VACANCY MIGRATION ENERGY IN ALUMINUM: A
DETERMINATION BY NUCLEAR MAGNETIC RELAXATION

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VACANCY MIGRATION ENERGY IN ALUMINUM: A
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Aluminum of 99.998% purity has been investigated with the technique of nuclear magnetic relaxation in the coordinate system rotating at the natural frequency of Al^{27} nuclei. The activation energy for vacancy migration is determined, at each base-line (equilibrium) temperature setting, from the ratio of the mean time between successive atomic jumps in the specimen under thermal equilibrium conditions and that immediately after pulsed heating. The value obtained is 0.55 eV with the standard deviation of 0.04 eV in the temperature range from 260°C to 310°C. At higher temperatures, however, the measured values of the activation energy exhibit a variation with temperature. This temperature dependency is explained as being primarily associated with the generation of vacancies during the experiment. The generation rates are estimated from supplementary experiments and the effects of vacancy generation are analyzed. Other possible systematic errors and imprecisions are also examined.

From the data taken under equilibrium conditions, the activation energy for self-diffusion is determined to be 1.32 eV with the estimated standard deviation of 0.02 eV in the temperature range from 240°C to 500°C; the pre-exponential factor is $0.144 \text{ cm}^2/\text{sec}$ with the estimated error limit (not the standard deviation) of $0.003 \text{ cm}^2/\text{sec}$.

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. THEORIES OF NUCLEAR MAGNETIC RELAXATION IN THE ROTATING FRAME	8
A. Introduction: General Comments and Motional Effects	8
B. Description of the Theories	13
III. EXPERIMENTAL APPARATUS AND PROCEDURE	22
A. Apparatus	22
1. Electronics	22
2. Current Pulser	27
3. High Temperature Probe	31
B. Specimen Preparation	36
C. Experimental Procedures	38
1. Measurement of the Spin-Lattice Relaxation Time in the Rotating Frame	38
2. Technique for Setting Experimental Conditions	41
3. Calibration of the RF Field	46
4. Temperature Measurement	47
5. Measurement of the Spin-Lattice Relaxation Time in the Laboratory Frame	48
IV. THE ANALYSIS OF ERROR	49
A. Introduction: Error Equation	49
B. The Oscillatory Character of the $M_x(t)$ Curve	50
C. The Static Field Off-Resonance	55
D. Deviation from the Phase Condition	60
E. Variation in the Magnitude of H_1	61
F. Temperature Non-uniformities within the Specimen Volume	63
G. Uncertainties in the Temperature Step $\Delta\theta$	63
H. Temperature Gradient in the Specimen	66
I. Conclusion: the Estimated Error in E_m	69

V. EXPERIMENTAL RESULTS AND DISCUSSION	74
A. The Electronic Contribution to the Spin-Lattice Relaxation	74
B. Self-Diffusion	79
C. Activation Energy for Vacancy Migration	88
D. Vacancy Generation	97
E. Conclusion	115

APPENDIX

A. SUMMARY OF PREVIOUS WORKS ON SELF-DIFFUSION IN ALUMINUM	117
B. SUMMARY OF VALUES OF VACANCY FORMATION ENERGY IN ALUMINUM	122
C. SUMMARY OF PREVIOUS WORKS ON THE VACANCY MIGRATION ENERGY IN ALUMINUM	123
D. CALCULATION OF p AND g FOR VACANCY DIFFUSION IN AN FCC LATTICE	126
E. CORRECTION FOR VACANCY GENERATION DURING THE $T_{1\rho}$ MEASUREMENT	129
F. THE RELATION BETWEEN THE APPARENT MIGRATION ENERGY AND THE FRACTION OF VACANCY GENERATION	135
G. EXPERIMENTAL DATA.	137

REFERENCES	139
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VITA	144
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I. INTRODUCTION

Within experimental error, self-diffusion coefficients for most materials, especially face-centered cubic metals, are found to be satisfactorily describable by a simple Arrhenius equation,

$$D = D_0 \exp(-Q/k\theta) \quad (1)$$

where the pre-exponential factor D_0 and the activation energy Q are considered to be independent of temperature θ ; k is the Boltzmann constant. Some body-centered cubic metals do not obey the Arrhenius equation, and for a metal with a non-cubic structure more than one Arrhenius equation is used to express its self-diffusion coefficient along the principal axes in a single crystal. (1)

From voluminous experimental evidence and theoretical consideration, monovacancies in crystal structures have been demonstrated to be the major imperfections which are the basis of the predominant mechanism for atomic diffusion in almost all pure metals and substitutional solid solutions. An atomistic analysis of the vacancy mechanism for self-diffusion in cubic substances gives

$$\begin{aligned} D &= \frac{r^2}{6\tau} \\ &= \frac{1}{6} r^2 \nu Z \exp[(S_m + S_f)/k] \exp[-(E_m + E_f)/k\theta] \end{aligned} \quad (2)$$

where τ is the mean time between successive atomic jumps, r is the jump distance, ν is taken to be the vibrational frequency of an atom about its equilibrium position in the jump direction, Z is the number of nearest neighbor sites, S represents the non-configurational entropy terms, and E represents the activation energy terms; the subscript f denotes the vacancy formation and the subscript m denotes the vacancy migration. For self-diffusion coefficients as determined with the technique of radio-active isotope tracers, the right hand side of Eq. (2) must be multiplied by a correlation factor f which is the fraction of jumps of a tracer atom that are effective in causing random diffusion.⁽¹⁾ In the techniques of nuclear magnetic resonance in pure metals the nuclei of concern that are nearest neighbors of vacancies are indistinguishable so it might appear that the question of correlation effects should not arise. However, under certain circumstances, the correlation factor in one form or another must be considered as it affects the interpretation of data. This discussion is deferred to Chapter V. If r and the S terms are independent of temperature, a comparison between the experimental Eq. (1) and the theoretical Eq. (2) indicates

$$Q = E_m + E_f$$

and

$$D_0 = \frac{1}{6} r^2 \nu Z \exp[(S_m + S_f)/k]$$

(3)

which are true for self-diffusion by a single mechanism, namely, monovacancies. Clearly, r varies with temperature due to thermal expansion of the lattice. In addition, theoretical considerations show that both the S terms and the E terms are not necessarily independent of temperature.⁽²⁾ However D_0 and Q are found to be independent of temperature within experimental error. When a deviation from the Arrhenius equation occurs, at least in the case of a face-centered cubic metal, it is usually attributed to the existence of competing mechanisms. Specifically at high temperatures, divacancies may be created in appreciable quantities in addition to monovacancies; at low temperatures, fast atomic transport along dislocations or in grain boundaries may become important in spite of the fact that only a small fraction of the atoms are influenced by these defects.

Self-diffusion in metals may be investigated by direct measurement of mass flow in the specimen, employing a radio-active isotope tracer. It may be studied also by means of some physical processes which are related to atomic transport in the specimen and for which a theoretical model can be constructed to interpret the experimental data. Such phenomena are, for examples, annealing of dislocation loops after quenching and nuclear magnetic resonance. The difficulties associated with these indirect methods arise from the fact that the theoretical models are very often based on assumptions, and thus some unknown factors may

render their validity questionable. The previous works on self-diffusion in aluminum are summarized in Appendix A. The values of Q obtained by different investigators range from 1.25 eV to 1.5 eV.

The activation energy for vacancy formation in pure aluminum has been studied mainly with either dilatation method or with quench methods. The dilatation method consists of simultaneous observations of the thermal expansion of the lattice parameter and of the gauge length of the specimen, and hence provides a direct quantitative measure of the vacancy concentration as a function of temperature, $C = \exp(S_f/k) \exp(-E_f/k\theta)$. The values of S_f and E_f are obtained from the Arrhenius plot. The dilatation experiment has also supplied a conclusive proof that vacancies are the predominant point defects in metals. The quench methods retain the vacancy concentration at different elevated temperatures by quick cooling of the specimen to a low temperature where the effect of vacancy migration is negligible. Resistance measurements at liquid-nitrogen or -helium temperature are often used in these experiments. (It is an advantage that the lattice contribution to the total electric resistivity is greatly reduced at such a low temperature so that accuracy is increased in the measurements of the vacancy contribution.) According to Matthiessen's rule, the increment in residual resistivity after quenching is proportional to the concentration of vacancies that have been

frozen in. Other methods such as micro-calorimetry or thermoelectric power also have been employed. Previous works dealing with vacancy formation energy for aluminum are listed in Appendix B. The results obtained for aluminum by different investigators range from 0.70 eV to 0.79 eV, but the most quoted value is 0.76 eV for E_f and 2.4 k for S_f .

The activation energy for vacancy migration has been obtained mostly by analyzing the annealing kinetics of quenched specimens. A review of the various methods used in the annealing studies may be found in articles by Doyama.⁽³⁾ In this approach to the determination of the vacancy migration energy, the main complication is the complex behavior of vacancies during the quenching and the annealing processes. Depending on the quenching temperature, the cooling medium, the specimen size, and the annealing temperature, various types of vacancies may be formed. Thus the central effort becomes, very often, the identification of migrating defects. The migrating defects are identified by their activation energies for migration. The vacancy migration energy has been estimated also from the irradiation and cold-work experiments. For aluminum different methods give values of the migration energy for a monovacancy ranging from 0.55 eV to 0.62 eV and those for a divacancy ranging from 0.46 to 0.5 eV. The earlier works on the migration energy are summarized in Appendix C. In the present study, we hope to provide an alternative method for the determination of

the migration energy for a monovacancy by using the techniques of nuclear magnetic relaxation in the rotating frame.

It has been known for a long time that the relaxation times associated with nuclear magnetic resonance signals of a metal are sometimes strongly dependent on temperature. This temperature dependency is explained as a result of diffusion of the nuclei involved.^(4,6) To observe the motional effects, a very powerful technique, when applicable, is to measure the spin-lattice relaxation time in the coordinate system rotating at the natural frequency of the nuclei involved, in the present case Al^{27} . The relation between this relaxation time and the mean time between successive atomic jumps will be described in Chapter II.

In the present experiments, the mean time between successive atomic jumps is analyzed for pure aluminum under both thermal equilibrium and non-equilibrium conditions. The specimen is heated up to an equilibrium temperature θ within the region where the motional effect on the spin-lattice relaxation time in the rotating frame dominates the relaxation process. The non-equilibrium condition is created by a pulsed heating with an ideally instantaneous increase of temperature equal to $\Delta\theta$. From Eq. (2), the mean time between successive atomic jumps in the specimen under thermal equilibrium conditions is

$$\tau_b = \tau_o \exp(E_f/k\theta) \exp(E_m/k\theta); \quad (4)$$

immediately after the temperature step, under non-equilibrium conditions,

$$\tau_p = \tau_o \exp(E_f/k\theta) \exp[E_m/k(\theta + \Delta\theta)] \quad (5)$$

in which no change in the vacancy concentration is assumed, that is $C_p = C_b \propto \exp(-E_f/k\theta)$. The subscript b denotes the equilibrium (base) state and p, the non-equilibrium (pulsed) state. Combination of Eqs. (4) and (5) gives

$$E_m = k \frac{\theta(\theta + \Delta\theta)}{\Delta\theta} (\ln\tau_b - \ln\tau_p) \quad (6)$$

By substituting the measured values of θ , $\Delta\theta$, τ_b and τ_p , the value of E_m is determined from Eq. (6).

The experimental technique and apparatus are presented in Chapter III. Some possible deviations from ideal experimental conditions are discussed in Chapter IV for further improvement. The experimental results are analyzed in Chapter V.

II. THEORIES OF NUCLEAR MAGNETIC RELAXATION IN THE ROTATING FRAME

A. Introduction: General Comments and Motional Effects

Before proceeding to the theories being used in the present study, it may be beneficial to describe here some general concepts and motional effects in nuclear magnetic relaxation. Further background may be found in the books by Slichter⁽⁴⁾ and Abragam.⁽⁵⁾

In the case of many isotopes, a nucleus in its ground state possesses a non-zero spin angular momentum $\hat{I}\hbar$ and a dipolar magnetic moment $\vec{\mu}$. The relationship between these two quantities is collinear and can be expressed by $\vec{\mu} = \gamma\hbar\hat{I}$, where γ is called the gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π , and the spin I is either an integer or a half-integer. For aluminum, the isotope Al^{27} has a natural abundance of 100%, $I = 5/2$, $\gamma/2\pi = 11.094 \times 10^2 (\text{sec-G})^{-1}$, and an electric quadrupolar moment. Since aluminum possesses a face-centered cubic lattice, electric quadrupolar interactions vanish unless the crystalline symmetry is disturbed by some kind of imperfections and hence will not require consideration in the present study.

In a transient experiment on nuclear magnetic relaxation, the spin system of a substance is subjected to two kinds of external magnetic fields. Applied along the Z axis as usually designated, a static field H_0 interacts with the nuclei to cause $(2I + 1)$ energy levels with an equal spacing of $\hbar\gamma H_0$ in the laboratory frame.

(Zeeman effect). The relative population of these levels is governed by the Boltzmann distribution when in thermal equilibrium at temperature θ . The magnetization is $M_x = M_y = 0$ and $M_z = M_0 = CH_0/\theta$, where C is Curie's constant for the nuclei. The situation in the rotating frame will be described in the next section. An oscillating field, usually in the radio-frequency range, is applied in the X-Y plane, perpendicular to H_0 . The rf field is in the form of a pulse sequence which is programmed in such a way that it first disturbs the thermal equilibrium of the spin system and then facilitates the observation of the relaxation process of interest in the X-Y plane. According to quantum theory, the rf field causes transitions between adjacent Zeeman levels effectively only when its frequency coincides with the natural frequency $\omega_0 = \gamma H_0$ of the spin system.

There are two basic relaxation processes in nuclear magnetism. Firstly, starting from a disturbed state, the spin system approaches thermal equilibrium with the lattice system at a rate characterized by the spin-lattice relaxation time T_1 . In the laboratory frame, the process is manifested by restoration of the magnetization toward its equilibrium value $M_z = M_0$. Secondly in addition to the external fields, each individual spin also experiences a local field H_L produced by all other spins in the system. The consequence is manifested by a broadening in the absorption mode of steady-state spectroscopy. On the other hand, coupling between the spins

allows energy transfer between them at a rate characterized by the spin-spin relaxation time T_2 . The T_2 process is manifested macroscopically by the decay of the transverse magnetization, $M_x = M_y$, produced by an rf pulse. The two phenomena are related by the approximate relation,

$$T_2^{-1} \approx \gamma H_L \approx \gamma \delta H \quad (7)$$

where δH is the part of the absorption line width that is contributed from the spin-spin interaction only. The remaining part of the absorption line width may be generated by differences in magnetic or electric fields at different nuclear sites. Such inhomogeneous broadening may be, for example, due to the gradients of the applied magnetic fields or the presence of impurities and imperfections in the crystal lattice. The same mechanism shows a faster free induction decay than would be expected from genuine spin-spin relaxation. The absorption line shape of steady-state spectroscopy and the transverse relaxation after a $\pi/2$ pulse are in fact related by a Fourier transform. However the dipolar component of the transverse decay of the magnetization is usually not exponential, making the definition of T_2 somewhat arbitrary. (This uncertainty creates some minor difficulties in the analysis presented in Chapter V.) The value of T_2 can be determined unambiguously from an absorption line or a free induction

decay only when the shape of the line is related to Gaussian, Lorentzian, or in the process of transition from Gaussian to Lorentzian.

Clearly the spin-spin interaction is always limited by the lifetime of the spin states and hence T_2 never exceeds T_1 . When T_2 is much shorter than T_1 , an internal equilibrium can be established inside the spin system, and a spin temperature θ_s may be postulated to describe this equilibrium state. The spin temperature is not necessarily equal to the lattice temperature, and T_1 may be considered to characterize the process by which θ_s changes toward θ .

Both T_1 and T_2 as observed are in general determined by the combined effect of several processes. A relaxation rate is defined as the inverse of a relaxation time and an observed rate is assumed to be simply the sum of the rates due to separate processes. In a metal, the T_1 process is achieved predominantly by the coupling of nuclear spins to the spin magnetic moments of the conduction electrons. For pure aluminum, the T_2 process consists of the dipolar interactions and the lifetime limit of the nuclear spin states, as described in the previous paragraph. Other complications due to field inhomogeneities from macroscopic and/or microscopic sources may be eliminated by using spin-echo method. ⁽⁵⁾

The quadrupolar effect is not considered in the present study. Both T_1 and T_2 may be modified by bodily motion of nuclei which will be described in the following.

Atomic motions cause fluctuations in the spin-spin couplings. The fluctuations weaken the spin couplings themselves when the mean time between successive atomic jumps becomes less than the spin-spin relaxation time under the rigid lattice condition, i.e., $\tau \leq (T_2)_{RL}$. The consequence is that T_2 becomes lengthened and, in steady-state spectroscopy, the absorption line is narrowed. The temperature at which the line becomes narrowed is called the narrowing temperature and, for aluminum, it is about 330°C. The dipole fluctuations may also induce transitions between the adjacent Zeeman levels and thus contribute a mechanism for the spin-lattice relaxation. The relaxation is evidently most effective when $1/\tau \approx \omega_0$ where ω_0 is the natural frequency of the nuclei; so the diffusional contribution to the spin-lattice relaxation $(T_1)_d$ shows a minimum as a function of temperature. However, for metal, the diffusional contribution is observable only when its relaxation rate becomes greater than that of the electronic contribution. Following the theory by Bloembergen, Purcell and Pound⁽⁶⁾ (often referred to as the BPP theory in NMR literature), the condition for observation⁽¹²⁾ may be reduced to $\tau < (\frac{\delta\omega_D}{\omega_0})^2 (T_1)_e$ where $\delta\omega_D \approx \gamma\delta H$ is the frequency corresponding to the fluctuating dipolar field, and $(T_1)_e$ is the electronic contribution to the spin-lattice relaxation time. For aluminum the condition is fulfilled only when H_0 is of the order of 10 G. For such a low field the magnetization is correspondingly small and thus the

signal is not detectable. In the following section theories are described that provide a technique to observe high field magnetization under effectively low field conditions. Several works applying the T_2 measurements to the problem of self-diffusion in aluminum are reviewed in Appendix A.

B. Description of the Theories

When the reference frame is chosen to rotate with a rotating magnetic field H_1 , at frequency ω , about an axis parallel to the direction of the static magnetic field $\vec{H}_0 = H_0 \hat{k}$, the dipolar magnetic moment of a nucleus experiences an effective field $\hat{k}[H_0 - (\omega/\gamma)] + iH_1$, where $\hat{i}$, $\hat{j}$ and $\hat{k}$ are unit vectors of the rotating frame. If ω is chosen equal to the natural frequency of the spin $\omega_0 = \gamma H_0$, the effective field is reduced to iH_1 . Since in the present study the magnitude of H_1 is chosen to be of the order of the local field H_L , which is 1.8 G in pure aluminum at 23°C, then, according to the estimate made in the last section, the diffusion effect on the spin-lattice relaxation in the rotating frame will be observable provided $\tau < (T_1)_e$. The minimum of the relaxation time is expected to occur near the narrowing temperature, because $\tau \approx \frac{1}{\omega_1} \approx \frac{1}{\delta\omega_D} \approx (T_2)_{RL}$, where $\omega_1 \equiv \gamma H_1$.

