about 5 at 2°K. It is expected that similar "giant oscillations" will occur also in the velocity of sound waves and that they can be used in a similar fashion to determine effective masses.

Experiments designed to determine the line shape of the "giant oscillations" with greater precision are now in progress. The results of such experiments should permit the use of Eq. (10) to determine the parameters β and α.

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STUDY OF ULTRASLOW ATOMIC MOTIONS BY MAGNETIC RESONANCE*

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Magnetic resonance has been widely used to study phenomena such as atomic diffusion and molecular reorientation. It is applicable[1] when the mean time, τ, between atomic jumps is either (a) sufficiently short to narrow the resonance linewidth or (b) of the correct magnitude to produce spin-lattice relaxation. Case (a) occurs when τ is less than $1/\Delta\omega$ where $\Delta\omega$ is the rigid lattice linewidth. Case (b) occurs when τ is of the order of $1/\omega_0$, where ω_0 is the Larmor frequency. Typically, case (a) is found when $\tau < 100$ μsec, case (b) when $\tau \sim 10^{-8}$ sec. In this Letter we report a new, experimentally simple technique which enables us to study motions of a much slower rate, the criterion being roughly $\tau < T_1$, where T_1 is the spin-lattice relaxation time.

The method is in many ways equivalent to case (b) with ω_0 set equal to zero; however, by means of a trick we achieve this condition with the actual field H_0 at a large value (10 000 gauss), thereby achieving important experimental advantages. An important problem in interpretation is understanding the effect of atomic motion on the relaxation time when the static field is comparable to or less than the local field of the neighboring nuclei ($\omega_0 \lesssim \Delta\omega$). The conventional theory of Bloembergen, Purcell, and Pound breaks down under these circumstances (in the limit of slow motion with which we are concerned). By generalizing the methods of Redfield et al.,[2,3] we have

been able to solve this problem.

In this Letter we report the results of measurements of self-diffusion in lithium metal, a system chosen because the previous work of Holcomb and and Norberg[4] gave information about τ. Combining their data with ours, we have measured τ for this system over eight decades, from 2×10^{-9} second to 2×10^{-1} second, extending their data by nearly four decades.

The experimental method is based on the technique of adiabatic demagnetization.[3] If a spin system is demagnetized adiabatically from a high field to zero field, the order remains the same throughout the cycle. In the high field, the order consists of an excess of spins pointing along the applied field. In zero field the order consists of alignment of spins preferentially along the local fields due to their neighbors. Ordinarily, the order in zero field can be maintained for a time comparable to the spin-lattice relaxation time. If atomic jumps take place the situation is changed. When a spin jumps, its orientation does not change since the jumping time is very short compared to any precession period. But the local field in the new site is different from that at the old one, since the dipolar coupling falls off strongly with distance. To some degree, therefore, jumping randomizes the spin orientation in the local field and destroys the order. Clearly we can maintain the order only for a time comparable to τ. We can therefore detect jumping by measuring

the rate of loss of order provided τ satisfies the criterion $\tau < T_1$.

It is easiest to observe the loss of magnetic order by studying the strength of a magnetic resonance. The use of a large H_0, which gives the greatest sensitivity, makes demagnetization to zero field more complicated. We therefore use the trick of performing the adiabatic demagnetization in the <u>rotating</u> reference frame[5]- that is, the frame which rotates at the frequency ω of the alternating field H_1, and in the sense of the precession. We describe the details below.

The fact that one could achieve an effective H_0 of zero in the rotating frame and thus study slow motion has been independently recognized by Lowe.[6] Since he has applied the conventional BPP theory to the problem, his results apply when H_1 is much bigger than the linewidth.

