Nuclear magnetic resonance determination of the activation volume for self-diffusion in aluminum

Ralph Duane Engardt
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NUCLEAR MAGNETIC RESONANCE DETERMINATION
OF THE ACTIVATION VOLUME FOR SELF-DIFFUSION
IN ALUMINUM

by

Ralph Duane Engardt

A Dissertation Submitted to the
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I. INTRODUCTION

The primary objective of this research was to determine the activation volume for self-diffusion of aluminum by the method of nuclear magnetic resonance (NMR). This method is not concerned with actual macroscopic mass flow, but with the rapidity of individual atom jumps. NMR, in contrast with the conventional tracer technique, should suffer very little by the higher rates of diffusion (1) which occur along grain boundaries, surfaces, and other avenues of high mass flow since relatively few atoms take part in this type of flow. NMR techniques employed by Holcomb and Norberg (2) have yielded activation energies of self-diffusion for lithium, sodium, and rubidium. Barnes, Engardt, and Hultsch (3) combined NMR with high pressure techniques to measure the activation volume of lithium. Similarly Hultsch and Barnes (4) also found the activation volume of sodium. The NMR determination of the activation volume for sodium agreed poorly with the results of tracer techniques (5); however, it agreed well with the predictions of the dynamical theory of diffusion (6). Tracer techniques are not applicable to the case of lithium because it does not have an isotope with a suitably long half-life; however, NMR was well suited to measure both the activation energy and volume. In fact, the large nuclear signal, convenient temperature range, and the magnitudes of the parameters of interest (the inverse line width $T_2$ and the nuclear spin
lattice relaxation time $T_1$) were near ideal.

NMR techniques were first used by Seymour (7) to study the temperature dependence of diffusion in metallic aluminum. Seymour's data were reinterpreted by Spokas (8) and by Spokas and Slichter (9) after they had investigated the relaxation times $T_1$ and $T_2$ as a function of temperature. They found it necessary to introduce an unknown interaction, independent of temperature, to interpret their data and determine an activation energy. In the present study it was hoped that the variation of the diffusion sensitive parameter $T_2$ with pressure in the temperature region $400^\circ\text{C}$ to $450^\circ\text{C}$ could be observed with sufficient accuracy to obtain a measure of the activation volume of aluminum.
II. THEORY OF DIFFUSION

Until recently diffusion was studied as a function of temperature only and the data almost without exception could be fitted to an Arrhenius equation,

$$D = D_0 \exp(-Q/RT)$$  \hspace{1cm} (1)

in which the "frequency factor" $D_0$ and the activation energy $Q$ are temperature independent. $D$ is called the diffusion coefficient or diffusivity.

A theory of diffusion must yield the above equation if it is to be successful. One such theory is the equilibrium theory of vacancy diffusion. The theory assumes that the diffusing atom must pass over a potential energy saddle point of height $G_m$, after which it falls into another vacant lattice site. It is assumed all states are in thermal equilibrium with the lattice and that all changes in the configuration coordinates occur in times long compared to the thermal relaxation times of the lattice. It has been shown (10) that the frequency of jumping in the presence of a vacant lattice site is given by

$$v'_i = \bar{v} \exp \left( -\frac{G_m}{kT} \right)$$  \hspace{1cm} (2)

where $\bar{v}$ is the "frequency of tries" at the barrier or the vibrational frequency. $G_m$ is the isothermal work necessary to move the atom slowly to the top of the potential barrier while allowing it to vibrate in a plane perpendicular to the
direction of the motion. The rate at which an atom jumps into a vacancy is proportional to the probability that a vacancy is present \( c \); that is,

\[
v_i = v_i' c
\]

where \( c \) is the probability that a vacancy is present, and \( v_i' \) is as defined before, the probability of jumping when a vacancy is present. The equilibrium concentration of vacancies is given by Keyes (12) as

\[
c = \exp\left(-\frac{G_f}{kT}\right) \tag{3}
\]

where \( G_f \) is the isothermal work necessary to form a vacancy. Therefore the frequency of jumping can be written as

\[
v_i = \bar{v} \exp[-(G_f + G_m)/kT] = \bar{v} \exp(-G_a/kT) \tag{4}
\]

where \( G_a \) is the sum of \( G_f \) and \( G_m \).

From the theory of random walk in three dimensions Chandrasekhar (13) has shown that

\[
D = \frac{1}{6} \sum_i v_i \delta_i^2 \tag{5}
\]

where \( \delta \) is the jump distance and the sum is taken over all the possible jumps to nearest neighbor positions. If \( v_i \) is the same for all directions as in a cubic crystal then

\[
D = \bar{v} \frac{1}{6} \sum_i \delta_i^2 = \bar{v} \gamma a^2, \tag{6}
\]
where $\frac{1}{6} \sum_1^n \delta_i^2$ is set equal to $\gamma a^2$, $a$ is the lattice constant and $\gamma$ is a factor which depends only on the crystal symmetry. For vacancy diffusion the atom jumps to a vacant nearest neighbor site. Considering a body centered cubic crystal, there are eight nearest neighbors at a distance of $(3/4)^{1/2} a$, so that

$$\gamma = \frac{1}{6a^2} \sum_1^8 \left( \frac{3}{4} a^2 \right) = 1 \quad (7)$$

For a face centered cubic lattice there are 12 nearest neighbors at a distance of $(1/2)^{1/2} a$, therefore

$$\gamma = \frac{1}{6a^2} \sum_1^{12} \left( \frac{1}{2} a^2 \right) = 1 \quad (8)$$

If Equations 4 and 6 are combined one has

$$D = \gamma a^2 \sqrt{\exp(-G_a/kT)} \quad (9)$$

Since $G_a$ is viewed as the isothermal work this can also be written as

$$D = \gamma a^2 \sqrt{\exp(S_a/k)} \exp(-H_a/kT) \quad (10)$$

The thermodynamic identity $G_a = H_a - TS_a$ has been used, where $S_a$ and $H_a$ are respectively the change in entropy and enthalpy associated with the formation and motion of a vacancy, and are often called the activation entropy and activation enthalpy. Then, if one identifies $\gamma a^2 \sqrt{\exp(S_a/k)}$ with $D_o$, $H_a$ becomes
the activation energy of Equation 1 (1).

To describe the results of recent measurements of the effect of hydrostatic pressure on the rates of diffusion Nachtrieb (5) has proposed interpreting the data in terms of an activation volume $V_a$. This he defined as

$$V_a = -kT \frac{\partial \ln (D/\gamma a^2 V)}{\partial p} \bigg|_T$$  \hspace{1cm} (11)

where $p$ is the pressure. In terms of the equilibrium theory this is

$$V_a = \frac{\partial G_a}{\partial p} \bigg|_T$$  \hspace{1cm} (12)

Since $G_a$ is the sum of two terms $G_m$ and $G_f$, the activation volume $V_a$ is also the sum of two terms $V_f$ and $V_m$. $V_f$ is the volume of formation of a vacancy, or simply the volume of a vacancy, and $V_m$ is the volume change necessary for the motion of a vacancy. That is, $V_m$ is the dilation of the lattice during a jump. A hard-sphere model predicts $V_m$ and $V_f$ to each be one atomic volume for close packed structures (1).

Experimental activation volumes, however, have been on the order of one-half an atomic volume (1). This would indicate that there is considerable relaxation inward on a vacancy. This agrees with the calculations of Tewordt (14) for face centered cubic copper. In these calculations the atoms in a large region I around the defect are treated as discrete particles. A second region, II, in which the atoms
are again treated as discrete particles, connects region I with an elastically deformed continuum. Tewordt found the change in volume of a crystal of face centered copper arising from the formation of a vacancy to be about one-half of an atomic volume. Tewordt also calculated the formation energies for interstitials, vacancies, and crowdion defects to be 2.5, 1, and 3.2 electron volts respectively, indicating that the vacancy mechanism for diffusion in copper is preferred.

Lazarus (1) has pointed out several objections to the equilibrium theory:

1. Quantum effects are ignored.

2. The diffusional jump is considered as basically reversible.

3. It is assumed that the jump takes place in a time long compared with the thermal relaxation time of an extensive part of the lattice, so that thermodynamic properties may be assigned to the excited state.

4. The model ignores the details of the atomic jumping process.

A dynamical theory of diffusion was proposed by Rice (6), in which attention is focused on one atom and the conditions necessary for it to jump. First, it must have a sufficient amplitude of thermal vibration in the direction of the jump to carry it from one lattice site to another. Second, the surrounding atoms must move apart in such a manner so as to
allow it to jump. The jump frequency is then

\[ \nu = \Sigma_{n.n.} \rho_{ij}^2 P(\delta) \]  

(13)

where \( \rho_{ij}^2 \) is the probability of finding an atom at site \( i \) and a vacancy at site \( j \). \( P(\delta) \) is the frequency of occurrence of the configuration in which the atom has sufficient amplitude and the neighboring atoms move apart at the proper time. The sum is taken over nearest neighbors. With the introduction of several restrictive assumptions Rice has obtained an approximate solution and two interesting predictions which may be compared with experiment (6). One prediction of the theory is that in the limit of low pressures there exists a law of corresponding states of the form

\[ \ln D \alpha T_M(p)/T \]  

(14)

where \( T_M(p) \) is the melting temperature at an elevated pressure. This prediction is well born out by the data of Hultsch and Barnes (4), for sodium and lithium. The theory (6) further shows that the temperature and pressure derivatives of the self-diffusion coefficient are related as

\[ \frac{H_a}{V_a} = \frac{H_M}{V_M} \]  

(15)
where $H_M$ is the heat of fusion and $V_M$ is the volume change upon melting.