In the present study, the magnetization in the rotating frame is prepared by nutating $M_0 = CH_0/\theta$ with a $\pi/2$ pulse from the Z direction into the X direction within a time very short compared

to any relaxation times. The H_1 field is immediately applied along the X axis following the $\pi/2$ pulse. Since the spacing $\hbar\gamma H_1$ of the Zeeman level in the rotating frame is comparable to the width of the dipolar energy distribution characterized by H_L , the cross relaxation time between the dipolar system and the Zeeman system is of the order of the time required by the dipolar energy to redistribute, that is the spin-spin relaxation time T_2 . The cross relaxation establishes an internal thermal equilibrium within the spin system, characterized by a spin temperature θ_s . The following simple thermodynamic consideration gives the magnetization $M_x(0)$ of the spin system when the internal equilibrium is reached. Immediately after nutation, the spin system has magnetization $\hat{M}_0$ in the effective field $\hat{H}_1$, the energy of the spin system is

$$E = -M_0 H_1 = -CH_0 H_1 / \theta \quad \text{at } t' = t(\pi/2)$$

After the internal equilibrium is reached the average energy of the spin system is ⁽⁷⁾

$$\begin{aligned} \langle E \rangle &= (1/k\theta_s) [\text{Tr}(\mathcal{H}_Z^2 + \mathcal{H}_D^2) / \text{Tr} \exp(-\mathcal{H}/k\theta_s)] \\ &= -C(H_1^2 + H_L^2) / \theta_s \quad \text{at } t' \approx t(\pi/2) + T_2 \end{aligned}$$

where $\mathcal{H}_Z$ is the Zeeman Hamiltonian, $\mathcal{H}_D$ is the dipolar Hamiltonian and $\mathcal{H}$ is the total Hamiltonian of the spin system in the rotating frame. Since the process is completed within a time shorter than any spin-lattice relaxation time, it is assumed that no energy

flows out of the spin system, so the two expressions for the energy must be equal; this leads to

$$\theta_s = \theta \frac{H_1^2 + H_L^2}{H_O H_1}$$

But $M_x(0) = CH_1/\theta_s$ and $M_O = CH_O/\theta$, so

$$M_x(0) = M_O \frac{H_1^2}{H_1^2 + H_L^2} \quad (8)$$

In practice, it is somewhat difficult to know when the internal equilibrium is accomplished.

Above the narrowing temperature, the relative motion between nuclei becomes sufficiently fast that the local field experienced by a given spin will fluctuate in time, and thus only the average value of the local field taken over a time long compared with the duration of a fluctuation is observed. Strictly speaking, Eq. (8) is no longer valid in this high temperature region. When H_1 is much larger than the time average of H_L , the cross relaxation between the dipolar and the Zeeman systems becomes very slow, and the internal equilibrium may not be established within the spin system as required by the argument that leads to Eq. (8). Nevertheless Eq. (8) gives the correct result, $M_x(0) = M_O$ in the high temperature region, if H_L is substituted by its time average.

The magnetization M_x decays in the H_1 field as a function of time t ,

$$M_x(t) = M_x(0) \exp(-t/T_{1\rho}) \quad (9)$$

which is characterized by the spin-lattice relaxation time in the rotating frame denoted by $T_{1\rho}$. The equilibrium magnetization, $(M_x)_{eq} = CH_1/\theta$, is of the order of $(H_1/H_0)M_0$ and is assumed to be zero as implicitly expressed in Eq. (9).

In the temperature range where $\tau < (T_{1\rho})_e$ holds, for metals, the spin-lattice relaxation time in the rotating frame consists of two processes, namely, the electronic contribution T_e and the diffusion contribution T_d (the subscript 1ρ are omitted for the sake of brevity). The observed rate is the sum of the rates due to separate processes, that is,

$$\frac{1}{T_{1\rho}} = \frac{1}{T_e} + \frac{1}{T_d} \quad (10)$$

It should be noted here that the local field H_L in the rotating frame arises from the secular terms in the dipolar Hamiltonian only. The non-secular terms vary as periodic time functions $\exp(\pm i\omega_0 t)$ and $\exp(\pm 2i\omega_0 t)$ and cause absorption lines at $\omega = 0$ and $2\omega_0$.⁽⁴⁾ These side lines are far away from the central line at $\omega = \omega_0$ when ω_0 is large, and hence the non-secular terms must be disregarded. So, even though the field is effectively low, the value of H_L in the rotating frame is the same as that expected for the high field case in the laboratory frame which is, for a specimen with randomly oriented crystalline grains,⁽⁸⁾

$$H_L^2 = \frac{1}{5} \gamma^2 \hbar^2 I(I+1) \sum_j R_{ij}^{-6} \quad (11)$$

where R_{ij} is the distance between spins i and j . For the low field case in the laboratory frame, the side lines overlap with the central line and the entire dipolar Hamiltonian is effectual. So the total local field $H'_L = \sqrt{5} H_L$ must be used in the theories concerning low field behavior of nuclei in the laboratory frame.

The electronic contribution to $T_{1\rho}$ is given by^(9,5)

$$\frac{1}{T_e} = \frac{1}{T_{1e}} \frac{H_1^2 + \alpha H_L^2}{H_1^2 + H_L^2} \quad (12)$$

where α is the ratio of the spin-lattice relaxation time at very high field (characteristic of the decay of the Zeeman Hamiltonian) to that at zero field (characteristic of the decay of the dipolar Hamiltonian). The value of α is sensitive to the degree of correlation between electron spin densities on adjacent nuclear sites. Redfield⁽¹⁰⁾ has suggested that $\alpha = 2$ if the electrons are completely uncorrelated, or $\alpha = 3$ if the electrons are completely correlated. However, Wolff⁽¹¹⁾ has set an extreme upper limit for the correlation effect of $\alpha = 2.2$, which is smaller than the observed values for many metals. The high field spin-lattice relaxation time T_{1e} is due to the Fermi hyperfine contact interaction between the conduction electrons and the nuclear spins and is proportional to the inverse of absolute temperature.⁽⁴⁾ As mentioned above, if H_1 becomes appreciably larger than H_L , the exchange of energy between the effective Zeeman Hamiltonian and the effective dipolar

Hamiltonian is slowed down. When the cross relaxation time becomes much longer than the spin-lattice relaxation time T_{1e} , the two Hamiltonians are uncoupled, and relax independently. In this high field case, the Zeeman Hamiltonian is the main part of the total effective Hamiltonian, and the relaxation time is T_{1e} as can be seen from Eq. (12). (It should be noted that Eq. (12) is not strictly valid in this high temperature case.)

Based on a strong collision concept, Slichter and Ailion⁽¹²⁾ have developed a theory for the diffusion contribution to the T_{1p} process in the temperature range below the narrowing temperature, hereafter referred to as the low temperature region, where $\tau \gg (T_2)_{RL}$, and have derived

$$\frac{1}{T_d} = \frac{H_L^2}{H_1^2 + H_L^2} \frac{2(1-p)}{\tau} \quad (13)$$

The quantity p defines the correlation of the dipolar interactions before and after an atomic jump, and is given by

$$p = \frac{1}{G} \sum_q [A_{qr}^2 + \sum_i A_{ir} A_{iq}] / \sum_i A_{ir}^2 \quad (14)$$

in which a nucleus at position r changes places with a vacancy at position q , and the i sum is performed over the whole specimen.

Since only about one atomic jump is needed to relax a spin, the q sum is performed over G nearest neighbor sites only. The term

A_{ij} is defined as

$$A_{ij} = \frac{\gamma^2 \hbar^2}{2} (1 - 3\cos^2 \theta_{ij}) / R_{ij}^3 \quad (15)$$

where θ_{ij} is the angle between the applied field and the inter-nuclear vector R_{ij} . The value of p is computed for diffusion by the vacancy mechanism for a face-centered cubic lattice in Appendix D. The result is $(1-p) = 0.777$ for a specimen with randomly oriented grains.

When atomic migration becomes rapid, in the temperature range above the narrowing temperature, hereafter referred to as the high temperature region, where $\tau \ll (T_2)_{RL}$, the dipolar system and the Zeeman system become uncoupled, and hence a spin requires many jumps to relax. Based on a BPP type theory, Douglass and Jones⁽¹³⁾ have derived an expression for the diffusion contribution to the $T_{1\rho}$ process in the high temperature region,

$$\frac{1}{T_d} = 3\gamma^2 H_L^2 (1-q) \frac{\tau}{1 + 4\omega_1^2 \tau^2} \quad (16)$$

where $\omega_1 = \gamma H_L$ and H_L^2 is given in Eq. (11). The factor $(1-q)$ accounts for the part of the dipolar interaction which is dependent on motion, and is given as

$$q = \frac{\sum_{q,i} A_{ir} A_{iq}}{\sum_{q,i} A_{ir}^2} \quad (17)$$

where the term A_{ij} is defined in Eq. (15). The expression for q is similar to that for p in Eq. (14) with two differences. First, there is an extra term A_{qr}^2 in the expression for p which takes

account of the fact that no spin exists at the lattice site q prior to the jump because it is a vacancy. It is not clear whether the same term should be included in Eq. (17) also since the vacancy at site q executes more than one jump to reach site r in the high temperature case, so g does not depend on the two end sites only. Second, the q sum in Eq. (17) as defined is performed over all lattice sites in the specimen, whereas in Eq. (14) it is over the nearest neighbor sites only, because many jumps take place before the relaxation is achieved in the former case. Most likely the q sum in Eq. (17) should be bounded by the extent of the maximum distance that a vacancy jumps within the relaxation time. If so, the value of g would be somewhat temperature dependent, and a random walk method would be required for its computation.

Actually, the random walk problem has been solved by Resing and Torrey⁽¹⁴⁾ for diffusion in solids as an extension of the BPP theory. Within the limits $\omega_0 \tau \gg 1$ and $(\delta\omega_D) \tau \ll 1$ they have shown that

$$(T_2)_d^{-1} = 2.765 \gamma^2 H_L^2 \tau \quad (18)$$

The algebraic manipulation with which Eq. (18) results from Torrey's theory is given in Appendix D. Since, in the region far above the narrowing temperature, T_2 is equal to $T_{1\phi}$, a comparison between Eq. (16) and Eq. (18) shows that $(1-g) = 0.922$.

To summarize this section,

$$M_x(t) = M_x(0) \exp(-t/T_{1\rho}).$$

For the low temperature region where $\tau \gg (T_2)_{RL}$,

$$M_x(0) = M_0 \frac{H_1^2}{H_1^2 + H_L^2}$$

and

$$\frac{1}{T_{1\rho}} = \frac{1}{T_{1e}} \frac{H_1^2 + \alpha H_L^2}{H_1^2 + H_L^2} + \frac{H_L^2}{H_1^2 + H_L^2} \frac{2(1-p)}{\tau}; \quad (19)$$

for the high temperature region where $\tau \ll (T_2)_{RL}$,

$$M_x(0) = M_0$$

and

$$\frac{1}{T_{1\rho}} = \frac{1}{T_{1e}} + 3\gamma^2 H_L^2 (1-g) \frac{\tau}{1 + 4\omega_1^2 \tau^2}. \quad (20)$$

The intermediate region is not described by either Eq. (19) or Eq. (20) when $H_1 \approx H_L$ is chosen. However, when $H_1 \gg H_L$ is chosen, Eq. (20) is valid for all three regions, since, under such a condition the dipolar system and the Zeeman system are uncoupled, and hence the weak collision theory prevails.

III. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Apparatus

1. Electronics

A block diagram of the electronic equipment used in the $T_{1\rho}$ measurements is shown in Fig. 1. The rig is of the cross coil type and consists of a transmitter, a broad-band receiver, and a signal averaging equipment. Except for some changes in design, the transmitter has a layout similar to that used by Fradin.⁽¹⁵⁾ The receiver is a commercial amplifier, International Microwave Corporation, model 30AS, solid state broad-band universal amplifier. The signal averaging equipment is a Princeton Applied Research Waveform Eductor TDH-9.

The transmitter consists of a 9.0 MHz crystal oscillator followed by a twin triode cathode follower buffer stage: one section supplies the reference signal, while the output of the other section is fed through a diode gated switch to divert the rf into either of two channels at different times. One channel is a direct connection to provide the $\frac{\pi}{2}$ pulse whose width is controlled by a gate from a Tektronix 163 pulse generator. The other channel contains a phase shifter and an attenuator, both of them continuously adjustable, to provide the locking field H_1 . The continuously adjustable attenuator is necessary because below the narrowing temperature $T_{1\rho}$ is strongly dependent on the size of H_1 and since the Q of

Figure 1. Block diagram of apparatus.

the transmitter coil is temperature dependent, the load condition changes accordingly. The two channels are recombined by an isolator (triode buffer stage) without any time lapse between pulses. The isolator is followed by gated amplifiers of which the final power stage is an Arenberg PG650C, modified for long pulses; the gating pulse is obtained from a Tektronix 161 pulse generator which controls the length of the H_1 pulse. For thermal equilibrium experiments, the repetition of the rf pulse sequence is timed with a waveform generator (0.1 ~ 10 sec/cycle). For pulsed heating experiments, the timing is manually controlled (120 ~ 150 sec/cycle). The transmitter coil is tuned and matched to the 93 ohms output impedance of the power stage of the transmitter. An rf pulse of about 20 G is obtainable with this equipment when the transmitter coil is at 23°C.

The tuned receiver coil is connected to a preamplifier which is two stages in the cascode configuration. The receiver, IMC model 30AS, has a voltage gain of 62 db in the range 3 to 80 MHz. Since it is impossible to make the receiver coil perfectly orthogonal to the transmitter coil geometrically, when the rf pulses are on, the receiver is seriously overloaded due to pick-up and the recovery may take as long as 30 μ sec. A switch is therefore placed between the preamplifier and the receiver to block these spurious signals. It consists of a commercial mixer, Hewlett-Packard, model 10514A. The mixer is essentially a double-balanced

diode modulator acting as a current controlled attenuator; when the dc control current is smaller, attenuation is larger. The control current is cut off for the duration of the rf pulses so as to block the spurious signals coming from the transmitter; the gate supplied to the current switch for the mixer is from the same Tektronix 161 pulse generator that provides the gate for the rf pulses. With the addition of the mixer, the recovery time is improved to about 12 μ sec. The mixer is also used as an attenuator to control the magnitude of the NMR signal.

The phase coherent method⁽¹⁶⁾ is used in detection. A continuous wave 9MHz reference signal is furnished by the master crystal oscillator through the buffer stage. After a phase shifter and an attenuator, the reference signal is added to the NMR signal from the preamplifier at the input to the mixer. The reference signal must be large enough to effect three purposes. The first is to bias the detector into the linear region. The second is to prevent the noise from being rectified that may cause erroneous output readings at low signal level. The third is to facilitate the adjustments required in calibrating the equipment. This will be described in a later section.

In order to improve the signal-to-noise ratio, a Waveform Eductor is used which operates essentially as a 100 channel box car integrator. Since the exact shape of the NMR signal is actually of no concern, the gate for each channel is left open

for a duration encompassing, say, a quarter of the free induction decay signal in order to accumulate more rapidly a conveniently large output voltage in the Eductor. The total time required for an experiment is thus shortened. The trigger for the Eductor is timed so that the spurious signal due to the pick-up from the rf pulse, which occurs preceding the free induction decay signal, is not included in the averaging. By measuring the difference in voltage between the first or the second channel timed to open during the signal and another on the base line, a voltage proportional to the nuclear magnetization is obtained.

The geometry and the performance of the transmitter and the receiver coils will be described in Section A3: High temperature probe.

2. Current Pulser

Pulsed heating in our non-equilibrium experiment is achieved by the discharging of current from a capacitor bank. A schematic diagram for the current pulser is shown in Fig. 2A. A silicon controlled rectifier C32B, made by General Electric, is used as a switch, denoted by ON SCR. Since the impedance of an SCR is extremely non-linear, although the resistance of the specimen is of the order of 0.1 ohm, the current was found at first to persist up to 2 seconds after the onset of a discharge from the capacitor bank. (The SCR will be automatically off when the

Figure 2A. Pulsed heating circuit. The gate of each SCR is coupled by a pulse transformer to the respective trigger circuit. $C_2 = 80 \mu\text{f}$, $R_2 \leq 47\Omega$, $R_1 \approx 10 \text{ k}\Omega$, and $C_1 = 4800 \mu\text{f}$ or $6400 \mu\text{f}$. The Zener diode Z is changed when the voltage of the capacitor bank C_1 is changed.

2B. Trigger circuit.

A

SPRAGUE
11 z 12

B

current decreases to about 15 ma.) Therefore another SCR, which is denoted by OFF SCR, is employed to turn off the current. The limiting resistor R_1 , that couples the variable power supply and the capacitor bank C_1 , must not be too small, otherwise the ON SCR will be difficult to turn off. The small resistor R_2 is placed in parallel with the gate and the cathode of the OFF SCR in order to prevent spurious triggering when the heating current is turned on.

The trigger circuit⁽¹⁷⁾ for each SCR consists of a unijunction transistor (UJT) 2N2646 and a capacitor C, as shown in Fig. 2B. The diode D (any diode will do) acts as a high impedance for the triggering pulse from Tektronix 162 Waveform Generator and as a low impedance for the discharging current from the capacitor C. The behavior of a UJT is such that when the peak voltage is exceeded as a consequence of the triggering pulse, a negative resistance results. The potentiometer R is adjusted so that the circuit acts as a one-shot current pulse generator. A trigger circuit is coupled to the gate of each SCR by a pulse transformer, Sprague 11Z12, which also provides isolation between the triggering circuit and the SCR circuit.

When both C_1 and C_2 are charged up to 100 V DC and C_1 is 4800 μ f, with the turn-off time equal to 3 msec, the temperature step in the specimen averages $9.33 \pm 0.11^\circ\text{C}$, in the temperature range from 260°C to 460°C . When both C_1 and C_2 are charged up to 130 V DC and C_1 is 6400 μ f, with the turn-off time

equal to 5 msec, the temperature step is 21°C , so the system gives a temperature step of about 0.39°C per joule stored in the capacitor bank. The temperature step $\Delta\theta$ is found to be slightly temperature dependent. The value of $\Delta\theta$ decreases about 0.2° as the equilibrium temperature is increased 100° . This is in good agreement with an estimate which included the temperature dependence of both the heat capacity and the resistivity of aluminum.⁽¹⁸⁾ In all cases, 2 msec are required for the reverse current to disappear, after the termination of the current pulse.

