

Nuclear Magnetic Resonance in Solid He³—The Exchange Bath

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We have performed spin-echo experiments on β -phase He³ and have measured the exchange interaction J between He³ atoms in a consistent way, both by the “exchange narrowing” of the line (exchange lengthening of T_2) and by the strong reduction of T_1 at low magnetic fields ($\gamma H_0 \approx J$). J is found to increase very rapidly with increasing molar volume, ranging from less than 20 kc/sec at a lattice constant of 3.4 Å to 90 kc/sec at 3.5 Å, and to about 300 kc/sec at 3.6 Å. These exchange interactions are much too small to account for the “departure from the Curie law” found by Adams, Meyer, and Fairbank. It is shown that the susceptibility is, in fact, “Curie law” (in their temperature range) and we believe that they were reporting—as a susceptibility anomaly—the effect of a long exchange bath-lattice relaxation time (observed for the first time in the present experiment). This exchange-lattice relaxation time varies as T^{-n} ($7 < n < 11$) and is ≈ 100 sec at 1°K for β -phase He³ of 3.5 Å lattice constant. The results for the exchange-lattice relaxation time are compared with a modification of a theory by Griffiths. A major mystery remains—the exchange-bath heat capacity as measured by the spin-echo method exceeds the calculated value by $> 10^3$. The exchange interaction is discussed and compared with the prediction of Saunders and others.

I. INTRODUCTION

NUCLEAR-magnetic-resonance measurements on He³, both liquid and solid, have contributed greatly to our knowledge of the behavior of a real Fermi liquid. Equilibrium properties such as nuclear susceptibility, and dynamical properties such as T_1 , T_2 , and the coefficient for atomic diffusion D , have all been measured by these techniques.¹ Liquid He³ has long been known to exhibit large departures from the Curie law at temperatures of the order of 0.6°K, at which it becomes degenerate.² At sufficiently low temperature,³

the atomic diffusion coefficient in degenerate liquid He³ goes as T^{-2} , as befits any true Fermi liquid.

Our understanding of the behavior of solid He³ has been much impeded by the following apparent paradox: Since 1960 it has been believed that the nuclear susceptibility of solid He³ exhibits a departure from the Curie law at temperatures below 0.3°K as evidenced⁴ by Fig. 1. Such deviations require, of course, an exchange interaction J such that

$$J/2\pi \approx (4kT_c/z\hbar) \sim 3000 \text{ MHz}, \quad (1)$$

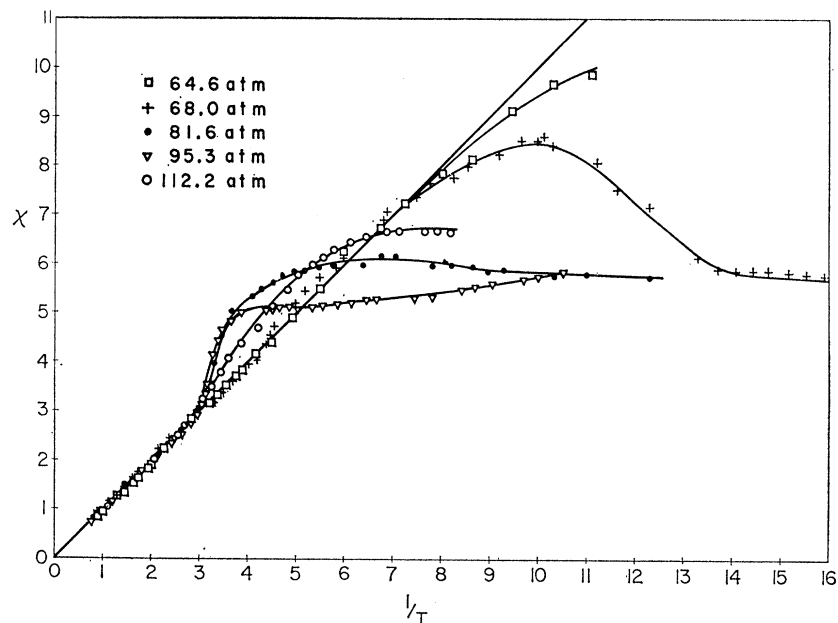


FIG. 1. Bulk susceptibility of He³ versus $1/T$, reported by E. D. Adams, H. Meyer, and W. M. Fairbank (Ref. 4).

¹ R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959).

² W. M. Fairbank, W. B. Ard, and G. K. Walters, Phys. Rev. **95**, 567 (1954).

³ A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **127**, 671 (1962).

⁴ E. D. Adams, H. Meyer, and W. M. Fairbank, *Helium Three* (Ohio State University Press, 1960), p. 57.

z being the number of nearest neighbors of a given atom. On the other hand, solid He^3 has long been investigated in both the α and β phases by the spin-echo method, and perfectly reasonable values of T_2 have been found. The large exchange interactions inferred from the susceptibility would have narrowed the line so much that T_2 would have been lengthened to 10^4 sec or more, or rather, would be limited only by T_1 , in contradiction to the experimental values of the order of some milliseconds. It has not been obvious how to reconcile this conflicting evidence.⁵

The experiments reported here, and their interpretation, form a continuation of the work published previously,^{1,6} using for the most part the same apparatus, except as noted. In this paper we describe some further measurements of spin relaxation T_1 and T_2 as well as nuclear susceptibility χ , in β -phase He^3 . For the most part, T_2 is found to be very long compared with the dipolar width, and we derive the nuclear exchange interaction J from the measured exchange narrowing of the line for the hexagonal close-packed (hcp) lattice of β -phase He^3 . An independent estimate of J may also be obtained, it turns out, from the low-field Zeeman-exchange relaxation (cross relaxation), and these two measurements of J are found to agree.

Specific-heat measurements down to⁷ 0.2°K failed to show any increase in specific heat due to an exchange interaction, thus setting 100 Mc/sec as an upper limit for $(J/2\pi)$ at a molar volume of 21.00 cm³.

At the lower temperatures ($T < 1^\circ\text{K}$) our observations are still quantitatively interpretable by the model of Fig. 2. At sufficiently low temperatures the direct relaxation from the Zeeman system to the lattice (T_{ZL}) is quenched, since the most effective mechanism (atomic diffusion) disappears with a large activation energy. On the other hand, an appropriate choice of the

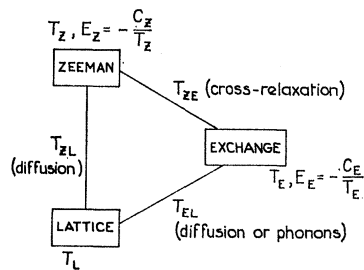


FIG. 2. Schematic diagram of the three-reservoirs model for the spin system and the lattice. E_Z and E_E are the energies and T_Z , T_E , and T_L are the temperatures. C_Z/T^2 and C_E/T^2 are the heat capacities. T_{ZE} , T_{EL} , and T_{ZL} are the relaxation times.

⁵ A preliminary report of the content of this paper was published by the authors in Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962 (to be published).

⁶ H. A. Reich, Phys. Rev. **129**, 630 (1963).

⁷ D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Letters **1**, 218 (1962). Cf. G. O. Zimmerman, H. A. Fairbank, M. Strongin, and B. T. Bertman, Bull. Am. Phys. Soc. **8**, 91 (1963). These limits on J cannot be taken at face value since, according to our result for T_{ZE} , the exchange system at 0.05–0.5°K is completely isolated from the lattice and thus does not exchange energy with it. Exchange integrals much larger than the limiting values claimed by these authors could thus exist and be undetected by their specific-heat measurements (at least in hcp He^3).

