

Observation of Ultra-Slow Translational Diffusion in Metallic Lithium by Magnetic Resonance*†

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The theory of a new magnetic-resonance technique for studying the ultra slow motion of atoms was presented in a previous paper. In this paper, we present its experimental confirmation for the case of translational diffusion in lithium metal. By this technique the mean time between atomic jumps τ can be measured provided that τ is less than the spin-lattice relaxation time T_1 , permitting study of much slower rates of motion than previously has been possible using magnetic resonance. For lithium metal we have measured over nine orders of magnitude from $\tau=10^{-9}$ sec to $\tau=1$ sec, thereby extending by nearly five decades the results previously obtained by Holcomb and Norberg using conventional techniques. We have applied a new spin-temperature theory to the analysis of our low-temperature results in the range of its validity, $T_1 > \tau > T_2$. By studying the variation of our relaxation time with the rf field strength H_1 , we have unambiguously demonstrated the validity of the spin-temperature theory and the invalidity of perturbation theories in describing relaxation due to infrequent atomic motions in weak applied fields.

I. INTRODUCTION

SELF-diffusion in metals has been studied by a variety of techniques. One of the most powerful of these techniques is magnetic resonance. In certain instances it has advantages over other techniques. For example, the use of radioactive tracers is limited to those materials which have a radioactive isotope of convenient half-life. Magnetic resonance does not measure the mass flow of an impurity atom, but measures instead the individual jumps of the abundant isotope. Conventional NMR techniques^{1,2} have been based on either (1) direct measurements of the motional narrowing of the linewidth or (2) measurements of the spin-lattice relaxation time T_1 in the vicinity of the T_1 minimum. The first technique can be used to study diffusion when the mean time between atomic jumps τ is less than the spin-spin relaxation time, $(T_2)_{R.L.}$ which is the inverse of the rigid lattice linewidth. The second technique is most useful when τ is of the order of the Larmor period. Since $(T_2)_{R.L.}$ is of the order of $100 \mu\text{sec}$ and the Larmor period is typically 10^{-8} sec, conventional magnetic resonance techniques can be used to study motions for which τ is less than $100 \mu\text{sec}$, but cannot be used to study slower motions.

This paper is a continuation of a previous paper³ in which we have described a new magnetic resonance technique⁴ for observing atomic motions. The present paper provides the experimental confirmation of the theory presented earlier. By this new technique the

range over which motions can be detected is greatly extended, thereby making possible the observation of slower atomic motions than had previously been possible by magnetic resonance. The criterion for the observability of motion by the new technique is that $\tau < T_1$. In this paper, the experimental technique is demonstrated for the case of translational diffusion in lithium metal, in which $T_1 \sim 0.15$ sec at room temperature. By combining our results with those of Holcomb and Norberg (HN),² we have measurements of τ over nine decades, from $\tau=10^{-9}$ sec to $\tau=1$ sec, thereby extending their data by nearly five decades. We have used the spin temperature theory³ to relate τ to the measured relaxation time for the slow motion data. In addition we have experimentally verified several consequences of the theory. In particular the failure of the Bloembergen-Purcell-Pound (BPP)⁵ type of perturbation theory is clearly demonstrated for the case of weak-field relaxation due to infrequent atomic motions.

Look and Lowe⁶ have independently realized that motional effects can be observed by a method similar to the one we describe. However, their theoretical treatment, which is based on a BPP-type theory, applies to the case of "weak collisions," and is therefore not applicable to the strong collision case described in this paper.

This paper will be organized into five sections. Section II will contain a brief discussion of the physical basis of the technique. (A more extended account is given in Ref. 3.) The experimental techniques and the apparatus will be described in Sec. III. In Sec. IV we will present and discuss the principal experimental results. Section V summarizes the conclusions. In the Appendix we calculate the parameter β , which is defined in Ref. 3,

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¹ H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1952).

² D. F. Holcomb and R. E. Norberg, *Phys. Rev.* **98**, 1074 (1955).

³ C. P. Slichter and D. C. Ailion, *Phys. Rev.* **135**, A1099 (1964).

⁴ A preliminary account of this research has been published by D. C. Ailion and C. P. Slichter, *Phys. Rev. Letters* **12**, 168 (1964).

⁵ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

⁶ D. C. Look and I. J. Lowe at the Fourth Omnibus Conference on the Experimental Aspects of Nuclear Magnetic Resonance, March 1963 (unpublished).

for the case of vacancy diffusion by nearest-neighbor jumps in a bcc lattice.

II. PHYSICAL BASIS

An approximate relationship which gives the contribution of diffusion to the spin-lattice relaxation time is

$$\frac{1}{(T_1)_d} \sim \frac{(\omega_d)^2 \tau}{1 + \omega_0^2 \tau^2}, \quad (1)$$

where ω_d is the frequency corresponding to the dipolar contribution to the linewidth and $1/(T_1)_d$ is the diffusion contribution to the relaxation rate. This formula was originally derived by Bloembergen, Purcell, and Pound.^{5,7} Equation (1) shows that there will be a minimum in $(T_1)_d$ when $\omega_0 \sim 1$.

Let us now examine the conditions under which diffusion manifests itself on spin-lattice relaxation. In general, the diffusion can be observed only if the relaxation rate due to atomic diffusion is greater than that arising from other mechanisms. In metals the conduction electrons provide the competing mechanism which limits the observability of diffusion. We thus have, for the case of slow motions ($\omega_0 \tau \gg 1$), that diffusion can be observed only if

$$\tau < (\omega_d/\omega_0)^2 (T_1)_e, \quad (2)$$

where $(T_1)_e$ is the relaxation time due to the conduction electrons.

In our experiment we effectively reduce ω_0 to zero. The BPP formula Eq. (1) was derived by treating the dipolar Hamiltonian as a perturbation on the Zeeman Hamiltonian and, as we shall show, is therefore invalid for the "rigid lattice" ($\omega_d \tau \gg 1$) when the applied field becomes comparable to or smaller than the local field due to the other nuclei.

There are two reasons for the failure. The first is that the Zeeman states are not the correct eigenstates when the dipolar Hamiltonian is as big as or bigger than the Zeeman Hamiltonian. In the limit of zero applied field, the correct eigenstates would be dipolar states, and ω_0 in Eqs. (1) and (2) should be replaced by a quantity of the order of ω_d . In this case the diffusion minimum should occur when $\tau \sim 1/\omega_d \sim (T_2)_{R.L.}$. Since this is the point where motional narrowing disappears, the zero-field T_1 minimum should be at the same temperature as that of the "neck" of the T_2 curve. If we replace ω_0 by ω_d in Eq. (2), we see that now we should be able to observe atomic motions in metals if $\tau < (T_1)_e$.