3. High Temperature Probe

A cross coil arrangement is used in the present experiment. The transmitter coil is placed with its axis perpendicular to the static field H_0 in order to have full utilization of the rf power since the only effective component of the rf field H_1 is that perpendicular to H_0 . The receiver coil is placed inside and at the center of the transmitter coil with its axis orthogonal to both the direction of H_0 and the axis of the transmitter coil in order to minimize inductive coupling between the two coils. The geometry of the cross-coil arrangement is shown in Fig. 3B

The transmitter coil is of the conventional curved rectangular type, 38 mm in height and 19 mm in diameter. There are four turns on each side and each side includes an angle of 120° . Two sides of the coil are connected in parallel. The coil is of 0.020"

pure platinum wire insulated with fiberglass sheathing, wound on a coil former machined from Lava Grade A⁽¹⁹⁾ and secured with Sauereisen adhesive cement No. 1. The calibration of the rf field is 1.05 ± 0.03 G per 100 V_{pk-pk} across the coil and 20 G can be obtained at 23°C. At elevated temperatures, however, due to changes in the Q of the transmitter coil, the rf field being generated is reduced; for example, 16 G is obtained at 500°C after retuning, with all other conditions being the same as those at 23°C. The rise time of the rf pulse envelope is 2 μ sec and the fall time is 4 μ sec.

The receiver coil consists of 18 turns of 0.010" pure silver wire, wound on quartz tubing, 12 mm O.D. and 18 mm long, which houses the specimen. The coil is secured and insulated with Sauereisen cement. At room temperature the Q of the coil plus its coaxial lead is approximately 25 with the specimen in the coil volume. The coil is tuned with a JFD piston type variable capacitor. When the temperature is raised the coil must be retuned.

The coil assembly, including the transmitter and the receiver coils, is centered inside a Lava tube which is machined with double threads on the outside surface to position a nichrome heater wire wound non-inductively. The power for the heater winding is supplied by a DC power supply. The temperature is maintained constant by stepless control of a West Instruments model JSCR Temperature Set Point Unit using a Pt-Pt + 10% Rh

thermocouple placed very close to the furnace winding. The furnace tube is sealed at both top and bottom ends with Lava blocks in order to minimize heat loss due to convection and improve the temperature uniformity within the specimen space.

The thermocouples used to measure the base-line temperature and the temperature steps are embedded in the specimen and will be described in the next section. The analysis of the temperature distribution in the specimen will be presented in Chapter IV.

The entire probe assembly described above is enclosed by a water-cooled brass jacket which fits into the 3" gap of a Magnion 12" electromagnet. The functions of the brass jacket are twofold, to prevent the magnet being heated by the furnace and to preserve an argon atmosphere inside the jacket so that the probe assembly will not be oxidized. The probe assembly is suspended from the cover of the jacket by three ceramic supporting rods and four coaxial conductors. Each of the coaxial conductors consists of a stainless steel grounded outer conductor and a copper wire inner conductor, with a ceramic tubing spacer. The pair of leads to the transmitter coil, the receiver coil lead and the heater winding lead are silver-soldered to each of these conductors which are soft-soldered to vacuum tight BNC connectors. The control thermocouple is brought out of the jacket through a Kovar seal. The probe assembly is shown in Fig. 3.

Figure 3A. High temperature probe. T is the transmitter coil form, F is the furnace. C's are four coaxial leads; shown are the two for the transmitter coil pair; not shown are one for the receiver coil and one for the heater wire. Also not shown are the supporting rods for the transmitter coil assembly and the controlling thermocouple.

3B. Coil arrangement. R represents the axis of the receiver coil. T represents the axis of the transmitter coil. H_0 represents the direction of the static field. The three are mutually orthogonal.

3C. The specimen S is an aluminum foil folded in a zigzag fashion with mica sheets as insulation. The receiver coil R is wound on quartz tubing that houses the specimen. To monitor the temperature of the specimen, two thermocouples, which are not shown, are spot-welded onto the aluminum foil, one at the center and the other at one of the ends.

A

B

C

B. Specimen Preparation

The specimen is 99.998% aluminum foil obtained from Material Research Corporation. The thickness of the foil is 25.4 microns which is somewhat smaller than the classical skin depth for aluminum of 29.8 microns at 23°C in an rf field of 9MHz. The foil is cut typically 12.7 mm wide by about 90 cm long and is folded in a zigzag fashion; each fold is about 7 mm long. A mica sheet is placed between each two adjacent surfaces as an insulator. Mica plates, being kindly supplied by Asheville-Schoonmaker Mica Company, are split into sheets 25.4 microns or less in thickness and are cut to a size slightly larger than the folds of the aluminum foil. Care must be taken not to let different parts of the aluminum foil come into contact. It was a matter of concern that the mica sheets, since they generate no heat, might not reach thermal equilibrium with the aluminum foil in time, and thus during the $T_{1\rho}$ measurement the temperature might be changing in the aluminum foil. An analysis presented in the next chapter should clarify this point. To avoid using insulators of a foreign material, anodized foils were also tried. The aluminum foil was folded first, and then was treated electrochemically in a 5.5% oxalic acid aqueous solution at room temperature, with 20 V across the electrodes, for 10 to 15 minutes. However, during experiment, when a high current was being passed through the foil, it was easily broken at the bends where the foil might have been

attacked chemically more easily than the flat faces. As to the form of the specimen, spirals wound non-inductively were also tried. However, the NMR signal obtained with the spiral form was found to be about a half of that with the zigzag form. The spiral form was not used in the experiments.

The pulsed-heating leads posed a serious problem, because an initial current of the order of 700 amperes was sent into the specimen which was in a magnetic field of about 8 kG; a design of great rigidity was necessary. An 18 gauge copper wire was silver-soldered onto a copper beryllium plate 0.4 mm thick and 4 mm wide. The entire lead was gold-plated to avoid oxidation. Two such plates were used to make a pressure contact with the specimen, and the whole assembly was then squeezed into the quartz tubing on which the receiver coil was wound. The lead wires were housed in and restrained by a $\frac{1}{4}$ " ceramic thermocouple tubing with four holes, because when the heating current is on, large, but equal and opposite, forces are exerted on the two lead wires. A coaxial lead would be better from the view point of these induced forces, but the difficulties associated with the connection to the specimen could not be solved. Fortunately no microphonics due to the vibration of the specimen were found to interfere with the NMR signal with the two-wire heating lead arrangement. The lead wires were soldered to a UHF connector, and were rf-grounded near the connector with a 0.1 μ f capacitor

in order to eliminate the antenna effect.

Two 0.001" Pt-Pt + 13% Rh thermocouples were attached to the aluminum using a spot-welder, one near the center and another near one of the ends. The 0.001" wires were then welded with a gas torch onto respective 0.005" Pt or Pt + 13% Rh wires which were housed in the holes in the supporting tubing. The thicker wires are used for their greater strength and ease of repair. The two 0.005" wires in one hole were insulated from each other by threading one of them in a fiberglass sheathing. The thermocouples were then carefully straightened by pulling the free ends so that no parts of the wires other than those inside the specimen touched the specimen, the heating leads, or each other. The thermocouple at the center of the specimen was soldered to two BNC connectors, while the one near the end was brought out through a Kovar seal. The supporting tubing together with the specimen was fixed to a vacuum-tight sealed box accommodating the connectors to the capacitor bank and to the temperature measuring equipments. The detail of the specimen assembly is shown in Fig. 3C.

C. Experimental Procedures

1. Measurement of the Spin-Lattice Relaxation Time in the Rotating Frame

In the present experiments, the frequency of the rf field $\omega = \omega_0$ is fixed at 9.0 MHz by the crystal controlling the master

oscillator. The static field in the Z direction is set at the resonance value $H_0 = \omega_0/\gamma$. The procedure for measuring $T_{1\rho}$ starts with a tilting rf pulse H_t applied for a duration equal to a $\pi/2$ pulse in the Y direction and hence nutates the equilibrium magnetization M_0 from along the Z direction into the X direction in the coordinate frame rotating at 9 MHz. The H_t pulse must be as large as possible so that its duration is short compared to T_2 , and thus the nutation of M_0 is effective. An rf field H_1 is applied along the X direction immediately upon the termination of the H_t pulse and the magnetization is allowed to relax in the H_1 field. But when the rf is on, it saturates the receiver system due to pick-up, so the relaxation of the magnetization in the H_1 field, $M_x(t)$, cannot be observed directly. The magnetization $M_x(t)$ at any particular time t is determined by abruptly terminating the H_1 field and measuring the initial magnitude of the resultant free induction decay signal which is directly proportional to $M_x(t)$. By plotting several $M_x(t)$ measurements as a function of t , $T_{1\rho}$ is obtained from

$$M_x(t) = M_x(0) \exp(-t/T_{1\rho})$$

In the low temperature region, the shortest H_1 pulse must be longer than T_2 which is the characteristic time for the spin system to attain internal equilibrium when $H_1 = H_L$.

The free induction decay portrays the spin-spin relaxation

which is of no direct concern in the present measurements, so the sweep of the Waveform Eductor is chosen to give the largest possible output in the first channel. For each $T_{1\rho}$ determination, $M_x(t)$ is measured more than seven values of t . Each $M_x(t)$ measurement requires, on the average, 10 inputs into the Eductor in the high temperature region and 50 inputs in the low temperature region. In an experiment involving a temperature step, the repetition period is about 120 seconds, so to complete the $T_{1\rho}$ determination about 3 hours is required in the high temperature region and more than 10 hours in the low temperature region.

In the low temperature region, if the magnitude of the H_1 field is large, the signal is large (see $M_x(0)$ expression in Eq. (8)), but the effect of diffusion on $T_{1\rho}$ is reduced (compare the two terms in Eq. (19)). The situation is reversed if the magnitude of the H_1 field is small. To make a compromise, in the present experiments the magnitude of H_1 field is chosen to be equal to the magnitude of the local field H_L at 23°C as determined by Fradin,⁽¹⁵⁾ i.e., $H_1 = 1.79$ G. In the high temperature region, the choice of the magnitude of the H_1 field is not so critical (see Eq. (20)). It should be remembered that if H_1 is very large so that the dipolar system and the Zeeman system become uncoupled, the argument used to explain the case of the high temperature region is valid for all temperature.

The pulsing procedure for the $T_{1\rho}$ measurement will be

designated the $H_t - H_l$ sequence henceforth. To measure T_{lp} under non-equilibrium (thermal pulse) conditions, the $H_t - H_l$ sequence is delayed 5 msec after the triggering of the heating current pulse, since the heating pulse requires 3 msec, and 2 msec more are needed for the reverse current to disappear in the case of the temperature step of 9.33°C .

2. Technique for Setting Experimental Conditions

The T_{lp} measurement described in the preceding section must be performed under two strict conditions: First, the system must be exactly at resonance, and second, the H_l pulse must be exactly 90° advanced in phase with respect to the H_t pulse. The effects of deviations from these two conditions will be examined in the next chapter. For a stable oscillator, once the phase has been set properly, the second condition does not demand frequent examination. But, in the low temperature region, a single T_{lp} measurement for the pulsed heating condition usually takes more than 10 hours for completion; drift in the static field is unavoidable during that time, and error is introduced into the experiment. A technique was thus developed to test these two conditions and to make corrections, if necessary, within a time shorter than 2 minutes, the approximate time required by the specimen to cool down to its base-line temperature. In the

following, some preliminary procedures and the testing technique will be described.

The temperature control unit for the furnace heater power supply is preset at an equilibrium temperature. After the specimen temperature is stabilized, the H_t pulse is maximized by adjusting the tuning capacitors in the last stage of the transmitter and in the matching network. Without the reference signal, the receiver coil is tuned to maximize the free induction decay signal. Then the reference signal is connected and the free induction decay signal is maximized by adjusting the phase shifter for the reference signal, so the reference signal is in phase with the NMR signal produced by the H_t pulse.

The testing technique consists of one step: eliminate the H_t pulse and apply the H_1 pulse only. The static field and the phase shifter for the H_1 pulse are adjusted, if necessary, so that no signal appears after the H_1 pulse. If the conditions are not met, it is possible to identify which one is not satisfied. When the phase of the reference signal is 90° lagging with respect to that of the NMR signal produced by the H_1 pulse, i.e., the phase condition is satisfied, Fig. 4A shows the case for the static field below resonance. Because the population of slow spins is larger than that of fast spins (where the speed of spins is with regard to the rf), the resultant magnetization rotates slowly clockwise relative to the reference signal

which is taken to rotate counterclockwise in the laboratory frame. The observed signal hence starts at zero and then passes through a negative extremum if the static field is not off resonance by more than half of the line width. Fig. 4B shows the case when the static field is above resonance. The explanation proceeds in the same manner but with the signs reversed. The above argument is known to hold when the reference voltage is much greater than the signal voltage.⁽²¹⁾ In the present work, the reference voltage was chosen somewhat greater than the largest NMR signal. On the other hand, when the resonance condition is fulfilled, the magnetization will be stationary with respect to the reference signal. Figs. 4C and D show cases if the phase condition is not satisfied, then only the component of the signal that is in phase with the reference signal will be observed; the shape of the observed signal is similar to that of a free induction decay with the polarity depending on the phase difference between the two signals.

During the non-equilibrium experiment, a quick test is provided by switching into the transmitter the gate from a second Tektronix 161 pulse generator which gives only an H_1 pulse with the length approximately equal to 0.126 msec, i.e., a $\pi/2$ pulse for H_1 equal to 1.79 G. Usually the phase condition is fulfilled, so the resonance condition is satisfied by adjusting the static field, if necessary, to make the observed signal null.

Figure 4 A - D. Schematic diagram describing the results of deviation from ideal phase and static field settings.

- A. 90° phase-shifted, but below resonance.
- B. 90° phase-shifted, but above resonance.
- C. On resonance, but phase angle larger than 90° .
- D. On resonance, but phase angle smaller than 90° .

4D. Functional diagram

- a. Current pulse
- b. Temperature step
- c. RF pulse sequence (the H_t - H_1 sequence)
- d. NMR signal

Where R represents the reference voltage, H_1 is that of the rf field, M represents the resultant magnetization nutated by the H_1 field. Y is the direction of the H_t ($\pi/2$) pulse. ϕ is the phase angle between the H_t and H_1 pulses.

3. Calibration of the RF Field

In the high temperature region where T_2 is long, H_1 is calibrated by adjusting the rf pulse width Δt_w to give consecutive nulls in the signal output corresponding to nutation angles of π , 2π ,, under the resonance condition. The width Δt_w in seconds and the height V in volts of the rf pulses are measured on the oscilloscope. Since the angle through which the nuclei precess is given by

$$\phi = \gamma H_1 \Delta t_w \quad (21)$$

By substituting π for ϕ and Δt_w for the difference in the pulse width corresponding to two consecutive nulls into Eq. (21), H_1 is obtained in gauss. Comparison between H_1 and the corresponding V gives the calibration of H_1 in gauss per V_{pk-pk} .

In the low temperature region, the signal decays faster, so the calibration is done by finding the maximum value of the initial height of the free induction decay signal. In this case ϕ is replaced by $\pi/2$ and Δt_w by the pulse width that gives the maximum signal. In all cases, an average of ten different rf pulse heights is taken in arriving at a final value of

$$H_1 = 1.05 \pm 0.03 \text{ G/100 } V_{pk-pk}$$

Periodic checks were made to determine whether calibration depended upon temperature or aging of the transmitter assembly.

No change in calibration was found during the time of the experiment.

4. Temperature Measurement

Two Pt-Pt + 13% Rh thermocouples are embedded in the specimen, one at the center and another near one end. The former is soldered to BNC connectors and is used for measuring the temperature difference before and after the current pulse. The latter is brought out through a Kovar seal and is used for measuring the equilibrium temperatures. (Extensions made of Pt and Pt + 13% Rh wires were prepared for the BNC connectors, so it is also possible to measure the equilibrium temperatures at the center of the specimen.) The equilibrium temperatures are determined by measuring the emf of the thermocouple having an ice-water cold junction with a Leeds and Northrup potentiometer.

The temperature difference and the cooling curve are observed by connecting the thermocouple to the oscilloscope with a high gain differential amplifier (Tektronix Type 1A7A) which has a maximum sensitivity of 10 μ V/cm on the oscilloscope screen and selective bandwidth. The base-line for temperature is established by adjusting the dc offset in the differential amplifier. Although the difference configuration was used at the input, the current pulse always overloads the amplifier and the initial 10 msec of the signal is lost in distortion. Therefore the

trace on the oscilloscope screen, that is the cooling curve, is photographed and extrapolation to the inception of the curve gives the temperature step at the time of the $T_{1\rho}$ measurement. The horizontal sweep rate of the oscilloscope is 5 sec/cm. The problems associated with temperature measurement will be analyzed in the next chapter.

5. Measurement of the Spin-Lattice Relaxation Time in the Laboratory Frame

To extract the diffusional contribution, the electronic part must be subtracted from the observed $T_{1\rho}^{-1}$. As has been discussed in the preceeding chapter, the electronic contribution in the rotating frame is equal to that in the laboratory frame in the temperature range above the narrowing temperature, thus we measure T_1 .

The technique of measuring T_1 consists of applying a π pulse at time zero followed by a $\pi/2$ pulse after an interval t . The pulse sequence will be called π - t - $\pi/2$ sequence. The π pulse inverts the magnetization which then returns to its equilibrium value M_0 with a time constant T_1 . By applying the $\pi/2$ pulse at time t the magnetization $M_z(t)$ is tilted into the X-Y plane where it can be observed. By plotting $\log(M_0 - M_z(t))$ as a function of t , the spin-lattice relaxation time T_1 is obtained from the reciprocal of the slope since⁽⁵⁾

$$M_z(t) = M_0[1 - 2 \exp(-t/T_1)] \quad (22)$$

IV. THE ANALYSIS OF ERRORS

A. Introduction: Error Equation

The migration energy for a vacancy is determined by substituting the experimental values of τ_b , τ_p , $\Delta\theta$ and θ into the equation

$$E_m = k \frac{\theta(\theta + \Delta\theta)}{\Delta\theta} (\ln \tau_b - \ln \tau_p) \quad (6A)$$

where all quantities have been defined in Chapter I. The expression for the relationship between errors is obtained by differentiating the above equation with respect to each parameter, noting that $\Delta\theta \ll \theta$,

$$\frac{dE_m}{E_m} = \frac{k\theta^2}{E_m \Delta\theta} \left(\frac{d\tau_b}{\tau_b} - \frac{d\tau_p}{\tau_p} \right) + 2 \frac{d\theta}{\theta} - \frac{d\Delta\theta}{\Delta\theta} \quad (23)$$

As for the first term on the right hand side of Eq. (23), since the determination of τ_b usually can be accomplished within 30 minutes, while the same for τ_p may require more than 10 hours, the causes of error such as drift in the static field can be more readily avoided in the former than in the latter, and thus $d\tau_p/\tau_p$ dominates. Because of the factor $\theta^2/\Delta\theta$ in its coefficient, the contribution of error to E_m from the first term increases rapidly for a higher equilibrium (base-line) temperature θ , and decreases for a larger temperature step $\Delta\theta$. By choosing typical

values in the low temperature region: $\theta = 550^\circ\text{K}$, $\Delta\theta = 9.5^\circ\text{K}$ and $E_m = 0.55 \text{ eV}$, the factor $k\theta^2/E_m\Delta\theta$ is found to be about 5, while in the high temperature region, for $\theta = 690^\circ\text{K}$, the same factor is about 8. In view of these rather large multiplication factors, the τ_p term is probably the single largest contributor to the error in the E_m determination.