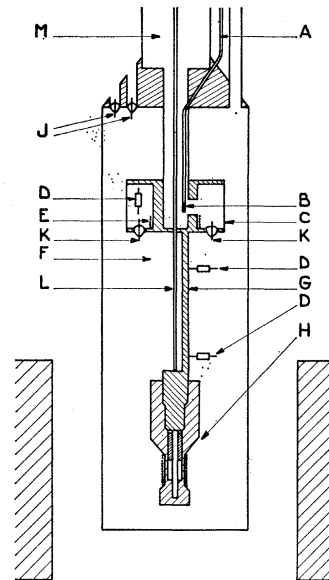


FIG. 3. Schema of low-temperature apparatus. The helium Dewars are of conventional design and are not shown. (A) Liquid He^3 for the refrigerator. (B) Capillary feed for throttling the liquid He^3 returning from the compressor. (C) Evaporator. (D) Carbon resistance thermometers. (E) Heater. (F) Guard space. (G) Copper rod insuring thermal contact between evaporator C and (H) Sample cell (see Ref. 6 for details of brass-nylon cell). (J) Seals used for rf leads. (K) Seals used for resistance leads. (L) Filling capillary for sample cell. (M) Pumping line for the He^3 refrigerator. Not shown are the leads to the sample cell and resistance thermometers.

magnetic field maintains the Zeeman-to-exchange cross relaxation (T_{ZE}) at a reasonable rate.⁶ In this case one can use the Zeeman system as a thermometer for the exchange bath, and we find it possible to measure accurately and directly the exchange bath-lattice relaxation time, T_{EL} . This relaxation time which varies as T^{-n} ($7 < n < 11$), essentially cuts off the cooling of the spin system as the lattice is cooled at reasonable rates. We believe that it is this effect which in α -phase He^3 was mistaken by Adams, Meyer, and Fairbank for a deviation from the Curie law. It must be stated here, however, that the heat capacity of the exchange bath of Fig. 2, as measured by the spin-echo method, is orders of magnitude higher than it should be (according to our measurements of J). In order to display this puzzle as explicitly as possible, we describe herein some of the details of the experiment which might otherwise be superfluous.

II. EXPERIMENTAL APPARATUS

The experimental apparatus was mainly that of Refs. 6 and 1. Electronic temperature regulation was added, using the circuit published by Sommers.⁸ In addition, the He^3 refrigerator was modified to use the small liquid capillary described by Ambler.⁹ These changes

⁸ H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

⁹ E. Ambler and R. B. Dove, Rev. Sci. Instr. **32**, 737 (1961).

facilitated the rapid achievement and stabilization of the desired experimental temperature which was vital to the measurements of the exchange-lattice relaxation time. It was possible to change the temperature from 0.5 to 2°K in a few seconds, without overshoot, and to return to a predetermined temperature below 1°K in about ten sec. (It should be noted that the porous plug used by Ambler is many orders of magnitude too coarse and presumably was usable only because the machining operation closed almost all the pores. We use powdered lead compacted to a leak rate of 3×10^{-4} cc STP He⁴/sec from 1 atm to vacuum at 300°K.)

The He³ we used was obtained from Oak Ridge National Laboratories; no He⁴ was detectable when analyzing the gas on a mass spectrometer ($\text{He}^4/\text{He}^3 < 10^{-3}$).

The cryogenics were somewhat simplified, as can be seen on Fig. 3, showing the experimental apparatus inserted within the He⁴ Dewar. In the He³ refrigerating system, the throttling of the returning liquid is accomplished by means of the capillary feed (B). The pressure across it increases with the increasing heat influx to the evaporator. The temperature in the evaporator (C) is controlled by means of an electronic temperature regulator,⁸ using the heater (E). The Constantan leads to the temperature-sensing resistances (D) and the above-mentioned heater are brought in through the pumping line (M) and the seals (K). The rf leads are brought in through the He⁴ bath, the seals (J) and the guard space (F); in the region of this space which experiences no strong magnetic field, the rf leads are made of niobium, in order to minimize the heat leak to the sample cell.

Data was taken at Zeeman frequencies from 400 kc/sec to 5.2 Mc/sec and at temperatures from 0.38

to 4.5°K. The molar volume ranged from 16.56 to 19.32 cc, and the maximum pressure at which data was taken with the nylon sample cell⁶ was 340 atm.

The technique of preparation of a solid with a desired molar volume differed somewhat from that of Reich. To form the solid at a known density, we start with an exchange gas as (either He³ or He⁴) in the guard space (F); the pumping line (M) being under vacuum, which insures thermal isolation of the upper part of the capillary (L) from the He⁴ bath. We then compress the liquid and cool it, by pumping on the He⁴ bath, slowly enough to insure thermal equilibrium of the sample cell. When the temperature reaches the freezing temperature T_f (point *a* on the phase diagram of Fig. 4), a plug of solid appears at the coldest point in the capillary, presumably somewhere between the evaporator and the sample cell. On further cooling, the material in the cell will freeze at constant volume, along the track *abc*, and, provided the capillary volume is negligible with respect to that of the sample cell, the density of the solid will be that of the liquid in presence of solid at the initial pressure. In order to verify this understanding of the situation we check that the temperatures T_f and T_m (at which solid appears and liquid disappears), agree with the freezing and melting temperatures given by the phase diagram.^{10,11} We take advantage of the large difference in spin-lattice relaxation time T_1 between the solid and the liquid. In the liquid, T_1 is of the order of one min, while in the solid, at our usual magnetic fields and at the freezing temperature, T_1 is always less than about 0.1 sec in the β phase. To detect when the solid appears, we look at the He³ signal in a recurrent display, with a repetition time of the order of the T_1 in the solid. To detect when the liquid disappears, we use a sequence of three 90° rf pulses; if the time interval between the second and the third ones is long compared with the T_1 in the solid, the "stimulated echo," if any, is only due to the spins in the liquid phase. In this manner, we often checked that the freezing and melting temperatures agree with those given by the phase diagram within about 0.01°. Although in our opinion it was more convenient than the technique used previously,⁶ this method still left something to be desired, since the bath needed to be warmed in order to change the molar volume of the sample.

β -phase He³ of the desired molar volume was prepared as described above and the temperature regulated to within a few millidegrees by the electronic regulator. The apparatus was tuned,⁶ and measurements were made of the longitudinal and transverse relaxation times T_1 and T_2 , as well as of the relative nuclear susceptibility by comparison with a reference signal. These data supplement those of Reich and are presented below.

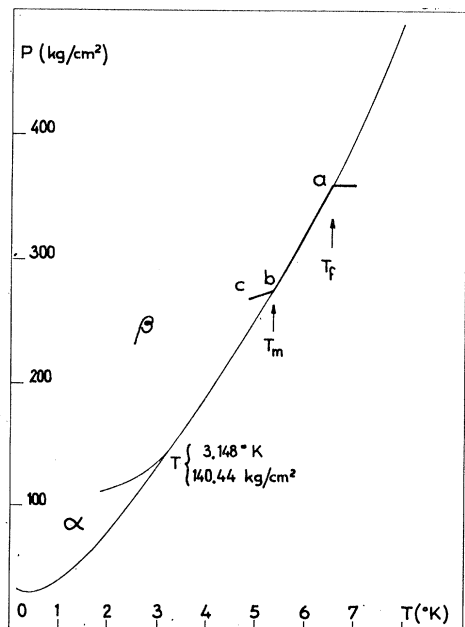


FIG. 4. Phase diagram for He³.

¹⁰ R. L. Mills and E. R. Grilly, Phys. Rev. **99**, 480 (1955).

¹¹ E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **8**, 1 (1959).

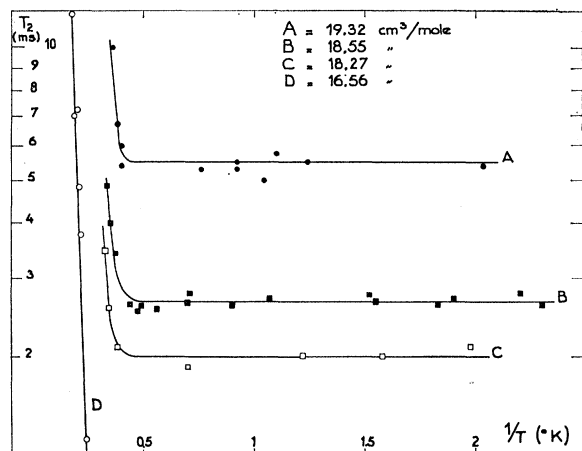


FIG. 5. $\text{Log} T_2$ versus $1/T$, for several different molar volumes. The curves A and B were taken at 1.6 Mc/sec, the curve C at 0.88 Mc/sec and the curve D at 2.2 Mc/sec. In Figs. 5, 7, and 8, the spin system is at the same temperature as the lattice for $1/T_L \leq 1.4$. As may be seen from Table III, the spin system does not cool below $\sim 0.7^\circ\text{K}$ during these T_1 , T_2 , and T_{ZE} measurements, and the relaxation times are simply plotted versus reciprocal lattice temperature on the abscissa. The curves are already demonstrably flat below $1/T = 1.4$, and even in equilibrium will probably run as shown.