The second difficulty with the BPP theory is that it is a weak collision theory which assumes that τ is much less than the relaxation time, with the result that many atomic jumps are required to relax the magnetization. In the case of zero field, however, most of the order is in the dipolar system, and thus fluctuations in the dipolar system strongly relax the Zeeman Hamiltonian, thereby

making the relaxation time comparable to τ . We have presented a strong collision theory based on the concept of spin temperature for the case of relaxation in weak applied fields due to infrequent atomic motions ($\omega_d \tau \gg 1$) in Ref. 3. It should be noted, however, that the BPP theory is valid for the motionally narrowed state—even for weak applied field—since the expansion parameter for the perturbation expansion is $\omega_d \tau$, and this quantity is less than unity in the motionally narrowed region.⁸

An experimental problem involved in an observation of relaxation in a weak applied field is that in a weak field the magnetic resonance signal is greatly reduced. This problem can be circumvented by using the technique of adiabatic demagnetization, which was previously employed by Anderson and Redfield⁹ and by Hebel and Slichter¹⁰ in studying spin-lattice relaxation in superconducting Al. In this process the external magnetic field is reduced to zero sufficiently slowly for the process to be thermodynamically reversible—that is, the order and thus the entropy will be maintained constant during this cycle. Even though the magnetization is zero when the applied field is zero, the order is *not* zero but is the same as it was in a large field before the demagnetization cycle. In a large magnetic field, the order consists in preferential alignment of the nuclei along this external field, whereas, in zero external field, the order consists in alignment of the individual nuclei along their particular local fields. So we can think of the order as being long range in large field and short range in zero field. It is because the local fields are randomly oriented that the net magnetization is zero in zero applied field. If, in the absence of irreversible processes, the system were to be adiabatically remagnetized, the magnetization would then be returned to the same value it had before the demagnetization process.

Let us now consider how long the order can be maintained in the demagnetized state. We first recognize that spin-lattice relaxation provides a heat flow dQ into the spin system. Since $d\sigma = dQ/\theta$, this heat flow results in an increase in entropy σ of the spin system corresponding to a loss of order. Therefore, if there were no atomic jumping, the order could be maintained for a time T_1 , where T_1 is the spin-lattice relaxation time due to the other processes. Since the process of jumping will cause an irreversible loss of order, it can be detected if the mean time between atomic jumps τ is less than T_1 . If, after jumping has occurred, the magnetic field is adiabatically increased to its original value, the magnetization will be less than it was before the demagnetization process since order has been destroyed. By observing the magnetization as a function of the time during which the field is zero, the relaxation can be studied. One may think of the diffusion process as a heat leak by which heat flows from the lattice to the

⁸ D. C. Ailion, thesis, University of Illinois (unpublished).

⁹ A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

¹⁰ L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

⁷ C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

dipolar system, resulting in a heating of the cold spins toward the lattice temperature.

In the experiment described in Secs. III and IV of this paper, spin-lattice relaxation due to diffusion in the demagnetized state is observed following an adiabatic demagnetization cycle. However, as a practical matter, the demagnetization is greatly simplified by a trick: The demagnetization is performed in the "rotating frame," i.e., a frame rotating in the sense of the nuclear precession at the frequency ω of the alternating field.¹¹ Redfield¹² has shown in the case of a solid that, if H_1 is sufficiently strong, that $\gamma^2 H_1^2 T_1 T_2 \gg 1$, and if $T_2 \ll \tau$, then the system is correctly described by a spin temperature in a frame rotating with H_1 . This means that Curie's law will hold in the rotating frame and that the magnetization \mathbf{M} will be parallel to \mathbf{H}_{eff} . \mathbf{H}_{eff} , the effective field in the rotating frame, equals $\mathbf{k}h_0 + \mathbf{i}H_1$ where h_0 , the field off resonance, equals $H_0 - \omega/\gamma$. By choosing ω exactly equal to γH_0 , we can cancel out the z field leaving H_1 the only field in the rotating frame. We thus can have the sensitivity corresponding to a large value of H_0 (~ 5000 G), and at the same time we can have the relaxation occur in a weak effective field.

As mentioned earlier, a strong collision theory is needed to describe the effects of atomic motion on the relaxation in weak field when $\omega_d \tau \gg 1$. Such a theory has been presented in our earlier paper³ and is based on two assumptions. The first assumption is that there is enough time between jumps for the dipolar and Zeeman systems to be characterized by the same temperature prior to each jump. This assumption allows us to formulate physical quantities of interest as diagonal sums which can be evaluated without determining the eigenfunctions.¹³ Since the time required for these two systems to cross relax to the same temperature is of order T_2 in the limit of weak applied field, we see that this assumption requires that $\tau \gg T_2$. In the case of large applied field the time required to reach a spin temperature becomes very long thereby causing this assumption to become invalid and a BPP type of theory to apply then.

The second assumption of the theory is that the sudden approximation of quantum mechanics can be applied to the jumping process. In other words, we assume that the actual time the nucleus spends jumping is so short that immediately after a diffusion jump the spins have the same orientation as they did immediately before the jump. Since the time that the nucleus spends actually jumping is of the order of 10^{-12} sec, the reciprocal of the lattice vibrational frequency, which is much shorter than the precession periods of any of the nuclei, we see that the sudden approximation is easily satisfied. If it were not satisfied and the nucleus jumped much more slowly, the nucleus would have time to align along

the new local field with the result that the jumping would *not* result in a loss of order and would not be observable by magnetic resonance.

The strong collision theory predicts that if H_0 is set exactly on resonance the magnetization $\langle M \rangle$ will decay to zero¹⁴ in a time T given by

$$\frac{1}{T} = \frac{1}{T_1} \frac{H_1^2 + \alpha H_L^2}{H_1^2 + H_L^2} + \frac{2(1-p)}{\tau} \frac{H_L^2}{H_1^2 + H_L^2}, \quad (3)$$

where the first term represents the contribution of the conduction electrons and the second term represents the contribution of diffusion. In the above equation $\alpha = 2$ if the spins of neighboring nuclei are flipped independently by the conduction electrons. H_L is a properly defined local field,³ and p is a parameter which represents the fact that the local field is not completely random after a jump. p is calculated in the Appendix for the case of vacancy diffusion in a bcc lattice.

If we represent the diffusion contribution by $(1/T)_{\text{diff}}$ we get

$$(T)_{\text{diff}} = \frac{\tau}{2(1-p)} \frac{H_1^2 + H_L^2}{H_L^2}. \quad (3')$$

We see that the relaxation time is proportional to τ in this region, thus guaranteeing the existence of a minimum in $(T)_{\text{diff}}$ somewhere around the neck of the T_2 curve.

If the field is not set exactly at resonance, the magnetization will not decay to a value zero, but will decay to a value M_{eq} which is given by¹⁴

$$M_{\text{eq}} = \frac{M_0 H_{\text{eff}} h_0}{h_0^2 + H_1^2 + \alpha H_L^2 + (T_1/\tau) 2(1-p) H_L^2}. \quad (4)$$

In the region where diffusion effects are important ($\tau \ll T_1$), the last term in the denominator dominates and M_{eq} is always small. If $\tau \gg T_1$, the last term can be neglected and

$$M_{\text{eq}} = \frac{M_0 H_{\text{eff}} h_0}{h_0^2 + H_1^2 + \alpha H_L^2}. \quad (4')$$

We verify both Eqs. (3') and (4') experimentally in this paper.

III. EXPERIMENTAL TECHNIQUE AND APPARATUS

A. Experimental Technique

In order to study translational diffusion in lithium metal, the time constant T for the decay of the total magnetization was measured as a function of the temperature θ over the temperature region 150 to 400°K.

In principle, the technique consists of starting with the external magnetic field H_0 off resonance. An rf field H_1 comparable to the local field H_L is now turned on, after which the external field H_0 is slowly brought to

¹¹ C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

¹² A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

¹³ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹⁴ This is true only if we neglect terms of the order of H_1/H_0 .