The steps in our experiment are as follows[5]: At $t = 0$ we have $H_1 = 0$, and the static field H_0 set exactly on resonance. By means of extra coils placed in the magnet gap, we take H_0 off resonance an amount h_0, of the order of 15 gauss, and slowly

return to resonance. By slowly we mean taking several milliseconds. We turn on an H_1 of about 1 gauss when the displacement of h_0 is at a maximum. This value of H_1 is comparable to the local field, H_L ($H_L = 1.2$ gauss for lithium metal). This sequence of events brings the magnetization M parallel to H_1 in the rotating frame. Since $H_1 \approx H_L$, M is less than M_0, the thermal equilibrium magnetization, and a substantial amount of the order is in alignment of spins along their local fields. We keep H_1 on for a variable time T at the end of which we turn off H_1 suddenly. We measure the amplitude of the free induction decay immediately after turnoff. This signal is proportional to M, and decays exponentially with T. We call the time-constant $(T_2)_{\text{eff}}$, the effective transverse relaxation time.

As we have mentioned, calculation of $(T_2)_{\text{eff}}$ is complicated by the fact that $H_1 \approx H_L$, so that the quantum states of the spin system in the rotating frame are not known. By applying the concept of a spin temperature in the rotating frame,[5,7] which is valid as long as $\tau > 1/\Delta\omega$, and $\gamma^2 H_1^2 > (\Delta\omega/T_1)$,[8] and
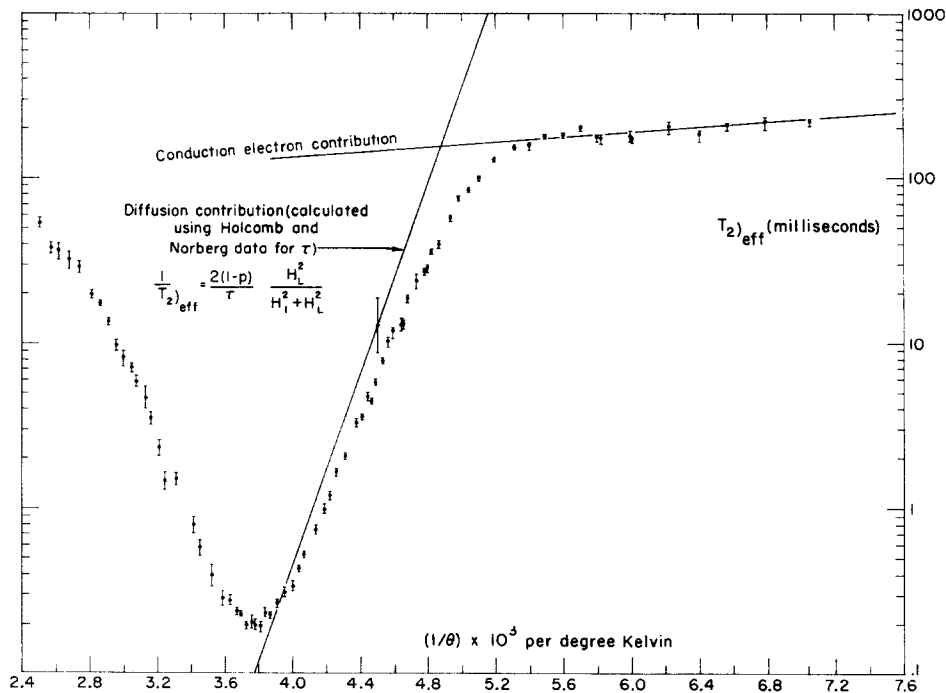

FIG. 1. $\ln(T_2)_{\text{eff}}$ vs $(10^3/\theta)$ for lithium metal. $(H_1/H_L)^2 = 1.19$. The conduction electron contribution is obtained by fitting the low-temperature data to a $(1/\theta)$ curve. The theoretical diffusion contribution shown is obtained by Eq. (1) using data of Holcomb and Norberg extrapolated from $(10^3/\theta) = 2.77/°K$, using their value of 13.2 ± 0.4 kcal/mole for E_D, the activation energy. The vertical bar on the theoretical curve at $(10^3/\theta) = 4.5/°K$ gives the diffusion contribution for the limits of error in E_D. At this temperature, their data are extrapolated five orders of magnitude.