More complete discussions of the theoretical and experimental situation can be found in the reviews by Lazarus (1), and Lazarus and Nachtrieb (15).
III. NUCLEAR MAGNETISM AND NUCLEAR SPIN RELAXATION TIMES

A. Nuclear Magnetism

Consider a sample of matter to consist of two parts, the nuclei, and the rest of the sample called the "lattice". For the moment, consider materials in which the nuclei are free of interactions with one another and with the lattice or equivalently consider a single nucleus. A nucleus which possesses angular momentum $I\hbar$ also has a collinear magnetic dipole moment $\mu$. These are related by

$$\bar{\mu} = \gamma \bar{I} \hbar$$  \hspace{1cm} (16)

The proportionality constant $\gamma$ is called the magnetogyric ratio (or the gyromagnetic ratio), and is different for different nuclear species. Planck's constant divided by $2\pi$ is represented by $\hbar$.

Such a nucleus when placed in a uniform magnetic field $H_0$ will precess about the direction of the field just as a spinning top will precess about the direction of the gravitational field. The angular rate of precession can be found by considering the torque on the nuclear dipole and setting it equal to the time rate of change of the angular momentum. The situation is depicted in Figure 1. The precession frequency is found from the following equations.
Figure 1. Classical precession of a spinning magnetic dipole in a large magnetic field $H_0$. 
Torque = time rate of change of angular momentum \( \tau = \frac{d}{dt} (\bar{I} \Theta) \) (17)

\[ \bar{\mu} \times \bar{H}_0 = \frac{d}{dt} (\bar{I} \Theta) \] (18)

\[ \gamma \bar{I} \Theta \times \bar{H}_0 = \frac{d}{dt} (\bar{I} \Theta) \] (19)

Therefore \( \frac{d(\bar{I} \Theta)}{dt} \) is perpendicular to \( \bar{I} \) and \( \bar{H}_0 \) and its magnitude can be expressed as \( |\bar{I}| \hbar \sin \theta \frac{d\varphi}{dt} \) as seen from Figure 1. Then we have

\[ \gamma |\bar{I}| \hbar |\bar{H}_0| \sin \theta = |\bar{I}| \hbar \sin \theta \frac{d\varphi}{dt} \] (20)

\[ \gamma |\bar{H}_0| = \frac{d\varphi}{dt} = \omega_0 \] (21)

where \( \frac{d\varphi}{dt} \) has been redesignated as \( \omega_0 \) and is called the Larmor frequency.

The potential energy of orientation of a nuclear magnetic dipole in a uniform magnetic field \( H_0 \) is

\[ E = -\bar{\mu} \cdot \bar{H}_0 = -\gamma \bar{I} \Theta \cdot \bar{H}_0 \] (22)

From the quantum mechanical properties of \( \bar{I} \) we obtain the quantized energy levels

\[ E_m = -\gamma \hbar H_0 m \] (23)

where \( H_0 \) has been chosen to be in the z-direction, and where \( m = (I, I-1, I-2, \ldots, -I) \) are the possible projections of \( \bar{I} \) on the z-axis. The magnitude of \( \bar{I} \) is \( [(I+1)]^{1/2} \). It is
possible to induce magnetic transitions between these levels. The selection rule for magnetic dipole transitions is $\Delta m = \pm 1$. If $m$ is increased $E$ is decreased and one has emission of energy. Alternately, if $m$ is decreased ($\Delta m = -1$) the energy of orientation of the nuclear magnetic dipole moment in the applied field is increased. This energy change $\Delta E$ is supplied by a rotating magnetic field which has a frequency given by the Einstein relation $\Delta E = \hbar \omega$

$$\Delta E = E_{m-1} - E_m$$

$$= (-\gamma \hbar H_0) [(m-1) - m] = \hbar \omega$$

and employing Equation 21 we have

$$\Delta E = \hbar \omega_o = \hbar \omega$$

Thus transitions may be induced by applying a rotating magnetic field at the Larmor frequency. In a real sample the nuclei interact with each other and the lattice. These interactions cause a broadening of the energy levels and the resonance condition is obtained for a spread of frequencies of the applied radio frequency field.

When a sample containing a large number of nuclei which interact weakly with each other and with the lattice is placed in an external field $H_0$ the nuclei distribute themselves in $2I + 1$ equally spaced energy levels. At equilibrium the populations of these levels will be determined by their
respective Boltzmann factors (16, p. 2), with the result that the lower the energy of a level the more densely it will be populated. The population difference between adjacent levels at room temperature and in the external fields normally available in the laboratory is of the order of only several per million. This population difference will however give rise to a net nuclear magnetization, call it \( M_o \), parallel to the applied field. Although each precessing nucleus may have a rotating component of magnetic moment perpendicular to the direction of \( H_o \), at equilibrium the relative phases of these components are random and no net rotating component of magnetization exists in the plane perpendicular to \( H_o \).

B. Spin-Lattice Relaxation Time

Suppose the equilibrium magnetization \( M_o \), initially aligned parallel to the applied field \( H_o \) is suddenly tipped by 90° into the x-y plane at time \( t = 0 \). Then \( M_z(0) = 0 \), \( M_{xy}(0) = M_o \), and \( M_{xy} \) rotates at the Larmor frequency in the x-y plane. If the nuclei are non-interacting this situation will not change. However, in a real sample \( M_{xy}(t) \) decays and \( M_z(t) \) grows to its equilibrium value. The latter process is often (16, p. 359) accurately described by the equation

\[
M_z(t) = M_o \left[ 1 - \exp\left(-t/T_1\right) \right]
\]  

(27)
The characteristic time $T_1$ is called the spin-lattice relaxation time, the thermal relaxation time, or the longitudinal relaxation time. It describes the rate of change of the energy of the nuclear spin system, or the rate at which the spin system exchanges energy with its surroundings, that is, the "lattice". Some important interactions in metals connecting the nuclear spin system to the lattice are discussed.

1. **Nuclear dipole coupling to the thermal motion of the lattice via the dipole fields of neighboring nuclei**

   A neighboring nucleus $j$ imbedded in an atom which is moving in the lattice produces a time-varying magnetic field at nucleus $i$. If the frequency spectrum of the motion of nucleus $j$ contains components at the Larmor frequency it can cause a transition in which energy is transferred between the lattice and nucleus $i$. The frequencies of thermal vibration are the order of $10^{13}$ per second. These frequencies are higher than the Larmor frequencies obtainable by a factor of $10^6$ and are not effective in inducing transitions. However, by varying the temperature, the frequency of diffusive motion of the atoms in a solid can be adjusted to give a spectrum of frequencies particularly rich at the Larmor frequency $\omega_0$. It is then expected that there will be a temperature at which $2\pi\nu = \omega_0$ and at this temperature the interaction will be most effective. This is strikingly evident in the $T_1$ measurements for lithium metal (2), but in aluminum metal this interaction
contributes negligibly to spin-lattice relaxation compared to the electron contribution \((8,9)\).

2. **Nuclear magnetic dipole - conduction electron magnetic dipole interaction**

   Since the electron magnetic dipole moment is about 1000 times larger than the nuclear dipole moment, one does not expect an energy exchange between a nuclear magnetic dipole and an electron magnetic dipole to be large enough to change the orientation of the electron spin. The interaction is instead viewed as a scattering of the electron into a higher or lower momentum state. The electrons which interact most effectively with the nucleus are those which have a large probability of being at the nucleus, and which also have accessible unoccupied energy states nearby. These are, in the case of aluminum, the conduction electrons near the Fermi energy. In many metals, including aluminum, the conduction electron relaxation of the nuclear spin system is characterized by a relaxation time \(T_{1e}\) which has the temperature dependence \((17)\)

   \[
   T_{1e}T = \text{constant}/K^2
   \]

   \((28)\)

   where \(K\) is the so called "Knight shift" and \(T\) is the absolute temperature. The constant in the above equation has been theoretically found by Korringa \((17)\). Knight \((18)\) observed that the laboratory field necessary to obtain resonance with a
nucleus in a metallic solid was less than the field necessary to obtain resonance for the same nucleus in a non-metallic solid. The difference $\Delta H$ in field arises from the polarization of the conduction electrons in the metal (18). $K$ is defined as $\Delta H/H$, and is temperature independent in the Korringa derivation. The temperature and pressure dependence of $K$ has been found to be very small (19) in the case of the alkali metals and $T_{le}$ is assumed to be essentially pressure independent in this research. The inverse temperature dependence of $T_{le}$ for aluminum is very well established and appears to be the only contribution to the spin-lattice relaxation in pure samples (8,9). The value of $T_{le}$ for T was found to be $1.35 \text{ seconds}^{-1}\text{K}$ over the temperature range of about $1^\circ\text{K}$ to about $930^\circ\text{K}$ (9,20,21).