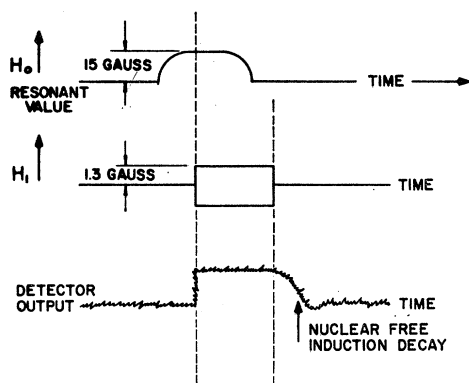


FIG. 1. The pulse sequence versus time. The upper picture shows the modulation field as a function of time; the middle picture shows the rf-pulse envelope as a function of time; and the lower picture shows the detector output including the nuclear signal as a function of time.

resonance. This process reduces the effective field from a value large compared to H_L to a value comparable to H_L . In addition, the direction of magnetization is changed during the demagnetization process from alignment parallel to H_0 to alignment parallel to H_1 . The rf field H_1 is now sharply turned off and the height of the free induction decay is measured. The cycle is then repeated, but with H_1 remaining on for a longer period of time following the return to resonance. The decrease in size of the free induction signal for different pulse lengths is thus a measure of the relaxation of the total magnetization in the presence of H_1 . The slope of a plot of the logarithm of the signal size versus the rf pulse length yields the relaxation time T of Eq. (3). This entire process is then repeated at a different temperature, thereby determining T at the new temperature.

In practice, the pulse sequence is as follows (see Fig. 1). At time $t=0$, the static field H_0 is set exactly on resonance, but $H_1=0$. By means of a pair of Helmholtz coils wound around the Dewar, the magnetic field is pulsed $h_0=14.8$ G off resonance. At this point, H_1 is sharply turned on (the rise time of H_1 is about $3 \mu\text{sec}$). H_1 is supplied from a stable crystal oscillator whose frequency is 7.507 Mc. The external field is now allowed to come slowly back to resonance. By slowly we mean that sufficient time (~ 3 msec) is allowed for the return to resonance to enable the nuclei to undergo many precessions about the effective field. If this condition is met, the return to resonance will result in the total magnetization being tilted from the z direction into the direction of H_1 . Actually, since $H_1=1.3$ G and $H_L=1.2$ G, the individual magnetic moments will be aligned finally along the resultant of H_1 and their individual local fields. Since the latter are randomly oriented, the magnetization along H_1 will be less than if H_1 were very large. In the limit that $h_0 \gg H_1, H_L$, we have that the resultant magnetization immediately after the demagnetization process will lie along H_1 and its value will

equal^{8,11,15}

$$M_f = M_0 H_1 / (H_1^2 + H_L^2)^{1/2}. \quad (5)$$

The demagnetization process can therefore be regarded in part as a tipping of the magnetization into the direction of H_1 , and in part as a reduction of the magnitude of the applied field. As we observed earlier, the relaxation will be more effective for smaller H_1 ; however, a larger H_1 will give a larger signal. A suitable compromise would be to have $H_1 \sim H_L$ in which case an appreciable fraction of the order would be stored in the local field, and yet the observed magnetization would still be an appreciable fraction of M_0 . Consequently, since $H_L=1.2$ G, we have used $H_1=1.3$ G.

An alternative way of treating the problem would have been to follow the adiabatic return to resonance with a second adiabatic demagnetization in which H_1 is reduced from a value large compared to H_L to a value small compared to H_L .^{15,16} In this case, the return to resonance would have the function only to tilt the magnetization into the H_1 direction, whereas the reduction in H_1 would demagnetize the system. We would then wait for a variable time in order to allow the system to relax, after which we would adiabatically increase H_1 back to its original value. We would then sharply turn off the pulse and observe the signal. If there had been no jumping, the signal would be M_0 . By observing the decrease in the signal as a function of the length of time that the nuclei spend in the demagnetized state, T can be determined. This procedure has the disadvantage that considerable time is required for the three adiabatic processes with the result that it would have been extremely difficult to use this technique to study motion in the region for which T is less than 10 msec.

It should be mentioned that it was not always possible, even without demagnetizing H_1 , to satisfy both the adiabatic condition and to have negligible relaxation during the demagnetization process. In the vicinity of the diffusion minimum, enough relaxation occurs during the return to resonance to cause the signal to be substantially reduced in size.

The measurements of T versus $1/\theta$ were done exactly at resonance. Since $M_{\text{eq}}=0$ at the center of the line,¹⁴ the center of the resonance line was determined at the beginning of each day's experiment by lowering the temperature to the conduction electron region and adjusting the magnetic field so that a null in the signal is observed for pulse lengths long compared to T . In this determination of the center of the resonance line, the z field was *not* pulsed and a long (one-second) rf pulse was turned on, after which the signal was observed. Since T is approximately 0.25 sec at the lowest temperatures obtained, a 1-sec pulse allows all the relaxation to be completed, so that the remaining magnetization is M_{eq} . The magnetic field is determined

¹⁴ F. M. Lurie and C. P. Slichter, Phys. Rev. **133**, A1108 (1964).

¹⁵ F. M. Lurie, thesis, University of Illinois (unpublished).

by means of a Shulman-type "Pound Box"¹⁷ whose proton probe was also in the magnet. The frequency of the Pound Box was adjusted so that the protons were on resonance and then measured on a Hewlett-Packard Model 124C frequency counter. By this technique it was possible to reproduce H_0 to 0.025 G.

In principle, one can also observe the resonance by pulsing on H_1 for a time long compared to T_2 but short compared to T .¹¹ Since the magnetization will be along the z direction initially, it will have no component along \mathbf{H}_{off} when the field is exactly at resonance, thereby resulting in a null. However, we observed that the position of the null determined in this way differed from the position of the null obtained by using pulses which are long compared to T . We concluded that the null obtained from the shorter pulse was incorrect since we observed that the phase of the rf relative to the reference changed during the pulse duration. This phase change resulted in an extra component of the magnetization along the x direction which caused the null to occur at a magnetic field value which was slightly different from the center of the line. Since this extra magnetization decays in a time of order T , the null occurs at the center of the resonance line if a pulse long compared to T is used.

