

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  $T_1 T = 1.85 \text{ sec deg}$  from a little over  $1^\circ \text{K}$  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  $360^\circ \text{C}$ . The intermediate temperature range runs from  $360$  to  $460^\circ \text{C}$ , in which the decay of  $M_{xy}$  is exponential. The high-temperature range extends from  $460^\circ \text{C}$  to the melting temperature  $660^\circ \text{C}$ . 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,<sup>18</sup> 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  $280$ – $360^\circ \text{C}$  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<sup>6</sup> over the entire temperature range 1 to above  $660^\circ \text{K}$  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.<sup>6,7</sup>

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  $450^\circ \text{C}$ ,  $T_2^{-1} = 1430 \text{ sec}^{-1}$  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  $400^\circ \text{C}$ ,  $(T_2)^{-1} = 3330 \text{ sec}^{-1}$  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.<sup>2,6,22</sup> 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,<sup>27</sup> and with that determined by Butcher<sup>9</sup> 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.<sup>6</sup> 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.<sup>6</sup>

At temperatures above  $450^\circ \text{C}$ , 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<sup>6</sup> 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  $360^\circ \text{C}$  and a slight reduction of  $T_1$ . Seymour and Flynn<sup>28</sup> 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,<sup>18</sup> 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.



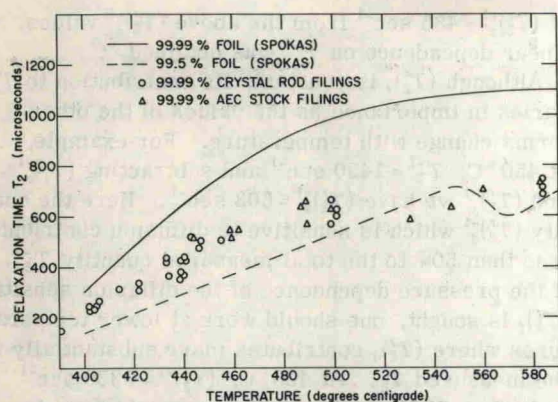


FIG. 3. Temperature dependence of the inverse linewidth relaxation time  $T_2$  in aluminum metal.

### 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<sup>6</sup> and others,<sup>28</sup> 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.<sup>6,7</sup>

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  $1.3 \pm 0.2 \text{ eV}$ , which is in good agreement with the value of  $1.4 \pm 0.1 \text{ eV}$  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  $\ln(\text{echo amplitude})$  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<sup>6</sup> 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<sup>6</sup>

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

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  $10^6 \text{ lines/cm}^2$  necessitates a not unreasonable nearest-neighbor interaction of  $\delta\nu_{\text{dis}} = \delta\omega_{\text{dis}}/2\pi = 2 \times 10^6 \text{ cps}$ .<sup>6</sup>

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

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

or

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

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

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