The thermal time constant of the solid He^3 is expected to be only a few seconds even at low temperatures where the major thermal impedence will be the Kapitza resistance between the copper axial tube and the surrounding solid He^3 sample. In our temperature range, for which the specific heat of the solid $\text{He}^3 C_v \propto T^3$, this thermal time constant is nearly independent of temperature and is observed to be less than 10 sec at 1.3°K .

III. RESULTS AND INTERPRETATION

A. Transverse Relaxation

The first observation to be made, in the whole range of densities and temperatures we cover, is that the transverse relaxation is exponential, an indication of some kind of narrowing of the line. This enables us to define a transverse relaxation time T_2 , equal to the inverse half-width at half-intensity of the resonance line observed in a cw method.

Measurements of the transverse relaxation time T_2 as a function of temperature, for various densities of the solid, give curves such as those of Fig. 5. In the high-temperature region of these curves, T_2 is diffusion-narrowed and proportional to the inverse of the correlation time τ_c for the diffusion [τ_c increases with decreasing temperature like $\tau_c = \tau_0 \exp(T_0/T)$]. In the low-temperature region, T_2 does not depend on temperature, being exchange-narrowed when $J \gg \tau_c^{-1}$. These exchange-narrowed relaxation times T_2^e are given in Table I.

The computation of the moments of the line raises a problem as to what is the magnetic dipole-dipole coupling of the spins when these are not completely localized (large zero-point motion). Strictly speaking, magnetic coupling between two given spins i

and j in the crystal is:

$$\mathcal{H}_{iij} = \gamma^2 \hbar^2 \langle \Psi_0 | r_{ij}^{-3} \{ \mathbf{I} \cdot \mathbf{I} - 3r_{ij}^{-2} (\mathbf{I} \cdot \mathbf{r}_{ij})(\mathbf{I} \cdot \mathbf{r}_{ij}) \} | \Psi_0 \rangle, \quad (1)$$

$|\Psi_0\rangle$ being the total orbital wave function, assuming the separation of spin and orbital coordinates to be valid, and γ being the gyromagnetic ratio of He^3 . If i and j are remote from one another ($r_{ij} \gg a$, a being the nearest-neighbor distance), this dipole-dipole coupling obviously reduces to

$$\mathcal{H}_{iij} = \gamma^2 \hbar^2 a_{ij}^{-3} \{ \mathbf{I} \cdot \mathbf{I} - 3a_{ij}^{-2} (\mathbf{I} \cdot \mathbf{a}_{ij})(\mathbf{I} \cdot \mathbf{a}_{ij}) \}, \quad (2)$$

\mathbf{a}_{ij} being the vector joining the lattice sites around which are spread the wave functions of atoms i and j . If i and j are neighbors, in replacing (1) by (2) one makes an error which is bigger the less localized are the individual wave functions of He^3 atoms. This error, largest for two atoms which are first neighbors, can be seen¹² to be of the order of $(\delta a)^{-2}$, $1/\delta$ being a measure of the width of individual wave functions (zero-point energy of the crystal increases with δ^{-2}). Theoretical computations¹³ yield values of the parameter which always make $(\delta a)^{-2}$ less than 4% in the range of densities which has been explored. We shall therefore neglect the correction for this error and use Eq. (2) for all the terms in the dipole-dipole coupling.

The computation of the second moment of the resonance line M_2 for a powder of crystallites in α phase (body-centered cubic) and in β phase (hexagonal close-packed) then gives [cf. Ref. 19, see Chap. IV, Eq. (39')]:

$$M_2^\alpha = 7.36I(I+1)(\gamma^4 \hbar^2 / a^6)$$

and

$$M_2^\beta = 8.67I(I+1)(\gamma^4 \hbar^2 / a^6), \quad (3)$$

a being in both cases the nearest-neighbor distance and γ the gyromagnetic ratio of the spins I . The reciprocal square root of M_2^β is of the order of 50 to 60 μsec for the molar volumes given in Table I.

Comparison of the measured T_2^e with $(M_2)^{-1/2}$ from Eq. (3) allows us then to compute an exchange interaction. We assume the only nonvanishing exchange interaction is between nearest neighbors and we define it as $\hbar J \mathbf{I} \cdot \mathbf{I}'$. We assume the only spin-spin tensor coupling is the magnetic dipole-dipole interaction.

We then compute the fourth moment M_4 for a powder, which gives for the two phases

$$M_4^\alpha = 66.95 [I(I+1)]^2 (\gamma^4 \hbar^2 J^2 / a^6),$$

and

$$M_4^\beta = 121.4 [I(I+1)]^2 (\gamma^4 \hbar^2 J^2 / a^6). \quad (4)$$

TABLE I. The measured exchange-narrowed transverse relaxation time T_2^e , and the exchange interaction J as a function of molar volume V , in the β -phase solid He^3 . The alignment temperature T_c is given by $T_c \approx 3(\hbar/k)J$. The nearest-neighbor distance a is given by $a = 2^{1/6}(V/N)^{1/3}$, N being the Avogadro number.

V (cm ³ /mole)	a (Å)	T_2^e (msec)	$J/2\pi$ (kc/sec)	$T_c \times 10^6$ (°K)
19.32	3.566	5.5	205	3
18.78	3.532	3.7	150	2.2
18.55	3.518	2.7	110	1.6
18.27	3.501	2.0	83	1.2
17.59	3.457	<1.1	<50	<0.8
16.56	3.388	<0.3	<15	<0.3

¹² S. R. Hartmann, Phys. Rev. **133**, A17 (1964).

¹³ E. M. Saunders, Phys. Rev. **126**, 1724 (1962).

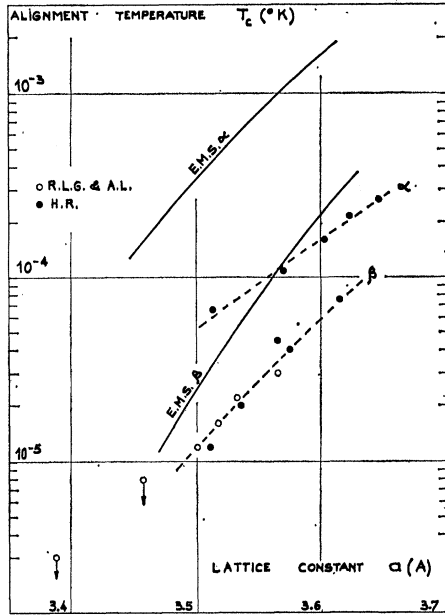


FIG. 6. Alignment temperature $T_c = (\hbar J/4k)$ versus the lattice constant a . We have calculated the solid lines according to the theory of Saunders, as discussed in our footnote 14. The open circles are given by our T_2 measurements, the measurements made for $a < 3.5$ Å giving only upper limits to T_c . The solid circles are given by Reich's measurements of T_2 .

The measured exchange-narrowed T_2^e is related to the computed second and fourth moments by the equation¹⁴

$$(T_2^e)^{-1} = (\frac{1}{2}\pi)^{1/2} (M_2)^{3/2} (M_4)^{-1/2}, \quad (5)$$

which leads to

$$(J/2\pi) = 17.35(T_2^e/V^2) \quad \text{for the } \alpha \text{ phase}, \quad (6a)$$

and

$$(J/2\pi) = 13.926(T_2^e/V^2) \quad \text{for the } \beta \text{ phase}, \quad (6b)$$

where the molar volume V is in cm³, T_2^e in milliseconds, and $(J/2\pi)$ in megacycles.

Table I gives the results of this computation of J as a function of the molar volume V . The alignment temperature $T_c = (z/4)(\hbar/k)J$, deduced from this computed value of J is also shown as a function of the nearest-neighbor distance a on Fig. 6, together with the alignment temperature computed, according to Eq. (6), from the T_2 measurements^{14a} of Reich.⁶ For the sake of

¹⁴ P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 169 (1953).