The rf field H_1 was calibrated using the 180° pulse method,^{15,16} by which the rf pulse length is adjusted to give consecutive nulls corresponding to 180°, 360°, etc. For this purpose, the Li⁷ resonance was observed at room temperature since the resonance line is motionally narrowed there, thus affording a more precise determination of the null. The calibration of H_1 so obtained was 4.30 ± 0.15 G/1000 V. The voltage is the peak-to-peak rf voltage across the transmitter coil and was

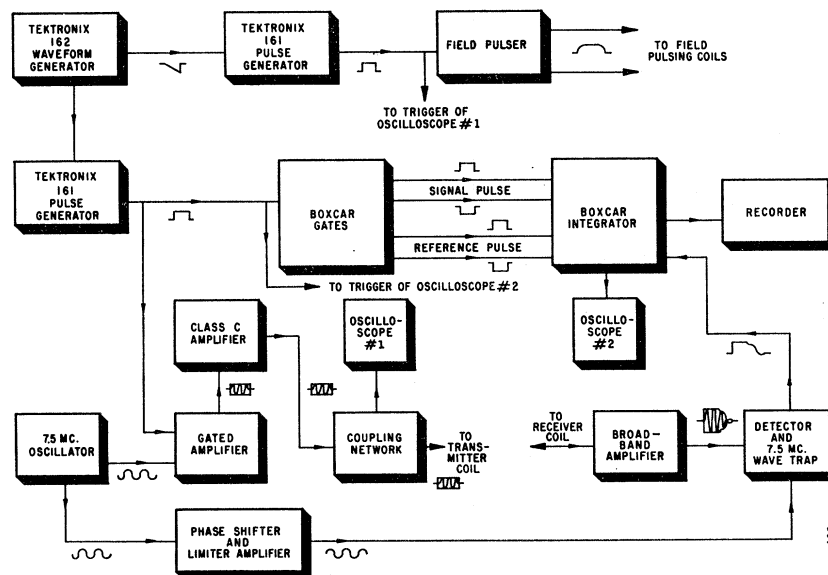
measured on the Tektronix 531A oscilloscope. Since we were interested only in the magnetic field, no attempt was made to calibrate the voltage scale of the scope. However, periodically the calibration was checked by repeating the above procedure. The internal consistency of this calibration with the theoretical value for H_L of 1.2 G in the rotating frame was demonstrated by performing a plot of the magnetization following an adiabatic return to resonance as a function of H_1 .⁸

The modulation field h_0 was measured as follows. It is known that when H_1 is turned on suddenly without any modulation of h_0 , the component of \mathbf{M} perpendicular to \mathbf{H}_{off} decays to zero in about T_2 . Thus, if one pulses on H_1 when one is exactly at resonance ($\mathbf{M} \perp \mathbf{H}_{\text{off}}$) the magnetization decays quickly to zero. Suppose then that we are initially off resonance at a field H_0' , but return exactly to resonance with the slowly varying h_0 pulse. When H_1 is pulsed on, the magnetization will quickly decay to zero. The signal observed when h_0 returns to zero will then be a null. We can thus measure h_0 by finding the value of H_0' that gives a null and using the relation $h_0 = |H_0' - \omega/\gamma|$. Since both ω/γ and H_0' could be accurately measured by means of a proton probe, the observation of this null provides a direct measure of h_0 .

B. Apparatus

A block diagram of the apparatus used in the T versus $1/\theta$ experiment is shown in Fig. 2. The rig is a cross-coil pulse rig, consisting of a transmitter, broad-band amplifier, phase sensitive detector, and boxcar integrator. The transmitter and the broad-band amplifier were used by Spokas in his thesis,¹⁸ and the field pulser is similar to the one used by Lurie.^{15,16} The

FIG. 2. Block diagram of the pulse apparatus.



¹⁷ J. M. Mays, H. R. Moore, and R. G. Shulman, Rev. Sci. Instr. 29, 300 (1958).

¹⁸ J. J. Spokas, thesis, University of Illinois (unpublished).

boxcar integrator is a double boxcar version of the Blume¹⁹ boxcar and is described in more detail elsewhere.⁸

The transmitter consists of a 7.5 Mc "tri-tet" crystal oscillator followed by a gated amplifier, the gating pulse for which is obtained from a Tektronix 161 pulse generator which is triggered from the sawtooth output of a Tektronix 162 waveform generator. The rf pulse is then amplified in a class C push-pull power amplifier. The output of the power amplifier is connected via an impedance matching coupling network to the transmitter coil. With this rig we were able to get a maximum of about 2500 V peak-to-peak across the transmitter coil, corresponding to an H_1 of about 10.8 G.

The receiver coil is connected to the input stage of a five-stage broadband amplifier synchronously tuned to 7.5 Mc with a bandwidth of about 600 Kc. The detector is a phase sensitive balanced detector which uses as a reference signal a 2- or 3-V signal obtained from the 7.5 Mc oscillator. The use of a reference voltage which is larger than the signal guarantees that the diode detector will at all times be biased into the linear region. For this reason noise is never rectified and positive and negative noise excursions are reproduced.

The signal height was obtained from the boxcar and continuously monitored on a Leeds and Northrup Model H recorder. An order-of-magnitude improvement in signal to noise was obtained by using the boxcar.

The pulse widths were determined photographically from a Tektronix 531A oscilloscope whose time scales

had been accurately calibrated against a Hewlett-Packard Model 124C frequency counter.

The adiabatic z -field demagnetization was accomplished by means of a cylindrical pair of Helmholtz coils wound around the outside of the Dewar. A pulse obtained from a Tektronix 161 pulser was passed through a shaping circuit and applied to the modulation coils. The shaping circuit consists of an integrator followed by a clipping circuit and is described elsewhere.¹⁶

The cryostat consists of a brass can which contains coolant and is connected by brass rods to the rf head which is in the magnet gap. The sample is cooled by means of heat conduction through the brass rods. Thermal isolation from the outside is obtained by placing the entire cryostat and rf head inside an evacuated glass Dewar with silvered walls. Elevated temperatures can be maintained with moderately good temperature stability by means of a 90- Ω nichrome heater non-inductively wound around the neck of the rf head. By making small adjustments in the heater current, it was possible to obtain different temperatures. By this technique it was always possible to hold the temperature of the sample constant to within 0.5°K.

In the temperature range below -45°C , the coolant used was liquid nitrogen. From -45 to $+5^\circ\text{C}$ we used as coolant a dry ice and acetone mixture. Above $+5^\circ\text{C}$ the cold bath was a mixture of ice and water. When using nitrogen as a coolant care had to be taken to prevent the formation of liquid oxygen.

