ is a constant. Therefore,

$$\frac{\partial \ln(T_2')_x^{-1}}{\partial T}\bigg|_P \simeq -2a^{-1}\left(\frac{\partial a}{\partial T}\right)_P = -4.6\times10^{-5}(^\circ\mathrm{K})^{-1}, \quad (9)$$

where the linear thermal expansion[29]

$$a^{-1}\left(\frac{\partial a}{\partial T}\right)_P = 2.3\times10^{-5}(^\circ\mathrm{K})^{-1}$$

has been employed. Therefore, the change in $(T_2')_x^{-1}$ for the temperature change 400–660 °C would be approximately 1%. This temperature dependence is far too small to be observed in this work.

In a similar manner, the pressure dependence of $(T_2')_x^{-1}$ is given by

$$\partial \ln(T_2')_x^{-1}/\partial P\,|_T \simeq -2a^{-1}\left(\frac{\partial a}{\partial P}\right)_T$$

$$= 0.92\times10^{-6}\ \mathrm{atm}^{-1}, \quad (10)$$

where the volume compressibility

$$\beta = -3a^{-1}\left(\frac{\partial a}{\partial P}\right)_T = 1.38\times10^{-6}\ \mathrm{atm}^{-1};$$

Ref. 29 has been used. The maximum pressure used in this work was 3000 bar, which would produce only a 0.3% change in $(T_2')_x^{-1}$. Therefore, $(T_2')_x^{-1}$ may be assumed to be independent of the pressure.

The assumption that the number of dislocations in an annealed sample is temperature independent is based upon considerations reviewed, for example, by Dekker.[30] Since theoretical calculations give an energy of formation of a dislocation to be 5–10 eV/atom, and since $kT$ at 600 °C is less than 0.1 eV, it follows that thermal activation cannot be responsible for the creation of a dislocation.[30] The density of dislocations in a solid is determined essentially by its history, i.e., by conditions under which the crystal was grown; the mechanical stresses it has experienced, which may generate new lengths of dislocations; and annealing. It is not possible to remove all dislocations by annealing. Although certain parts of a dislocation may be mobile, other parts may be hindered from moving by interaction with other dislocations or impurities, and high dislocation densities may be preserved in an annealed crystal. Therefore, dislocations are not in thermal equilibrium with the lattice and in this respect behave differently from vacancies and interstitials. From these considerations, one may infer that the dislocation densities present after annealing will remain approximately constant if no mechanical stress is applied.

Since the histories of the foil samples used by Spokas and the filed samples used in this work may be expected to be different, it is not unreasonable to expect the dislocation densities to be different, and therefore the values of $(T_2')_x^{-1}$ to differ.

The temperature dependence of $T_{1e}$ has been well established[6,7] and satisfies the equation $T_{1e}T = 1.85$ sec deg. $T_{1e}$ is assumed to be essentially pressure independent in this work. The pressure dependence of the Knight shift of aluminum was studied by Benedek and Kushida[31] and was found to be of the same order of magnitude as the error involved. They set an upper limit for the pressure-induced change in the Knight shift to 10 000 atm to be less than 1%. Assuming that the Korringa relationship,[32] $T_{1e}T \alpha K^{-2}$ applies, it follows that the pressure-induced change in $T_{1e}$ at 3000 atm would be less than 0.6%. This would have a negligible effect on the pressure dependence of $T_2$.

The decay of $M_{xy}$ is exponential only in the temperature range 380–450 °C, and the "$x$" interaction becomes relatively more important as the temperature is increased. Therefore, $(T_2')_d$ would contribute relatively more to $T_2$ at 380 °C than at higher temperatures and $T_2$ would be most sensitive to pressure near this temperature. Also, the validity of the assumptions that $T_{1e}$ and $(T_2')_x$ are independent of pressure would be less important at this temperature since their relative contributions to $T_2$ would be smaller. However, because of the limitations of the spin-echo apparatus discussed earlier, it was not possible to measure accurately values of $T_2$ less than 150 μsec. This made it necessary to work at temperatures above 390 °C.