3. **Interaction of the nuclear quadrupole moment with the electric field gradient of the lattice**

For a perfect cubic environment the electric field gradient at the nucleus is zero. In a real crystal, electric field gradients exist in the neighborhood of defects which destroy the cubic symmetry. This interaction (8) does not make an observable contribution to the spin-lattice relaxation time in aluminum, although it is thought to contribute to the inverse line width relaxation time $T_2$. 
C. Inverse Line Width Relaxation Time $T_2$

Again consider that the equilibrium magnetization $M_0$, initially in the z-direction and aligned with the applied field $H_0$, is tipped into the x-y plane at $t = 0$. If the nuclei are in a perfectly homogeneous field and are non-interacting, $M_0$ will rotate in the x-y plane at the Larmor frequency with constant amplitude, and the magnetization will be given by the real part of

$$M_{xy}(t) = M_0 \exp(i \omega t)$$

(29)

If the nuclei interact with each other, say through the dipole-dipole interaction, and with the lattice by some of the interactions already mentioned, the energy levels will be broadened, and the resonance absorption will take place over a width of frequencies. The frequency dependence of the absorption is described by a distribution function $g(\omega)$. This function is normalized so that

$$\int_{-\infty}^{\infty} g(\omega) \, d\omega = 1$$

(30)

Lowe and Norberg have shown (22) by a quantum mechanical theory and direct experiments that, except at very low temperatures, the decay of $M_{xy}(t)$ is the Fourier transform of the distribution function $g(\omega)$. $M_{xy}(t)$ for a sample of interacting nuclei is found by integrating the contributions of all rates of precession. Then
\[ M_{xy}(t) = M_0 \int_{-\infty}^{\infty} g(\omega) \exp(i\omega t) \, d\omega \]  
(31)

\[ = M_0 \exp(i\omega_0 t) \int_{-\infty}^{\infty} g(u + \omega_0) \exp(iut) \, du \]  
(32)

where \( \omega_0 \) is the mean Larmor frequency and \( u = \omega - \omega_0 \). Often a Lorentz distribution of precession frequencies occurs which has the form

\[ g(\omega) = \frac{b/\pi}{1 + b^2 (\omega - \omega_0)^2} \]  
(33)

\[ g(\omega + u) = \frac{b/\pi}{1 + b^2 u^2} \]  
(34)

In this case

\[ M_{xy}(t) = M_0 \exp(i\omega_0 t) \int_{-\infty}^{\infty} \frac{b/\pi}{1 + b^2 u^2} \exp(iut) \, du \]  
(35)

hence

\[ M_{xy}(t) = M_0 \exp(i\omega_0 t) \exp(-t/b) \quad (t \geq 0) \]  
(36)

and we see that the transverse magnetization decays exponentially with time constant \( b \). Another distribution frequently encountered is the Gaussian,

\[ g(\omega) = \frac{c}{\sqrt{2\pi}} \exp \frac{-c^2(\omega - \omega_0)^2}{2} \]  
(37)
and  \[ M_{xy}(t) = M_0 \exp(i\omega_0 t) \int_{-\infty}^{\infty} \frac{c}{\sqrt{2\pi}} \exp\left(-\frac{c^2u^2}{2}\right) \exp(\text{i}ut) \, du \] (38)

\[ = M_0 \exp(i\omega_0 t) \exp\left(-\frac{t^2}{2c^2}\right) \] (39)

Here the decay of the transverse magnetization is Gaussian and is characterized by the constant c. The definition of the transverse relaxation time (also called the inverse line width relaxation time) is implicit in the distribution function. The most commonly used definitions are shown in Table 1. To specify completely the decay of \( M_{xy} \) it is necessary not only to state the characteristic time, but to also state the shape of the decay or distribution function. With this understanding the inverse line width relaxation time is denoted by \( T_2 \), where \( T_2 = b \) for the Lorentz distribution, and \( T_2 = c \) for the Gaussian distribution.

The behavior of \( M_{xy}(t) \) after being tipped into the x-y plane is called a free induction decay. The word "free" refers to the fact that a driving radio frequency magnetic field is absent. "Induction" refers to the method by which the rotating magnetization is observed. The rotating dipole moment \( M_{xy}(t) \) induces a voltage proportional to \( M_{xy}(t) \) in a coil wrapped about the sample. This coil forms part of a tank circuit tuned to the Larmor frequency. The word "decay" refers to the decrease of the magnitude of \( M_{xy}(t) \) as a function of time or equivalently to the envelope of the induced radio
Table 1. Relationships between the parameters often used to describe the resonance absorption and the inverse line width relaxation time for the Lorentz and Gaussian distributions.

<table>
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<th>Normalized function</th>
<th>Fourier transform $\Delta w_a^1/2$</th>
<th>$\Delta w_b^\text{m.s.}$</th>
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<td>Lorentz distribution</td>
<td>$g(w) = \frac{b/\pi}{1+b^2(w-w_0)^2}$</td>
<td>$\exp(-t/b)$ $\frac{2}{b}$</td>
</tr>
<tr>
<td>Gaussian distribution</td>
<td>$g(w) = \frac{c}{\sqrt{2\pi}} \exp\left(-\frac{c^2}{2}(w-w_0)^2\right)$</td>
<td>$\exp\left(-\frac{t^2}{2c^2}\right)$ $\frac{2\sqrt{\ln4}}{c}$</td>
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$a\Delta w_{1/2}$ is the width of the resonance measured between points of half maximum absorption.

$b\Delta w_{\text{m.s.}}$ is the width of the resonance absorption measured between the points of maximum and minimum slope of the absorption.

frequency signal. The rapidity and shape of the decay are the quantities of interest for they are the direct result of the interactions of the nuclei with each other and with the lattice. Some of these interactions already mentioned lead to the reestablishment of the equilibrium magnetization along the z axis.

In general, without considering the details of the interactions, the decay of $M_{xy}$ can be decomposed into two parts. First, the growth of $M_z$ after a $90^\circ$ tipping is at the expense of $M_{xy}$ and contributes to its decay. Second, the loss of the in-phase condition in the x-y plane accelerates the decay.
The first process involves a change in energy of the nuclear spin system and is a $T_1$ or spin-lattice relaxation process. The second process conserves the energy of the spin system but destroys the phase relationships among the nuclei. The characteristic time associated with the destruction of the in-phase condition is appropriately called the phase memory time and is denoted by $T_2'$. For each interaction we have a $T_1$ and a $T_2'$ contribution to $T_2$. When both contributions lead to exponential decays the total rate of decay of $M_{xy}$ is

$$\frac{1}{T_{21}} = \frac{1}{T_{21}'} + \frac{1}{T_{11}}$$

(40)

for the $i$-th type of interaction. Here $(1/T_1') = \alpha (1/T_1)$, where $\alpha$ is a numerical coefficient of order unity and never greater than one and the precise value of which depends on the type of interaction \((23; 16, \text{p. 445})\). When more than one type of interaction is involved the total rate of decay is, assuming them to be independent, the sum of the rates of decay of the various interactions.

$$\frac{1}{T_2} = \sum_i \frac{1}{T_{21}}$$

(41)

The interactions contributing to the inverse line width relaxation time of aluminum will now be mentioned. The nuclear dipole-nuclear dipole interaction has a $T_2'$ contribution to $T_2$. In fact, this is the quantity of most interest
here because of its dependence on the rate of diffusion. The dipole-dipole interaction contribution to \( T_1 \) has been shown by Spokas (8) to be unobservably small in aluminum. The nuclear dipole-conduction electron interaction contributes to \( T_1 \), and is the only observable contribution to \( T_1 \). This is strongly implied by the fact that \( T_1 T \) is a constant for all temperatures \( T \) from a little over one degree absolute to above the melting temperature (9, 20, 21). The last interaction to be considered is called the "x"-interaction and was first observed by Spokas (8) and attributed to an interaction between the quadrupole moment of the nucleus and the electric field gradient at the nucleus arising from departures of the lattice from cubic symmetry in the neighborhood of dislocations. This interaction was assumed to be temperature independent by Spokas and will be discussed later. The total inverse line width relaxation time for aluminum assuming all processes lead to exponential decays is then given by

\[
\frac{1}{T_2} = \sum \frac{1}{T_{2i}} = \frac{1}{T_{2d}} + \frac{1}{T_{2x}} + \frac{1}{T_{2e}} \tag{42}
\]

The subscript \( d \) refers to the nuclear dipole-nuclear dipole interaction, the subscript \( x \) refers to the "x"-interaction mentioned above. Since the experimental behavior of \( T_1 \) shows no departure from \( T_1 T = \) a constant, the expected behavior of \( T_{1e} \) (16, pp. 359, 464), it has been assumed (8) that \( 1/T_{1d} \) and \( 1/T_{1x} \) are essentially equal to zero. Due to the shortness of
the correlation time of the electronic field "seen" by the nucleus $T_{2e}$ is equal to $T_{1e}$ (16, p. 460). We then obtain

$$\frac{1}{T_2} = \frac{1}{T_{2d}} + \frac{1}{T_{2x}} + \frac{1}{T_{1e}}$$  \hspace{1cm} (43)

D. Motional Narrowing

It has been observed in light metals and other substances that the line width is independent of temperature up to a certain temperature above which the line width decreases. This effect was first explained by Bloembergen, Pound and Purcell (24) in 1947 in a paper which is often cited in the literature today. It is shown that the line width decreases when the frequency of diffusive motion becomes as great as the low temperature line width measured in frequency units, that is narrowing begins when

$$2\pi \nu_1 = \Delta \omega_{1/2}$$  \hspace{1cm} (44)

where $\nu_1$ is the mean jump frequency of an atom.