by using the fact that spins do not reorient during an atomic jump, we find for lithium metal

$$(T_2^{-1})_{\text{eff}} = \frac{2(1-p)}{\tau} \frac{H_L^2}{H_1^2 + H_L^2} + (T^{-1})_{\text{cond}}, \qquad (1)$$

where p is a quantity representing the extent to which the local field a spin sees after a jump is randomly oriented relative to the value seen before a jump. (p can be calculated and is of order $1/10$ to $1/2$. For lithium metal $p = 0.52$.) $(T)_{\text{cond}}$ is the conduction-electron contribution to $(T_2)_{\text{eff}}$.[9]

Figure 1 shows a plot of $\ln(T_2)_{\text{eff}}$ vs $1/\theta$, where θ is the absolute temperature, for $(H_1/H_L)^2 = 1.19$. At low temperatures τ is very long and we find only the conduction-electron contribution. In the region $3.8 < 10^3/\theta < 5.4$, $(T_2)_{\text{eff}}$ is limited by diffusion. Note that for $(10^3/\theta)$ greater than about 4.0, τ is so slow that neither the conventional linewidth nor spin-lattice relaxation time shows signs of diffusion. This is, however, the region in which the spin-temperature theory applies. A solid line extrapolating $(T)_{\text{cond}}$ from its low-temperature values using $(T)_{\text{cond}} \propto (1/\theta)$ is drawn. From the Torrey theory, the data of Holcomb and Norberg yield $\tau = 5.5 \times 10^{-8}$ second at the T_1 minimum $(10^3/\theta = 2.77)$. Extrapolating using their activation energy of 13.2 ± 0.4 kcal/mole gives $\tau = 5.5 \times 10^{-3}$ sec at $(10^3/\theta) = 4.50$ with extremes of 8.0 msec or 3.8 msec for the range in activation energy. The experimental τ at this temperature from our data is 3.2 msec. Alternatively, use of our τ together with Holcomb and Norberg's[4] τ at the T_1 minimum gives an activation energy of 12.6 kcal/mole.

Figure 2 shows the H_1 variation of the dipolar contribution to $(T_2)_{\text{eff}}$. Equation (1) predicts a straight-line dependence as a function of $(H_1/H_L)^2$ intercepting the horizontal axis at -1. We have chosen the slope to give the best fit, although in principle the slope is given by Eq. (1). Such a line is shown and gives a good account of the data. For $(H_1/H_L)^2 \gg 1$, the spin-temperature theory breaks down[8] since the dipolar and Zeeman systems cannot cross relax and a BPP theory applies. Then the slope of the graph should increase by a factor of $4/3$. Literal application of the BPP theory to low H_1's would give a straight line through the origin, clearly in disagreement with the facts.

A full account of the theory, the definition and calculation of p, the application to molecular reorientation, and details of the experimental technique will be published shortly. We wish to
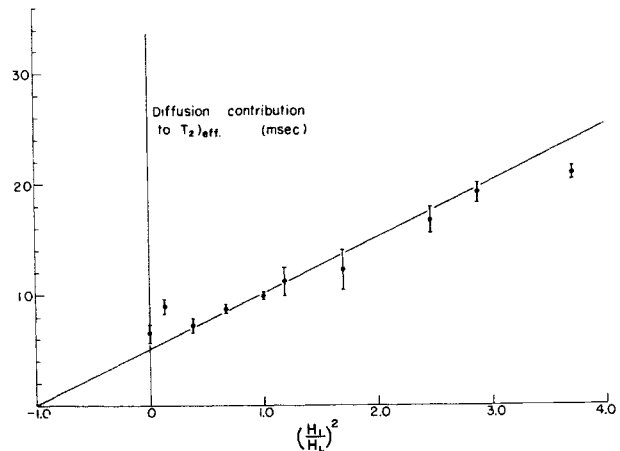
FIG. 2. The diffusion contribution to $(T_2)_{\text{eff}}$ vs $(H_1/H_L)^2$ for $(10^3/\theta) = 4.57/°K$ $(218.5°K)$. Equation (1) predicts a straight line intercepting the horizontal axis at the (fictitious) $(H_1/H_L)^2 = -1$. The slope has been chosen to fit the data best, though in principle it is given when τ is known. The BPP theory if used predicts a straight line passing through the origin and clearly does not apply for these low H_1's.

