

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

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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  $T_2$ ,  $(T_2^D)_d$ , was found to depend on temperature according to  $[\ln(T_2^D)_d]^{-1} \propto T^{-1}$  in accordance with theory, yielding an activation enthalpy for self-diffusion of  $1.3 \pm 0.2$  eV, in good agreement with previous determinations. The pressure dependence of  $(T_2^D)_d$ , deduced from ten independent experimental runs, yielded an activation volume for self-diffusion of  $0.71 \pm 0.13$  in units of the atomic volume of aluminum, with no discernible systematic dependence on the temperature (cited uncertainty is the standard deviation). Nine of the ten determinations fall within the range  $0.71 \pm 0.20$ . The result is consistent with expectations based on monovacancy diffusion in aluminum.

### I. INTRODUCTION

For the elementary metals, the vacancy mechanism 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)  $\Delta H_a$ .<sup>1</sup> 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.<sup>1</sup>

Pulsed-NMR methods were first employed in the

study of self-diffusion in metals by Holcomb and Norberg<sup>2</sup> 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<sup>3,4</sup> to measure the activation volume for self-diffusion in lithium and sodium.

Seymour<sup>5</sup> employed NMR methods (steady state) to study the temperature dependence of diffusion in aluminum. His data were reinterpreted by Spokas<sup>6</sup> and by Spokas and Slichter<sup>7</sup> 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<sup>8</sup> 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<sup>9</sup> and Butcher, Hutto, and Ruoff<sup>10</sup> measured the effect of pressure on the steady-state creep of aluminum. Beyeler and Adda<sup>11</sup> utilized the radioactive-tracer technique and pressures to 10 kbar. Norris<sup>12</sup> studied the annealing of dislocation loops at pressures to 60 kbar. In another series of experiments, Emrick and McArdle<sup>13</sup> 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<sup>14</sup> 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<sup>15</sup> 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,<sup>16</sup> and on the length changes accompanying quenching, by Tuler.<sup>17</sup> 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<sup>2</sup> 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<sup>6</sup> and by Spokas and Slichter<sup>7</sup> 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

$$(T_2)_i^{-1} = (T'_2)_i^{-1} + (T'_1)_i^{-1}, \quad (1)$$

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.<sup>18,19</sup>

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.<sup>6</sup> 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<sup>7,20,21</sup> 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

$$(T'_2)_d^{-1} = (T_2)^{-1} - (T'_2)_x^{-1} - (T_1)^{-1} \quad (2)$$

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<sup>22</sup> for the case of liquids, and by Holcomb and Norberg<sup>2</sup> 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<sup>2</sup>

$$(T'_2)_d^{-1} = 4\gamma_N^4 \hbar^2 1(1+1)N/5Dd. \quad (3)$$

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<sup>23</sup>

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

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

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

leads to the expression<sup>4</sup>

$$\Delta V_a = -RT \left( \frac{\partial \ln(T'_2)_d}{\partial P} - 6 \frac{\partial \ln a}{\partial P} - \frac{\partial \ln \nu_0}{\partial P} \right)_T. \quad (6)$$

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,<sup>4</sup>

$$\Delta V_a = -RT \left[ \left( \frac{\partial \ln(T'_2)_d}{\partial P} \right)_T + \beta(2 - \gamma_G) \right]. \quad (7)$$

This last expression is used in the present work to obtain values of  $\Delta V_a$  from the pressure dependence