Let us now rephrase the phenomenon in terms of relaxation times. The inverse line width relaxation time $T_2$ is often found to be independent of temperature up to a certain temperature above which $T_2$ increases. For many metals we know that $T_{1e}$ is temperature dependent, in the form $T_{1e} \propto T$ a constant, and we would expect $T_2$ always to be temperature dependent because it includes a contribution from $T_{1e}$. In the light
metals and in aluminum $1/T_{le}$ is very much smaller than $1/T_2$ in the rigid lattice region, and contributes an immeasurably small temperature dependent term to $1/T_2$. Therefore in the rigid lattice region $1/T_2$ is, to a very good approximation, equal to $1/T_2'$ for the light metals. Consider how the phase memory time $T_2'$ is affected by diffusion. Let the phase memory time in a completely rigid lattice be denoted by $T_2'$. Let us also consider that we measure the phase memory time by observing the free induction decay of $M_{xy}$ in a perfectly homogeneous external field following a 90° tipping of $M_z$. In the rigid lattice a nucleus $j$ precessing at a frequency $\omega_0 + \Delta \omega$ will monotonically increase its phase angle with respect to nuclei precessing at $\omega_0$ (the mean Larmor frequency), and the in-phase condition will be destroyed appreciably in a time $T_{2R}'$ by definition. Furthermore, as long as the field seen by nucleus $j$ does not change in a time shorter than $T_{2R}'$ the in-phase condition will be destroyed with the same characteristic time $T_{2R}'$. However, when the diffusive motion becomes rapid enough, the field at nucleus $j$ will change several times in the time $T_{2R}'$ and the phase angle between nucleus $j$ and nuclei precessing at frequency $\omega_0$ will not increase monotonically, but will sometimes increase and at other times decrease. Thus, the dephasing in the presence of rapid diffusion becomes less effective, and the phase memory time increases. In contrast, when there is no diffusive motion a nucleus which sees a
constant field different from $H_0$ steadily accumulates a larger and larger phase angle with respect to nuclei precessing at $\omega_0$.

The increase in the dipolar phase memory time with the increase in diffusion was treated theoretically by Bloembergen, Pound, and Purcell (24) for liquids and later extended to solids by Holcomb and Norberg (2). Other treatments are also presented by Abragam (16). All treatments result in the same dependence of $T_2'$ on the diffusion coefficient $D$ when the phase memory time is appreciably increased from the rigid lattice value (24; 16, p. 460). The Holcomb and Norberg result is

$$\frac{1}{T_{2d}'} = \frac{4\gamma_N^2 I(I+1)N}{5Da}$$

(45)

Here $\gamma_N$ is the nuclear gyromagnetic ratio, $N$ is the number of nuclei per unit volume, $D$ is the self-diffusion coefficient, and $a$ is the nearest neighbor distance.

The diffusion coefficient given by Equation 10 is

$$D = \left[2\gamma_a^2 \exp(S_a/k)\right] \exp(-H_a/kT)$$

The expression in the brackets is practically independent of temperature, and is often treated as a constant, $D_0$ (1). Equations 10 and 45 may be combined to give

$$T_{2d} = \frac{5a}{4\gamma_N^2 I(I+1)N} D_0 \exp \left(-\frac{H_a}{kT}\right)$$

(46)
and hence

$$\frac{\delta \ln T'_{2d}}{\delta (1/T)} \bigg|_p = -\frac{H_a}{k}$$  \hspace{1cm} (47)

where the temperature independent terms are removed by differentiation. The temperature dependence of $a$ and $N$ are neglected as these terms contribute less than 1% to the activation energy $H_a$.

The activation volume $V_a$ was defined by Equation 11 as

$$V_a = -kT \frac{\delta \ln(D/a^2N)}{\delta p} \bigg|_T$$

Now Equation 45 can be written in the form

$$D = \text{constant} \times T_2 \frac{d}{da}$$  \hspace{1cm} (48)

where the constant includes terms that are independent of temperature and pressure. We have used $N = N_0/a^3$, where $N_0$ is the total number of nuclei in the sample. Then

$$V_a = -kT \frac{\delta \ln(\text{const.} \times T'_2 a/\gamma)}{\delta p} \bigg|_T$$  \hspace{1cm} (49)

or

$$V_a = -kT \left[ \frac{\partial \ln T'_2}{\partial p} - 6 \frac{\partial \ln a}{\partial p} - \frac{\partial \ln \gamma}{\partial p} \right] \bigg|_T$$  \hspace{1cm} (50)

Introducing the volume compressibility $K$ and the Grüneisen constant $\gamma_G$, using
$$K = -3 \left. \frac{\partial \ln a}{\partial p} \right|_T$$

and

$$\gamma_G = - \left. \frac{\partial \ln \nu}{\partial \ln \nu} \right|_T$$

we obtain

$$V_a = -kT \left[ \left( \frac{\partial \ln T}{\partial p} \right)_T + K(2 - \gamma_G) \right]$$

This equation will be used in this work to derive values of $V_a$ from measurements of $T'_{2d}$.

E. Spin Echoes

To measure $T_2$ (the characteristic decay time of $M_{xy}$) by the free induction decay method it is necessary to have a perfectly homogeneous magnetic field $H_o$, or at least one where the dephasing effect due to a distribution of precession frequencies across the sample caused by a field gradient is much smaller than the irreversible dephasing effect caused by the interactions of the nuclei with each other and the lattice.

The fact that the departures from the mean precession frequency due to an inhomogeneity are time independent makes it possible to reverse this dephasing effect at, say, a time $\tau$ and observe a momentary magnetization $M_{xy}(t)$ at time $2\tau$ which is equal to the magnetization that would have existed at that time in a perfectly homogeneous field $H_o$. $H_o$ has been assumed to be in the z-direction. This technique was first developed
30

and explained by Hahn in 1950 (25).

We shall now describe the phenomenon in an artificially simple way. Consider the relaxation times $T_1$ and $T_2$ to be infinite. Let the equilibrium magnetization $M_0$ be tipped $90^\circ$ from the z-direction into the $xy$-plane at time $t = 0$. If the external field is perfectly uniform $M_{xy}$ will precess about the z-direction indefinitely with constant magnitude. If the field is inhomogeneous there will be a static spread of precession frequencies across the sample which will lead to a time increasing phase difference between the magnetization of different parts of the sample. It is convenient to consider the reconstruction of the in-phase condition from the viewpoint of a coordinate system which is rotating at the mean Larmor frequency $w_0$. For convenience, consider the sample to be divided into five regions, each of which is in a different external field, such that the precession frequencies are $w_0$, $w_0 \pm \Delta w$, and $w_0 \pm 2\Delta w$. Let the macroscopic magnetization of each region be called an isochromat of magnetization and be denoted by $M(w_0 + x\Delta w)$, where $x = 0, \pm 1, \pm 2$. The solid vectors in Figure 2 represent the situation in the $x'y'$-plane of the rotating coordinate system some time $\tau$ after the magnetization $M_0$ has been tipped into the $x'y'$-plane. At this time Figure 2 indicates there is still a net component of magnetization along the $y'$-axis, but that it is decreasing. If at this time each isochromat is rotated about the $x'$-axis
Figure 2. The isochromats of magnetization are shown in a coordinate system rotating at the mean Larmor frequency \( \omega \). The solid vectors represent the isochromats just prior to a rotation of 180° about the \( x' \)-axis, and the dashed vectors represent the isochromats just after the rotation. The dashed curve indicates the 180° rotation of the \( +2 \Delta \omega \) isochromat. The small curved vectors orthogonal to the isochromat vectors indicate the precessional rates of the isochromat vectors in the rotating frame.
by 180° (this is indicated by the dashed curve in the figure) the isochromats will be positioned as shown by the dashed vectors. The sense of precession of each isochromat still remains the same because they are still in the same fields as before. All isochromats will now converge on the \(-y'\)-axis giving rise to a momentary net magnetization equal to the original magnetization, (since it was assumed that the nuclei were independent of each other and of the lattice). The time required after the 180° rotation for the regrouping is equal to the time \(T\) that the isochromats were allowed to dephase before the 180° rotation was effected. Therefore the in-phase condition occurs momentarily at time \(2T\), and is called by Hahn a "spin-echo". The 90° or 180° rotations about the \(x'\)-axis are accomplished in practice by applying (for a controlled short period of time) a large magnetic field rotating about the \(z\)-direction at the Larmor frequency. The sequence of events is a 90° Larmor frequency magnetic field pulse, a variable dephasing time \(\tau\), a 180° Larmor frequency magnetic field pulse, and then the appearance of an echo at time \(2\tau\). The techniques used to measure \(T_1\) and \(T_2\) will be discussed next.
IV. EXPERIMENTAL TECHNIQUE AND APPARATUS

A. Spin-Echo Techniques

To measure the relaxation times $T_1$ and $T_2$ using pulse techniques one most often starts from the equilibrium condition with $M_o$ aligned along the applied constant field $H_o$. A radio frequency magnetic field $H_1$, rotating at the mean Larmor frequency and perpendicular to $H_o$, is applied to the sample for a short controllable time $t_w$, satisfying the condition $t_w << T_1, T_2$. In practice a linearly oscillating field is applied to a coil wrapped about the sample. This field can be decomposed into two oppositely rotating fields. The field component which rotates in the same sense as the Larmor precession will be effective; the other component will have negligible effect. This rotating magnetic field of controllable duration is called a radio frequency (RF) pulse or simply a pulse. Consider the situation in a reference plane rotating at the mean Larmor frequency. The axis of rotation is chosen parallel to $H_o$ and is called the $z'$-direction and is coincident with the $z$-direction. In this frame $H_1$ has constant direction and magnitude. Choose this direction to be the $x'$-axis. $H_1$ applies a torque to $M_o$ which is perpendicular to both $H_1$ and $M_o$ and which causes $M_o$ to rotate about $H_1$ at a constant rate given by $H_1 t_w$. The angle of rotation about $H_1$ is given by $H_1 t_w$ (25).
A 90° or π/2 pulse tips the equilibrium magnetization into the y-axis and satisfies the condition $H_1 t_w = \pi/2$. If the duration of the pulse is such that $\gamma H_1 t_w = \pi$ the equilibrium magnetization will be rotated 180° about the x'-axis and be aligned with the -z'-axis. To tip the magnetization intact, the field $H_1$ must be much larger than the internal fields, or $t_w$ much shorter than $T_1$ and $T_2$ (16, p. 33).