The second term $d\theta/\theta$ is negligibly small, because the precision in the reading of θ is better than 0.5°K . This argument is valid in the case of E_m which is determined for each temperature. On the other hand, the value of the activation energy for self-diffusion is obtained by a least square fit of τ as a function of θ , therefore correspondence between τ and θ is crucial. In other words, the accuracy of Q depends more on the precision of the absolute temperature reading than E_m .

The contribution of the third term $d\Delta\theta/\Delta\theta$ is straightforward. In the following, several factors that may cause imprecision in the determination of τ will be discussed and systematic errors in E_m associated with temperature will be analyzed.

B. The Oscillatory Character of the $M_x(t)$ Curve

For aluminum, the free induction decay after the rf pulses has an oscillatory character at temperatures in the rigid lattice region. As the spin system relaxes in the H_1 field to reach an

internal equilibrium, the oscillation also appears in the curve of M_x as a function of t . The data in Fig. 5 are taken in an H_1 field of 1.79 G at room temperature.

As described in Section II B, the validity of the relaxation equation

$$M_x(t) = M_x(0) \exp(-t/T_{1\rho}) \quad (9A)$$

requires establishment of an internal equilibrium within the spin system which, although no definite time can be set, is expected to be achieved in a time comparable to T_2 when H_1 is of the order of H_L . For aluminum T_2 is about 50 μ sec at room temperature. However, Fig. 5 indicates that the internal equilibrium is actually reached at a much longer time; after 0.3 msec, deviations from a straight line in the semi-logarithmic graph are less than 3% of the magnitude of $M_x(t)$. In the following the effect of these deviations will be examined.

Since the value of τ is directly related to $T_{1\rho}$, the error in τ is proportional to the error in $T_{1\rho}$. The relation of error between the magnitude of signal $V(t)$ and $T_{1\rho}$ is obtained from differentiation of the $M_x(t)$ expression above,

$$\left| \frac{d\tau}{\tau} \right| = \left| \frac{dT_{1\rho}}{T_{1\rho}} \right| = \frac{T_{1\rho}}{t} \left| \frac{dM_x(t)}{M_x(t)} \right| = \frac{T_{1\rho}}{t} \left| \frac{dV(t)}{V(t)} \right| \quad (24)$$

where the receiver system is assumed to possess perfect linearity

Figure 5. Data taken at 23°C, showing oscillatory character of $M_x(t)$. The initial part of the curve gives a decay time constant of about 0.04 msec which is approximately equal to the spin-spin relaxation time in the rigid lattice region. Data points after $t = 1$ msec give $T_{1\rho} = 3.24$ msec. The H_1 field used is 1.79 G.

so that $V(t)$ is proportional to $M_x(t)$. Eq. (24) shows that, for the same accuracy in the reading of signal size, measurements over a relatively greater range of the H_1 pulse length t will result in a smaller error in the determination of $T_{1\rho}$. However, the signal is smaller for a longer pulse, and hence of lower accuracy. So we may assume that, in a general case,

$$(d\tau/\tau) \approx (dV/V) \quad (25)$$

In the present section, the oscillatory character appears only in the early part of the $M_x(t)$ curve, so Eq. (24) must be used directly. Since $T_{1\rho}$ is always longer than T_2 which is taken to be the characteristic time for the establishment of the internal equilibrium within the spin system, $(T_{1\rho}/t)$ is always larger than 1. If the deviation from the Eq. (9) is 3% as stated above, the error in τ will be greater than 3%, depending on the magnitude of $(T_{1\rho}/t)$. However this systematic error affects both τ_b and τ_p by the same amount and in the same direction when the data are taken with the same H_1 pulse length, its contribution to the uncertainty in E_m is probably very small. On the other hand, in the determination of the activation energy for self-diffusion, this fact must not be overlooked, since only τ_b is used in this case. Fortunately as temperature is raised, the amplitude of the oscillation is diminished. Nevertheless, to avoid this uncertainty, most of the $T_{1\rho}$ measurements use a length of 0.5 msec

as the shortest H_1 pulse; for temperatures at which $T_{1\rho}$ is shorter than 0.5 msec the shortest pulse used is 0.2 msec to 0.4 msec, depending on the case.

C. The Static Field Off-Resonance

Fig. 6 shows the results when the static field H_0 is set deliberately off-resonance by ± 0.1 G. The values of the offset were read directly from the dials on the power supply to the magnet and were not calibrated. When at resonance, M_x plotted as a function of t falls on a straight line in a semi-logarithmic graph that gives $T_{1\rho} = 3.18$ msec from the slope. When off resonance, the portions of data points that are more or less on a straight line give an apparent value of $T_{1\rho} = 2.8$ msec for the case of $(H_0 - 0.1 \text{ G})$, and 3.6 msec for the case of $(H_0 + 0.1 \text{ G})$. So there is an error of about 10% in the determination of $T_{1\rho}$ for an offset of 0.1 G. It is possible to adjust all the data points in a set, adding or subtracting by the same amount in magnetization, depending on the case, so as to make them fit on a straight line in Fig. 6. This operation demonstrates the fact that when the static field is off-resonance, a residual magnetization exists along the X direction even though the H_1 field may be applied much longer than $T_{1\rho}$. This phenomenon is, in fact, used in one common method of adjusting H_0 to the resonance condition. (12,15)

Figure 6. Apparent deviation of $M_x(t)$ from exponential decay when the static field is not adjusted to the exact resonance.

Theoretically the equilibrium magnetization along the X direction under the off-resonance condition is given by⁽¹²⁾

$$(M_{eq})_x = M_o \frac{H_1 h}{h^2 + H_1^2 + \alpha H_L^2 + (T_1/\tau) 2(1-p)H_L^2} \quad (26)$$

where h is the amount of off-resonance in the static field. The value of $(M_{eq})_x$ estimated from the data in Fig. 6 is consistent with that calculated from Eq. (26) in which the last term in the denominator is omitted because τ is much greater than T_1 at room temperature. In the low temperature region, T_1 is about 3 msec, while τ ranges from 0.2 msec to 10 msec, so $(M_{eq})_x$ is smaller than it is at room temperature and becomes still smaller as the temperature is increased. Nevertheless, the effect of $(M_{eq})_x$ on the $T_{1\rho}$ determination is not always small, especially at the low temperature end of the low temperature region ($\tau \approx 10$ msec). Comparing with the room temperature case of 10%, the error in $T_{1\rho}$ is estimated to be 4% for a static field offset of 0.1 G at the midpoint in the low temperature region where τ is 0.7 msec. (Here we use Eqs. (25) and (26) with $\alpha = 2.86$ and $H_1 = H_L$.) However the resonance condition was frequently checked during the experiment, and, as will be presented in Section V A, the overall uncertainty (i.e., 99% confidence limit) in the room temperature case is, in reality, 6.5% and not 10% as given above, so a more reasonable estimate for the error in $T_{1\rho}$ is probably 2% rather than 4%.

In the high temperature region, Eq. (26) is not applicable, because its derivation is based on the assumption that the spin system adiabatically attains internal thermal equilibrium in a time shorter than $T_{1\rho}$. Since, in this case, the spins are weakly coupled to each other, the Curie's law holds even in an effectively low field, therefore, along the X direction in the rotating frame, the component of the equilibrium magnetization is $(M_x)_{eq} = CH_1/\theta$, regardless of h . As compared with the initial magnetization $M_x(0) = M_0 = CH_0/\theta$, the magnitude of $(M_x)_{eq}$ is negligibly small and hence it introduces no error in the determination of $T_{1\rho}$ in the high temperature region. (It should be noted that, in Eq. (26), a term of order $M_0 H_1/H_0$ is omitted.)

Another cause of error in $T_{1\rho}$ due to being off-resonance is instrumental. A phase coherent method is used in the detection of the signal.⁽¹⁶⁾ The output of the detector can be written as

$$V(t) = B + A(t) \cos (\gamma h t - \phi) \quad (27)$$

where B and A are the respective amplitudes of the reference and the NMR voltages at the detector, t is the time measured from the terminus of the rf pulses and ϕ is the phase difference between the reference and the NMR signals which is, in the present section, assumed to be zero if it has been adjusted properly. The signal is usually measured at $t \approx 25 \mu\text{sec}$; for an accuracy of 2% in determination of the NMR signal $A(t)$, the allowed deviation from

resonance is $h \leq 1.2$ G. Since the field offset of such a magnitude is unlikely to occur, the error in $T_{1\rho}$ due to this cause is very small.

D. Deviation from the Phase Condition

A correct $T_{1\rho}$ measurement requires that H_1 be applied exactly along the X axis. Eq. (27) shows that deviation from the in-phase condition changes the NMR signals by a factor of $\cos \phi$ which will not contribute any error in $T_{1\rho}$ if ϕ is the same for all the data points. When the deviation is more than, say, 10° , the scattering of the data points is large and seems to possess an oscillatory character. Since the phase can be adjusted probably better than 5° by using the technique described in the preceding chapter, the error in $T_{1\rho}$ due to this source is negligible for the case of equilibrium experiments.

In a pulsed heating experiment, drift in the frequency of the oscillator or changes in the properties of the components used in the phase shifter for the H_1 field may alter the phase condition. Drift in the frequency of the oscillator is about 5 ppm which also changes the resonance condition and the equivalent offset is about 0.005 G. The drift is too small to be effective in changing the phase condition or the resonance condition.

The phase shifter for the H_1 pulse consists of a parallel resistor and capacitor in series with an inductor. For this circuit the phase angle ϕ as a function of resistor R , capacitor C , and inductor L at frequency ω is

$$\tan \phi = \frac{R}{\omega L + \omega C R^2 (\omega^2 C L - 1)} \quad (28)$$

In order to obtain a 90° phase shift the conditions are $\omega C = R^{-1}$ and $\omega L = R/2$. In reality the components R , L , and C are not ideal and the operation of the circuit may also depend on its layout, so the analysis is more complicated. However known temperature coefficients of R , L , and C components may be used to estimate the possible change in ϕ . The results show that it is very small. The above equation also shows that ϕ is insensitive to a change in ω of about 5 ppm.

E. Variation in the Magnitude of H_1

When H_1 is of the order of H_L , the variation in the magnitude of H_1 has a serious effect on $T_{1\rho}$ only for the experiments conducted below the narrowing temperature. The electronic contribution to $T_{1\rho}$ is expressed as

$$T_e = T_{1e} \frac{H_1^2 + H_L^2}{H_1^2 + \alpha H_L^2}$$

Differentiation of the T_e equation with respect to H_1 gives

$$\frac{dT_e}{T_e} = \frac{1}{2} \frac{dH_1}{H_1} \quad (29)$$

where $H_1 = H_L$, as chosen in the present experiment, and $\alpha = 3$ is assumed. Since the H_1 field can be set to within 1% accuracy, the error in T_e is correspondingly small. However when the H_1 pulse is long, the rf amplitude droops by about 8% at 5 msec. The upper limit of the error in T_e may be set at 4%, which is smaller than that introduced by the static field being off-resonance. Fortunately, since $T_{1\rho}$ in the temperature range of interest is around 1 msec or less, the occasion that calls for a pulse length longer than 5 msec is rare. The only exception is the determination of T_e at room temperature.

The diffusional contribution to $T_{1\rho}$ is expressed as

$$T_d = \frac{\tau}{2(1-p)} \frac{H_1^2 + H_L^2}{H_L^2}$$

Differentiation of the T_d equation with respect to H_1 gives

$$\frac{dT_d}{T_d} = \frac{dH_1}{H_1} \quad (30)$$

when $H_1 = H_L$. Thus, for the same magnitude of error in H_1 , the error in T_d is twice as large as that in T_e . But again it will

be small, if the H_1 field is set within 1% accuracy. As mentioned in the previous chapter, because of change in the Q of the transmitter coil as the temperature is changed, the magnitude of H_1 is carefully calibrated before each experiment.

The error in E_m due to variation in H_1 is negligible since the variation affects both equilibrium and non-equilibrium experiments in the same magnitude and direction, so $(d\tau_b/\tau_b - d\tau_p/\tau_p)$ vanishes.

F. Temperature Non-uniformities within the Specimen Volume

The temperature distribution in the specimen region has been investigated with the specimen removed from its space inside the center section of the furnace. The temperature gradient is found to be less than $1^\circ\text{C}/\text{cm}$. When the specimen is in its place the situation is believed to be vastly improved. The specimen is one piece of aluminum foil and a receiver coil of silver wire is wound around it; both tend to equalize the temperature of the materials inside the specimen volume.

G. Uncertainties in the Temperature Step $\Delta\theta$

The arrangement of thermocouples inside the specimen has been described in Section III B and the method used in the determination of the temperature step after the current pulse has been described in Section III C 4.

For a Pt-Pt + 13% Rh thermocouple, 1 μV emf is, on an average, equivalent to 0.1°C in the temperature range of the present experiment, from 260°C to 450°C . By narrowing the bandwidth of the Tektronix type 1A7A difference amplifier to DC - 100 Hz, the noise level of the signal is reduced to about 2 μV . To obtain the temperature step, the cooling curve is extrapolated to its inception with an uncertainty of about 2 μV . Honeywell Service Manual 59095M is used to convert emf to temperature which is tabulated to a micro-volt; however, an uncertainty of 1 μV seems probable for a temperature difference of about 10°C . Therefore the systematic error in temperature reading is estimated to be 3 μV , that is, 0.3°C .

In the determination of E_m , the individual corresponding temperature steps were used for the calculation in the respective cases. The arithmetic average of all the temperature steps in the entire temperature range investigated is 9.33°C with a standard deviation of 0.11°C , i.e., about 1%. Therefore the overall uncertainty (99% confidence limit) of the $\Delta\theta$ term in Eq. (23) is not more than $\pm 6\%$, derived from three times the standard deviation plus the systematic error.

In addition the nature of the measurement requires serious consideration. Since the thermocouple is placed between the aluminum foil and the mica insulation, it monitors actually an average temperature of the two materials, but not the true temperature of the aluminum foil, provided the contact of the

thermocouple to both materials is perfect. When a current pulse is discharged through the aluminum foil as the foil is being heated, thermal energy is transferred from the aluminum to the mica; but the temperature rise in the mica lags behind that in the aluminum. Although the current discharge curve and all properties⁽¹⁸⁾ of mica and aluminum required in the analysis are known, the temperature of the aluminum foil as a function of time is very difficult to derive exactly. Instead, we attempt to estimate the time required by the mica to approach thermal equilibrium with the aluminum. A set of graphs in the book by Kreith⁽²⁰⁾ were used extensively in the temperature analysis. The graphs appear as Fig. 4-8 on page 149 of the book and are titled "Dimensionless temperature distribution in a wall subjected to a sudden change in environmental temperature."

Because of the high thermal conductance of aluminum as compared to that of mica, the temperature of the aluminum foil is assumed to be uniform across its thickness at all times. Also a perfect contact between the aluminum foil and the mica sheets, and hence an infinite unit-surface conductance h , is assumed; in other words, no temperature difference exists between the contact surfaces of the mica sheets and the aluminum foil. For Biot's modulus hL/k equal to infinity, the graphs show that the center of the mica sheet reaches 99.9% of its surface temperature within 0.673 msec. The properties⁽¹⁸⁾ used in the estimate are, for the

mica sheet, average half thickness $L = 12.7$ microns, thermal conductivity $k = 0.514 \times 10^{-2}$ cal/sec-cm-°K, specific heat $C_p = 0.26$ cal/g°K, and density $\rho = 2.845$ g/cm³. Since T_{10} is always measured at 2 msec after the termination of the current pulse, the entire specimen, including the aluminum foil and the mica sheets, may be assumed to be in thermal equilibrium at that time, and hence the measurements of the temperature step are valid.

H. Temperature Gradient in the Specimen

At two moments in the course of an $M_x(t)$ measurement, the temperature gradient in the specimen is of particular concern: firstly at the instant immediately prior to the application of the heating pulse, and secondly, during the measurement.

Since it is impractical, after the previous heat pulse, to wait for the specimen to achieve complete thermal equilibrium with its surroundings before proceeding, the next pulse is applied when the trace of the cooling curve on the oscilloscope screen reaches the base-line temperature. The temperature gradient then present in the specimen may create ambiguity in the base-line for the temperature step. The error in E_m arising from this situation enters through the $d\theta/\theta$ term in Eq. (23), so it will not be severe if the temperature gradient is not large. The temperature gradient in the specimen at the base-line temperature was checked as follows. The temperature at the center of the specimen was

monitored with the oscilloscope and its base-line was established by adjusting the dc offset of the differential amplifier. The temperature at one end of the specimen was measured with the Leeds and Northrup potentiometer and the equilibrium (base-line) temperature was recorded. The specimen was then pulse-heated, and the temperature decay was observed on the oscilloscope. When the trace reached the base-line, the temperature at the end of the specimen was again measured with the potentiometer. No difference between the two temperatures, before and after pulsed heating, was observed at the end of the specimen when the center of the specimen was at the base-line temperature, so the temperature gradient in the specimen at the base-line temperature may be regarded to be small. It was not possible to measure the gradient directly with the oscilloscope, because the thermocouples will also monitor the voltage drop between the two measuring points during the current pulse, and hence the detecting instrument may be damaged. (The temperature gradient at the base-line is estimated later in this section.)

A serious problem may be encountered if the average temperature and/or the temperature gradient in the specimen change during a T_{1p} measurement, because the error in E_m is contributed by the $d\tau_p/\tau_p$ term in Eq. (23).

The cooling curve at the center of the specimen is found to be an exponential decay function with a time constant of

approximately 27 sec. Therefore a time of approximately 260 msec is required for the temperature of the specimen to drop 1%. Since the measurement of T_{1p} is always completed within 7 msec after the termination of the heating pulse, it may be assumed that no changes occur in the temperature of the specimen during the T_{1p} measurement.