The temperature of the sample was determined by

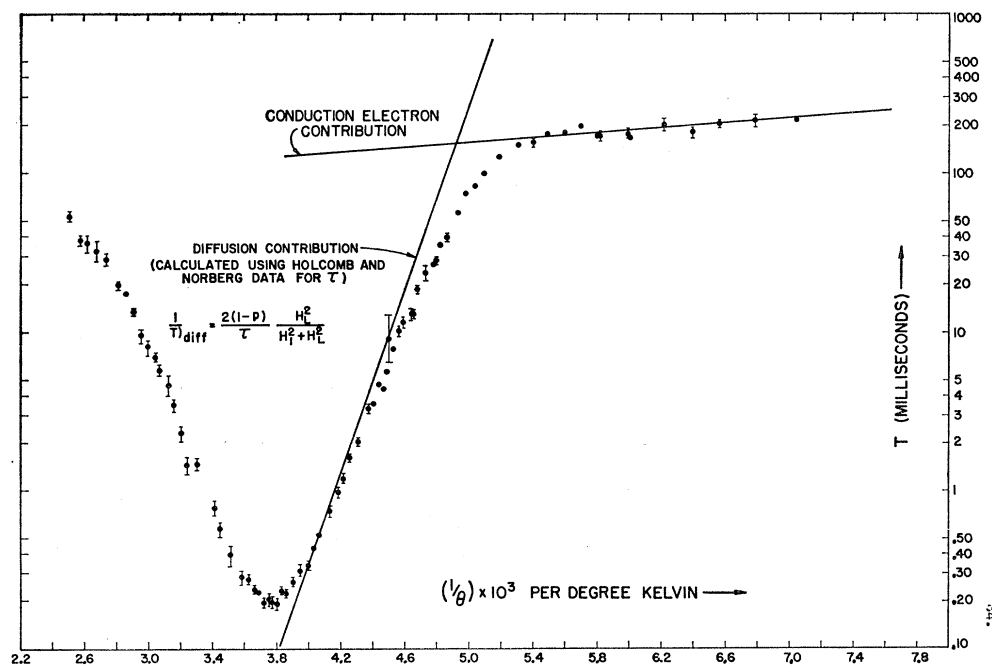


FIG. 3. $\ln T$ versus $10^3/\theta$. $H_1=1.3$ G. The conduction electron contribution is obtained by fitting the low-temperature data to a $(1/\theta)$ curve. The "theoretical" diffusion contribution shown is obtained from Eq. (3') using data of Holcomb and Norberg extrapolated from $(10^3/\theta)=2.77/^\circ\text{K}$, using their value of 13.2 ± 0.4 kcal/mole for the activation enthalpy Q . The vertical bar on the theoretical curve at $(10^3/\theta)=4.5/^\circ\text{K}$ gives the diffusion contribution for the limits of error in Q . At this temperature their data are extrapolated five orders of magnitude.

¹⁹ R. J. Blume, Rev. Sci. Instr. 32, 1016 (1961).

means of a copper-constantan thermocouple placed directly in the sample. The emf was read on a Rubicon potentiometer and converted to temperature by means of revised thermocouple tables.²⁰

The lithium sample was in the form of a dispersion of small particles in mineral oil. Examination with a microscope revealed that the mean radius of these particles was 15μ , which is considerably smaller than the classical skin depth for 7.5 Mc at the temperatures studied. A spectrochemical analysis of the Li sample after preparation by the Anderson Physical Lab (Champaign, Illinois) revealed that it was 99.98% pure with regard to metallic impurities.

IV. EXPERIMENTAL RESULTS

A. T versus $1/\theta$

Figure 3 exhibits the results of measurements of T at various temperatures for $H_1=1.3$ G. There is a high-temperature region to the left of the minimum and a low-temperature region to the right. The spin-temperature theory applies in the low-temperature region. Here, T_2 is constant, and the conventional linewidth measurement shows no motional effects. In the region to the left of the minimum, T_2 exhibits motional narrowing and is equal in magnitude to T . In either region T is the resultant of two curves, one due to the conduction electrons and one due to diffusion. Since $1/T$ is a transition probability, we can write

$$1/T = 1/(T)_{\text{diff}} + 1/T_e, \quad (6)$$

where $1/T_e$ equals the contribution of the conduction electrons to the relaxation rate.

In the low-temperature region where our spin temperature theory applies, we get

$$T_e = T_{1e} [(H_1^2 + H_L^2) / (H_1^2 + \alpha H_L^2)], \quad (7)$$

where T_{1e} is the conduction electron contribution to T_1 .

Since $T_{1e} \propto 1/\theta$, we see that in the asymptotic region at low temperatures T should be proportional to $1/\theta$. The line drawn on the graph gives a $1/\theta$ dependence. It is chosen to give the best fit through our data. In addition, the magnitude of T_e observed experimentally is in good agreement with the predictions of Eq. (7), thus confirming the fact that the conduction electrons are the dominant source of spin-lattice relaxation at low temperatures.

In the high-temperature region where Torrey's theory, based on BPP, applies

$$T_e = T_{1e}. \quad (8)$$

In order to obtain $(T)_{\text{diff}}$, it is necessary to subtract off the conduction electron contribution.

We note the following interesting features. First, the

²⁰ R. L. Powell, L. P. Caywood, Jr., and M. D. Bunch, in *Temperature, Its Measurement and Control in Science and Industry*, edited by C. M. Herzfeld (Reinhold Publishing Corporation, New York, 1962) Vol. 3, part 2.

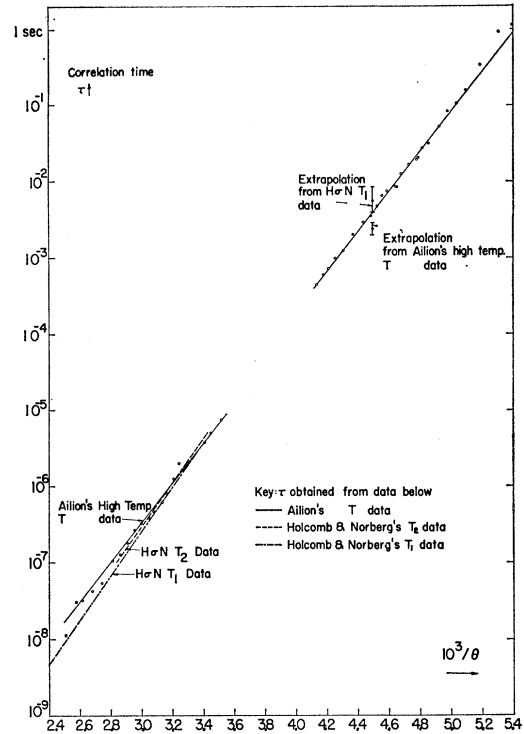


FIG. 4. $\ln \tau$ versus $10^3/\theta$. The experimental points taken in our experiment are shown. Also shown are the slopes obtained from Holcomb and Norberg's data. The values of τ in the high-temperature region were obtained from Torrey's theory, whereas the values of τ in the low-temperature region were obtained using the spin-temperature theory, specifically Eq. (3).

diffusion minimum occurs approximately at the "neck" of the T_2 curve as we predicted for the limit of small applied field. Second, at temperatures above the minimum, T is very close to being equal to Holcomb and Norberg's value of T_2 .² This is analogous to the statement that above a T_1 minimum, T_1 must be independent of H_0 and in most cases equals T_2 . The third feature to be noted is that in the low-temperature region the slope of $(T)_{\text{diff}}$ versus $1/\theta$ is comparable in magnitude but opposite in sign to the slope for the high-temperature region. This is consistent with the idea that $(T)_{\text{diff}} \propto 1/\tau$ above the minimum and $(T)_{\text{diff}} \propto \tau$ below the minimum. From the slopes of the curve, we can determine activation energies for the diffusion process. It is to be noted that these activation energies do not depend greatly on the specific theories used to relate τ to T .

From the measured values of T versus $1/\theta$ we can obtain a plot of the mean jump time τ versus $1/\theta$. We used Torrey's theory²¹ to relate $(T)_{\text{diff}}$ to τ in the low-temperature region. We have plotted the results in Fig. 4. On this plot we have superimposed the results

²¹ H. C. Torrey, *Phys. Rev.* **92**, 962 (1953); H. C. Torrey, *ibid.* **96**, 690 (1954); H. A. Resing and H. C. Torrey, *ibid.* **131**, 1102 (1963).

of HN's T_2 and 3 Mc T_1 measurements. Resing and Torrey²¹ have corrected Torrey's earlier work for an error in the BPP formulas. We have reanalyzed HN's data using the corrected theory.

Since $T=T_2$ in the high-temperature region, we used Resing and Torrey's theory to relate T to τ in this region. There is a numerical coefficient in Torrey's theory which acts as a scale factor. We have determined it from HN's measured values of the T_1 minimum at 3 Mc.