^{14a} Note added in proof. All the $J/2\pi$ from our Table I used to plot the points in Fig. 6 are obtained directly by the use of Eq. (6) on experimental T_2^e measurements at such low temperatures that thermally activated diffusion has ceased. It should be noted that the values of J shown in Ref. 6, Table II are all in error by a factor $\sim 1.2 \times 2\pi$ (see Ref. 23, note 6). This error has been corrected roughly in the values of J derived from these data and plotted in Figs. 2 and 3 of Ref. 12. Both these authors, however, have made the gross error of obtaining the exchange-narrowed T_2^e from the relation $1/T_2 = 1/T_2^e + 1/T$, where T_2 is the observed time constant of the experimental decay of transverse magnetization (as measured by the spin-echo method) and T_1 is the time constant of decay of longitudinal component. This procedure is completely incorrect, since T_1 and T_2^e are both due to precisely the same cause

comparison, we show also on Fig. 6 two solid lines which are results of numerical calculations making use of the theory of Saunders¹³ for the ground state of solid He³ in the α and the β phases.¹⁵ We find the agreement with the experimental results to be surprisingly good, considering various criticisms of Saunders' theory and the approximations made therein.

B. Spin-Lattice Relaxation

The alignment temperatures given in the fifth column of Table I being well below the lowest temperature reached in our experiments, the nuclear spin system is then always paramagnetic. As far as spin-lattice relaxation is concerned, we can regard the system as an ensemble of three heat reservoirs (Fig. 2): (1) the Zeeman energy of the He³ spins in a dc magnetic field H , (2) the exchange energy of the He³ spins, and (3) the lattice energy, containing all the spin-independent terms (lattice vibrations).

Zeeman-Lattice Relaxation

A flow of energy is expected to occur directly from the Zeeman reservoir to the lattice with a time constant T_{ZL} , through the thermally activated diffusion¹⁶ already exhibited by T_2 measurements in the temperature range where $\tau_c^{-1} \gg J$. This mechanism, acting alone, will give a relaxation time, determined by the spectral amplitude of the local field at the frequency $\omega = \gamma H$:

$$T_{ZL} = \tau_c (H/H_D)^2, \quad \text{when } \tau_c^{-1} \gg \omega. \quad (7)$$

H_D is the field at a spin caused by its neighbors and is of order of magnitude $(M_2^{1/2}/\gamma)$. Figures 7 and 8, which show the variation of the observed spin-lattice relaxation time T_1 with temperature for two different molar volumes and various magnetic fields, exhibit the

(exchange-modulated dipolar interaction). We claim that the observed T_2 is given by T_2^e of Eq. (6) for $\gamma H \ll J$, and by $\frac{1}{2}T_2^e$ for $\gamma H \ll J$. Since $T_1 = T_2$ for $H \rightarrow 0$, the procedure used by Reich and Hartmann would give $J = \infty$ if computed from precise experimental data taken at low fields! Thus, in addition to the numerical errors, Reich's J from T_2 is too large by a factor 6.3 at $V = 22.48$ cm³ mole⁻¹, 5.0 at 22.05 cm³ mole⁻¹, 2.8 at 21.70 cm³ mole⁻¹, etc. The correct values of J from Reich's T_2 data are plotted in our Fig. 6. The good agreement exhibited by Reich and Hartmann for J obtained from T_1 and J obtained from T_2 at $V = 20.1$ cm³ mole⁻¹ thus obtains throughout the density range.

¹⁵ For those numerical calculations, using the notations of Ref. 13, we first compute the single-particle density parameter δ^2 with the appropriate coefficients for each lattice [Eq. (41) in Ref. 13], and then compute the exchange interaction J by means of Eq. (59) in Ref. 13. The solid line for the α phase in our Fig. 6 is the analog of the solid line in Fig. 6 of Ref. 13. It is to be noted that the fourth coefficient inside the brackets of the right-hand member of Eq. (42) in Ref. 13, defined as $(2B^2C_{14}/189C_6)$ is erroneous and equal to 2.098 rather than 4.44, for a bcc lattice. Also, Eq. (62) in Ref. 13 should read $\theta = -\sum_{\lambda} J_{\lambda}/4$, due to the different way the author and we define the quantity J . Our numerical calculations are made with the correct coefficients. Saunders' theory contains several major approximations and, indeed, some nontrivial errors. We are preparing a detailed criticism and extension of his theory, to be published soon.

¹⁶ H. C. Torrey, Phys. Rev. **92**, 962 (1953).

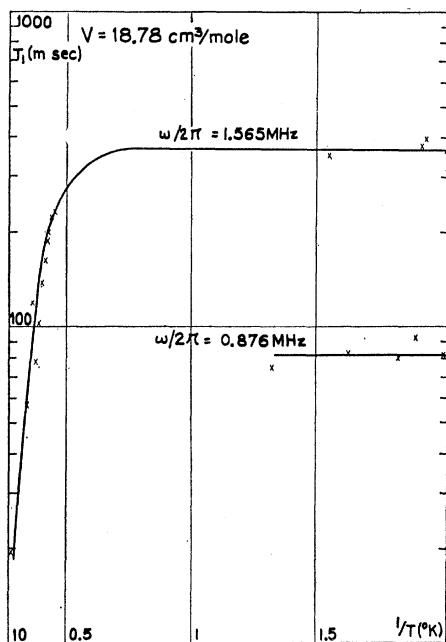


FIG. 7. The observed relaxation time T_1 as a function of the inverse temperature $1/T$ for a constant molar volume $V=18.78$ cm^3/mole and two different Larmor frequencies.

thermally-activated diffusion-induced Zeeman-lattice relaxation in the high-temperature region where it is more efficient.

Zeeman-Exchange Relaxation

A flow of energy will also occur between the Zeeman and exchange reservoirs through a cross-relaxation mechanism induced by spin-spin tensor interactions, the cross-relaxation time T_{ZE} being independent of the lattice temperature. When the diffusion becomes negligible, the Zeeman energy relaxes to the lattice through the exchange reservoir. In Figs. 7 and 8 the temperature-independent regions of the T_1 curves then illustrate situations where the bottleneck for the flow of energy from the Zeeman system to the lattice is the Zeeman-exchange relaxation time T_{ZE} to which we ascribe the observed temperature-independent T_1 . Table II shows T_{ZE} for various molar volumes and various magnetic fields in β -phase solid He^3 .

Assuming Eq. (2) to be valid, this cross-relaxation time T_{ZE} can be shown to vary with the dc field H according to:

$$1/T_{ZE} = f(\gamma H/J)/T_2^e, \quad (8)$$

where $f(x)$ is a dimensionless function decreasing rapidly when x increases, which only depends on the particular crystalline lattice type (bcc for α phase, and hcp for β phase).

In the limit of zero magnetic field, T_{ZE} must be equal to the transverse relaxation time which is well known¹⁷

¹⁷ R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).

TABLE II. The Zeeman-exchange relaxation time T_{ZE} in seconds, as a function of the Larmor frequency ($\omega/2\pi$) and of the molar volume V .

V (cm^3/mole)	$(\omega/2\pi)$ (kc/sec)			
	408	876	1565	1800 2500
19.32	7×10^{-8}	2×10^{-2}	6×10^{-2}	0.72
18.78		8.2×10^{-2}	0.37	
18.55			1.9	
18.27		0.85		> 300
17.59				> 600

to be T_2^e when $\gamma H \gg J$ and $\frac{3}{10}T_2^e$ when $\gamma H \ll J$. Thus $f(0) = 10/3$.

Figure 9 is a test of Eq. (8): (T_{ZE}/T_2^e) is plotted against $(\gamma H/J)^2$ on a semilogarithmic scale, for various dc fields H and various molar volumes. We have used smoothed values of J and T_2^e in the plotting of the points, making use of the dashed curve of Fig. 6 and of Eq. (6b). Neither a straight line nor the free-hand curve is a very good fit to the data. Nevertheless, the data seem to conform reasonably well to Eq. (8) which, like Eqs. (3) to (6), is based on the assumption that the spin-spin tensor coupling is given by Eq. (2), which then seems confirmed too.