An estimate of the temperature gradient present is obtained by using the graphs in the book by Kreith.⁽²⁰⁾ For the following two reasons, the specimen may be treated as an infinite mica slab of 4 mm in thickness with a certain uniform temperature distribution. Firstly, since the thermal conductivity of aluminum is 100 times larger than that of mica, the aluminum foil may be regarded as a short circuit for heat flow, and may be omitted from consideration in the present situation. Secondly, the specimen is clamped at each side with a copper plate of 0.4 mm thickness. Since conduction is much more effective than convection or radiation, heat is assumed to be dissipated predominantly through the copper plate. Heat transfer is therefore reduced to a one-dimensional problem. The only unknown in the present analysis is the unit-surface conductivity of the specimen assembly. The difficulty is overcome by matching the cooling curve obtained at the center of the specimen to the curves in the book by Kreith⁽²⁰⁾ for the center of the slab. The latter may be regarded as a set of universal cooling curves. The corresponding Biot's modulus is found to be $hL/k \approx \frac{1}{4}$. By using a half width $L = 0.2$ cm and

other parameters for mica as cited in the preceding section, the Fourier modulus is calculated to be $at/L^2 = 1.73 \times 10^{-4} t$ where a is the thermal diffusivity $k/\rho C_p$, and t is time in msec. By using the two moduli, the temperature distribution at any time can be estimated from the graphs. It is found that cooling of the specimen is too slow to have a detectable temperature gradient even at $t = 100$ msec. Changes in the temperature gradient in the specimen may thus be considered to be very small during the T_{1p} measurement. The same procedure gives 0.054°C for the temperature difference between the center and the external surface of the specimen assembly when $t = 120$ sec which is the period of the heating pulses. Therefore the uncertainty in the base-line for the temperature step is very small as asserted before.

The present analysis shows that the systematic error in E_m due to changes in the temperature and its gradient is very small.

I. Conclusion: the Estimated Error in E_m

To conclude this chapter, the uncertainty in our result for E_m will be discussed on the basis of the error analysis presented above.

Non-uniformities of temperature in the specimen and ambiguities in the base-line for the temperature step have negligible contributions to the θ term in Eq. (23) and hence to E_m also.

The uncertainty in the temperature step $\Delta\theta$ is estimated to be less than $\pm 6\%$. Therefore its contribution to the error in E_m is probably less than $\pm 6\%$.

The following imprecision and systematic error are believed to contribute a negligible error to the magnitude of the NMR signals: deviation from the phase condition, variation in the amplitude of the H_1 field and changes in temperature and its gradient in the specimen during a $T_{1\rho}$ measurement. The oscillatory character in $M_x(t)$ curve may contribute error to the activation energy for self-diffusion but not to the migration energy.

The remaining source of error in E_m is imprecision in setting the resonance condition for the static field. Fig. 7 shows a typical result obtained at $\theta = 283.8^\circ\text{C}$ with $\Delta\theta = 9.21^\circ\text{C}$. The scattering of the data points in the pulsed heating experiment may be explained by drift in the static field. Such drift can be immediately rectified in the case of an equilibrium experiment, which requires only 30 minutes to complete. In a pulsed heating experiment, although the experimental conditions were frequently checked, fluctuation in the static field could not be avoided at all times. The uncertainty in the signal size and hence in τ_p attributed to this cause has been estimated to be about 2% in the low temperature region and small in the high temperature region.

Figure 7. Typical data taken at $\theta = 283.8^\circ\text{C}$ with temperature step $\Delta\theta = 9.21^\circ\text{C}$. The H_1 field used is 1.79 G.

A cause of scattering in the pulsed heating data that hitherto has not been mentioned is the long-term stability of the experimental equipment. Judging from the data taken in the high temperature region, it may contribute an error of 3% to the signal size and hence to τ_p . If imprecision in the equilibrium experiment is assumed to be negligibly small, then $[(d\tau_b/\tau_b) - (d\tau_p/\tau_p)]$ is about 5% in the low temperature region and about 3% in the high temperature region. With multiplication factors of 5 and 8 for the respective regions, the first term in Eq. (23) contributes an error of 25% to the determination of E_m . Together with the $d\Delta\theta/\Delta\theta$ term, the overall uncertainty (99% confidence limit) in the experimental result may amount to 30%.

Some non-ideal conditions in the experiment will not have any adverse effect on the determination of $T_{1\rho}$. Field inhomogeneities in H_0 and H_1 never constitute a mechanism for the spin-lattice relaxation, while the consequence of a broad $\pi/2$ pulse may be loss in signal size. In short, if a non-ideal condition does not change from experiment to experiment, it will contribute systematic error to both T_b and τ_p in the same way, so the value of E_m will not be affected. A serious systematic error due to generation of vacancies during the $T_{1\rho}$ measurement will be discussed in the next chapter.

V. EXPERIMENTAL RESULTS AND DISCUSSION

A. The Electronic Contribution to the Spin-Lattice Relaxation

In metals, the dominant relaxation mechanism by which nuclear spins approach thermal equilibrium with the lattice is usually the hyperfine interaction. In the present investigation, the value of T_1 for aluminum has been determined as 6.3 msec at 23°C by employing the π -t- $\pi/2$ pulse sequence. This value is consistent with that of 6.25 msec obtained by other workers.^(15,16,22) Spokas and Slichter⁽¹⁶⁾ have summarized three independent sets of data taken over a temperature range from 1°K to 930°K and found $T_1\theta = 1.85 \text{ sec-K}^\circ$. As explained in Section II A, for aluminum, diffusion effects may occur in a magnetic field of less than 10 G but they never appear in the T_1 process under high field conditions. An identical $T_1\theta$ product is reported by Fradin⁽¹⁵⁾ over a temperature range from 400°C to 660°C.

Theoretically ($T_{1e}\theta$) is not necessarily temperature independent. In fact the theoretical expression⁽⁴⁾ for T_{1e} contains quantities involving Fermi surface parameters that may be slowly varying functions of temperature due to volume expansion and atomic motions; some metals exhibit temperature dependence for ($T_{1e}\theta$). The theoretical expression is very often written as a form of the Korringa relation⁽⁴⁾ $T_{1e}\theta K^2 = \text{constant}$, where K is the Knight shift, a measurable quantity. The temperature coefficient of K is very

small in the case of aluminum.⁽²⁵⁾ This indicates indirectly that $(T_{1e}\theta)$ is indeed temperature independent for aluminum.

Recently $(T_{1e}\theta)^{-1}$ of Cu^{63} and Cu^{65} have been found⁽²⁶⁾ to rise sharply at high temperatures near the melting point. The sharp rise is attributed to a quadrupolar interaction with diffusing lattice imperfections. The same phenomenon has not been reported for aluminum, although an excess broadening of the absorption line is observed at high temperatures and has been interpreted as being a result of quadrupolar coupling to the strain field of dislocations.⁽¹⁶⁾ In the present experiment, the product $T_1\theta$ will be considered to be constant for aluminum.

In the rotating frame, the electronic contribution to $T_{1\rho}$ is related to T_{1e} by the equation, from Eq. (12),

$$T_e = T_{1e} (H_1^2 + H_L^2) / (H_1^2 + \alpha H_L^2) \quad (31)$$

At room temperature, the effect of diffusion is very small, and $T_{1\rho}$ is simply equal to T_e . By employing the $H_t - H_L$ pulse sequence, T_e has been determined in the present experiment at 23°C for H_1 equal to H_L which is 1.79 G.⁽¹⁵⁾ The arithmetic average of ten measurements is $T_e = 3.24$ msec with a standard deviation of 0.07 msec (and thus an overall uncertainty of $3(0.07)/3.24=6.5\%$).

Since $(T_{1e}\theta)$ is constant, Eq. (31) shows that $(T_e\theta)$ is constant also, provided H_L is temperature independent, which is true in the low temperature region. As described in Section II B,

Eq. (31) is not rigorously correct for the high temperature region where the hypothesis of a unique spin temperature for the Zeeman system and the dipolar system is no longer valid, and T_e is equal to T_{le} in this case. Nevertheless it will be interesting to examine the transition of T_e from the low temperature region to the high temperature region by using Eq. (31), because an abrupt change in T_e at a certain temperature is improbable.

As mentioned in Section II A, if there are no complications from field inhomogeneities the line shape of the absorption mode in cw spectroscopy (or its Fourier transform, the transverse decay of magnetization after an rf pulse) defines the nature of the dipolar local field H_L . At room temperature, the line shape for aluminum resembles a Gaussian but has a more flattened central region and less marked wings. As the temperature approaches 325°C it becomes more nearly Gaussian; above 325°C it progressively narrows and changes to a Lorentzian. At 360°C the transition is complete. Above 450°C, although the line continues to narrow, deviations from a Lorentzian begin to be observable. The deviation is interpreted as due to a quadrupolar interaction of nuclei with the strain field of dislocation. (16)

The nature of the line shape and more particularly the second moment in the rigid lattice region are still not clearly understood; however, the initial decay time after a $\pi/2$ pulse is slowly lengthened as the temperature is raised. (16) Above 325°C the

relative motion between aluminum nuclei becomes sufficiently fast so that the local field experienced by a given spin will fluctuate rapidly in time. The criterion for this situation to occur has been described in Section II A. We observe only the average value of the local field taken over a time long compared with the duration of a fluctuation. This average value becomes progressively smaller than the instantaneous value, hence the absorption line in cw spectroscopy is narrowed. Fluctuation also retards exchange of energy between spins, so the transverse time T_2 becomes longer.

In Eq. (31) the time average values instead of the instantaneous value of the local field are used for H_L in the high temperature case which is estimated, at each temperature, from the data of T_2 reported by Spokas⁽¹⁶⁾ and Fradin⁽¹⁵⁾, using the approximation relation

$$T_2^{-1} \approx \gamma H_L \quad (7A)$$

The value of H_L is 1.79 G as used throughout the entire experiment, and α is calculated to be 2.86 from Eq. (31) using the values at room temperature, $T_e = 3.24$ msec, $T_{1e} = 6.25$ msec, and $H_1 = H_L = 1.79$ G.

The T_e thus calculated is plotted as a function of $1/\theta$ in Fig. 8 shown as a dotted line which, on the high temperature side, rapidly approaches the relation

$$T_{1e}\theta = 6.25 \text{ msec} \times 296^\circ\text{K} = 1.85 \text{ sec-}^\circ\text{K} \quad (32)$$

and, on the low temperature side, rapidly approaches the relation

$$T_e \theta = 3.24 \text{ msec} \times 296^\circ\text{K} = 0.953 \text{ sec-}^\circ\text{K} \quad (33)$$

The transition occurs between 320°C and 395°C where the validity of Eqs. (32) and (33) must be questioned. The dotted curve itself will not be used in the subsequent analysis of the data because of the following two reasons. Firstly, the values of T_2 used in the calculation of H_L are not necessarily correct on the low temperature side. Since they have been obtained from the free induction decay curves which possess an oscillatory character, no unique T_2 and thus H_L can be determined this way. Secondly the value of α used is determined arbitrarily with two data points only for convenience in the analysis and bears no other significance. The theoretical consideration of α has been described below Eq. (12) in Chapter II. Experimentally, Anderson and Redfield⁽²³⁾ obtained $\alpha = 2.57 \pm 0.25$ at 4.2°K . Hebel and Slichter⁽²⁴⁾ obtained $\alpha = 3.35 \pm 0.35$ at 4.2°K . Both values were measured in the laboratory frame using the field cycling scheme. Fradin⁽¹⁵⁾ obtained $\alpha = 3$ at room temperature in the rotating frame. Tunstall and Brown⁽²²⁾ obtained $\alpha = 2.15 \pm 0.07$ in the laboratory frame by using a three-bath model to analyze their data measured for temperatures between 1.3°K and 295°K . Further study appears needed to clarify the uncertainty in α , and indeed to clearly define its significance in aluminum.

B. Self-Diffusion

Illustrated in Fig. 8 are the results of the $T_{1\rho}$ measurement under equilibrium conditions at various temperatures where atomic diffusion becomes an important mechanism for the spin-lattice relaxation in the rotating frame. The magnitude of the H_1 field is 1.79 G throughout the entire experiment. To obtain the diffusional contribution, the electronic contribution must be subtracted from the observed values of $T_{1\rho}$. Since the relaxation rates are additive, we have

$$\frac{1}{T_d} = \frac{1}{T_{1\rho}} - \frac{1}{T_e} \quad (34)$$

The possible relaxation due to quadrupolar sources mentioned previously is believed to be small⁽¹⁵⁾ and is neglected.

To obtain T_e , Eq. (32) is used in the high temperature region and Eq. (33) is used in the low temperature region. The data points taken at temperatures between 375°C and 395°C are treated as belonging to the high temperature region, notwithstanding the fact that the analysis in the preceding section appears to indicate that, in this transition region, the dipolar system and the Zeeman system are neither completely uncoupled nor strongly coupled to allow use of Eq. (32) or Eq. (33) in the respective case. However due to other reasons which will be mentioned later in the present section (see below Table I), the data points in this

Figure 8. The experimental value of $T_{1\theta}$ for aluminum at each equilibrium (base-line) temperature is represented by a solid circle. The solid lines are electronic contribution to $T_{1\theta}$ as extrapolated from the values determined at 23°C: $T_e \theta = 1.85 \text{ sec-}^\circ\text{K}$ for the high temperature region and $T_e \theta = 0.953 \text{ sec-}^\circ\text{K}$ for the low temperature region. The dashed curve shows T_e as estimated from Eq. (31), using the time-average values of the local field for H_L .

temperature range are not included in the analyses of self-diffusion and vacancy migration energy.

A careful measurement of T_e is essential in the determination of the self-diffusion coefficient. This is especially true in the case of aluminum whose T_{1p} values span only about a decade in the region where diffusion effects become important. If the value used for T_e differs from the true value, the T_d values derived from Eq. (34) will deviate from Arrhenius rule. The same difficulty will not occur in the determination of the vacancy migration energy, because a systematic error in T_e affects both τ_b and τ_p in the same way.

In the low temperature region where $\tau \gg (T_2)_{RL}$, the diffusional contribution to T_{1p} is related to the mean time τ between successive atomic jumps by

$$T_d^{-1} = 2(1-p)H_L^2 / (H_1^2 + H_L^2) \tau \quad (13A)$$

The factor p is computed in Appendix D for a face-centered cubic lattice. The average for a specimen with randomly distributed grains is $(1-p) = 0.777$. The value of H_1 is 1.79 G. The value of H_L^2 measured at 23°C is 3.2 G². However, T_2 is reported⁽¹⁶⁾ to be 56 μ sec at 297°C where, as mentioned in the preceding section, the absorption line is nearly Gaussian. By using Eq. (7), the corresponding H_L^2 is estimated to be about 2.3 G². The theoretical value as calculated from Eq. (11) is 2.37 G², using a

value for the lattice parameter of $4.078\text{\AA}$ at 300°C .⁽²⁷⁾ Evidently, the value of H_L^2 as estimated from T_2 data is much closer to the theoretical value in the low temperature region than the experimental value obtained at 23°C . For this reason, the 300°C theoretical value of $H_L^2 = 2.37\text{ G}^2$ will be used in the present work in the low temperature region. The variation of H_L^2 due to thermal expansion of the lattice constant is small between 240°C and 310°C . We feel that this choice of H_L^2 , although somewhat arbitrary, has as much justification as direct use of the experimental value obtained at room temperature.

In the derivation of Eq. (13) the spin system is assumed to reach internal thermal equilibrium between successive vacancy jumps and be describable by a spin temperature before each jump. However, the time between two successive vacancy jumps is $\tau_v = (N_v/N)\tau$, where N is the number of atoms and N_v is the number of vacancies in the specimen. On the other hand, the characteristic time for the spin system to establish internal equilibrium is about T_2 when $H_1 = H_L$. In the region where T_d becomes important, T_2 is invariably longer than τ_v for aluminum, and thus, immediately prior to a vacancy jump, one of the neighboring nuclei that has participated in the preceding jump is still hot. To take this situation into account, Slichter and Ailion⁽¹²⁾ have suggested the right hand side of Eq. (13) be modified by $(G-1)/G$ for the hot spin and $(G-2)/G$ for the

possible correlated jump. (For the latter, however, the correlation factor f used in the radio-active isotope experiment may be a more logical choice.) The symbol G denoted the number of nearest neighbor sites: 12 for an fcc lattice.

In the high temperature region where $\tau \ll (T_2)_{RL}$, the diffusional contribution to $T_{1\rho}$ is expressed as

$$T_d^{-1} = 3\gamma^2 H_L^2 (1-g) \tau / (1 + 4\gamma^2 H_L^2 \tau^2) \quad (16A)$$

where $(1-g)$ is given in Appendix D as 0.922. The value of H_1 is 1.79 G. The value of H_L^2 is calculated as 2.325 G^2 by substituting the lattice parameter of $4.093 \text{ \AA}$ at 425°C ⁽²⁷⁾ in the theoretical expression Eq. (11). The reason for using the theoretical value of H_L^2 is the same as given in the case of the low temperature region. Since the concept of spin temperature is not valid in the high temperature region, no correction factor is required for Eq. (16).

The values of τ thus obtained are plotted as a function of $1/\theta$ in Fig. 9, using the theoretical values for H_L^2 and without any corrections for the effects of hot spins or for the deviation in T_e from Eqs. (32) and (33). Fig. 9 also shows the position of the results, using $H_L^2 = 3.2 \text{ G}^2$ and, in the low temperature region only, the correction factor $f(G-1)/G$, where f is the correlation factor equal to 0.78 for an fcc lattice. By assuming the validity of Arrhenius rule

Figure 9. The mean time between successive atomic jumps as a function of the inverse absolute temperature.

As explained in the text, the points are obtained by using the values of H_L^2 calculated from the theoretical expression Eq. (11) with the lattice parameter adjusted to thermal expansion in each temperature region. The dotted line shows the agreement between the results in the high and the low temperature regions in this analysis.

On the other hand, if the experimental value $H_L^2 = 3.2 \text{ G}^2$ at 23°C is used, the solid lines indicate the position of the results which are also corrected, in the low temperature region only, for the effects of hot spins.

$$\tau = \tau_0 \exp(Q/k\theta), \quad (35)$$

the constants of self-diffusion in aluminum are determined for each temperature region by a least square fit, and the results are tabulated as follows:

Table I
Self-Diffusion in Aluminum

θ	240 - 310°C	395 - 500°C
Q	$1.324 \pm 0.013 \text{ eV}$	$1.313 \pm 0.011 \text{ eV}$
τ_0	$0.946 \times 10^{-15} \text{ sec}$	$0.987 \times 10^{-15} \text{ sec}$

where the error limits are the standard deviation. Data points taken between 375°C and 393°C are not included in the analysis because some systematic errors appear to be associated with these points and deviation from Arrhenius rule is observed. The reason for the error is tentatively ascribed to possible contamination of the specimen, since these points are the last to be taken in the entire experiment. As described in the preceding section, this temperature range also includes the transition in T_e .

By using the relation

$$D_0 = a^2/12\tau_0 \quad (36)$$

the average of the two temperature regions gives

$$Q = 1.32 \pm 0.02 \text{ eV}$$

$$D_0 = 0.144 \pm 0.003 \text{ cm}^2/\text{sec}$$

where the lattice parameter a used is $4.078\text{\AA}$ in the low temperature region and $4.093\text{\AA}$ in the high temperature region. The error limits are estimated for Q from the standard deviations and for D_0 from the difference between the values in the two temperature regions. The values are in good agreement with $Q = 1.31 \text{ eV}$ and $D_0 = 0.176 \text{ cm}^2/\text{sec}$, deduced by Volin and Balluffi⁽²⁸⁾ from several sources. Results obtained by other investigators on self-diffusion in aluminum are summarized in Appendix A.