In the low-temperature region we used the formula

$$(T)_{\text{diff}} = \frac{\tau}{2(1-p)} \frac{H_1^2 + H_L^2}{H_L^2} \frac{G}{G-1}, \quad (9)$$

to relate $(T)_{\text{diff}}$ to τ .

The factor $G/(G-1)$, where G is the number of nearest neighbors, is included to correct for the fact that the vacancy jumps so frequently that an atom which has just jumped is still "hot" at the time of the vacancy's next jump.³ Thus, even though most of the atoms in the solid are at a spin temperature, there will be a trail of hot spins left behind the vacancy. The factor $G/(G-1)$ corrects for the fact that one of the spins next to the vacancy is hot and thus should not contribute to the relaxation. In addition, the correct τ for a particular temperature would be the measured τ multiplied by an additional factor $(G-2)/G$ in order to take into account correlations in successive jumps. We have omitted this factor since it multiplies both the high- and low-temperature data. (A detailed discussion of these corrections is found in Ref. 3.)

The quantity p is calculated in the Appendix for the case of vacancy diffusion in a bcc lattice and is found to have the value $p=0.266$.²²

A number of observations can be made. First, it is noted that we have no information in the region corresponding to the minimum of $(T)_{\text{diff}}$. This is due to the fact that the assumptions used in both the low-temperature and the high-temperature theory are invalid in this region. However, if $H_1 \gg H_L$, the minimum would occur at a higher temperature and it would then be possible to determine τ in the temperature range corresponding to the vicinity of the diffusion minimum for $H_1=1.3$ G. The use of large H_1 's causes serious experimental problems when working with metals. In particular, a large H_1 will induce eddy currents in the lithium particles, thereby heating them. Following the rf pulse, the hot particles give up heat to the mineral oil. The thermocouple will measure the temperature of the mineral oil, but will not directly determine how much hotter the particle is during the pulse. This rf heating did not, however, appear to be a serious problem for $H_1=1.3$ G. We note that τ has been measured over a range of nearly nine orders of magnitude.

²² The preliminary account of this work described in Ref. 4 contains an incorrect value of p due to an algebraic error.

There is a small discrepancy between the slopes obtained by HN and our slopes. HN measured an activation enthalpy equal to 13.2 ± 0.4 kcal/mole. A least-square fit of our high-temperature data yields the value 11.79 ± 0.28 kcal/mole, whereas our low-temperature result is 11.97 ± 0.16 kcal/mole. The error signs are the standard deviations. It is seen that our two slopes agree within experimental error, but are 10% lower than HN's slope. The exact source of this discrepancy is not understood. It is interesting to note that Hultsch and Barnes,²³ using magnetic resonance have reported an activation energy for Li of 12 kcal/mole which agrees with our measurements. On the other hand, Naumov and Ryskin,²⁴ using the mass spectrograph technique, measured an activation energy of 13.49 kcal/mole. Our results, however, agree with Nachtrieb's²⁵ theoretical estimate of 11.34 kcal/mole better than do the other results.

With respect to the discrepancy, we note first that our own results are internally consistent between the high- and low-temperature regions. We do not therefore attribute the discrepancy to a failure of the spin-temperature theory. It is true that we used a technique different from HN for measuring T_2 in the high-temperature region (we observe relaxation in the presence of H_1 , whereas they used $H_1=0$); however, their T_1 and T_2 data were consistent with each other. One is therefore inclined to suspect a sample dependence. Their lithium contained 0.3% sodium, whereas ours contained less than 0.02% of metallic impurities.

Holcomb and Norberg's pioneering work was the first magnetic resonance study to use a boxcar integrator. It was performed before the advent of phase coherent detection, with the result that their detector rectified the noise. It is conceivable that the correction factor which they had to employ may have been an additional source of error, but the reason why a different slope could result is hard to conceive.

We have plotted two additional points at $10^3/\theta=4.5$ corresponding to extrapolations of HN's T_1 data and of our $(T)_{\text{diff}}$ data. These points are extrapolations over many orders of magnitude. Note that the low-temperature data were analyzed using a very different theory. We believe that the small discrepancies between our low-temperature line and the extrapolation of our high-temperature points are probably not significant, and are due partly to the differences in slope and partly to the experimental uncertainty of HN's T_1 minimum which was used to calibrate our high-temperature $(T)_{\text{diff}}$ data. Probably, the main source of scatter in our data is temperature instability.

In order to verify Eq. (7) for the conduction electron contribution to T_1 , it was necessary to measure T_1 over

²³ R. A. Hultsch and R. G. Barnes, Phys. Rev. **125**, 1832 (1962).

²⁴ A. N. Naumov and G. Ya. Ryskin, Zh. Techn. Fiz. **29**, 189 (1959) [English transl.: Soviet Phys.—Tech. Phys. **4**, 162 (1959)].

²⁵ N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, J. Chem. Phys. **20**, 1189 (1952).

TABLE I. T_1 , θ versus θ

Temperature ($^{\circ}$ K)	T_1 (msec)	$T_1\theta$ ($^{\circ}$ K sec)
79.0 ± 0.1	470 ± 14	37.1 ± 1.1
127.0 ± 3.7	276 ± 16	35.1 ± 3.0
170.9 ± 1.1	220 ± 6	37.6 ± 1.2
217.8 ± 0.1	201 ± 6	43.8 ± 1.3
Average 38.4		

the temperature range 79 to 218 $^{\circ}$ K. The results obtained by the two pulse technique are shown in Table I.

Since diffusion effects should be negligible over this range, we see from our results that $T_1\theta = 38.4$ sec $^{\circ}$ K as compared with $T_1\theta = 44$ sec $^{\circ}$ K obtained by Anderson and Redfield.⁹ If the value of T_1 obtained from $T_1\theta = 38.4$ is used in Eq. (7), the predicted value of T_e is about 15% lower than the experimental value. If $T_1\theta = 44$ is used, we then get perfect agreement between our theoretical and experimental values of T_e . This suggests that possibly our T_1 measurements were subject to some unknown systematic error. An alternative explanation for this discrepancy would assume the presence of paramagnetic impurities which interact with nuclear moments over a range of many atomic distances and can thus simultaneously flip many nuclei. These impurities would thus relax the Zeeman energy, but would have no effect on the dipolar energy. Such impurities could explain the discrepancies in our results.⁸ However, it should be pointed out that Redfield and Blume²⁶ have obtained similar discrepancies in their studies of saturation in lithium. The paramagnetic impurity should have little effect on diffusion since it does not relax the dipolar energy. Our spectrochemical analysis suggests that iron might be the most likely candidate as the paramagnetic impurity in our sample.

B. $(T)_{\text{diff}}$ versus $(H_1/H_L)^2$

In this section we verify the predictions of our theoretical formula Eq. (3') and the failure of the theory of BPP in describing relaxation due to slow diffusion in the limit of low applied field.

We can rewrite Eq. (3') as

$$(T)_{\text{diff}} = \frac{\tau}{2(1-p)} [(H_1/H_L)^2 + 1]. \quad (10)$$

In the limit of slow motions ($\omega_d\tau \gg 1$), it can be shown^{3,8} that Torrey's answer, which is based on BPP, can be written as

$$(T)_{\text{diff}} = \frac{4}{3} \frac{\tau}{2(1-p)} (H_1/H_L)^2. \quad (11)$$

Figure 5 shows a plot of $(T)_{\text{diff}}$ as a function of $(H_1/H_L)^2$ for small H_1 at $218.3 \pm 0.5^{\circ}$ K. We note that the y intercept is nonzero as is required by our theory.