Simultaneous Relaxation of the Zeeman System to the Lattice and to the Exchange Bath

In this case the relaxation rate T_1^{-1} is not equal to $T_{ZL}^{-1} + T_{ZE}^{-1}$. The spin relaxations induced by the local field variations caused by diffusion and those induced by the exchange are not additive. The situation is completely different from that of a system in which there exist two relaxation times T_{ZLA} and T_{ZLB} induced

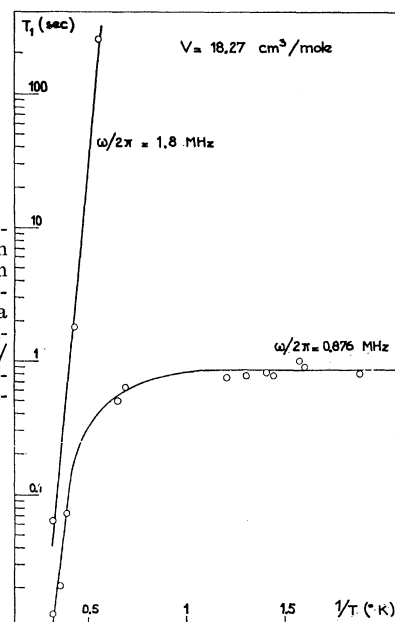
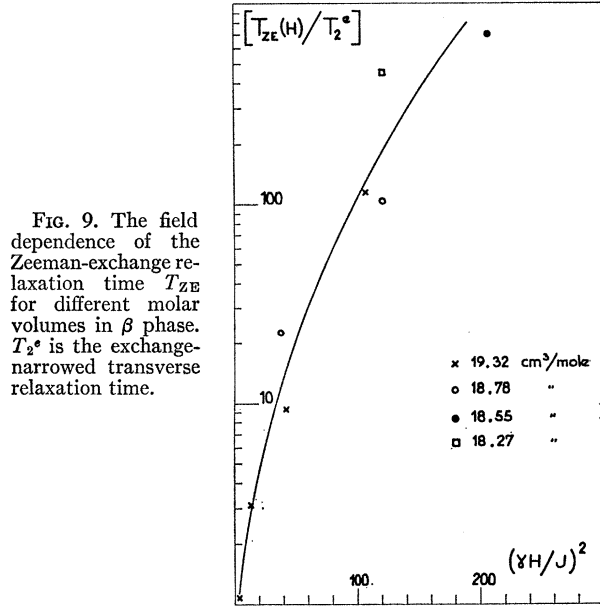


FIG. 8. The observed relaxation time T_1 as a function of the inverse temperature $1/T$ for a constant molar volume $V=18.27$ cm^3/mole and two different Larmor frequencies.



by local fields of some other diffusing atoms of types A and B. In this latter case one does have

$$T_1^{-1} = (T_{ZLA})^{-1} + (T_{ZLB})^{-1}.$$

A phenomenological theory in order to calculate T_1 in our case can be made as follows:

If one had no exchange interaction and only atomic diffusion, the correlation function for the modulation of the local field would be

$$G(\tau) = \frac{1}{4}(\gamma H_D)^2 \exp(-|\tau|/\tau_c), \quad (9)$$

where the spectral density of the local field is:

$$J(\omega) = \int_{-\infty}^{+\infty} G(\tau) e^{-i\omega\tau} d\tau. \quad (10)$$

This correlation function (9) is well known to lead for the dipolar spin-lattice relaxation time for a system of like spins to the formula of BPP:

$$\frac{1}{T_1} \propto J(\omega) + 4J(2\omega), \quad (11)$$

and

$$\frac{1}{T_1} = \frac{1}{2}(\gamma H_D)^2 \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right]. \quad (12)$$

In the long-correlation-time approximation ($\omega\tau_c \gg 1$), Eq. (12) reduces to Eq. (7).

In the limit when diffusion is negligible and one has only exchange modulation of the dipolar field, the correlation function is usually^{14,17} taken as Gaussian:

$$G(\tau) = \frac{1}{4}(\gamma H_D)^2 \exp(-\frac{1}{2}\omega_e^2 \tau^2), \quad (13)$$

the parameter ω_e being of the order of the exchange interaction J . In the case of simultaneous exchange and diffusion modulation of the dipolar field, we define the following correlation function:

$$G(\tau) = \frac{1}{4}(\gamma H_D)^2 \exp(-|\tau|/\tau_c) \exp(-\frac{1}{2}\omega_e^2 \tau^2), \quad (14)$$

which obviously reduces to Eq. (9) or Eq. (13) when either exchange or diffusion is negligible. The two parameters H_D and ω_e which enter so far only phenomenologically, are yet to be defined precisely. The Fourier transform¹⁸ of Eq. (14) gives the spectral density

$$J(\omega) = \frac{1}{4}(2\pi)^{1/2}(\gamma^2 H_D^2 / \omega_e) \text{Re}W(x+iy),$$

with

$$x \equiv \omega / \omega_e \sqrt{2}, \quad y \equiv 1 / \omega_e \tau_c \sqrt{2},$$

and

$$W(z) \equiv \exp(-z^2) \left\{ 1 + \frac{2i}{\sqrt{\pi}} \int_0^z \exp(t^2) dt \right\}.$$

Making use of Eq. (11) one finds for the relaxation time

$$T_1^{-1} = \frac{1}{4}(2\pi)^{1/2}(\gamma^2 H_D^2 / \omega_e) \{ \text{Re}W(x+iy) + 4 \text{Re}W(2x+iy) \}, \quad (15)$$

which is very close to Eq. (50) of Ref. 12. The previously published version of this formula [Eqs. (12) and (13) of Ref. 6] contains several errors and should be ignored.

In order to define H_D , we shall fit Eq. (7) with the formulas given by Torrey^{19,20} in the limit $\omega\tau_c \gg 1$:

$$\frac{1}{T_1} = \frac{32\pi}{5} \frac{\gamma^4 \hbar^2 I(I+1) N g}{a^3 V k^3 \omega^2 \tau_c},$$

with $k=0.743$ and $g=0.2857$ for a fcc lattice and $k=0.763$ and $g=0.2808$ for a bcc lattice. For a powder of crystallites of these structures, the second moments are M_2^β and M_2^α [Eq. (3)], since powder second moments are the same in face-centered-cubic and hexagonal-close-packed lattices. For both fcc and bcc lattices, numerical computation gives $(\gamma H_D)^2 \approx 2.2 M_2$.

In the limit of negligible diffusion Eq. (15) reduces to

$$T_1^{-1} = \frac{1}{4}(2\pi)^{1/2}(\gamma^2 H_D^2 / \omega_e) \{ \exp(-\omega^2 / 2\omega_e^2) + 4 \exp(-2\omega^2 / \omega_e^2) \}, \quad (16)$$

which can be used to define the function f introduced in Eq. (8). Setting $f(0)=10/3$ and using Eq. (5), one finds

$$\omega_e = \frac{3}{4}(\gamma H_D)^2 (M_4^{1/2} / M_2^{3/2}). \quad (17)$$

¹⁸ *Tables of Integral Transforms*, edited by A. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, pp. 15 and 387.

¹⁹ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. X.

²⁰ H. A. Resing and H. C. Torrey, *Phys. Rev.* **131**, 1102 (1963).

Putting $(\gamma H_D)^2 = 2.2 M_2$ and using Eq. (3) and (4), one finds for the α and β lattices

$$\omega_e^\alpha = 1.76J [zI(I+1)]^{1/2},$$

and

$$\omega_e^\beta = 1.78J [zI(I+1)]^{1/2}, \quad (18)$$

z being the number of nearest neighbors. As expected one finds ω_e of the order of magnitude of J and roughly proportional to \sqrt{z} .

This simple derivation of T_1 in the case of simultaneous relaxation of the Zeeman system to the lattice and to the exchange bath will prove useful for a consistent discussion of our results and those of other experimenters.

Exchange Bath-Lattice Relaxation

a. As it might be evidenced in T_1 . At a low enough temperature, $T_{ZL}^{-1} \ll T_{ZE}^{-1}$, and energy flow between the Zeeman system and the lattice passes through the exchange bath, which presents an opportunity to measure T_{ZE} . The exchange bath-lattice relaxation time T_{EL} will only manifest itself, for instance after a single 90° pulse, if the two following conditions are fulfilled:

(1) $T_{EL} \gtrsim T_{ZE}$, else the exchange bath will always be at lattice temperature and one will measure only T_{ZE} unless the specific heat C_E/T^2 of the exchange bath is very small compared with that C_Z/T^2 of the Zeeman system.

(2) $C_E \lesssim C_Z$. If the heat capacity of the exchange bath (C_E/T^2) very much exceeds that of the Zeeman system (C_Z/T^2), the exchange bath will remain at lattice temperature and one will measure only T_{ZE} . Since, in Fig. 2

$$C_Z = \frac{1}{4} N (\hbar \gamma H)^2 k^{-1},$$

and

$$C_E = \frac{3}{8} N z (\hbar J)^2 k^{-1}, \quad (19)$$

one would expect to satisfy condition (2) if one works at a field such that T_{ZE} varies rapidly with H , i.e., $\gamma H \geq z^{1/2} J$.