C. Activation Energy for Vacancy Migration

The results for T_{1p} measurements following pulsed heating are converted to τ_p by means of the equations used in the preceding section in the respective temperature regions, where the subscript p denotes a quantity after pulsed heating. The subscript b will denote the value of a quantity at the equilibrium (base-line) temperature θ . To obtain T_e , θ is substituted by $(\theta + \Delta\theta)$ in Eqs. (32) and (33) where $(\theta + \Delta\theta)$ is the temperature during the T_{1p} measurement after the current pulse. The values of the respective τ_p have been evaluated in the preceding section. The activation energy for vacancy migration is obtained by

substituting τ_p , τ_b , θ , and $\Delta\theta$ in

$$E_m = (\ln\tau_b - \ln\tau_p)k\theta(\theta + \Delta\theta)/\Delta\theta \quad (6A)$$

The values of E_m thus obtained are plotted for the corresponding $(\theta + \Delta\theta)$ in Figure 10.

In the low temperature region, i.e., $(\theta + \Delta\theta)$ ranging from 265°C to 320°C, no correlation between the migration energy and temperature is detected and the arithmetic mean of the vacancy migration energy in aluminum is

$$E_m = 0.55 \pm 0.04 \text{ eV}$$

The error limit indicates the standard deviation. In the preceding chapter, a systematic error in E_m from the bias in the reading of $\Delta\theta$ has been placed at 3%, which is equivalent to about 0.02 eV. (Therefore the overall uncertainty, i.e., 99% confidence limit, in the determination of E_m in the low temperature region is ± 0.14 eV as calculated from 3 times the standard deviation plus the systematic error.)

In the high temperature region, the data points obtained between 385°C and 402°C will not be considered for the same reasons mentioned in the preceding section (below Table I) to exclude τ_b in the θ range between 375°C and 393°C from the determination of the self-diffusion coefficient. For the rest of the high temperature region, the determined value for the migration energy appears

Figure 10. The experimentally determined values of the vacancy migration energy in aluminum plotted for the corresponding temperatures $(\theta + \Delta\theta)$. The temperature step $\Delta\theta$ is, on the average, 9.33°C . The delay time of the rf pulse sequence is 5 msec with respect to the triggering of the current heating pulse.

to increase from about 0.56 eV at 410°C to nearly 0.61 eV at 450°C.

Although it can not be denied on theoretical grounds^(2,29) that both migration energy and formation energy for a vacancy may be dependent on temperature, the activation energy for self-diffusion in aluminum has been found, in Section V B, to be nearly the same for all temperatures from 240°C to 310°C and from 390°C to 500°C. Since Flynn⁽²⁹⁾ has estimated that the fractional extent to which the migration energy may change with temperature is three times larger than that of the formation energy, it is apparently not possible that the two energies change by equal amounts but with opposite signs. To be consistent with the constant value of Q obtained in the present study, the observed behavior of the migration energy with temperature must be indicative of other than a simple temperature dependence of E_m .

This temperature dependence of the apparent migration energy can be explained on the basis of vacancy generation during the course of the T_{1p} measurement. For simplicity, $d\tau_b$ may be assumed to be zero. As the base-line temperature is raised, the amount of vacancies generated following the pulsed heating will be larger at the time when T_{1p} is measured, and hence the systematic error $d\tau_p$ will be more negative. (It should be recalled that, in Eq. (6), definition of τ_p is under the condition that no vacancies are generated during its T_{1p} measurement.) Then according to

Eq. (23), the apparent value of E_m will become larger at higher base-line temperature. In the next section we consider the problems associated with vacancy generation.

To determine the migration energy for a vacancy, the conventional methods generally consist of creating excess vacancies in a specimen by quenching, irradiation, or deformation, and subsequently annealing the specimen at suitable temperatures. The physical property most often observed is electric resistivity. Measurements are usually taken at liquid-nitrogen or -helium temperature so that the migration of vacancies is effectively suppressed. The low temperature also provides the advantage that the lattice contribution to the resistivity is greatly reduced and hence accuracy is increased for the measurement of the residual resistivity caused by the excess vacancies.

The annealing kinetics of a quenched metal is complicated by the complex behavior of vacancies during quenching and annealing procedures. Various vacancy products may be formed, depending on the quenching temperature, the cooling medium, the specimen size, and the annealing temperature. Very often the activation energy observed is only apparent and some interpretation is necessary to determine what the migrating defects are, and also whether any interactions or reactions between defects are present. The identification of the migrating defects is achieved through their migration energies. Since the contribution to the electric

resistivity from various vacancy configurations cannot be distinctly separated in most cases, the respective migration for each defect cannot be directly measured. The only exception is probably the migration energy for a monovacancy which may be measured for a specimen quenched from a relatively low temperature. Therefore values are chosen for their consistency with the theory on which the annealing process is interpreted. Based on theoretical considerations, a higher migration energy is assigned to a monovacancy and a lower one to a divacancy. The experimental information on the properties of trivacancies and larger vacancy complexes is extremely scarce; very often they enter into the interpretation as end products rather than active species. Isochronal annealing of a quenched metal reveals that it is divided into two stages in a temperature spectrum. The first stage is believed to be the migration of monovacancies and/or divacancies to be annihilated at sinks or to form larger aggregates which lead to black spots, dislocation loops, voids, etc. The second stage is dissociation of these aggregates. (30)

The interpretation of the point defect phenomena in irradiated specimens is necessarily more complicated than in quenched specimens because depleted zones and various types of interstitials are also generated in addition to vacancies. The same is true in cold-worked specimens because dislocations are created in addition to vacancies and interstitials. The temperature spectra for the

isochronal annealing of these specimens reveals four or five distinct stages. For irradiated specimens, the first two stages are divided into several substages.⁽³¹⁾ The stage designated as stage III is believed to be due to the migration of monovacancies to the sinks.⁽³²⁾ However, there is also a proposal⁽³³⁾ that stage III is due to the annihilation of freely migrating dumbbell interstitials at vacancies.

Based on the conventional methods described above, in the case of aluminum, the value of the migration energy for a monovacancy was reported as about 0.55 eV or 0.6 eV and that for a divacancy was 0.46 eV or 0.50 eV. The results of other workers on the migration energy in aluminum is summarized in Appendix C.

In the present study, the value of the activation energy for self-diffusion in aluminum has been obtained as $Q = 1.32$ eV. If the formation energy for a monovacancy is taken as $E_f = 0.76$ eV which is generally accepted as the best value, then the results obtained for Q and E_m in the present study are consistent with each other by the relation

$$Q = E_m + E_f \quad (3A)$$

provided that the vacancies observed are predominantly monovacancies. This proviso is probably true, since the concentration of divacancies is believed to be negligibly small at temperatures from 260°C to 320°C where 0.55 eV has been determined for the

vacancy migration energy in the present study. However, recent publications show lower values for E_f : 0.73 eV⁽³⁴⁾ and 0.71 eV⁽³⁵⁾ (see Appendix B); therefore 0.6 eV for E_m is closer to the value expected if $Q = 1.32$ eV. It will be shown in the next section that the data on vacancy generation in the present study are consistent with 0.55 eV for E_m .

The impurities in the specimen play an important role in the results of the conventional methods, although not all of the effects are understood at present. Garr and Sosin⁽³⁶⁾ have reported that the activation energy for stage III annealing in irradiated aluminum increased from 0.46 eV to 0.63 eV with decreasing purity. For a quenched aluminum, the migration energy for a monovacancy can be directly measured only at temperatures below about 300°C. At 300°C with $E_f = 0.76$ eV and $S_f = 2.4$ k, the vacancy concentration is about 2 ppm which is of the same order as the impurity concentration. In the present study the migration energy is also obtained at temperatures below about 300°C. However the effect of impurities in the present study is probably less than that in the quenching method, since the T_{10} measurement is conducted at elevated temperatures whereas the annealing is usually performed at temperatures below 0°C. Because the concentration of vacancy-impurity atom pairs is proportional to $\exp(B_{vi}/k\theta)$ where B_{vi} denoted the binding energy of an impurity atom to a monovacancy, more vacancies will be trapped by impurity atoms in the quenching method than in the NMR method.

In the present method, if the concentration of vacancy-impurity pairs does not change significantly between the equilibrium state and the pulsed heating state, the systematic error due to impurities will affect both τ_b and τ_p in the same way and hence it will not contribute any error to E_m . There is a possibility that vacancy-impurity pairs may be dissociated by the pulsed heating; however in our experiment this kind of impurity effect is probably small because the impurity concentration is not sufficiently large to contribute a significant quadrupolar local field.

Trapping of vacancies by impurities may impede⁽⁴³⁾ or assist⁽⁴⁴⁾ the migration of vacancies, depending on the nature of the impurities, and may change the effective value of the migration energy.

D. Vacancy Generation

We have investigated the generation of vacancies due to the temperature step by measuring a series of $T_{1\rho}$ at various times t after termination of the current pulse. The temperature step for these experiments was 21°C, and the measurements of $T_{1\rho}$ were performed at four base-line temperatures: 400°C, 420°C, 440°C, and 462°C. The delay time t between termination of the current pulse and application of the rf pulse sequence was varied from 7 msec to 35 msec. Based on the analysis of Chapter IV, we may assume no temperature variation or gradient in the specimen during the course of the $T_{1\rho}$ measurement. Since the repetition time for the

current pulses was about 150 seconds, the difference of temperatures at the surface and at the center of the specimen was estimated to be 0.04°C at the time when the specimen was cooled down to the base-line temperature just before the next pulse, so the uncertainty in the base-line temperature was negligible.

The results are shown in Fig. 11 where $\log(1-f)$ is plotted as a function of the delay time t . The fractional extent f to which the vacancies are generated is defined as

$$1-f \equiv \frac{C_{\infty} - C}{C_{\infty} - C_0} = 1 - \frac{C - C_0}{C_{\infty} - C_0} \quad (37)$$

where C is the instantaneous vacancy concentration at time t , and C_0 is the vacancy concentration at zero delay time, assumed to be the equilibrium concentration at the base-line temperature θ . C_{∞} is the vacancy concentration at fictitious infinite delay time, i.e., the equilibrium concentration at the step temperature $(\theta + \Delta\theta)$. The implicit assumption associated with Eq. (37) is that, immediately before application of the current pulse, the equilibrium concentration equal to C_0 is present in the specimen at the base-line temperature. As mentioned before, the average time constant of the cooling curve for the specimen assembly in the present experiment is 27 seconds. In view of the fact that a cooling rate of more than $10^4^{\circ}\text{C}/\text{sec}$ is generally required for a metal to freeze-in the vacancy supersaturation, this assumption should be excellent.

Figure 11 $(1-f) = (C_{\infty} - C)/(C_{\infty} - C_0)$

Kinetics of vacancy generation at the base-line temperatures: 462°C, 440°C, 420°C, and 400°C.

The temperature step for all cases is 21°C.

Solid circles and the dotted lines represent the results as calculated from T_{10} data. Open circles and the solid lines represent the results after the correction for vacancy generation during a single T_{10} measurement. The chain lines are the best fit lines for the data points. The open triangles are calculated from the 9° set by using Eq. (43). The solid triangles are the values if the 9° set has the same vacancy generation rates as the 21° set. The abscissa is the time delay after triggering of the current pulse which lasts 5 msec, and 2 msec more are required for the reverse current.

For simplicity in calculation, Eq. (37) is rewritten as

$$1-f = \frac{\tau_{p\infty}^{-1} - \tau_p^{-1}}{\tau_{p\infty}^{-1} - \tau_{po}^{-1}} \quad (38)$$

which is obtained from the following consideration. The average time between successive atomic jumps τ is expressed, in general, as

$$\frac{1}{\tau} = 12\nu C \exp(S_m/k) \exp(-E_m/k\theta) \quad (39)$$

where C is the instantaneous vacancy concentration, and is not necessarily equal to the equilibrium vacancy concentration. Since Eq. (37) is associated with a single temperature only, that is the step temperature $(\theta + \Delta\theta)$, the term $\exp[-E_m/k(\theta + \Delta\theta)]$ is a constant, and Eq. (39) shows that the inverse of τ is proportional to C . Eq. (38) is obtained by direct substitution for C in Eq. (37) of the corresponding τ .

In Eq. (38), $\tau_{p\infty}$ is the equilibrium value at $(\theta + \Delta\theta)$ which is obtained from Arrhenius' equation for τ using the experimental values of

$$\tau_o = 0.966 \times 10^{-15} \text{ sec} \quad \text{and} \quad Q = 1.32 \text{ eV}$$

The value of τ_{po} is obtained from the equilibrium value at θ , but is corrected for increased motion at the temperature step by the factor

$$\exp\left[\frac{E_m}{k} \left(\frac{1}{\theta} - \frac{1}{\theta + \Delta\theta}\right)\right] \quad \text{with } E_m = 0.55 \text{ eV}$$

The value of τ is obtained by analyzing $T_{1\rho}$ with Eq. (34) and Eq. (16) for each delay time; the value of T_e used in this calculation is that at $(\theta + \Delta\theta)$.

A more rigorous, but still not entirely accurate, treatment of the data points in Fig. 11 is to correct for the variation in vacancy concentration during a single $T_{1\rho}$ measurement. All measurements started with the shortest H_1 pulse length of 0.5 msec; the longest pulse lengths used were 1.4 msec at 400°C, 2 msec at 420°C, and 3.5 msec at 440°C and 462°C. From Fig. 11 it is clear that the difference in pulse lengths between the shortest and the longest is not short enough (compared with the time constant for vacancy generation in the temperature region between 421°C and 483°C) to allow us to ignore the change in $(1-f)$ during the $T_{1\rho}$ measurement. The equation used in the correction is derived in Appendix E as

$$(C_i t_f - C_f t_i) (T_{1\rho})_i^{-1} = C_f (t_f - t_i) (T_{1\rho})^{-1} - (C_f - C_i) t_i (T_e)^{-1} \quad (40)$$

where $T_{1\rho}$ and T_e are observed values and $(T_{1\rho})_i$ is the corrected value; the subscript i denotes the quantities associated with the shortest H_1 pulse, and the subscript f denotes those with the longest H_1 pulse. The values of C_i and C_f are estimated from the dotted lines in Fig. 11 which pass through the data points before being corrected for the above effect. The solid lines are drawn through the points after correction, and give the

half-time as follows:

$(\theta + \Delta\theta)$	°C	421	441	461	483
$t_{0.5}$	msec	29.5	23.2	19.4	13.9

In Fig. 11, the kinetics of the vacancy generation is implicitly assumed to be an exponential function of time. If vacancy generation is controlled by diffusion of vacancies away from dislocations, it can be expressed by^(37,38,39)

$$1-f = \exp(-AND_v t) \quad (41)$$

where A is a geometrical factor and is approximately equal to 1, N is the density of dislocations, and D_v is the diffusion coefficient of monovacancies for which $E_m = 0.55$ eV, $D_0 = 0.144$ cm²/sec, and $S_f = 2.4k$ are used in the present analysis.

Eq. (41) is obtained on the basis of the following assumptions. First, vacancies are present only as monovacancies. Second, each dislocation emits vacancies rapidly enough to maintain local equilibrium at its core. Third, all interactions between vacancies and dislocations are neglected. Fourth, dislocations are fixed in space and arranged in a regular array of parallel straight lines.⁽³⁹⁾ When a dislocation emits or absorbs point defects it moves as a result. Jackson⁽³⁷⁾ and Balluffi and Seidman⁽³⁹⁾ have considered the effect of dislocation climb on vacancy generation.

At present, the problem of vacancy generation can be solved only phenomenologically, as indicated by Eq. (41). Atomistic detail of the generation mechanism still cannot be described quantitatively.⁽⁴⁰⁾ Emission and absorption of point defects by dislocations are generally believed to occur at jogs.⁽⁴¹⁾ For a metal with a high stacking fault energy, such as aluminum, the formation energy for a jog is relatively small and thus the production of vacancies at dislocations is thought to be efficient. The second assumption stated above is thus probably valid for aluminum without any qualifications. In addition to the aforementioned assumptions, it is also implicitly assumed in the derivation of Eq. (41) that vacancies leave dislocations non-preferentially, that is, not necessarily at jogs. After being dissociated from jogs, vacancies are believed to migrate rapidly along dislocations before emission.

It should be noted that Eq. (41) is valid for vacancy annihilation as well as vacancy generation. This fact may be used to vindicate the assumption that follows Eq. (37). Fig. 11 shows that the time constant for vacancy generation is less than 35 msec for all cases. Since the time constant for vacancy annihilation is probably of the order of that for vacancy generation, it may be assumed that when the specimen is cooling with a time constant of 27 seconds, the vacancy concentration in the specimen is always maintained in a quasi-equilibrium state.

The values of the half-time obtained from Fig. 11 are plotted semilogarithmically as a function of the inverse absolute temperature in Fig. 12. By using Eq. (41), the density of dislocations N is estimated from the position of the resulting straight line, with slope $E_m = 0.55$ eV, in Fig. 12 as $N = 2.13 \times 10^7 \text{ cm/cm}^3$. In view of possible large strains caused by the large current flowing in the specimen placed in a high magnetic field, this value of the dislocation density appears to be low. Although many reports⁽⁴²⁾ indicate that dislocations in aluminum are easily eliminated, the probable answer is that the distribution of dislocations is not completely random, so the mean diffusion distance for vacancies after generation is longer than that expected from the average dislocation density determined by assuming a completely random distribution.

The main purpose of this section is, however, not the vacancy generation itself but its effect on the determination of the vacancy migration energy. The apparent value of the migration energy is derived in Appendix F as

$$E = E_m + \frac{\theta + \Delta\theta}{\Delta\theta} (E_f - kS_f + k\theta \ln C) \quad (42)$$

where E is the apparent value and E_m is the real value of the migration energy. All other terms are defined as before. It is also shown in Appendix F that when $\Delta\theta$ is much less than θ , Eq. (42) simplifies to

Figure 12. Vacancy generation half-time plotted as a function of the inverse absolute temperature.

The line is drawn with vacancy migration energy equal to 0.55 eV. Since $1-f = \exp(-\text{AND}_v t)$ and $D_v = D_{vo} \exp(-E_m/k\theta)$, for $f = 0.5$ and θ replaced by $\theta + \Delta\theta$, the half-time is

$$\ln t_{0.5} = \frac{E_m}{k(\theta + \Delta\theta)} + B$$

where $B = \ln(\ln 2 / \text{AND}_{vo}) = \text{constant}$.

$$E \approx E_m + fE_f \quad (43)$$

where f is defined by Eq. (37). Because of its simplicity, Eq. (43) will be used in the following discussion. The difference in the values of E as calculated from Eqs. (42) and (43) is less than 2% under the conditions used in the preceding section for the determination of E_m : at temperatures below 450°C and a delay time of 5 msec. The results obtained in the preceding section will be referred to as the 9° set hereafter, and those in the present section, the 21° set. Fig. 12 (the 21° set) indicates a half-time $t_{0.5} = 21.2$ msec at $(\theta + \Delta\theta) = 450^\circ\text{C}$ which gives f at 5 msec as 15%. With $E_f = 0.76$ eV and $E_m = 0.55$ eV, the apparent migration energy E is calculated as 0.66 eV, using Eq. (43). On the other hand, Fig. 10 (the 9° set) indicates that experimentally $E \approx 0.61$ eV at the same temperature. The other values of E are also calculated from the 21° set at several different temperatures and appear to be about 8% larger than the 9° set in all cases. In the following, some conceivable causes for this discrepancy between the two sets will be examined.