$T_2$ was measured as a function of pressure for several isotherms between 394 and 449 °C, using samples of 325 mesh (44 μ) filings obtained from a single-crystal rod of 99.99% purity. The $T_2$ measurements were made by means of the conventional 90°-$\tau$-180°-$\tau$ echo sequence. After each application of this sequence, a time greater than $10T_1$ was allowed to elapse for the nuclear spin system to return to equilibrium. The sequence was repeated approximately 50 times for each value of $\tau$. Echo amplitudes were recorded by either multiple-exposure Polaroid photography of the oscilloscope display, or by means of the strip-chart output of a boxcar integrator. Figure 4 furnishes an example of a $T_2$ determination, and a plot of $\ln T_2$ as a function of pressure is shown in Fig. 5 for a run made at 408 °C. The temperature, data-recording method, and activation volume for each of the experimental runs are summarized in Table I.

The activation volume for self-diffusion is proportional to $\partial \ln(T_2')_d/\partial P\,|_T$, and is given by Eq. (7). Other values used in Eq. (7) were $\beta = 1.38\times10^{-6}$ atm$^{-1}$,[29] and $\gamma_G = 2.1$.[33] The last term of Eq. (7) is then less than 1% of the first term, and can be neglected. The required $(T_2')_d$ values were obtained from the values of $T_2$, $(T_2')_x$, and $T_{1e}$ and Eq. (2), assuming that the latter two quantities were pres-

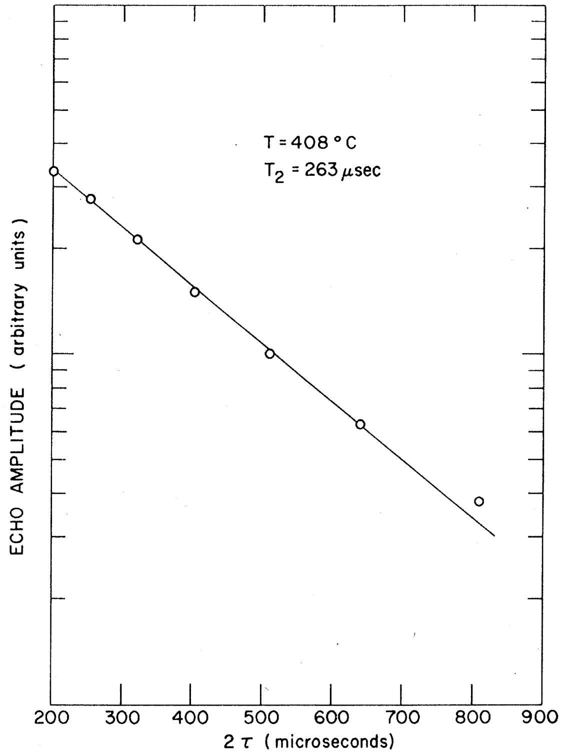

FIG. 4. Logarithm of the echo amplitude as a function of $2\tau$ at 408 °C in aluminum, $T_2 = 263$ μsec.

sure independent. Figure 5 exhibits $T_2$ and the resulting $(T_2')_d$ as a function of pressure at 408 °C. At this temperature the absolute value of the slope of $\ln(T_2')_d$ vs $P$, which determines the activation volume noted in the figure, is 40% greater than the absolute value of the slope of $\ln T_2$ vs $P$. At 446 °C, the absolute value of the slope of $\ln(T_2')_d$ vs $P$ is 130% greater than the absolute value of the slope of $\ln T_2$ vs $P$. The activation volumes determined from the $(T_2')_d$ values show no consistent temperature dependence over this rather small temperature range although the importance of $(T_2')_x$ to the derived values of $(T_2')_d$ changes appreciably. This observation supports the value of $(T_2')_x$ found from the temperature dependence of $T_2$ at 1 atm and previously discussed.