The spin lattice relaxation time $T_1$ can be determined by measuring the recovery of $M_z$ as a function of time following a 90° pulse. A 90° pulse is determined by applying a pulse to a sample in equilibrium and maximizing the free induction signal using the shortest possible pulse duration. The xy-component of the precessing magnetization induces a voltage in the coil about the sample. If we apply two such pulses in immediate succession $M_o$ will be tipped 180° to the -z'-axis, and no free induction signal will be observed. After a time greater than 10 $T_1$ the sequence is repeated with a time $\tau$ between the two 90° pulses. The second pulse tips $M_z(\tau)$ into the xy-plane, and thus the amplitude of the free induction signal following the second pulse will be proportional to $M_z(\tau)$. By repeating this procedure for different values of $\tau$ including $\tau >> T_1$, $T_1$ can be obtained from the slope of $\ln[M_o - M_z(\tau)]$ versus $\tau$.

Methods of measuring $T_2$ were discussed earlier. One method was to measure the time constant of the free induction decay following what we now call a 90° pulse in a perfectly
homogeneous magnet. The other method was to use an inhomogeneous field \( H_0 \) and obtain a spin-echo by rotating the magnetization about the \( x' \)-axis by 90° at \( t = 0 \) and then at a later time \( \tau \) rotating the isochromats 180° about the \( x' \)-axis and observing an echo at \( 2\tau \). These rotations are accomplished by the radio frequency pulses. The field inhomogeneity causes the free induction decay after the pulses to decay artificially fast. This is actually desirable so that the free induction signal after the second pulse will not interfere with the echo. The shape of the echo is (25) that of two free induction decays back-to-back. The amplitude \( E \) of the echo at time \( 2\tau \) is proportional to the magnitude of \( M_{xy}(2\tau) \). Therefore if

\[
M_{xy}(2\tau) = M_{xy}(0) \exp(-2\tau/T_2)
\]

then

\[
E(2\tau) = E_0 \exp(-2\tau/T_2)
\]

and a plot of \( \ln E \) vs. \( 2\tau \) can be fitted with a straight line with slope \(-1/T_2\). In the case of aluminum metal at temperatures below 360°C the decay of \( M_{xy} \) is definitely not exponential but is more nearly Gaussian. Kubo and Tomita (23) treat the case of a system with a Gaussian low temperature (rigid lattice) decay and a high temperature exponential decay. Their treatment allows one to find the dependence of the decay shape on the diffusion in the transition region. They warn, "One needs be careful about the assumption of a Gaussian shape
for the limit of the rigid lattice case. As is well known, this is approximately true in condensed phases, where the number of interacting neighbors is large enough to allow the approximate validity of the central limit theorem. The decay shape of aluminum is surely not Gaussian in the rigid lattice as evidenced by the spin-echo free induction decay and also by the steady state NMR line shape (8,26).

B. Spin-Echo Apparatus

A block diagram of the spin-echo apparatus is shown in Figure 3. The system was constructed according to a previously published designs (27,28). A crystal controlled oscillator operating at 5.25 megacycles per second supplies the radio frequency to the radio frequency 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 5.25 megacycle per second signal is allowed to pass through the radio frequency gate upon receipt of a pulse from the pulser. This radio frequency pulse is then sent to the frequency doubler and transmitter, where the frequency is doubled only on receipt of a pulse from the gate amplifier. The purpose of gating the doubler is to minimize the leakage to the sample at the resonance frequency. This is important for samples which have long spin lattice relaxation times.
Figure 3. Block diagram of the spin-echo apparatus
The transmitter develops pulses of sixteen hundred volts without a load. When coupled to the sample circuitry and pressure vessel and the pulse voltage at the transmitter output decreases to approximately 400 volts peak-to-peak. Pulse widths of ten to fifteen microseconds are sufficient to produce a 90° pulse with respect to aluminum. This corresponds to a rotating magnetic field of 25 gauss. 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 microseconds yield a 90° pulse for protons at 10.5 megacycles per second. This corresponds to a field of about 60 gauss.

The details of the sample circuitry are shown in Figure 4. The sample is placed in the coil of the tuned tank circuit. This coil not only delivers the large radio frequency pulses to the sample but also receives the microvolt signals from the precessing nuclear magnetization. These microvolt signals are amplified by a L.E.L. IF Amplifier Model 2809 tuned to 10.5 megacycles per second. It has a band width of one megacycle per second and a gain of $10^6$.

The recovery time of the receiver was originally estimated to be near its nominal value of 20 microseconds, as it took this long after the end of a radio frequency pulse for the detected receiver output to fall from its saturated value to near zero. Attempts to reduce this with switching circuits
Figure 4. Schematic of the sample circuitry showing the tuned tank circuit and receiver protecting diodes
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 radio frequency output of the receiver. It was found that after a pulse had been applied to the sample circuitry, the receiver was saturated for 20 microseconds 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 microseconds after the pulse. Accurate amplitude measurements are restricted to echoes which occur 75 microseconds or more after the second pulse, or more than 150 microseconds after the first pulse. This limitation is important if the inverse line width relaxation time $T_2$ is about this short. A radio frequency output was added prior to 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 volts at the detector proved sufficient to bias it into the linear region.
The linearity was checked by observing the inverse line width relaxation time $T_2$ of protons in a sample of water doped with $\text{MnCl}_2$. To restrict diffusion in a field gradient and to obtain a signal-to-noise ratio comparable to that found in the aluminum samples the sample was heavily diluted with sand.

The 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" (28). When multiple exposure pictures are normally taken the baseline is exposed many times and becomes broad, masking the echoes of small amplitude. The Tektronix Model 535 A oscilloscope used for this work is equipped with an intensifier that allows one to intensify the echo only and dim the rest of the trace as desired. A suitable setting decreases the width of the baseline and increases the accuracy of measuring small echoes. This occurs because large excursions of the noise occur less frequently than the small excursions and the film can discriminate against these if the baseline is not overexposed.

A two channel "boxcar integrator" was constructed similar to one described in the literature (28). The output of the amplifier detector is fed into the "boxcar integrator" where one channel samples the amplitude of the nuclear signal and another channel samples the amplitude of the noise. Each
channel stores the information as a charge on a low loss capacitor. The charges are then fed by separately adjustable resistors to capacitors which bias each half of a difference amplifier. If the sampling is repeated many times, the signal amplitude will continue to be presented and averaged while the noise amplitude, being both positive and negative, averages to zero. In this manner the signal-to-noise ratio is improved. The difference voltage is continuously recorded by a Varian G-10 strip chart recorder. A third triggering pulse from the pulser was used in conjunction with a delay in the boxcar integrator so that the sampler automatically tracked the echo.

The time between pulses was adjusted by a step switch and was measured by a Berkeley Universal Counter Model 7360 R or a Hewlett Packard Electronic Counter Model 524 D.

C. The Magnet

This work was carried out in a Harvey Wells twelve inch low impedance model L128 electromagnet with a three inch air gap. The associated power supply was a Harvey Wells model HS-1050 with a stability of one part in $10^5$ at 5000 Oe.

D. Pressure Equipment

The pressure generating apparatus is shown in Figure 5. Pumps 1 and 2 are Blackhawk model P228, capable of generating 40,000 psi. The intensifier, manganin gauge, and the pressure
Figure 5. Block diagram of the pressure generating apparatus
tubing used to connect the generating system to the pressure vessel are products of Harwood Engineering Co. The intensifier increases the pressure by a factor of 14, and has a maximum pressure rating of 140,000 psi. The Bourdon gauge, made by the Heise Co., was the pressure standard for this experiment. It was calibrated by the manufacturer up to 50,000 psi. and found to have an error of less than 25 psi. at all pressures. This calibration was checked up to 25,000 psi., one-half full scale, on a dead weight gauge by the Ames Laboratory Instrument Shop and found to be within the accuracy claimed by the manufacturer. The Bourdon gauge was then used to calibrate the manganin gauge to 50,000 psi. The calibration was linear and was linearly extrapolated to higher pressures. The manganin gauge contains two manganin wire resistances enclosed in a large stainless steel vessel. These resistances form two arms of a simple Wheatstone bridge. One of these resistances is pressurized and the other remains at one atmosphere. The resistance of manganin is pressure dependent, and this change of resistance is detected by the Wheatstone bridge arrangement. A helipot was used to balance the bridge, and the sensitivity permitted a measurement of pressure to ± 200 psi.

The design of the pressure vessel is rather conventional and is shown in Figure 6. The body of the vessel was machined of A286, a precipitation hardenable stainless steel. This is a
Figure 6. Stainless steel pressure vessel used for spin-echo experiments. The outside diameter of the vessel is 2 1/8 inches.
non-magnetic alloy which retains its strength to above 450°C. The material was obtained from Republic Steel Corporation, and hardened to Brinell number 321 by following the manufacturer's directions. The plug was machined of another high temperature non-magnetic stainless steel 19-9DL, also obtained from Republic Steel. This material is not hardenable by heat treatment.

