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°-τ–180°-τ 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 τ. 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-

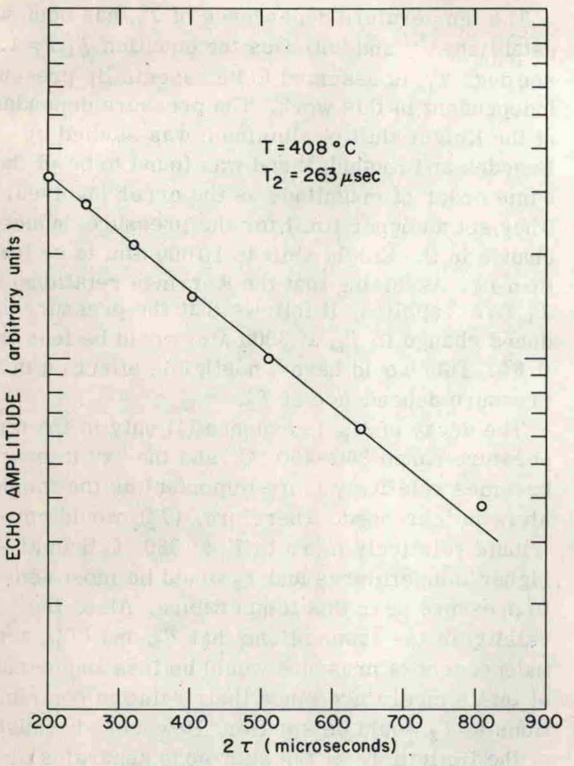

FIG. 4. Logarithm of the echo amplitude as a function of 2τ at 408 °C in aluminum, $T_2 = 263$ μsec.

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 ΔV_f, assuming that diffusion occurs by a vacancy mechanism.[13,15–17] Finally, one measurement has been made of the motional volume ΔV_m.[14] These results are summarized in Table II. The value of ΔV_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 ΔU_f^1 and ΔU_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,

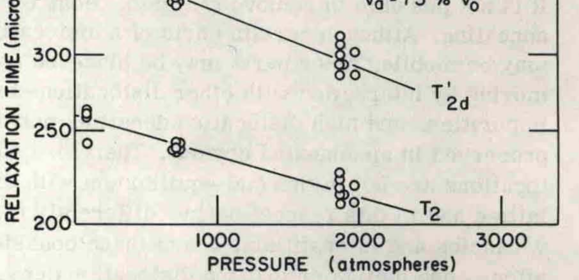

FIG. 5. Experimental values of the inverse linewidth relaxation time T_2 of aluminum as a function of pressure at a temperature of 408 °C. Also shown is the corresponding pressure dependence of $(T_2')_d$ derived from the T_2 dependence using Eq. (2) to remove the "x" interaction and the conduction electron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