One should then expect to see nonexponential recovery after a 90° pulse (for a small range of C_E/C_Z), or at least a variation of " T_1 " with temperature as T_{EL} varied itself with temperature. Down to the lowest temperature available to us, however, we observe a temperature-independent relaxation time T_1 (Figs. 7 and 8) which we ascribe to the Zeeman-exchange relaxation time T_{ZE} (Table II).

b. As it might be evidenced by response time of the spin system to change of lattice temperature. If the Zeeman system and the exchange bath are closely coupled by the choice of a small external magnetic field, then the time constant for approach of the Zeeman temperature to the lattice temperature will be $T_r = T_{EL}(C_E + C_Z)/C_E$. If $C_E \gg C_Z$, $T_{EL} = T_r$ can be measured directly in this way. In order to investigate this possibility, we meas-

TABLE III. The response time T_r of the spin system to change of lattice temperature as a function of the inverse temperature, for constant molar volume $V = 18.55 \text{ cm}^3/\text{mole}$.

$T_L^{-1} (\text{K}^{-1})$	T_r (min)
1	1
1.14	1.4
1.25	14
1.45	30
1.70	200
1.90	216
1.984	>2000

ured the susceptibility, i.e., the Zeeman temperature T_Z as a function of lattice temperature T_L .

For a molar volume $V = 18.55 \text{ cm}^3/\text{mole}$, we find the susceptibility to obey Curie's law for lattice temperature $T_L > 1^\circ\text{K}$. If we cool the sample to a temperature below 1°K , we initially measure a susceptibility that is well below the value corresponding to Curie's law. At constant lattice temperature, the susceptibility then grows with time and for $T_L > 0.7^\circ\text{K}$, reaches within 10% the value corresponding to Curie's law with a time constant T_r , increasing with decreasing temperature. Taking for granted then that the limiting susceptibility is given by Curie's law for any temperature in our range, we measure the time constant T_r given by Table III.

We observed the same behavior of the susceptibility for a molar volume $V = 18.27 \text{ cm}^3/\text{mole}$.

Appendix A shows that our results obtained in this way are not falsified by material thermal time constants.

c. Calculation of exchange bath-lattice relaxation time T_{EL} . Two mechanisms can be proposed for T_{EL} :

(1) Atomic diffusion gives rise to a relaxation time T_{EL} which is of the order of the correlation time τ_c , as shown in Appendix B. It should be noted that $T_{EL} \sim (H_D/H)^2 T_{ZL}$, i.e., that the diffusion-induced exchange-lattice relaxation rate is $10^6 - 10^8$ times more rapid than the diffusion-induced Zeeman-lattice relaxation rate. A single atomic jump suffices to bring a spin into essentially random orientation with respect to the local exchange field (at high temperatures) and thus the exchange-lattice relaxation time is nearly that for a single jump. On the other hand, a single atomic jump into a random field H_D in the presence of an external field $H \gg H_D$ corresponds to a mean-square angular departure from the external field $\theta^2 \sim (H_D/H)^2$, requiring on the average $(\theta^2)^{-1}$ jumps for full relaxation.

(2) Thermal vibrations are well known to be a negligible relaxation mechanism for nuclear Zeeman energy, essentially because they modulate relatively little the dipolar interactions between the nuclei. The situation is different for exchange energy because the exchange integral which depends on the overlap of the nuclear wave functions varies much more rapidly with the interatomic distance than the dipolar interaction. Exchange-lattice relaxation through ther-

mal vibrations was studied by Griffiths.²¹ As usual, two processes can be considered: In the first one (direct process) a single phonon is absorbed or emitted, the frequency being J , and T_{EL}^{-1} being proportional to the small fraction of the phonon spectra around the frequency J ; in the second one (Raman process), one phonon is absorbed and one phonon is emitted, the difference of their frequencies being J . Since the whole phonon spectrum is covered in the Raman process, this can be seen to be overwhelmingly more important and leads to²¹:

$$\xi = (C_{\text{E}}/T_{\text{EL}}) = \frac{3}{128} N_{\text{Z}}(z-1)\pi^{11/3}6^{1/3} \left(\frac{Na^3}{V}\right)^{4/3} \frac{LJ^2\hbar^4 T^2}{m^2\omega_0^3 \theta^7} W, \quad (20)$$

where

$$W = 2T^5 \int_0^{\theta/T} \frac{y^6 e^y dy}{(e^y - 1)^2}.$$

$\theta = (\hbar\omega_0/k)$ is the Debye temperature, m is the atomic mass of He³, and

$$L = \sum_{rs} \left(\frac{\partial^2 J}{\partial x^r \partial x^s} \right)^2 = (J'')^2 + \frac{2(J')^2}{a^2}.$$

J' and J'' being the first and second derivatives of the exchange integral, supposed isotropic, with respect to the interatomic distance. For an hexagonal close-packed lattice, Eq. (19) and (20) give

$$T_{\text{EL}}^{-1} = 530(\hbar^2 L/m^2\omega_0^3)(T^2/\theta^7)W. \quad (21)$$

In the limit $T \ll \theta$, $W \sim 1464 T^5$. Since J varies very rapidly with a , in a small interval around some equilibrium value a , J can be written, for instance, as¹³

$$J(r) \approx J(a) \exp\left[-\frac{1}{2}\delta^2(r^2 - a^2)\right].$$

It is then easy to see that

$$(J''a/J')^2 \sim (\delta a)^4 \gg 1,$$

so that L can be taken as $(J'')^2$. Since the Debye temperature is known from specific-heat measurements²² and J'' can be taken from Fig. 6, the exchange-lattice relaxation time induced by thermal vibrations can be calculated from Eq. (21).

d. Interpretation of our experimental results. The fact that the exchange-lattice bottleneck was not observed in T_1 measurements can be accounted for either by a short T_{EL} or by a large exchange heat capacity C_{E} . For $T = 0.5^\circ\text{K}$, $V = 18.78 \text{ cm}^3/\text{mole}$, and taking $(J''/2\pi) \sim 10 \text{ Mc/sec}/\text{\AA}^2$ from Fig. 6, Eq. (21) gives $T_{\text{EL}} = 10^6 \text{ sec}$, which is longer than T_1 by a factor 10^6 . Diffusion-induced T_{EL} is much longer if the only diffusion is that of the 23°K activation energy we measure above 2°K ; such diffusion would lead to a $T_{\text{EL}} = 2 \times 10^{19}$

sec for $T = 0.5^\circ\text{K}$, $V = 18.78 \text{ cm}^3/\text{mole}$. As for the exchange heat capacity, Eq. (19) gives $C_{\text{E}} \ll C_{\text{Z}}$, taking into account the value of J given in Table I.

On the other hand, our T_r measurements could be explained by a large exchange heat capacity, the time constant T_r being identified with the exchange-lattice relaxation-time T_{EL} . We tried, without success, to heat the exchange reservoir and thus decrease the susceptibility at constant lattice temperature ($T_{\text{L}}^{-1} = 1.984$), by applying 90° pulses every second ($\sim T_1$) for one minute, at a Larmor frequency $(\omega/2\pi) = 1.6 \text{ Mc/sec}$. This gives us a lower limit for the ratio of the heat capacity of the exchange system to that of the Zeeman system $C_{\text{E}}/C_{\text{Z}} > 10^3$. This limit is still compatible with the fact that no anomaly in the specific heat of solid He³ has been observed down to 0.3°K ,^{7,22} suggesting an exchange interaction smaller than 60 Mc/sec .

The law of temperature dependence of our measured values of T_r (Table III) cannot definitely be ascertained. T_r could vary with temperature as T^{-n} ($7 < n < 11$), but our measurements could as well be explained by a diffusion-induced exchange-lattice relaxation due to an entity present in concentration c , diffusing according to

$$D_{\text{E}} = D_0 e^{-T_0/T}, \quad (22)$$

with $T_0 \sim 7^\circ\text{K}$ which would give $T_{\text{EL}} \sim (a^2/6cD_{\text{E}})$. If this entity is not very different from ordinary atoms, $D_0 \sim 5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, which then gives $c \sim 10^{-10}$. It would be possible to assume the presence of substitutional He⁴ which would diffuse with a low activation energy and distort the wave functions of its neighboring He³ nuclei, possibly increasing the local He³-He³ exchange interactions. This He⁴ could then increase the global exchange heat capacity and act as an exchange-lattice relaxation process. Still it is hard to see how such a low concentration of He⁴ could be sufficient to increase so much the global exchange heat capacity. One is then led to assume some crystal defects present in the crystal and able to distort it enough to increase by a large amount the exchange interactions of two He³ in their neighborhood.