(Before proceeding with the examination, it should be recalled that according to the error analysis presented in Chapter IV, a systematic difference of merely 1% in the T_{10} measurement for the two sets is sufficiently large to produce a discrepancy of about 8% in the determination of the migration energy. The

most probable error in the T_{10} measurement is the long-term stability of the experimental equipment, in the high temperature region. There is a possibility that it would introduce a systematic difference between the two sets.)

Eq. (43) indicates that changes in the apparent value E for the migration energy are due to changes in f , while Eq. (41) indicates that, for a given delay time, any change in f is due to changes in the dislocation density N and/or the monovacancy diffusion coefficient D_v . The discussion proceeds most easily by dealing with the values of half-time. At 450°C , the 21° set (Fig. 12) gives a half-time of 21.2 msec, while the 9° set (Fig. 10) gives $E \approx 0.61$ eV, for which, with $E_f = 0.76$ eV and $E_m = 0.55$ eV, the value of f at 5 msec is calculated from Eq. (43) as 7.9% corresponding to a half-time of about 40 msec.

We first consider what two values of E_m would be required in order to accommodate these two different values of $t_{0.5}$. (The 21° set was taken several months after the 9° set, using the same specimen, and there is a possibility of contamination, the effect of which would be to alter E_m derived from our data.) If the dislocation density is assumed to be the same for the 21° and 9° sets (not necessarily to be $N = 2.13 \times 10^7 \text{ cm/cm}^3$), then the product $D_v t_{0.5}$ must be constant, according to Eq. (41). Using, for the 9° set, $E_m = 0.55$ eV in the exponent of D_v and $t_{0.5} = 40$ msec, the 21° set (for which $t_{0.5} = 21.2$ msec) requires that E_m be 0.51 eV.

If the lowering of the migration energy is a true phenomenon, it may be due to contamination of the specimen. The effect of impurities on the determination of E_m has been discussed in the preceding section and is believed to be small. The essential change in E_m will be discussed here. De Jong⁽⁴⁴⁾ has explained that the effective value of the vacancy migration energy in a dilute fcc alloy will be smaller than that in a pure metal if solute atoms move faster than solvent atoms, but the migration energy will not be affected if solute atoms move slower. Following de Jong's theory, a decrease in E_m of 0.04 eV at 700°K requires impurities having an activation energy for solute diffusion in the solvent lower than the activation energy for self-diffusion of the solvent by more than 0.36 eV. The diffusion data show this difference in activation energies for diffusion in aluminum to be less than 0.1 eV.⁽⁴⁵⁾ So de Jong's theory does not explain the discrepancy in our case. (It should be noted that de Jong's theory is developed specifically for the diffusion of supersaturated concentration of vacancies. Its application here is merely to check the possibility of changes in E_m due to contamination.) Although de Jong's theory shows that retardation of vacancy migration is only to be expected under special experimental conditions, the retardation is probably more general⁽⁴³⁾ than suspected. The effects of impurities are not all understood at present.

On the other hand, if the change in the state of the specimen is solely due to a variation in dislocation density, then the product $Nt_{0.5}$ is a constant. Using the value of half-time given before: 21.2 msec for the 21° set and 40 msec for the 9° set, the dislocation density is estimated for the case of the 9° set as $1.13 \times 10^7 \text{ cm/cm}^3$, if that for the case of the 21° set is $2.13 \times 10^7 \text{ cm/cm}^3$.

In the present experiment, the temperature step was created by passing a current pulse through the specimen which was aluminum foil folded in a zigzag configuration. Dislocations may be produced by stresses due to the large current and also due to its presence in a high magnetic field. Firstly, the current induces magnetic fields which tend to push the folds apart and introduce stresses in the foil. Since the induced magnetic fields are proportional to the current, the stresses caused by the current alone are proportional to the square of the current. Secondly, the presence of the high magnetic field interacts with the current and introduces much larger stresses in the foil than those caused by the current alone. These stresses are probably proportional to the current and will be the only ones considered here.

Instead of directly solving the problem of stress distributions, only a qualitative estimate will be attempted.

The dislocation density is proportional to the stored energy⁽⁴¹⁾ and thus, in turn, proportional to the square of the applied

stresses. Since the stresses are assumed to be proportional to the current, the dislocation density is proportional to the electric energy dissipated in the specimen, and hence is proportional to the temperature step. Therefore the number of dislocations created in the case of the 21° set is about twice as large as that in the case of the 9° set. If the dislocation density is initially low, then this argument appears to give relative magnitudes of the dislocation density for the two sets which are consistent with the values estimated from the experimental data.

In Fig. 11, the points associated with the shortest delay times appear to indicate a relatively slow initial vacancy generation in contradiction to the case of gold.⁽³⁷⁾ Because the period of the current pulses was only 150 seconds and the data points were taken in succession, when the shortest delay times were in use the dislocation density was relatively small, and as the experiment progressed to longer delay times, part of the dislocations created by the current pulses was accumulated, so the rate of vacancy generation became gradually larger than that which would be expected from the initial dislocation density. For each point in Fig. 11 about 200 current pulses were used.

An alternative explanation is based on the fact that $t = 0$ for the delay time is arbitrarily set at the triggering of the current pulse. The current pulse decays with a time constant of about 1.93 msec at $\theta = 420^\circ\text{C}$, so the temperature rise in the

aluminum foil has the same or a somewhat longer time constant because heat is simultaneously transferred to the mica sheets. This means that the time required by the specimen to reach 90% of the temperature step is 2.2 msec or longer for the 21° set. By drawing best fit straight lines through data points in Fig. 11, we find that they intersect the 100% line at about 2.5 msec which may be taken as the new $t = 0$ for the delay time in the 21° set.

In Fig. 11, the open triangles indicate the values of $(1-f)$ as calculated from the 9° set by using Eq. (43). The solid triangles indicate the values of $(1-f)$ if the 9° set has the same vacancy generation rates as the 21° set, and are obtained by drawing a line parallel to the best fit line for the 21° set and intersecting the 100% line at 1.5 msec. (It should be noted that the turn-off time is 3 msec in the 9° set and 5 msec in the 21° set, so $t = 0$ for the delay time in the 9° set may be taken to be 1.5 msec here.) Clearly the discrepancy between the two sets can be partly explained by this ambiguity in setting $t = 0$ for the delay time. (The half-times for these best fit lines are all 2.5 msec less than those obtained previously and the new estimate for the dislocation density is 2.44 cm/cm^3).

After the experiment, the aluminum foil was treated with Tucker's etch for observation. The grain size in the used specimen was found to be, on the average, 0.3mm, i.e., about 12 times the thickness of the foil. The thickness of the foil is 25.4

microns which is about 120 times larger than the average distance between two adjacent dislocations if the density of dislocations is $2.13 \times 10^7 \text{ cm/cm}^3$. Since the amount of vacancy generation is related exponentially to the distance between two adjacent sources (a function similar to Eq. (41)) if vacancy diffusion is the controlling factor, the contribution from grain boundaries and surfaces is probably very small. Furthermore, a surface may not be a good source (sink) because of unavoidable oxide film.⁽⁴⁷⁾ However, Bokshtein et al.⁽⁴⁶⁾ found that time constants for vacancy generation in 99.99% pure aluminum specimens of 0.27 to 0.53 mm thickness were 1.0 to 4.3 sec (average) respectively. They concluded that dislocations are ineffective as vacancy sources (sinks) due to the pinning effect of the Cottrell clouds, and the main sources (sinks) are the free surfaces and grain boundaries. Since aluminum possesses a high stacking fault energy, the formation of jogs is considered to be easy and hence dislocations are usually regarded as good sources (sinks) in aluminum. An alternative explanation of their results is that dislocation density was very low in their specimen because of prolonged heating at high temperatures, and was not increased significantly by the pulsed heating which they used in the experiment. It should be noted that Pochapsky⁽⁷³⁾ performed the same experiment using 99.9% pure aluminum wire of 0.127 mm diameter and concluded the time constant for the generation of vacancies was

shorter than a millisecond. Both experiments gave unusually high values for vacancy formation energy in aluminum; Pochapsky obtained 1.17 eV and Bokshtein et al. obtained 0.85 eV. In addition, Bokshtein et al. found that copper solute atoms greatly retarded vacancy migration and hence the vacancy generation rate.

E. Conclusion

The migration energy for a vacancy in aluminum has been found to be 0.55 eV with the standard deviation of 0.04 eV and a systematic error of 0.02 eV in the temperature range between 260°C and 320°C. A value of 0.55 eV to 0.62 eV is generally determined in the quenching, the cold-work, and the irradiation experiments.

In the temperature region between 380°C and 450°C, the apparent migration energy increases with increasing temperature. The temperature dependency was explained as being due to the generation of vacancies during the experiment. The temperature step used in this experiment was 9.33°C.

The kinetics of vacancy generation between 420°C and 480°C has been found to be consistent with a model based on vacancy diffusion as the controlling factor and with the migration energy for a vacancy equal to 0.55 eV. The temperature step used to study the generation rate was 21°C.

The apparent migration energy estimated from the experiment using the 21°C temperature step was found to be about 8% higher

than that obtained in the experiment using the 9.33°C temperature step at the same final temperature $(\theta + \Delta\theta)$. The discrepancy was tentatively ascribed to the difference in the number of dislocations created by different magnitudes of current pulses used in the two experiments, and systematic error due to ambiguity in setting $t = 0$ for the delay time.

Possible systematic errors and imprecisions were analyzed. The main uncertainty in the determination of the vacancy migration energy was found to be deviation from the resonance condition and long term stability of the experimental equipment. The error in the value of the temperature step also contributes the error in E_m .

From the data obtained at equilibrium temperatures, the activation energy for self-diffusion in aluminum has been determined as 1.32 eV with the standard deviation of 0.02 eV; the pre-exponential factor is $0.144 \text{ cm}^2/\text{sec}$ with the error limit of $0.003 \text{ cm}^2/\text{sec}$.

APPENDIX A

SUMMARY OF PREVIOUS WORKS ON SELF-DIFFUSION IN ALUMINUM

The first attempt to determine the self-diffusion coefficient for aluminum was made by Seymour⁽⁴⁸⁾ with the application of cw nuclear magnetic resonance spectroscopy. Summarized in Table II are the results obtained by Seymour and those by others which will be described later in this appendix.

As mentioned in Section II A, the absorption line of a solid narrows above a certain temperature where the mean time between atomic jumps τ becomes shorter than the spin-spin relaxation time. Seymour related the peak-to-peak derivative width of the narrowing resonance line directly to τ . The mistake in this treatment of line width lies in the failure to take the line shape transition into account. For a powdered specimen, the resonance curve commonly approximates a Gaussian in the rigid lattice region and changes gradually to a Lorentzian above the narrowing temperature. The problem of the line shape transition has been solved by Kubo and Tomita.⁽⁴⁹⁾

Flynn and Seymour⁽⁵⁰⁾ tried to rectify the error in the light of the theory by Kubo and Tomita. However they found that the theory is not applicable in the case of aluminum, because, as mentioned in Section V B, the rigid lattice line shape of the aluminum resonance curve is not truly Gaussian. Instead, they used

Table II
Self-Diffusion in Aluminum

Method	Temperature Range °C	D_0 cm ² /sec	Q eV	Reference
NMR linewidth measure.	---	4×10^{-6}	0.91	Seymour (48)
NMR θ_n concept	---	---	1.3 ~ 1.4	Flynn & Seymour (50)
NMR T_2 measurement	360-520	---	1.4 ± 0.1	Spokas & Slichter (16)
NMR linewidth measure.	330-460	0.1	1.33 ± 0.04	Stoebe, <u>et al.</u> (51)
NMR $T_{1\rho}$ measurement	240-547	0.035	1.25 ± 0.04	Fradin & Rowland (15)
Radio-active isotope Al ²⁶	450-650	1.71	1.48	Lundy & Murdock (52)
Radio-active isotope Al ²⁶	400-610	---	1.5	Beyeler & Adda (54)
2nd stage anneal. resistivity	130-169	---	1.33 ± 0.05	Federighi (55)
2nd stage anneal. void shrinkage*	85-209	0.176	1.31	Volin & Balluffi (28)

* A best fit for the data taken from References (51), (15), (52), and (28) itself.

the concept of the narrowing temperature suggested by Spokas and Slichter⁽¹⁶⁾ to estimate the value of Q .

To avoid the difficulties due to the line shape transition, Stoebe et al.⁽⁵¹⁾ treated only the data of line width above the narrowing temperature of 330°C. As mentioned in Section V B, the line shape deviates from Lorentzian above 450°C. To eliminate this anomaly, they assumed that all contributions to the line width were Lorentzian and were constant except for the dipolar interaction. In reality, however, the line shape is Lorentzian only within the temperature range between 360°C and 450°C, and the non-dipolar contributions are not all constant. The instrumental term is constant, the anomalous term probably is also constant, but the life-time term, that is the electronic term, is dependent upon temperature.

To avoid the difficulties associated with the analysis of line width, Spokas and Slichter⁽¹⁶⁾ utilized Hahn's echo method which provides an operational definition and hence an unambiguous determination of the spin-spin relaxation time. They also explained that the anomaly existing above 450°C was due to a quadrupolar effect caused by the strain field around dislocations.

The best NMR technique for the investigation of diffusion problems is the $T_{1\rho}$ measurement of Slichter and Ailion.⁽¹²⁾ Because of the application of the H_1 field during the $T_{1\rho}$ process, the anomalous contribution above 450°C is diminished.⁽¹⁵⁾ As

described in Section II B, the theory of Slichter and Ailion applies to the region below the narrowing temperature. This enabled Fradin and Rowland⁽¹⁵⁾ in their work on aluminum to include the range from 240°C to 550°C.

There are only two known direct determinations of self-diffusion in aluminum. Both employed the radio-active isotope Al^{26} which has a very long half-life and correspondingly an activity barely sufficient for the purpose. Because in the tracer technique no assumptions are made other than the boundary conditions for solving the diffusion equation, its results are expected to be much more reliable and unambiguous than those obtained from the indirect methods. However Lundy and Murdock⁽⁵²⁾ reported that an oxidation layer was probably present between the two parts of each diffusion couple and necessarily changed the boundary conditions. The barrier effect was temperature dependent and was not observed above 600°C. Since the barrier effect may affect the determination of the absolute values of the diffusion coefficient, its temperature dependence may result in a wrong value for the activation energy for self-diffusion in aluminum.

The activation energy for self-diffusion is also obtained from the shrinkage rates of vacancy products such as dislocation loops, stacking faults, voids, etc. The temperature spectrum of isochronal annealing for a metal reveals that the annealing

process is achieved in two stages. The first stage occurs between -100°C and 0°C in aluminum, and is believed to be due to migration of vacancies to sinks or to form clusters. The second stage is centered at about 150°C and is due to dissociation of the clusters. Most of the investigations utilizing this phenomena were performed with transmission electron microscopy and were primarily devoted to the determination of stacking fault energy. Their Q values are not tabulated in Table II. Volin and Balluffi⁽²⁸⁾ compiled their own diffusion data obtained by observing the shrinkage of voids together with several results reported by other workers, and obtained a best fit value for D_0 and Q .

Several works used resistivity measurement to study the second stage annealing. Only the result obtained by Federighi⁽⁵⁵⁾ is given in Table II.

APPENDIX B

(Table III)

SUMMARY OF VALUES OF VACANCY FORMATION ENERGY IN ALUMINUM

Dilatation Method

E_f (eV)	S_f/k	Reference	
0.77	1.5	Feder & Nowick	(56)
0.75 ± 0.07	2.4	Simmons & Balluffi	(27)
0.71 ± 0.04	1.76 ± 0.56	Bianchi, <u>et al.</u>	(35)

Quenching Method

E_f (eV)	Reference	
0.76 ± 0.04	Bradshaw & Pearson	(53)
0.76 ± 0.03	Panseri & Federighi	(57)
0.79 ± 0.04	DeSorbo & Turnbull	(58)
0.75 ± 0.02	Detert & Ständer	(59)
0.77 ± 0.02	Kabemoto	(60)
0.76 ± 0.02	Duckworth & Burke	(61)
0.76 ± 0.02	Takamura	(62)
0.73 ± 0.03	Bass	(34)

Miscellaneous Methods

E_f (eV)	Method	Reference	
0.77	Resistivity	Simmons & Balluffi	(27)
0.70 ± 0.03	Heat Capacity	Guarini & Schiavini	(63)
0.74	Thermoelectric Power	Bourassa, <u>et al.</u>	(64)

APPENDIX C

SUMMARY OF PREVIOUS WORKS ON

THE VACANCY MIGRATION ENERGY IN ALUMINUM

In conventional methods the lattice defects are identified by their migration energies during annealing of a quenched, irradiated, or cold-worked specimen.

The temperature spectrum of the isochronal annealing of quenched aluminum reveals a two stage process. The first stage is associated with the migration of monovacancies and/or divacancies to be annihilated at sinks or to coagulate into clusters. The second stage is associated with the dissociation of the vacancy clusters, such as stacking faults, prismatic loops, etc., formed at the first stage. The work in this field has been summarized by Federighi⁽³⁰⁾, and the best value for the migration energy is given as 0.62 ± 0.05 eV for a monovacancy and 0.46 eV for a divacancy. Doyama and Koehler⁽⁶⁵⁾ have reported the migration energy for a divacancy as 0.50 ± 0.04 eV.

Irradiated aluminum reveals four stages in the isochronal annealing. The first two stages are composed of numerous sub-stages. Stage III, as designated, is believed by the majority of researchers in this field to be due to migration of monovacancies as identified by the activation energy for the process which is about 0.62 eV. Others, however, assert interstitial mechanisms. Herschbach and Jackson⁽⁶⁸⁾ have postulated a model in which the

freely migrating split interstitial is responsible for the majority of the recovery in stage III and vacancies migrate at the end of stage III. Frank and Seeger⁽³³⁾ have proposed that stage III is due to the annihilation of freely migrating dumbbell interstitials at vacancies. Clearly the species and nature of the defects migrating in stage III are still controversial. As for the activation energy of stage III, Federighi et al.⁽⁶⁶⁾ obtained 0.61 ± 0.03 eV; Frois and Dimitrov⁽⁶⁹⁾, 0.56 ± 0.06 eV; McReynolds et al.⁽⁷⁰⁾, about 0.55 eV; Sosin and Rachal⁽⁶⁷⁾, 0.45 ± 0.06 eV; and Lwin, Doyama, and Koehler⁽³²⁾, 0.62 ± 0.04 eV.