The radio frequency lead was brought into the vessel through the plug. It was insulated from the plug by Alundum tubing until it entered the pressure chamber, at which point it was hard soldered to a solid stainless steel cone. This cone seated in a hollow cone of pyrophylite which acted as an insulator and pressure seal. The pyrophylite was obtained from the American Lava Corporation and is often called lava. The lava cones were hardened by raising the temperature 100°C an hour to 1000°C. The cone had an included angle of 60°, which was chosen as it is the standard included angle for center drills and thereby simplified construction of the plug seat and lava cones. The stainless steel cone had a 3/8 inch stem about 1/16 inch in diameter extending into the pressure chamber. A small hole was drilled through the stem near the end to accommodate the end of the sample coil which was threaded through this hole, wrapped around the stem, and soft soldered to it. Although soft solder melts at about 250°C this did not seem to cause any trouble. One of the most
consistently occurring difficulties was a sudden loss of the echo and the inability to tune the sample circuit. Sometimes this was due to an open circuit at the beginning or end of the sample coil. More often there was not an open circuit and it was supposed that a short or at least a radio frequency short had occurred somewhere in the plug or sample coil. These shorts sometimes would disappear as the pressure was returned to zero, leading one to suspect that the short had occurred at the lava seal.

Two holes were drilled part way into the bottom of the vessel to accommodate thermocouples. One hole was 9/16 inch from the center line and 3/8 inch deep. The other hole was 1/2 inch from the center line and 1/2 inch deep. The thermocouples were obtained from Aero-Research Instruments Company Inc. The thermocouple wires are chromel and alumel; they are insulated from each other and from the protective stainless steel sheath by magnesia powder. The calibration was specified to meet the standards of the Instrument Society of America. The National Bureau of Standards Thermocouple Tables were used to convert the thermoelectromotive force to a temperature on the Centigrade scale. The calibration was checked at liquid nitrogen and boiling water temperature.

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 DC 200, 200 centistokes. This fluid "crosslinked" at these elevated temperatures and upon disassembly of the pressure vessel was found to contain a putty-like 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 DC 550 silicone fluid was also tried. This lasted longer than DC 200, 200 centistokes but it too would crosslink after prolonged time at high temperatures. Finally Dow Corning DC 200, 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.
E. Sample Preparation

Two sources of 99.99% aluminum were used. One source was a single crystal rod of aluminum purchased from Monocrystals Company. The radio frequency penetration depth in aluminum is 28 microns at 10.5 megacycles 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 microns) 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 gauss magnetron magnet. These aluminum filings were put in a pyrex glass tube, 9 mm in outside diameter and about 3 cm in length, and mixed with Dow Corning DC 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 DC 200, 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 in a temperature dependence study.
V. RESULTS AND CONCLUSIONS

A. Spokas' Work

Spokas (8,9) employed the spin-echo technique to measure the spin-lattice relaxation time $T_1$ and the inverse line width relaxation time $T_2$ in 99.99% aluminum foil as a function of temperature from 77°K to above the melting point. Spokas was interested in obtaining the activation energy for self-diffusion from the temperature dependence of $T_{2d}$ in the motionally narrowed region. However, $T_{2d}$ 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°K to above the melting point. This is the dependence expected for an uncomplicated nuclear spin-conduction electron spin interaction (16, p. 357). The inverse line width relaxation time $T_2$ is best studied by considering the decay of $M_{xy}$ in three temperature ranges. The first is the low temperature range extending from the rigid lattice condition to 360°C. The intermediate temperature range is 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 (23), 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° to 360°C were not amenable to interpretation, although the qualitative change in decay shape was as expected, that is, a smooth change from the rigid lattice shape to an exponential decay shape.

In the intermediate temperature region the decay shape was exponential. Abragam (16, p. 292) has shown that in the range of high temperatures and short correlation times, such that the narrowed line width 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. Furthermore the decay is exponential. If only the nuclear spin-conduction electron interaction and the nuclear dipole-nuclear dipole interaction were present the dipolar phase memory time $T_{2d}$ could be found directly from the measured values of $T_1$ and $T_2$. The temperature independence of $T_1 T$ for aluminum over the entire temperature range 1°K to above 660°K (8) is the expected result if the only relaxation
mechanism contributing to $T_1$ is $T_{1e}$. Therefore $1/T_2$ was expected to be given by

$$1/T_2 = 1/T_{2d} + 1/T_{1e}$$  \hspace{1cm} (56)

According to the theory of diffusional narrowing (2,24)

$$1/T_{2d} \propto 1/D \propto \exp \left( -H_a/kT \right)$$  \hspace{1cm} (57)

where $D$ is the diffusion coefficient, $H_a$ is the activation energy for diffusion and $k$ is the Boltzmann constant. Therefore a plot of $\ln 1/T_{2d}$ against $1/T$ should yield a straight line with slope $H_a/k$. $1/T_{2d}$ values calculated from Equation 54 did not give a straight line; however, Spokas found that a straight line could be obtained if a constant were subtracted from all values of $1/T_2 - 1/T_{1e}$. The constant giving the best fit of the data to a straight line was called $1/T_{2x}$ and had a value of 435 sec$^{-1}$. The relaxation time $T_2$ is thus given by

$$1/T_2 = 1/T_{2d} + 1/T_{1e} + 1/T_{2x}$$  \hspace{1cm} (58)

Although $1/T_{2x}$ is constant, its contribution to $1/T_2$ varies in importance as the values of the other terms change with temperature. For example, at $450^\circ$C, $1/T_2$ is 1430 sec$^{-1}$ and subtracting $1/T_{1e}$ and $1/T_{2x}$ we have $1/T_{2d}$ equal to 603 sec$^{-1}$. Here the quantity $1/T_{2d}$ which is sensitive to diffusion contributes less than 50% to the total measured quantity $T_2$. If
the pressure dependence of the diffusion sensitive $T_{2d}'$ is being sought one should work at lower temperatures where $T_{2d}'$ contributes more substantially to the measured quantity $T_2$. At $400^\circ C$, $1/T_2$ is $3330 \text{ sec}^{-1}$ and $1/T_{2d}'$ is $2530 \text{ sec}^{-1}$, which is a much more favorable situation, as the diffusion sensitive term accounts for about 75% of the measured quantity. Spokas' introduction of the "x"-interaction was justified on the basis that the theory of dipole-dipole narrowing requires $T_{2d}'$ to continue to increase as the diffusion increases $(2,8,24)$. The simple form of the "x"-interaction is supported by agreement of an activation energy of 1.4 ev, derived from the slope of $\ln(1/T_{2d}')$ against $1/T$, with that predicted by Nowick (29), and determined by Butcher (30) using steady state creep measurements. This value is also in agreement with the prediction of a semi-empirical formula and the "narrowing temperature" found by Spokas (8). 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' thesis (8).

At temperatures above $450^\circ C$ 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 (8) to be the
expected behavior if the "x"-interaction were 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 99.95% aluminum foil they showed a marked reduction in $T_2$ at temperatures above 360°C and a slight reduction of $T_1$.

B. Seymour's Work

Previous to the work of Spokas, E. F. W. Seymour (7) measured the temperature dependence of the width of the frequency distribution $g(w)$ of aluminum nuclei by a steady state resonance experiment and inferred from these data an activation energy of 0.91 electron volts. The possible reasons why his analysis resulted in this lower activation energy are enumerated by Spokas (8, p. 70):

"Surely Seymour's arbitrary line width parameter reflects to some degree the changing shape and not solely a decrease in breadth because of narrowing. The resonance curve was found in the present work to be very nearly Lorentzian only above 360°C. Seymour obtained few points above 360°C. In addition, Seymour's data above 360°C are least reliable since they were subjected to a magnet correction. Also the dipolar interaction is not the sole contributor to the observed line width. In particular, thermal relaxation processes plus an unexpected additional interaction were found, in the present experiments, to completely dominate the observed line breadth above 500°C. An undetected line width contribution would affect the analysis of the motional narrowing
in such a way as to give a low activation energy. It is proposed that some combination of the circumstances outlined above had an adverse influence on Seymour's result."

After the publication (9) of Spokas' work, Seymour and Flynn (26) conducted a careful study of diffusional narrowing of the nuclear magnetic resonance in aluminum and copper using steady state resonance techniques. They found the variation of line shape and width of the Cu resonance followed quantitatively the theory of Kubo and Tomita (23), and found an activation energy for self-diffusion in copper. But, in the case of aluminum they concluded:

"The presence of this considerable additional line width, of uncertain origin, inhibits a precise analysis by means of the theory of Kubo and Tomita. We have however computed the line shapes corresponding to the theoretical dipole interaction and the activation energy deduced by Spokas and Slichter from their high temperature measurements. The latter would be expected to be wider throughout the transition owing to the extra interaction present. The experimental curves are indeed consistently wider than the computed ones, although the difference is too small to allow any deduction about the shape characteristic of the excess width alone, or about its temperature dependence. We therefore conclude that the steady state results are not inconsistent with the activation energy assumed."

C. Present Results

The object of this work was to measure the pressure dependence of the inverse line width relaxation time $T_2$ in order to determine the activation volume for self-diffusion in aluminum. The diffusion sensitive parameter is the dipolar
phase memory time $T_{2d}$. This parameter, however, can not 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' work. As shown by Spokas (8) and others (26) 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 $T_2$ versus temperature runs were conducted for samples of different origins. Data points were taken mainly in the temperature region of interest in this experiment ($400^\circ$ to $440^\circ$C). The results are shown in Figure 7. One source of samples was a single crystal rod of 99.99% aluminum obtained from Monocrystals Company. 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 microns) to insure reasonably uniform penetration of the radio frequency 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 $440^\circ$C the value of $T_2$ obtained in this work was 430 microseconds compared to the
Figure 7. The temperature dependence of the inverse line width relaxation time $T_2$.
99.99% FOIL (SPOKAS)
99.9% FOIL (SPOKAS)
99.99% CRYSTAL ROD FILINGS
99.99% AEC STOCK FILINGS
values obtained by Spokas of 640 microseconds for 99.99% aluminum foil and 290 microseconds for 99.5% aluminum foil.