TABLE I. Summary of experimental runs to determine the activation volume for self-diffusion in aluminum.

| Temperature (°C) | Method | $\Delta V_a/V_0$ |
|---|---|---|
| 394 | boxcar | 0.62 |
| 408 | photo | 0.75 |
| 408 | boxcar | 0.52 |
| 411 | photo | 0.97 |
| 411 | boxcar | 0.66 |
| 435 | boxcar | 0.65 |
| 438 | photo | 0.64 |
| 446 | photo | 0.76 |
| 448 | photo | 0.87 |
| 449 | photo | 0.65 |

An average activation volume for self-diffusion of 71% of an atomic volume was determined by a weighted average of the activation volumes in 10 independent runs. Each value was arbitrarily weighted by the square root of the number of data points used in its determination. The data were not weighted with respect to temperature. The final result is $\Delta V_a/V_0 = 0.71 \pm 0.13$, where the cited uncertainty is the standard deviation. A value of $\Delta V_a/V_0 = 0.71 \pm 0.20$ includes 9 of the 10 determinations.

## V. DISCUSSION AND CONCLUSIONS

As indicated in the Introduction, a number of measurements have now been made of the activation volume for self-diffusion in aluminum, utilizing a variety of experimental techniques.[9–12] In addition, several measurements have been made of the volume of formation $\Delta V_f$, assuming that diffusion occurs by a vacancy mechanism.[13,15–17] Finally, one measurement has been made of the motional volume $\Delta V_m$.[14] These results are summarized in Table II. The value of $\Delta V_f^1$, which Tuler[17] inferred from the length-change measurements of Detert and Ständer,[16] depends critically upon the equilibrium single-vacancy concentration at the quench temperature, a quantity which in turn depends critically upon the divacancy binding energy $B_2 = \Delta U_f^2 - 2\Delta U_f^1$, where $\Delta U_f^1$ and $\Delta U_f^2$ are the energies of formation of the monovacancy and divacancy, respectively. Values of $B_2$ range from 0.17 eV found by Doyama and Koehler[34] to 0.57 eV found by Bourassa *et al.*[15] Under these circumstances, the equilibrium vacancy concentration at,

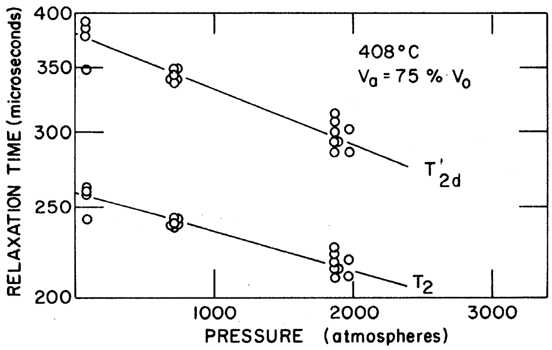

FIG. 5. Experimental values of the inverse linewidth relaxation time $T_2$ of aluminum as a function of pressure at a temperature of 408 °C. Also shown is the corresponding pressure dependence of $(T_2')_d$ derived from the $T_2$ dependence using Eq. (2) to remove the "$x$" interaction and the conduction electron contributions. $(T_2')_d$ dependence and Eq. (7) yield an activation volume for self-diffusion of 75% of an atomic volume.

e.g., 400 °C, varies over a considerable range,[35] so that with $B_2 = 0.25$ eV, e.g., one obtains $\Delta V_f^1 = 0.80\ V_0$ from the Detert and Ständer data. The value of $\Delta V_f^1$ cited by Tuler corresponds to $B_2 = 0.35$ eV.

The striking feature of the data summarized in Table II is, of course, the spread in the values of the activation volume $\Delta V_a$, ranging roughly $0.6–1.25 V_0$. By contrast, the activation volumes of other fcc metals are consistently less than one atomic volume. Thus, in gold,[36] $\Delta V_a = 0.71\ V_0$; in silver,[37] $\Delta V_a = 0.89\ V_0$; and in lead, $\Delta V_a = 0.71\ V_0$ in one case,[38] and $\Delta V_a = 0.64\ V_0$ in a second case.[39] All of these measurements were made using the radioative-tracer technique.