Thomson, Meyer, and Dheer (henceforth referred to as TMD) have recently published²³ susceptibility measurements which do not exhibit the very high temperature (0.3°K) deviations from Curie law which had previously appeared.⁴ TMD attribute the previous results to the fact that the measurements had been done on a 1% He⁴ in He³ solid, whereas their new work was with He³ of purity better than 99.97%.

The new results of TMD, which exhibit a Curie-Weiss law with a Curie temperature varying with molar volume, are in contradiction with specific-heat measurements as well as with our measurements of J .

²¹ R. B. Griffiths, Phys. Rev. **124**, 1023 (1961).

²² E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

²³ A. L. Thomson, H. Meyer, and P. N. Dheer, Phys. Rev. **132**, 1455 (1963). (Also private communication, for which we are grateful.)

On the other hand, they find at a Larmor frequency $\omega/2\pi=3.3$ Mc/sec for $V=19.5$ cm³/mole in the β phase, T_1 varying rapidly with temperature below 1°K as

$$T_1^{-1}=2e^{-2/T}(\text{sec}^{-1}). \quad (23)$$

Our T_1 measurements never exhibited such a low activation energy; presumably our sample is quite different from that of Ref. 23.

For $V=19.5$ cm³/mole, in the β phase, TMD find a Curie-Weiss constant (called θ in Ref. 23) $T_e=0.12^\circ\text{K}$; their exchange interaction would then be $J/2\pi=(kT_e/3h)=700$ Mc/sec. At their Larmor frequency $(\omega/2\pi)=3.3$ Mc/sec, (thus small compared with $J/2\pi$), it would be impossible to observe a relaxation rate smaller than $(10/3)(T_e)^{-1}$, which according to Eq. (6), is equal to 6.5 sec. Actually we can consider the plateau in the $T_1(T)$ curve of TMD (in fact only defined by two points) to be due to Zeeman exchange relaxation: $T_{ZE}=140$ sec. Solving then Eq. (16) for J , noting that $\exp(-\omega^2/2\omega_e^2)\gg\exp(-2\omega^2/\omega_e^2)$ and taking into account Eqs. (6), (17), and (18), we find $(J/2\pi)=150$ kc/sec. Interpolation of the dashed curve of Fig. 6 for β phase would predict $(J/2\pi)=250$ kc/sec. We consider the agreement as acceptable considering the large number of assumptions which led us to Eqs. (15) to (18). We conclude that the sample of TMD had a J in good agreement with ours—their 700 Mc/sec figure we believe to be in error.

As for the temperature variation of T_1 exhibited by Eq. (23), it can be accounted for by the presence of some impurity (even He⁴) diffusing according to Eq. (22) with $T_0=2^\circ\text{K}$ and $D_0\sim 5\times 10^{-5}$ cm² sec⁻¹. If the impurity is present in fractional concentration c with respect to the He³, it will give the He³ atoms (if they are otherwise frozen) an effective diffusion coefficient $D=cD_E=(ca^2/6\tau_E)$ and a correlation time $T_e=(\tau_E/c)$. If we then fit Eq. (23) with

$$T_1^{-1}=(\gamma H_D/\omega)^2(6cD_0/a^2)\exp(-T_0/T),$$

taking $(\gamma H_D/2\pi)=5.8$ kc/sec, we find $c\sim 3\times 10^{-6}$. This would explain why TMD did not observe our response time T_r ; it is shown in Appendix B to be of the order of τ_e which would reach $T_{EL}=140$ sec only at 0.14°K.

The real difficulty is to understand how our sample could be so pure that $T_r\sim 10^5$ sec at 0.5°K, whereas T_1 in TMD's sample at 0.5°K was $\sim 10^2$ sec. An alternative is to imagine that somehow the sample of TMD does not have the excess exchange specific heat that ours has, so that T_{EL} can be observed as T_1 .

All of these effects must eventually be explained and these rather tentative and mutually exclusive hypotheses of the previous 7 paragraphs are advanced here in order to make plain the magnitude of the dilemma. Further work with purer He³ and with doped He³ will be required to solve the puzzle.

IV. CONCLUSION

These experimental results for T_1 , T_2 , and J are in good agreement with the data of Reich who used largely the same apparatus but a different sample. The magnitude of J is consistent with the lack of a measurable contribution to the heat capacity at low temperature^{7,22} and the very long response time T_r would in any case prevent the flow of energy between exchange bath and lattice at low temperatures and thus the thermal measurement of the heat capacity of the exchange bath at 0.1~0.3°K. The only internal inconsistency in our point of view is the source of the unknown large heat capacity of the exchange bath. We have been unable to imagine a contribution to the exchange specific heat which would not also lead to an exchange-lattice relaxation time shorter than T_r .

We have previously pointed out⁵ that this $T_r(T)$ would offer a ready explanation to the apparent departure of susceptibility⁴ (Fig. 1) from the Curie law at temperatures many orders of magnitude greater than $(\hbar J/k)$. The susceptibility, although Curie law in this entire range, would appear to fall below the Curie law at low temperatures because the spins do not actually come to the temperature of the lattice in a finite time.

We are unable to reconcile the low-temperature susceptibility measurements of TMD²³ with their relaxation measurements or with our own results. Their T_1 results, on the other hand, are internally consistent, although incompatible with our own. It seems probable that the difference between our T_1 (temperature-independent below 1°K) and their T_1 (thermally activated with a 2°K activation energy below 1°K) arises from the different defect structure of our samples. Further work is necessary to determine the nature of the important defects and their mode of influence.

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APPENDIX A: DISCUSSION OF THE SPIN-SYSTEM RESPONSE TIME TO CHANGE OF LATTICE TEMPERATURE

Before explaining our measured T_r as a lattice-temperature-dependent rate of energy flow from exchange bath to lattice, we considered the possibility T_r might be simply a manifestation of a long thermal-equilibrium time constant between the He³ and the metallic portions of the sample cell, to which the thermometers were attached. It is well known that such purely thermal time constants do become long at low temperature. The following argument shows that no part of the temperature dependence of T_r can be ascribed to such a thermal resistance, and if there were such a resistance it would mean that the true T_r varies

even more rapidly than the variation exhibited by Table III.

Recall the way in which T_τ is measured: The magnetic field H is maintained at a value such that $T_1 \sim 1$ sec. The Zeeman system thus serves as a convenient thermometer for the exchange bath, to which it is coupled supposedly much more strongly than to the lattice. The sample is brought to thermal equilibrium at some temperature $T_0 \sim 1^\circ\text{K}$, such that T_τ is neither very long nor very short ($T_\tau \sim 10^2$ sec). The sample cell is then cooled suddenly to a low temperature and the rate of change of Zeeman temperature is measured as (dT_Z/dt) , for $T_Z = T_0$. It is this rate of change of Zeeman temperature (and thus exchange bath temperature) which is a strongly *decreasing* function of the lower temperature of the sample cell, to which the heat is flowing, i.e., the flow of heat from our thermometer at fixed high-temperature T_0 *decreases* rapidly as the temperature T_S of the sink is reduced. Not only does this behavior violate the laws of physics in systems in which heat flow is governed by a diffusion equation with arbitrary temperature dependence of the conductivity,²⁴ but it is also inconsistent with the studies on thermal contact below 1°K ,²⁵ all of which show results for the heat flow from constant source temperature T_H to a sink at temperature T_S which can be put in the form

$$\dot{Q} = T_H^p - T_S^p, \quad 1 < p < 4. \quad (\text{A1})$$

This heat flow never decreases with decreasing T_S . Therefore, we consider it established that we are not measuring by T_Z the temperature of the lattice, but have exhibited in fact a true relaxation phenomenon between the exchange bath and the lattice.

APPENDIX B: CALCULATION OF THE DIFFUSION-INDUCED EXCHANGE-LATTICE RELAXATION TIME

As usual we neglect the exchange interaction between nuclei which are not first neighbors. The exchange Hamiltonian can then be written

$$\mathcal{H}_e = \frac{1}{2} \hbar J \sum'_{i \neq j} \mathbf{I}^i \cdot \mathbf{I}^j, \quad (\text{B1})$$

\sum' being restricted to spins i and j which are first neighbors. Any given nucleus actually jumps from one crystalline site to another, thus modulating the exchange Hamiltonian \mathcal{H}_e . If we assume the temperature to be low enough for the resonance line to be exchange-narrowed rather than diffusion-narrowed, the jumping frequency τ_c^{-1} is small compared with J , which makes it meaningful to ascribe a temperature to the exchange bath and write its density matrix:

$$\rho = \frac{[1] - \beta \mathcal{H}_e}{\text{Tr}[1]}, \quad (\text{B2})$$

²⁴ R. L. Garwin, Rev. Sci. Instr. **27**, 826 (1956).