Stage IV of irradiation experiment is believed to be due to migration of trapped vacancies after being dissociated from impurity atoms.⁽⁶⁶⁾ If the specimen is quenched prior to irradiation, there will be stage V which is associated with self-diffusion.⁽⁶⁶⁾

The annealing spectrum of cold-worked aluminum also consists of four stages, excluding stage I but including stage V. For stage III, which is also believed to be due to migration of vacancies, Ceresara et al.⁽⁷¹⁾ obtained an activation energy of 0.57 ± 0.01 eV. Frois and Dimitrov⁽⁷²⁾ obtained 0.58 ± 0.05 eV.

It may be of interest to mention some theoretical works on vacancy migration energy. Wynblatt⁽⁷⁴⁾ has postulated a pairwise potential based on the Morse function for atomic interactions in crystal to compare the energy of a vacancy having relaxed

surroundings and the energy of a saddle point configuration. The result for aluminum is $E_m = 0.66$ eV. Flynn⁽²⁹⁾ has used a harmonic theory to treat the atomic displacements that cause diffusion jumps as a summation of phonon amplitudes. The result for aluminum is $E_m = 0.83$ eV.

APPENDIX D

CALCULATION OF p AND q FOR VACANCY DIFFUSION IN AN FCC LATTICEA. Calculation of p

The theory of Slichter and Ailion⁽¹²⁾ is valid in the low temperature region where $\tau \gg (T_2)_{RL}$. The correlated lattice sum p is defined as

$$p = \frac{1}{G} \sum_q [A_{qr}^2 + \sum_i A_{ir} A_{iq}] / \sum_i A_{ir}^2 \quad (D1)$$

where r denotes the initial position of an atom which jumps to q , the initial position of a vacancy, and G is the number of the nearest neighbor sites. The q sum is over the nearest neighbors only, which are all equivalent, so calculation for one term is sufficient. The dipolar interaction is given by

$$A_{ij} = \frac{\gamma^2 \hbar^2}{2} \frac{1 - 3 \cos^2 \theta_{ij}}{R_{ij}^3} \quad (D2)$$

where θ_{ij} is the angle between the applied field and the inter-nuclear vector R_{ij} .

Following the calculation given by Ailion and Slichter, for a powder,

$$\sum_i A_{ir}^2 = \frac{\gamma^2 \hbar^2}{4} \frac{4}{5} \sum_i R_{ir}^{-6} = \frac{\gamma^4 \hbar^4}{4} \frac{4}{5} \left(\frac{115.631}{a^6} \right) \quad (D3)$$

where a is the lattice parameter. The i sum was carried out on an IBM 360 and included 56,500 lattice sites.

$$A_{qr}^2 = \frac{\gamma^4 \hbar^4}{4} \frac{4}{5} \left(\frac{a^2}{2}\right)^{-3} = \frac{\gamma^4 \hbar^4}{4} \frac{4}{5} \left(\frac{8}{a^6}\right) \quad (D4)$$

and

$$\begin{aligned} \sum_i A_{ir} A_{iq} &= \frac{\gamma^4 \hbar^4}{4} \sum_i (R_{ir} R_{iq})^{-3} \left\{ -\frac{2}{5} + \frac{6}{5} (X_{ir} X_{iq} + Y_{ir} Y_{iq} + Z_{ir} Z_{iq})^2 (R_{ir} R_{iq})^{-2} \right\} \\ &= \frac{\gamma^4 \hbar^4}{4} \left(\frac{14.254}{a^6} \right) \end{aligned} \quad (D5)$$

where the i sum again included 56,500 lattice sites. It should be noted that for a nearest neighbor jump in an FCC lattice is of the type

$$X_{iq} = X_{ir} \pm (a/2)$$

$$Y_{iq} = Y_{ir} \pm (a/2)$$

$$Z_{iq} = Z_{ir}$$

where X , Y , and Z are interchangeable, so the calculation of only one set of X , Y , and Z is necessary. Substituting Eqs. (D3), (D4), and (D5) and Eq. (D1), we obtain

$$p = 0.223 \quad \text{or} \quad (1-p) = 0.777$$

B. Calculation of q

In the high temperature region where $\tau \ll (T_2)_{RL}$ we require the lattice sum g . The difficulties of its direct evaluation from the definition Eq. (17) have been mentioned in Section II B. By analogy with the case of a T_1 minimum, T_{10} is mostly equal to T_2 above the T_{10} minimum, however $\omega_0 \tau \gg 1$ is always true for aluminum in a high field. (It should be noted that $T_1 = T_2$ only when $\omega_0 \tau \ll 1$.) For simplicity, we consider the region where $\gamma H_L \tau \ll 1$. Under these two conditions, Resing and Torrey's⁽¹⁴⁾ expression for T_2 , after some rearrangement and using Eq. (11) for H_L^2 (Van Vleck's expression), is

$$T_2^{-1} = \frac{9}{2} \gamma^2 H_L^2 \tau G(k, 0) \quad (D6)$$

where $G(k, 0) = 0.6145$ for the fcc lattice. By equating Eq. (D6) to Douglass and Jones'⁽¹³⁾ expression for T_d in the weak collision case,

$$T_d^{-1} = 3 \gamma^2 H_L^2 (1-g) \tau \quad (D7)$$

we have

$$(1-g) = 0.922$$

In Eq. (D7) the factor $(1+4\omega_1^2 \tau^2)$ is omitted because in the present experiment $H_1 = \omega_1/\gamma \approx H_L$ and by assumption $\gamma H_L \tau \ll 1$.

APPENDIX E

CORRECTION FOR VACANCY GENERATION DURING THE $T_{1\rho}$ MEASUREMENT

As the vacancy concentration increases, the mean time between successive atomic jumps decreases, and hence $T_{1\rho}$ increases in the high temperature region. Shown in Fig. 13A, with exaggerated difference in the slopes, the dotted straight lines indicate the $T_{1\rho}$ curves as they would appear if, during the measurement, the vacancy concentration stayed constant at C_0 or C_∞ as designated. The solid line demonstrates a possible locus of M_x decay, starting with a slope parallel to the C_0 line and smoothly changing to a slope parallel to the C_∞ line. In such a situation the magnetization does not relax as an exponential function of time and, rigorously speaking, a unique $T_{1\rho}$ does not exist. In reality, however, curvatures of the $\log M_x$ vs. t plot is very slight, and an apparent $T_{1\rho}$ may be determined, shown in Fig. 13 B as a solid straight line. Point i locates the instantaneous magnitude of M_x at the shortest H_1 pulse length t_i , while point f locates that at the longest H_1 pulse length t_f .

The slopes of the M_x decay curve at point i and f in Fig. 13A may be regarded as the inverse of the instantaneous values for $T_{1\rho}$ at the respective times. The two tangents at points i and f do not intersect the ordinate at the same point. However, since the variation of the slope is small, we may postulate a

Figure 13. A. The schematic locus of the transverse magnetization as a function of time if vacancies are generated during the course of the measurement. (For clarity, the difference in the slopes of the C_0 and C_∞ is greatly exaggerated.)

B. Approximate representation of Fig. A as used in derivation of Eqs. (E11) and (E12). From the slope of the solid line the apparent $T_{1\rho}$ is obtained from experiment, disregarding the vacancy generation.

A

B

common initial magnetization designated as M_1 in Fig. 13B. We may also assume that if there were no changes in the vacancy concentration, the magnetization would relax with a time constant $(T_{1\rho})_i$ and pass through point i at time t_i , when C is equal to C_i , in other words, point i satisfies

$$\ln M_i - \ln M_1 = -t_i / (T_{1\rho})_i \quad (E1)$$

where M_i is the magnetization at point i. The subscript x is dropped for simplicity. A similar argument for point f leads to

$$\ln M_f - \ln M_1 = -t_f / (T_{1\rho})_f \quad (E2)$$

when C is equal to C_f . All the quantities appearing in Eq. (E2) are defined in the same way as in Eq. (E1). The postulated M_1 can be eliminated by combining Eqs. (E1) and (E2),

$$\ln M_i - \ln M_f = [t_f / (T_{1\rho})_f] - [t_i / (T_{1\rho})_i] \quad (E3)$$

The relation between the two relaxation times is obtained as follows. Although $(T_{1\rho})_i$ and $(T_{1\rho})_f$ are assumed quantities, nevertheless they must obey the relaxation equations applicable for vacancy concentrations C_i and C_f

$$(T_{1\rho})_i^{-1} - T_e^{-1} = A\tau_i$$

and

$$(T_{1\rho})_f^{-1} - T_e^{-1} = A\tau_f$$

(E4)

where $A = 3\gamma^2 H_L^2 (1-g)$, and the factors $(1+4\omega_1^2 \tau^2)$ are dropped for simplicity in calculation. In general, $4\omega_1^2 \tau^2$ is less than 1.

Also the Arrhenius' rule gives

$$\tau_i = \tau_o C_i^{-1} \exp[E_m/k(\theta+\Delta\theta)]$$

and

(E5)

$$\tau_f = \tau_o C_f^{-1} \exp[E_m/k(\theta+\Delta\theta)]$$

By combining Eqs. (E4) and (E5), we have

$$\frac{C_i}{C_f} = \frac{(T_{1\rho})_f^{-1} - T_e^{-1}}{(T_{1\rho})_i^{-1} - T_e^{-1}} \quad (E6)$$

On the other hand, the apparent relaxation time $T_{1\rho}$ is obtained by fitting the data points in an actual measurement to the equation

$$M_x = M_2 \exp(-t/T_{1\rho})$$

where M_2 is the extrapolation of the line through the data i and f to time zero. Therefore, at point i we have

$$\ln M_i - \ln M_2 = -t_i/T_{1\rho} \quad (E7)$$

and at point f

$$\ln M_f - \ln M_2 = -t_f/T_{1\rho} \quad (E8)$$

Combining Eqs. (E7) and (E8) we have

$$\ln M_i - \ln M_f = (t_f - t_i)/T_{1\rho} \quad (E9)$$

By comparing Eq. (E9) with Eq. (E3), we have

$$[t_f/(T_{1\rho})_f] - [t_i/(T_{1\rho})_i] = (t_f - t_i)/T_{1\rho} \quad (E10)$$

Using the relation Eq. (E6) we have

$$(Rt_f - t_i)(T_{1\rho})_i^{-1} = (t_f - t_i)(T_{1\rho})^{-1} - (1 - R)t_f(T_e)^{-1} \quad (E11)$$

and

$$(Rt_f - t_i)(T_{1\rho})_f^{-1} = R(t_f - t_i)(T_{1\rho})^{-1} + (1 - R)t_i(T_e)^{-1} \quad (E12)$$

where R is C_i/C_f , which is estimated from the measured values in Fig. 11. Error in Eqs. (E11) and (E12) arises from the assumption that relaxations in both cases of C_i and C_f have the same initial magnetization M_1 . Because the initial magnetization of the C_i line is probably much closer to M_1 than that of the C_f line, Eq. (E11) is probably more accurate than Eq. (E12) and is used for the correction in Section V D.

APPENDIX F

THE RELATION BETWEEN THE APPARENT MIGRATION
ENERGY AND THE FRACTION OF VACANCY GENERATION

With the assumption that no vacancies are generated at the time when T_{1p} is measured, the apparent migration energy E is obtained by analyzing the experimental data with the equation

$$\frac{\tau_b}{\tau_p} = \exp \frac{E}{k} \left(\frac{1}{\theta} - \frac{1}{\theta + \Delta\theta} \right) \quad (F1)$$

In reality the vacancy concentration C at the time of measurement may be different from the equilibrium concentration C_o at the base-line temperature, so

$$\frac{\tau_b}{\tau_p} = \frac{C}{C_o} \exp \frac{E_m}{k} \left(\frac{1}{\theta} - \frac{1}{\theta + \Delta\theta} \right) \quad (F2)$$

By equating Eqs. (F1) and (F2) we obtain

$$E = E_m + \frac{\theta + \Delta\theta}{\Delta\theta} (E_f - S_f \theta + k\theta \ln C) \quad (F3)$$

The effect of vacancy generation during the measurement is not considered.

Eq. (F3) may be simplified as follows. Since

$$1-f = \frac{C - C_o}{C_\infty - C_o}$$

then

$$\ln C = \ln C_o + \ln \left(1 + f \frac{C_{\infty} - C_o}{C_o} \right)$$

but

$$\ln \left(1 + f \frac{C_{\infty} - C_o}{C_o} \right) = \ln \left[1 - f + f \exp \frac{E_f}{k} \frac{\Delta \theta}{\theta(\theta + \Delta \theta)} \right]$$

$$\approx \ln \left[1 + f \frac{E_f}{k} \frac{\Delta \theta}{\theta(\theta + \Delta \theta)} \right]$$

$$\approx f \frac{E_f}{k} \frac{\Delta \theta}{\theta(\theta + \Delta \theta)}$$

where in the first and second approximations the terms higher than

$$\frac{1}{2} \left[f \frac{E_f}{k} \frac{\Delta \theta}{\theta(\theta + \Delta \theta)} \right]^2 \quad \text{and} \quad \frac{1}{2} \left[f \frac{E_f}{k} \frac{\Delta \theta}{\theta(\theta + \Delta \theta)} \right]^2$$

respectively, are omitted. The approximation will be correct if

$\Delta \theta$ is much less than θ and f is small. Therefore Eq. (F3) becomes

$$E \approx E_m + f E_f \quad (F4)$$

because $E_f - S_f \theta = -k \theta \ln C_o$.

APPENDIX G

EXPERIMENTAL DATA

$\theta^{\circ}\text{C}$	$(T_{1\rho})_b$ msec	$(T_{1\rho})_p$ msec	$\Delta\theta^{\circ}\text{C}$	$10^3/\theta$ $^{\circ}\text{K}^{-1}$	τ_b sec	E_m eV
239.2	1.65	--	--	1.952	9.186×10^{-3}	--
239.5	1.56	--	--	1.951	6.201	--
246.5	1.5	--	--	1.925	5.291	--
252.0	1.342	--	--	1.905	3.344	--
255.7	1.272	1.18	9.42	1.891	2.815	0.515
258.9	1.175	1.075	9.39	1.880	2.231	0.555
262.3	1.108	1.0	9.37	1.868	1.920	0.608
263.9	1.108	1.016	9.26	1.863	1.929	0.519
267.5	1.01	0.91	9.23	1.850	1.550	0.579
268.4	0.99	0.893	9.22	1.847	1.484	0.563
269.0	0.955	0.86	9.42	1.845	1.372	0.543
270.4	0.931	0.839	9.41	1.840	1.303	0.530
271.6	0.926	0.832	9.41	1.836	1.291	0.547
272.0	0.902	0.808	9.4	1.835	1.224	0.552
273.3	0.87	0.775	9.29	1.831	1.141	0.574
273.5	0.828	0.725	9.5	1.830	1.037	0.623
274.8	0.82	0.734	9.27	1.826	1.020	0.530
277.0	0.792	0.703	9.38	1.818	9.595×10^{-4}	0.557
277.4	0.762	0.677	9.27	1.817	8.954	0.546
278.9	0.71	0.629	9.26	1.812	7.938	0.540
279.8	0.727	0.642	9.47	1.809	8.274	0.552
280.6	0.672	0.591	9.46	1.806	7.260	0.548
281.9	0.663	0.584	9.23	1.802	7.112	0.554
283.8	0.612	0.538	9.21	1.796	6.277	0.547
285.5	0.604	0.53	9.31	1.791	6.161	0.550
285.7	0.584	0.512	9.21	1.790	5.853	0.553
286.5	0.557	0.489	9.31	1.787	5.456	0.532
287.7	0.566	0.5	9.3	1.784	5.594	0.512
291.7	0.482	0.422	9.18	1.771	4.450	0.534
292.9	0.475	0.415	9.18	1.767	4.364	0.543
293.7	0.454	0.393	9.38	1.765	4.103	0.562
294.9	0.429	0.369	9.38	1.761	3.802	0.580
298.4	0.378	0.331	9.13	1.750	3.226	0.514
301.0	0.348	0.296	9.42	1.742	2.906	0.603
302.2	0.325	0.273	9.41	1.739	2.670	0.644
303.1	0.317	0.283	9.20	1.736	2.589	0.426
305.0	0.29	0.25	9.18	1.730	2.324	0.555
305.5	0.281	0.241	9.39	1.729	2.237	0.560

$\theta^{\circ}\text{C}$	$(T_{1\rho})_b$ msec	$(T_{1\rho})_p$ msec	$\Delta\theta^{\circ}\text{C}$	$10^3/\theta$ $^{\circ}\text{K}^{-1}$	τ_b sec	E_m eV
308.1	0.268	0.232	9.38	1.721	2.116×10^{-4}	0.527
308.7	0.274	0.236	9.17	1.719	2.173	0.561
310.0	0.245	0.213	9.17	1.715	1.904	0.520
310.8	0.244	0.209	9.33	1.713	1.897	0.573
375.0	0.283	0.304	9.31	1.543	1.178×10^{-5}	0.554
379.8	0.308	0.333	9.28	1.532	1.038	0.534
382.1	0.324	0.351	9.26	1.527	9.650×10^{-6}	0.523
384.5	0.339	0.37	9.25	1.521	9.057	0.553
385.8	0.35	0.422	9.34	1.518	8.667	1.102
389.3	0.379	0.411	9.33	1.510	7.781	0.488
390.2	0.39	0.43	9.32	1.508	7.490	0.580
392.8	0.415	0.454	9.31	1.502	6.900	0.531
395.1	0.426	0.464	9.4	1.497	6.662	0.502
397.2	0.448	0.493	9.49	1.492	6.235	0.555
400.2	0.488	0.54	9.46	1.485	5.572	0.591
402.7	0.518	0.568	9.47	1.480	5.151	0.543
407.1	0.568	0.599	9.43	1.470	4.557	0.328
408.1	0.59	0.644	9.43	1.468	4.331	0.536
410.2	0.615	0.669	9.42	1.464	4.094	0.524
416.9	0.723	0.789	9.4	1.450	3.272	0.582
418.2	0.74	0.806	9.38	1.447	3.165	0.578
420.3	0.77	0.833	9.37	1.442	2.988	0.546
429.2	0.957	1.025	9.24	1.424	2.145	0.560
433.9	0.966	1.04	9.42	1.415	2.106	0.603
436.4	1.03	1.12	9.51	1.410	1.893	0.713
439.0	1.1	1.161	9.38	1.405	1.690	0.506
441.0	1.14	1.214	9.38	1.401	1.583	0.607
441.8	1.135	1.205	9.38	1.399	1.594	0.579
448.0	1.24	--	--	1.387	1.343	--
451.6	1.375	--	--	1.380	1.082	--
462.3	1.53	--	--	1.360	8.270×10^{-7}	--
473.3	1.68	--	--	1.339	6.203	--
484.6	1.845	--	--	1.320	4.293	--
496.3	1.915	--	--	1.298	3.453	--

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