In the case of aluminum, Butcher, Hutto, and Ruoff first suggested the possibility that the large activation volume which they observed might be due to the dominance of divacancies over monovacancies at high temperatures.[10] The thermoelectric power and resistivity measurements of Bourassa *et al.*[15] were interpreted in terms of a three-defect model comprising the monovacancy, the divacancy, and the vacancy-interstitial bound pair. As indicated in Table II, the formation volume of the divacancy is roughly twice as great as that for the single vacancy. When these values are combined with the motional volumes obtained by Buescher and Emrick,[14] total activation volumes are obtained: $\Delta V_a^1 \leq 0.78\ V_0$ for the single vacancy and $\Delta V_a^2 = (1.13–1.62) V_0$ for the divacancy. These findings have been discussed in detail in the paper by Buescher and Emrick.[14]

The question remains as to why some measurements of $\Delta V_a$ yield values consistent with expectations for monovacancy diffusion while others are consistent with divacancy diffusion. Thus, for example, the radioactive-tracer measurements of Beyeler and Adda[11] yield, in the case of aluminum, $\Delta V_a = 1.29\ V_0$, whereas for gold these authors obtained $\Delta V_a = 0.72\ V_0$. Similarly, whereas divacancy effects may be expected to dominate at high temperatures, the creep measurements of Butcher *et al.*[10] were made at relatively low temperatures,

TABLE II. Summary of activation volume results for self-diffusion in aluminum. Superscripts 1 and 2 refer to vacancies and divacancies, respectively.

| Method | Ref. | Temp. range (°C) | Specimen purity (%) | Quantity measured | $\Delta V/V_0$ |
|---|---|---|---|---|---|
| Steady-state creep | 9 | 260–280 | 99.999 | $\Delta V_a$ | 0.79 |
| Steady-state creep | 10 | 270–290 | 99.999 [a]<br>99.9999 [b] | $\Delta V_a$ | 1.36 |
| Tracer diffusion | 11 | 440–610 | not specified | $\Delta V_a$ | 1.29 |
| Dislocation annealing | 12 | up to 280 | "zone refined" | $\Delta V_a$ | 0.44–0.87 |
| NMR | this work | 390–450 | 99.99 | $\Delta V_a$ | 0.70 |
| Length change with quenching | 16, 17 | 400 | 99.99 | $\Delta V_f^1$ | 1.23 |
| Quenched-in resistivity | 13 | 420 | 99.999 | $\Delta V_f^1$ | 0.62 |
| Thermoelectric power | 15 | 25–600 | 99.9999 | $\Delta V_f^1$ | 0.54 |
| Thermoelectric power | 15 | 25–600 | 99.9999 | $\Delta V_f^2$ | 0.96 |
| Resistivity | 15 | 300–400 | 99.9999 | $\Delta V_f^1$ | 0.60 |
| Resistivity | 15 | 300–400 | 99.9999 | $\Delta V_f^2$ | 1.45 |
| Annealing of excess quenched resistivity | 14 | 330 | 99.999 | $\Delta V_m^1$ | 0.18[c] |
| Annealing of excess quenched resistivity | 14 | 580 | 99.999 | $\Delta V_m^2$ | 0.17 |

[a] Polycrystal wire.

[b] Single-crystal rod.

[c] This value contains some contribution from divacancies.

lower in fact, than the NMR experiments reported here. The dislocation annealing experiments of Norris[12] were also made at relatively low temperatures, but in this case a $\Delta V_a$ consistent with monovacancy diffusion was found.

There does appear to be a tenuous correlation between sample purity and $\Delta V_a$ value, however. Less pure aluminum appears to correlate with the monovacancy value for $\Delta V_a$. This correlation is not very strong, but the present measurements, as well as those of Norris,[12] were made with aluminum of less than 99.999% purity. In addition, the measurements by Butcher,[9] which yielded $\Delta V_a = 0.79\ V_0$, were very likely made with somewhat less pure aluminum than were the later measurements by Butcher, Hutto, and Ruoff.[10] Finally, the value of $\Delta V_f$ inferred from the length-change measurements of Detert and Ständer,[16] as discussed above, ranges down to the monovacancy value depending upon the choice of the divacancy binding energy $B_2$. These observations suggest that, for reasons which we do not propose to speculate on, the imperfections present in less pure aluminum inhibit the formation of divacancies.

In conclusion, the series of pulsed NMR measurements reported here have obtained a value of the activation volume for self-diffusion in aluminum of $\Delta V_a = (0.71 \pm 0.13) V_0$. This result is consistent with expectations based on monovacancy diffusion in aluminum.

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