Although the $T_2$ values were smaller, it was possible, using the procedure outlined in the review of Spokas' work, to find a temperature independent value of $1/T^*$ (870 sec.$^{-1}$) such that the $\ln(1/T^*$) yielded a linear dependence on $1/T$ in the temperature range 400°C to 580°C. At temperatures above 590°C the filed samples sintered and were useless for spin-echo experiments. The linear dependence of $\ln(1/T^*)$ on $1/T$ is expected according to the theory of Bloembergen, Purcell and Pound (24) and others (2,9) when the phase memory time has appreciably increased from the rigid lattice value. The activation energy determined by this dependence was 1.3 ± 0.2 electron volts, which is in good agreement with the value of 1.4 ± 0.1 electron volts 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 Figure 7 are determined from the "initial" decay rates. Since the data at high temperature often are slightly non-linear, 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' $T_2$ data at higher temperatures. The pressure dependence of $T_2$ was not determined for temperatures appreciably above 450°C because the strength of the pressure vessel materials decreases
rapidly for temperatures above approximately 450°C.

It was proposed by Spokas (8) that the "x"-interaction is a static uncorrelated nuclear quadrupole-electric field gradient interaction, in which the electric field gradients arise mainly from dislocation lines. Furthermore, the line width (8) caused by this interaction is approximately given by

\[ \frac{1}{T_{2x}} \sim \delta \omega_{\text{dis}} \left( \frac{a}{l} \right) \]  

(59)

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 (8). Taking a realistic dislocation density of \( 10^6 \) lines/cm² necessitates a not unreasonable nearest neighbor interaction of \( \delta \omega_{\text{dis}} = \frac{\delta \omega_{\text{dis}}}{2\pi} = 2 \times 10^6 \) cps (8).

In order to examine the temperature dependence of \( \frac{1}{T_{2x}} \), 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 \( \frac{1}{a^2} \). Equation 59 becomes

\[ \frac{1}{T_{2x}} \sim \left( \frac{A}{a^2} \right) \left( \frac{a}{l} \right) \]

or

\[ \frac{1}{T_{2x}} \sim \frac{A}{al} \]
where \( A \) is a constant. If it is assumed that the total number of dislocations is constant it follows that the mean distance \( t \) between randomly dispersed dislocations is proportional to \( a \) and the relationship becomes

\[
\frac{1}{T_{2x}} \sim \frac{B}{a^2},
\]

where \( B \) is a constant. Therefore

\[
\left. \frac{\partial}{\partial T} \frac{3(1/T'_{2x})}{1/T_{2x}} \right|_p \sim -2(1/a) \left( \frac{\partial a}{\partial T} \right)_p = -4.6 \times 10^{-5} (C^0)^{-1} \quad (60)
\]

where the linear thermal expansion, \( 1/a \left( \frac{\partial a}{\partial T} \right)_p = 2.3 \times 10^{-5} (C^0)^{-1} \) (31) has been employed. Therefore, the change in \( 1/T'_{2x} \) for the temperature change 400\(^\circ\)C to 660\(^\circ\)C would be approximately one percent. This temperature dependence is far too small to be observed in this work.

In a similar manner the pressure dependence of \( 1/T'_{2x} \) is given by

\[
\left. \frac{\partial}{\partial P} \frac{3(1/T'_{2x})}{1/T_{2x}} \right|_T = -2 \frac{1}{a} \left( \frac{\partial a}{\partial P} \right)_T = 0.92 \times 10^{-6} \text{ atm}^{-1} \quad (61)
\]

where the volume compressibility \( K = -3(1/a) \left( \frac{\partial a}{\partial P} \right)_T = 1.38 \times 10^{-6} \text{ atm}^{-1} \) has been used (31). The maximum pressure used in this work was 3000 atmospheres, which would produce only a 0.3 percent change in \( 1/T'_{2x} \). Therefore, \( 1/T'_{2x} \) will be assumed to be pressure independent.
The assumption that the number of dislocations in an annealed sample is temperature independent is based upon considerations reviewed by Dekker (32, p. 95). Since theoretical calculations give an energy of formation of a dislocation to be 5 to 10 electron volts per atom, and since $kT$ at 600°C is less than 0.1 electron volts, it follows that thermal activation cannot be responsible for the creation of a dislocation (32). The density of dislocations in a solid is determined essentially by its history, that is, 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 \( \frac{1}{T_{2x}} \)
to differ.

The temperature dependence of \( T_{le} \) has been well estab­
lished (8) and satisfies the equation \( T_{le} \propto = 1.85 \) second-
degrees. \( T_{le} \) is assumed to be essentially pressure independent
in this work. The pressure dependence of the Knight shift of
aluminum was studied by G. B. Benedek and T. Kushida (19) 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 per­
cent. Assuming that the Korringa relationship (17), \( T_{le} \propto K^{-2} \)
applies, it follows that the pressure induced change in \( T_{le} \) at
3,000 atm. would be less than 0.6%. This would have a negli­
gible effect on the pressure dependence of \( T_2 \).

The decay of \( M_{xy} \) is exponential only in the temperature
range 380°C to 450°C, and the "x"-interaction becomes relative­
ly more important as the temperature is increased. Therefore,
\( T_{2d} \) 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 \( T_{le} \) and \( T_{2x} \) are independent of pressure would be less
important at this temperature since their relative contribu­
tions to \( T_2 \) would be smaller. However, due to the limitations
of the spin-echo apparatus discussed earlier, it was not
possible to measure accurately values of \( T_2 \) less than 150
microseconds. This made it necessary to work at temperatures above 390°C.

The inverse line width relaxation time $T_2$ was measured as a function of pressure for several isotherms between 394°C and 449°C. The samples used consisted of 325 mesh (44 micron) filings obtained from a single crystal rod of 99.99% aluminum. The relaxation times $T_2$ were determined by measuring the spin-echo amplitude as a function of the time $2\tau$, where $\tau$ is the time between the 90° and 180° pulses in the sequences 90°-τ-180°-τ-echo. After each application of this sequence, a time greater than 10 $T_1$ was allowed for the nuclear spin system to return to the equilibrium value. The sequence was repeated approximately 50 times for each value of $\tau$. The echo amplitudes were recorded by either multiple exposure Polaroid photography of an oscilloscope display, or by a stripchart output of a "boxcar integrator". The negative reciprocal of the slope of a graph of the logarithm of the echo amplitude as a function of $2\tau$ yields the relaxation time $T_2$. Figure 8 is an example of a $T_2$ determination. The logarithm of the $T_2$ values so determined were then plotted as a function of pressure at several fixed temperatures, and are shown in Figures 9a to 13b. The "boxcar integrator" was used to obtain the $T_2$ values shown in Figures 9a, 10a, 11a, 11b; the other $T_2$ data were obtained photographically. The activation volume for self-diffusion is proportional to the slope of $\ln T_2$. 
Figure 8. The logarithm of the echo amplitude as a function of $2\tau$ at 408°C. $T_2$ is 263 microseconds.
$T = 408^\circ C$
$T_2 = 263 \mu s$
Figure 9a. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a constant temperature of $394^\circ C$. The line drawn through the data corresponds to an activation volume for self-diffusion of 62% of an atomic volume.

Figure 9b. Experimental values of the inverse line width relaxation time $T_2$ of aluminum as a function of pressure at a temperature of $408^\circ C$. Also shown is the corresponding pressure dependence of $T_{2d}$ derived from the $T_2$ dependence using Equation 59 to remove the $"x"$-interaction and the conduction electron contributions. The $T_{2d}$ dependence and Equation 62 yield an activation volume for self-diffusion of 75% of an atomic volume.
Figure 10a. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 408°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 52% of an atomic volume.

Figure 10b. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 411°C. The solid and dashed lines correspond to activation volumes for self-diffusion of 97% and 65% of an atomic volume respectively.
Figure 11a. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 411°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 66% of an atomic volume.

Figure 11b. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 435°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 65% of an atomic volume.
Figure 12a. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 438°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 64% of an atomic volume.

Figure 12b. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 446°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 76% of an atomic volume.
Figure 13a. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 448°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 87% of an atomic volume.

Figure 13b. Experimental values of the inverse line width relaxation time $T_2$ for aluminum as a function of pressure at a temperature of 449°C. The line drawn through the data corresponds to an activation volume for self-diffusion of 65% of an atomic volume.
versus pressure $p$ at constant temperature and is given by

$$V_a = -kT \left[ \left( \frac{\Delta \ln T_{2d}}{\Delta p} \right)_T + K(2 - \gamma_G) \right]$$

(62)

which corresponds to Equation 53. Here $K$ is the volume compressibility, $\gamma_G$ the Grüneisen constant, and $k$ is the Boltzmann constant. The value used for the compressibility was $1.38 \times 10^{-6}$ (atmospheres)$^{-1}$ (31). A value of $\gamma_G$ equal to 2.1 was used (12). The last term of Equation 62 is then less than 1% of the first term, and can be neglected. The required $T'_{2d}$ values were obtained from the values of $T_2$, $T'_{2x}$, $T'_{1e}$ and Equation 43, assuming $T'_{2x}$ and $T'_{1e}$ were pressure independent. Figure 9b exhibits $T_2$ and the resulting $T'_{2d}$ as a function of pressure at 408°C. At this temperature the absolute value of the slope of $\ln T'_{2d}$ versus $p$, which determines the activation volume noted, is 40% greater than the absolute value of the slope of $\ln T_2$ versus $p$. At 446°C the absolute value of the slope of $\ln T'_{2d}$ versus $p$, which determines the activation volume noted, is 130% greater than the absolute value of the slope of $\ln T_2$ versus $p$. The activation volumes determined from $T'_{2d}$ values show no consistent temperature dependence over this temperature range although the importance of $T'_{2x}$ to the derived values of $T'_{2d}$ changes appreciably. This observation supports the value of $T'_{2x}$ found from the temperature dependence of $T_2$ at one atmosphere and previously discussed.
An average activation volume for self-diffusion of 70% of an atomic volume was determined by a weighted average of the activation volumes stated in Figures 9a to 13b. 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. A value of $V_A = 70\% \pm 20\% V_0$ includes nine of the ten determinations.