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Aspects of Nuclear-Magnetic-Resonance Spectroscopy, Mellon Institute, Pittsburgh, Pennsylvania, March 1963 (unpublished). We are indebted to Dr. P. Mansfield for calling our attention to the abstract of Look and Lowe's paper in the program of that meeting. They report a disagreement between the theory and experiment for the H_1 dependence. The difficulty may possibly arise from their application of a BPP-type theory to analyze the

data.

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DETERMINATION OF THE PROTON-PROTON $^1S_0$ SHAPE PARAMETER*

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Modification of the effective-range expansion for the $^1S_0$ nucleon-nucleon state to include the effect of the one-pion-exchange contribution (OPEC) by means of the partial-wave dispersion relation[1,2] or the fixed-angle dispersion relation[3] leads to the prediction that the shape parameter, P, in the expansion $q\cot\delta_0 = -1/a + \frac{1}{2}r_e q^2 - Pr_e^3 q^4 + \cdots$ is positive. This is also predicted by potential models which include the long-range one-pion-exchange potential (OPEP) and either an intermediate-range attraction plus repulsive core[4] or energy-independent boundary condition at intermediate range[5] whose parameters are adjusted to fit the effective range, r_e, and scattering length, a. A more quantitative prediction is provided by including the electrostatic repulsion in the partial-wave dispersion relation[2] and using two additional parameters to fit observed phase shifts at 95 and 310 MeV as well as a and r_e; this calculation[6] gives $P = +0.024$. This prediction is of opposite sign to that made by an energy-independent boundary condition at intermediate range,[7,8] an energy-dependent boundary condition[9] which fits the high-energy (i.e., up to 310 MeV) $^1S_0$ phase shifts,[10,11] or hard-core potentials with intermediate-range attractive tails,[12] which do not include the OPE effect. Since the OPE predictions have been quantitatively confirmed in higher angular momentum states,[13] and since the qualitative features of the phase shifts empirically determined in the 100- to 300-MeV range are in good agreement with models based on the exchange of known bosons and strongly interacting boson systems ("resonances") between the two nucleons (for a brief discussion of these qualitative features and references, see reference 11), it is important to test the consistency of these descriptions with the interaction in the S states as rigorously as possible. This is particularly true since the mod-

els in best agreement with the high-energy scattering experiments predict only 2 MeV of the observed 8-MeV binding for the three-nucleon systems,[14] and the latter calculation is more sensitive to the details of the S-state interactions than the high-energy scattering. One of the few tests available is the prediction of the shape parameter. Since the effective-range expansion fails to converge above 10 MeV,[1] this test can only be made by means of very low-energy nucleon-nucleon experiments. Existing n-p data are not of sufficient precision to yield definite conclusions.[11] In this Letter we show that the recently reported experiment on p-p scattering near the interference minimum at 0.3825 MeV[15] and the p-p differential cross sections measured at 1.397, 1.855, 2.425, and 3.037 MeV[16] can be analyzed to yield a precise value of the shape parameter. This analysis is only possible because the latter experiments also yield a precise value for the J-weighted average of the ^3P phase shifts, and because we claim to have a sufficiently quantitative understanding of the multirange character of the nucleon-nucleon interaction to use this value to predict the individual $^3P_{0,1,2}$ phase shifts.

The energy at which the minimum in the p-p 90° cross section occurs is claimed by Brolley, Seagrave, and Beery[15] to have been determined to better than ±200 eV, and the energy at which the minimum occurs is given by Gursky and Heller[17] as 0.3825 MeV. This value is preliminary, but even if the final result should differ by 200 or 300 eV, none of the conclusions drawn below would be affected. In the absence of vacuum polarization effects, this would imply a $^1S_0$ phase shift of 0.25408 ± 0.00020 rad at precisely that energy; the uncertainty is assigned by assuming that the minimum actually was at 0.3823 (or 0.3827) MeV and then computing the phase shift to be expected