²⁶ A. G. Redfield and R. J. Blume, Phys. Rev. **129**, 1545 (1963).

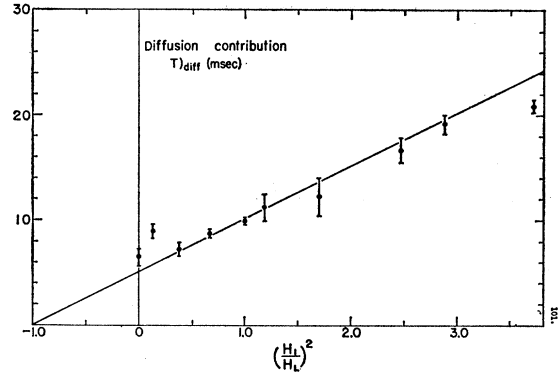


FIG. 5. $(T)_{\text{diff}}$ versus $(H_1/H_L)^2$ for low H_1 at $218.3 \pm 0.5^{\circ}$ K. Equation (3') predicts a straight line intercepting the horizontal axis at the (fictitious) point $(H_1/H_L)^2 = -1$. The slope has been chosen to fit the data best, though in principle it is given when τ is known. The Torrey theory of Eq. (11) predicts a straight line passing through the origin and clearly does not apply for these low H_1 's.

Torrey's theory predicts that $(T)_{\text{diff}} = 0$ when $H_1 = 0$. The agreement of the data with the straight line which intersects the horizontal axis at $(H_1/H_L)^2 = -1$ shows that the expression in brackets in Eq. (10) is correct. This figure thus clearly demonstrates the validity of the spin-temperature theory and the failure of the BPP type of theory in the limit of zero applied field.

C. M_{eq} versus h_0

Finally, we verify Eq. (4') for the equilibrium magnetization as a function of the field off resonance in the case of a completely rigid lattice. The formula in that circumstance was first derived by Redfield⁹ and subsequently by Solomon and Ezzratty.²⁷

In our experiment we used a one-second rf pulse, but did not pulse the z field. The experiment was performed at 123 $^{\circ}$ K to eliminate diffusion effects. The signal obtained following the pulse is the x component of M_{eq} which is given below.

$$(M_{\text{eq}})_x = M_0 H_1 h_0 / (h_0^2 + H_1^2 + 2H_L^2), \quad (12)$$

where we have used the value $\alpha = 2$ assuming the conduction electrons flip the spins independently.

Figure 6 is a plot of $(M_{\text{eq}})_x$ as a function of h_0 for $H_1 = 1.3$ G at $\theta = 123^{\circ}$ K. The solid line is a plot of the theoretical Eq. (12). M_0 was determined by normalizing to the experimental data.

The slight asymmetry is probably due to the amplifier's being tuned slightly to one side of the resonant value. For larger values of h_0 , the measured signal is less than the actual signal. This is because the beat frequency becomes great enough to cause the average value of the signal measured in the boxcar gate to be considerably less than the peak signal. This difficulty could easily be avoided by using narrower boxcar gates,

²⁷ I. Solomon and J. Ezzratty, Phys. Rev. **127**, 78 (1962).

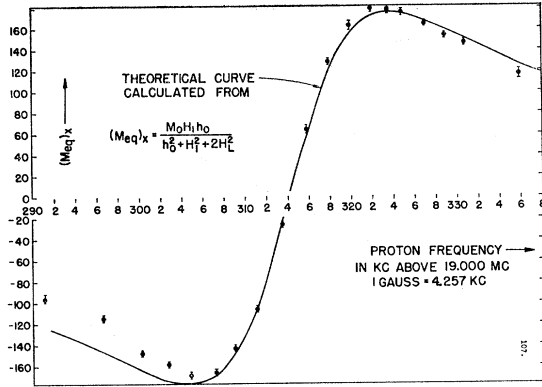


FIG. 6. $(M_{eq})_x$ versus h_0 for $\theta = 123^\circ\text{K}$ and $H_1 = 1.3\text{ G}$. The points were obtained using a long (one second) rf pulse without any modulation field. At this temperature, the diffusion contribution is negligible. The solid curve shows the prediction of Eq. (12) using $\alpha = 2$. M_0 was determined by fitting the peaks of the curve to the experimental points. The agreement is a verification of Redfield's hypothesis.

but in that case it would take longer to obtain each point.

V. CONCLUSIONS

The data in Sec. IV constitute the principal experimental results of this paper. As stated in the introduction, we have successfully demonstrated in lithium metal the feasibility of the new technique for observing slow atomic motions provided the jump time τ is less than the conduction electron spin-lattice relaxation time T_1 . If the spin-lattice relaxation at low temperatures is due to mechanisms other than the conduction electrons as in insulating crystals or in polymers in which T_1 is often very long, it may be possible by this technique to measure jump times which are hours in length. The possibility of being able to measure the activation energy over so many orders of magnitude may allow the experimenter to perceive a small temperature dependence of the activation energy. Such a temperature dependence could be, for example, due to the existence of more than one type of diffusion process, like, for example, jumps to next-nearest-neighbor positions. We have not, however, found such effects for

$$\sum_i A_{ir}^2 = \frac{\gamma^4 \hbar^4}{4} \sum_i \left\{ 1 - 6 \left(\frac{X_{ir} \alpha_x}{R_{ir}} \right)^2 - 6 \left(\frac{Y_{ir} \alpha_y}{R_{ir}} \right)^2 - 6 \left(\frac{Z_{ir} \alpha_z}{R_{ir}} \right)^2 + 9 \alpha_x^4 \left(\frac{X_{ir}}{R_{ir}} \right)^4 + 9 \alpha_y^4 \left(\frac{Y_{ir}}{R_{ir}} \right)^4 + 9 \alpha_z^4 \left(\frac{Z_{ir}}{R_{ir}} \right)^4 + 54 \alpha_x^2 \alpha_y^2 \left(\frac{X_{ir} Y_{ir}}{R_{ir}^2} \right)^2 + 54 \alpha_y^2 \alpha_z^2 \left(\frac{Y_{ir} Z_{ir}}{R_{ir}^2} \right)^2 + 54 \alpha_x^2 \alpha_z^2 \left(\frac{X_{ir} Z_{ir}}{R_{ir}^2} \right)^2 \right\}. \quad (\text{A4})$$

If we average over all angles as for a powder we find

$$\begin{aligned} \langle \alpha_x^2 \rangle_{av} &= \langle \alpha_y^2 \rangle_{av} = \langle \alpha_z^2 \rangle_{av} = \frac{1}{3}, \\ \langle \alpha_x^2 \alpha_y^2 \rangle_{av} &= \langle \alpha_x^2 \alpha_z^2 \rangle_{av} = \langle \alpha_y^2 \alpha_z^2 \rangle_{av} = 1/15, \\ \langle \alpha_x^4 \rangle_{av} &= \langle \alpha_y^4 \rangle_{av} = \langle \alpha_z^4 \rangle_{av} = \frac{1}{5}. \end{aligned} \quad (\text{A5})$$

translational diffusion in lithium over the temperatures at which we worked.