Another attempt has been made to determine the activation volume for self-diffusion in aluminum using NMR techniques. F. Tuler (33) studied the pressure dependence of the inverse linewidth relaxation time $T_2$ in aluminum powder but was not successful in determining an activation volume for self-diffusion. Commercially available 99.99% aluminum powder was used in the pressure dependence study, and a filed 99.999% sample was used in a comparative temperature dependence study. The two samples yielded different $T_2$ values at the same temperature and one atmosphere. The $T_2$ values obtained for the higher purity sample were slightly less than those obtained in this work. The $T_2$ values obtained for the lower purity sample were yet less and were approximately equal to those obtained by Spokas for a 99.5% aluminum foil sample. Tuler states (33, p. 47)

"Pressure dependent data were only taken for the 99.99% aluminum powder. The manufacture of the 99.999% aluminum powder by filing produced extremely irregular and elongated particles. The packing factor of the filed powder was approximately one-half that of the 99.99% aluminum powder..."
which was composed of particles with a much more regular (approaching spherical) shape. Since the signal-to-noise was quite marginal to begin with, the decrease in the true sample size due to the lower packing factor of the filed powder made measurements of the 99.999% aluminum powder impossible in the probe in the pressure vessel."

Tuler further states (33, p. 58)

"An extra broadening dominating the observed linewidth complicates the data sufficiently to make extraction of the desired self-diffusion contribution to the linewidth behavior virtually impossible."

And finally (33, p. 57)

"Because the extra broadening is the major part of the secular dipolar linewidth, no absolute value can be obtained for the pressure change in the linewidth due to vacancy formation and motion."
VI. DISCUSSION AND CONCLUSIONS

There is not a large body of experimental data regarding the effect of hydrostatic pressure on diffusion. Table 2 with the exceptions of the last two entries was taken from compilations by Lazarus and Nachtrieb (15) and Hultsch and Barnes (4).

Table 2. Comparison of predicted and experimental values of the activation volume for self-diffusion for various pure metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Structure</th>
<th>Method</th>
<th>Quantity measured</th>
<th>$V_a$ Experimental Percent</th>
<th>$V_a$ Calculated Equation 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>bcc</td>
<td>NMR</td>
<td>$V_f + V_m$</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td>Sodium</td>
<td>bcc</td>
<td>NMR</td>
<td>$V_f + V_m$</td>
<td>41</td>
<td>42</td>
</tr>
<tr>
<td>Sodium</td>
<td>bcc</td>
<td>tracer</td>
<td>$V_f + V_m$</td>
<td>52</td>
<td>42</td>
</tr>
<tr>
<td>Lead</td>
<td>fcc</td>
<td>tracer</td>
<td>$V_f + V_m$</td>
<td>72</td>
<td>74</td>
</tr>
<tr>
<td>Lead</td>
<td>fcc</td>
<td>creep</td>
<td>$V_f + V_m$</td>
<td>85</td>
<td>74</td>
</tr>
<tr>
<td>Silver</td>
<td>fcc</td>
<td>tracer</td>
<td>$V_f + V_m$</td>
<td>89</td>
<td>82</td>
</tr>
<tr>
<td>Gold</td>
<td>fcc</td>
<td>quench</td>
<td>$V_m$</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>Aluminum</td>
<td>fcc</td>
<td>NMR</td>
<td>$V_f + V_m$</td>
<td>70^a</td>
<td>76</td>
</tr>
<tr>
<td>Aluminum</td>
<td>fcc</td>
<td>creep</td>
<td>$V_f + V_m$</td>
<td>63^b</td>
<td>76</td>
</tr>
</tbody>
</table>

^aThis work.

^bSee Reference 30.
In several experiments the activation volume measured is the sum of the volume for formation $V_f$ of the defect and the volume change $V_m$ necessary for motion of the defect (presumably a vacancy). Within the accuracy of current techniques there is no definite evidence to indicate that the activation volume is temperature dependent, and there is little evidence to indicate that the activation volume is a function of pressure, although most work has been carried out at pressures up to 10,000 atm (15).

As shown in Table 2 most systems show a very similar activation volume, or in other words similar pressure dependence of the diffusion rates. The diffusion rates all decrease exponentially with pressure, and yield activation volumes of the same order of magnitude as the atomic volume. The activation volume is not noticeably dependent on the crystal structure or compressibility of the material. It is, for example, larger for silver than for sodium which is much more compressible.

The activation volume as defined by Equation 11 can be identified as a physically meaningful volume only if the assumptions regarding the diffusion process are describable in terms of the equilibrium theory. As noted earlier in section II, the theory contains a number of uncertain hypotheses. The comparison of measured activation volumes with those derived by various models is then a check on the models and the validity.
of the equilibrium theory (15).

The "hard sphere" model is the simplest description of a solid. The diameters of the spheres are equal to the nearest neighbor distance. For this model the relative atomic volumes of lattice defects can be estimated. Considering a face-centered cubic lattice, \( V_f \) is equal to 1 atomic volume, as no relaxation is possible around the vacancy. The motion volume \( V_m \) is about 0.8 atomic volume (15), and therefore \( V_a \) is equal to 1.8 atomic volumes. For a body-centered cubic lattice, with no relaxation inward on the vacancy, \( V_f \) would be 1 atomic volume and \( V_m \) would be zero (15). If inward relaxation occurs \( V_f \) decreases and \( V_m \) increases, and the activation volume remains about 1 atomic volume (15). These estimates show that the simplest model agrees to within a factor of two or three with the values in Table 2; however, the hard sphere model consistently overestimates the activation volumes, particularly for metals.

Tewordt's model for the lattice distortion about a vacancy in face-centered cubic copper was discussed earlier. He calculated an inward relaxation about a vacancy in copper to be in the range of 45 to 53\% (14). Therefore, the \( V_f \) is about one-half an atomic volume.

As cited in Ref. (15), Huntington and Seitz estimate that the barrier atoms are displaced about ten percent in the jump process. This is consistent with the experimental value of \( V_m \).
equal to $15\%$ shown for gold in Table 2. Tewordt's calculation of considerable inward relaxation about a vacancy in face-centered cubic metals is supported by the fact that measured values of the total activation volume are less than one atomic volume in these metals. A detailed comparison between theory and experiment is not justified however because values of $V_f$ alone are not available for face-centered cubic metals, and the theoretical values of $V_m$ are very approximate (15). However, combining Tewordt's value for the volume of formation $V_f$ with the Huntington and Seitz estimate of the motional volume $V_m$ would give a total activation volume $V_a$ of 55 to 63% for face-centered copper. This value is similar to the activation volume of $70\% \pm 20\%$ determined in this work for face centered cubic aluminum.

As mentioned earlier, Rice and Nachtrieb (6) have proposed a law of corresponding states between diffusion and melting. According to this model the activation volume for diffusion $V_a$ is related to the volume change on melting $V_M$ by (Equation 15)

$$\frac{V_a}{H_a} = \frac{V_M}{H_M}$$

where $H_a$ and $H_M$ are respectively the activation enthalpies for diffusion and melting. This relation gives good agreement with the measured activation volumes for metals as shown in Table 2. If the values $H_M = 2.57$ kcal/gm atom = .1113 e.v./atom (34),
\[ V_M = 0.060 \, V_o \quad (35), \quad \text{and} \quad H_a = 1.4 \text{ e.v./atom} \quad (8) \] are considered known, Equation 15 yields an activation volume of 76% for aluminum. The agreement of the experimental determinations of \( V_a \) and the values calculated using Equation 15 is shown in Table 2 for several metals.

The continuum model developed by Keyes (12) predicts a relationship between the activation volume for self-diffusion and the Gibb's free energy for self-diffusion

\[ V_a = k' K G_a \quad (63) \]

where \( k' \) is a dimensionless constant equal to approximately 4, and \( K \) is the isothermal compressibility. Setting \( G_a \) equal to 1.4 ev/atom results in a predicted activation volume of approximately 80% \( V_o \).

An activation volume of 63% ± 25% of the atomic volume has been found by B. M. Butcher (30) using the effect of hydrostatic pressure on steady-state creep in the temperature range 250° to 280°C. He also has reported an activation energy for self-diffusion in aluminum of 1.39 ev in this temperature range, in excellent agreement with the value of 1.4 ± 0.1 ev found using nuclear magnetic resonance techniques (8). Although macroscopic mass flow is measured in creep experiments, the values obtained for the activation energy and activation volume agree well with those obtained by nuclear magnetic resonance. However, recent work by Butcher et al. (36) has yielded an activation volume of
$135 \pm 11\% V_0$ which is in sharp contrast with his earlier work. Measurements by Detert and Stander (37) of the change in length of samples quenched from $400^\circ\text{C}$ also imply a rather large activation volume of approximately $123\% V_0$. 
VII. REFERENCES