The small discrepancies between our results and those of HN are probably not fundamental. Since the high- and low-temperature slopes agree in our sample, but disagree with those obtained by HN, we suspect that the discrepancies are due to differences in the impurity content of the two samples.

The primary source of scatter in our data is thought to be due to temperature instability, which could be reduced by an automatic temperature control.

In addition to verifying both the failure of the BPP type of weak collision theory and the validity of the spin temperature strong collision theory, the experiment described in Sec. IV.B also provides verification of Redfield's hypothesis of a spin temperature in the rotating frame. Further verification of Redfield's hypothesis is given in the observations of M_{eq} of Sec. C.

APPENDIX: CALCULATION OF p FOR VACANCY DIFFUSION BY NEAREST-NEIGHBOR JUMPS IN A BCC LATTICE

The definition of p is given in Ref. 3. It is

$$p = \frac{1}{G} \sum_q [A_{qr}^2 + \sum_i A_{ir} A_{iq}] / \sum_i A_{ir}^2, \quad (\text{A1})$$

where r = initial position of atom which jumps, q = initial position of vacancy, G = number of nearest neighbors to the vacancy. Now,

$$A_{ir} = \frac{\gamma^2 \hbar^2}{2} \frac{1 - 3 \cos^2 \theta_{ir}}{R_{ir}^3}, \quad (\text{A2})$$

where θ_{ir} = the angle between the applied field and the internuclear vector \mathbf{R}_{ir} .

Suppose the applied field has direction cosines α_x , α_y , α_z with respect to axes fixed in the crystal with origin at site r . Then

$$\cos \theta_{ir} = \frac{\alpha_x X_{ir}}{R_{ir}} + \frac{\alpha_y Y_{ir}}{R_{ir}} + \frac{\alpha_z Z_{ir}}{R_{ir}}, \quad (\text{A3})$$

where X_{ir} , Y_{ir} , and Z_{ir} are the components of \mathbf{R}_{ir} .

We then obtain

$$\begin{aligned} \sum_i A_{ir}^2 &= \frac{\gamma^4 \hbar^4}{4} \frac{1}{5} \sum_i \frac{1}{R_{ir}^6}, \\ &= \frac{\gamma^4 \hbar^4}{4} \frac{23.2336}{a^6}, \end{aligned} \quad (\text{A6})$$

where a is the lattice parameter. The sum over i was carried out on an IBM-7094 digital computer and included 35 000 atoms.

If we are considering a powder, we must average over all directions. We find that the average value of A_{qr} is independent of q and is given by

$$A_{qr}^2 = \frac{\gamma^4 \hbar^4}{4} \frac{1}{5} \frac{1}{(3a^2/4)^3} = \frac{\gamma^4 \hbar^4}{4} \frac{1.8963}{a^6}. \quad (\text{A7})$$

Now

$$\sum_i A_{ir} A_{iq} = \frac{\gamma^4 \hbar^4}{4} \sum_i \frac{(1 - 3 \cos^2 \theta_{ir})(1 - 3 \cos^2 \theta_{iq})}{R_{ir}^3 R_{iq}^3}, \quad (\text{A8})$$

where $\cos \theta_{iq}$ is given by an expression analogous to Eq. (A3). Since we are considering only nearest-neighbor jumps, we have for one jump that

$$\begin{aligned} X_{iq} &= X_{ir} + \frac{1}{2}a, \\ Y_{iq} &= Y_{ir} + \frac{1}{2}a, \\ Z_{iq} &= Z_{ir} + \frac{1}{2}a, \end{aligned}$$

and

$$R_{iq} = [(X_{ir} + \frac{1}{2}a)^2 + (Y_{ir} + \frac{1}{2}a)^2 + (Z_{ir} + \frac{1}{2}a)^2]^{1/2}. \quad (\text{A9})$$

Note that since we are averaging over a powder, all jumps are the same. When we average over a powder, we get

$$\sum_i A_{ir} A_{iq} = \frac{\gamma^4 \hbar^4}{4} \sum_i \frac{1}{R_{ir}^3 R_{iq}^3} \times \left\{ \frac{2}{5} + \frac{6}{5} \frac{(X_{ir} X_{iq} + Y_{ir} Y_{iq} + Z_{ir} Z_{iq})^2}{R_{ir}^2 R_{iq}^2} \right\}. \quad (\text{A10})$$

Evaluating this sum on the IBM computer, we obtain

$$\sum_i A_{ir} A_{iq} = (\frac{1}{4} \gamma^4 \hbar^4) (4.2895/a^6). \quad (\text{A11})$$

Therefore, we get for p

$$p = \frac{\left\{ \frac{1}{8} \times 8 \frac{\gamma^4 \hbar^4}{4} \frac{1.8963}{a^6} + \frac{\gamma^4 \hbar^4}{4} \frac{4.2895}{a^6} \right\}}{\frac{\gamma^4 \hbar^4}{4} \frac{23.2336}{a^6}} = 0.2663. \quad (\text{A12})$$

Photoelectric Properties of Cleaved GaAs, GaSb, InAs, and InSb Surfaces; Comparison with Si and Ge

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Work function and photoelectric threshold, yield, and energy distributions are given for nearly perfect atomically clean (110) surfaces of GaAs, GaSb, InAs, and InSb of known doping cleaved in a vacuum of 10^{-10} Torr, and are compared with results on cleaved (111) Si and Ge. The spectral-yield curves are made up of one or more distinct linear portions. Each of these is interpreted as a direct optical excitation in the bulk for which \mathbf{k} is conserved during emission, and the transitions are tentatively identified. GaAs and InAs, like Si, exhibit appreciable gaps (0.76 eV for GaAs) between the Fermi level and the top of the valence band at the surfaces and show only one linear rise in yield up to 6.3 eV. GaSb and InSb, like Ge, have the Fermi level coincident with the top of the valence band at the surface, and exhibit two different linear rises in yield. Surface states, while present in sufficient density to cause band bending, do not yield appreciable emission compared to valence-band states.

I. INTRODUCTION

THERE is relatively little literature concerning the photoelectric emission and work functions of the III-V compound semiconductors. This is partly due to the fact that these materials have become available in well defined single crystals only recently. The work reported by Haneman¹ and Haneman and Mitchell² on broken GaAs and InSb surfaces represents the total presently available. In view of the great interest in the III-V compounds the measurements of

photoelectric emission spectra, emitted electron kinetic energy distributions and work functions which have been reported for atomically clean cleaved (111) Si³ and Ge⁴ have been extended in this work to the cleaved (110) surfaces of GaAs, GaSb, InAs, and InSb. The results are analyzed to give work functions, position of the Fermi level at the surface and some details concerning the band structure of the compounds.

¹ D. Haneman, *Phys. Chem. Solids* **11**, 205 (1959).

² D. Haneman and E. W. J. Mitchell, *Phys. Chem. Solids* **15**, 82 (1960).

³ F. G. Allen and G. W. Gobeli, *J. Appl. Phys.* **35**, 597 (1964).

⁴ G. W. Gobeli and F. G. Allen, in *Proceedings of the International Conference on the Physics and Chemistry of Surfaces* (North-Holland Publishing Company, Amsterdam, 1964).