²⁵ J. C. Wheatley, D. F. Griffing, and T. L. Estle, Rev. Sci. Instr. **27**, 1070 (1956).

the temperature of the exchange bath being $T_E = (k\beta)^{-1}$.

The exchange-lattice relaxation rate can then be written²⁶:

$$T_{\text{EL}}^{-1} = \frac{1}{2} \frac{\sum_{nm} W_{mn} (E_m - E_n)^2}{\text{Tr} \mathcal{H}_e^2}. \quad (\text{B3})$$

W_{mn} is the transition probability between two eigenstates m and n of the Hamiltonian \mathcal{H}_e having energies E_m and E_n induced by the perturbation $\mathcal{H}_1(t)$ which arises from the diffusion modulation of \mathcal{H}_e and will now be defined precisely. W_{mn} is given²⁷ by the spectral density $J(\omega_{mn})$ related by Eq. (10) to the correlation function $G_{mn}(\tau)$ defined as:

$$G_{mn}(\tau) = \hbar^{-2} \{ \langle m | \mathcal{H}_1(t-\tau) | n \rangle \langle n | \mathcal{H}_1(t) | m \rangle \}_{\text{av}}. \quad (\text{B4})$$

The reciprocal correlation time $(\tau_c')^{-1}$ of $G(\tau)$ being small compared with the frequencies ω_{mn} (which is reasonable since τ_c' is *a priori* of the same order of magnitude as τ_c), we can assume the spectral density $J_{mn}(\omega)$ of $G_{mn}(\tau)$ to satisfy:

$$J_{mn}(\omega) \sim \frac{2G_{mn}(0)}{\omega^2 \tau_c'} = \frac{1}{\pi \omega^2 \tau_c'} \int_{-\infty}^{+\infty} J_{mn}(\omega) d\omega,$$

when

$$\omega \tau_c' \gg 1.$$

Then

$$T_{\text{EL}}^{-1} = \frac{\hbar^2 \sum_{nm} J(\omega_{mn}) \omega_{mn}^2}{2 \text{Tr} \mathcal{H}_e^2} = \frac{1}{\tau_c'} \frac{\text{Tr} \langle \mathcal{H}_1^2 \rangle_{\text{av}}}{\text{Tr} \mathcal{H}_e^2}. \quad (\text{B5})$$

Let us now consider two specific nuclei i and j diffusing through the crystal. We write the exchange interaction between these nuclei

$$\mathcal{H}_{ij} = \hbar J \mathbf{I}^i \cdot \mathbf{I}^j \delta_{ij}, \quad (\text{B6})$$

δ_{ij} being a function of the distance $|\mathbf{r}^i - \mathbf{r}^j|$ between the two nuclei: δ_{ij} is 1 when they are first neighbors (of which each atom has z) and 0 otherwise. Since, because of atomic diffusion, two spins which at a given time do not interact may later become neighbors, δ_{ij} is a function of time.

We then write the perturbation $\mathcal{H}_1(t)$ of the exchange interaction due to the diffusion:

$$\mathcal{H}_1(t) = \frac{1}{2} \hbar J \sum'_{i \neq j} \mathbf{I}^i \cdot \mathbf{I}^j \delta_{ij}(t), \quad (\text{B7})$$

\sum' not being a restricted sum as \sum' .

Assuming $\langle \delta_{ij} \delta_{i'j'} \rangle_{\text{av}} = 0$ when $i \neq i'$, $j \neq j'$, it is readily seen that:

$$\frac{\text{Tr} \mathcal{H}_e^2}{zN} = \frac{\text{Tr} \langle \mathcal{H}_1^2 \rangle_{\text{av}}}{N \sum_i \langle \delta_{ij} \rangle_{\text{av}}}, \quad (\text{B8})$$

$$\frac{1}{T_{\text{EL}}} = \frac{1}{\tau_c'} \frac{1}{z} \frac{\sum_i \langle \delta_{ij}^2 \rangle_{\text{av}}}{z},$$

²⁶ L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

²⁷ See Ref. 19, p. 273.

and

$$G_{mn}(\tau) = \frac{1}{2} J^2 \sum_{i \neq j} \langle \delta_{ij}(t) \delta_{ij}(t+\tau) \rangle_{\text{av}} |\langle m | \mathbf{I}^i \cdot \mathbf{I}^j | n \rangle|^2.$$

In order to calculate τ_c' , we may as well calculate the correlation time of

$$K(\tau) = \sum_i \langle \delta_{ij}(t) \delta_{ij}(t+\tau) \rangle_{\text{av}}$$

which we shall define by the condition that

$$S(\omega) \sim (2/\omega^2 \tau_c') K(0) \quad \text{for } \omega \tau_c' \gg 1,$$

where

$$S(\omega) = \int_{-\infty}^{+\infty} K(\tau) e^{-i\omega\tau} d\tau.$$

Then

$$T_{\text{EL}}^{-1} = \frac{K(0)}{z\tau_c'} = (2z)^{-1} \lim_{\omega \rightarrow \infty} [\omega^2 S(\omega)]. \quad (\text{B9})$$

This can be computed using the theory of random flights, in the same way as Torrey used it to treat the nuclear spin relaxation by translational diffusion.¹⁶ It is easily found that for a hexagonal close-packed lattice (β -phase He³), in the limit $\omega \rightarrow \infty$, $S(\omega) \sim (32/\omega^2 \tau_c)$, which gives for the exchange-lattice relaxation time

$$T_{\text{EL}} = \frac{3}{4} \tau_c. \quad (\text{B10})$$

Approximately the same result will hold for any lattice.

Second-Order Hyperfine Structure in Hydrogenic Atoms*

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A calculation of the hyperfine splittings in the $1s$ and $2s$ levels of hydrogenic atoms is made. Second-order terms in the nuclear magnetic dipole moment and terms of comparable magnitude arising from nuclear structure effects are calculated. Also included is a term derived by the use of "uncrossed" and "crossed" photon diagrams; this term is necessary because the one-electron Dirac Hamiltonian which is used evidently does not properly take certain quantum electrodynamic effects into account. In order to compare with experiment the ratio of the hyperfine splitting in the $2s$ state to the splitting in the $1s$ state is taken and evaluated for the case of the hydrogen atom; this result is combined with a previous result and the final theoretical value of $\frac{1}{3}(1.00003445 \pm 0.00000002)$ is in agreement with the experimental value of $\frac{1}{3}(1.000034495 \pm 0.000000060)$. Complete agreement has not yet been reached with respect to the splittings themselves. The calculation consists in solving the separated radial equations arising from the Dirac Hamiltonian in which the nuclear magnetic moment and the finite size of the nucleus are considered as perturbations. An iteration scheme is devised which uses certain properties of the unperturbed solution; this method may well have applications elsewhere.

I. INTRODUCTION

THE present paper is concerned with an attempt at a relativistic calculation of contributions to the shift and splitting of energy levels in the s states of hydrogenic atoms arising from hyperfine structure (hfs) interaction in second order. The consideration of this problem was prompted originally by the existence of two apparent discrepancies between experiment¹ and

first-order hfs calculation.^{2,3} More recent experimental values⁴ do not remove the discrepancies. The first was in respect to the ratio of hfs splittings in the $2s$ and $1s$ states of hydrogen. Since that time some errors in the original calculations have been uncovered by Zwanziger⁵ and their correction has eliminated the discrepancy. A recent calculation by Sternheim⁶ gives additional terms to the ratio; the agreement between theory and experi-

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¹ P. Kusch, Phys. Rev. **100**, 1188 (1955); and J. W. Heberle, H. A. Reich, and P. Kusch, Phys. Rev. **101**, 612 (1956).

² M. Mittleman, Phys. Rev. **107**, 1170 (1957).

³ For a review of the subject see G. W. Series, *Spectrum of Atomic Hydrogen* (Oxford University Press, London, 1957), especially Chap. XI.

⁴ F. M. Pipkin and R. H. Lambert, Phys. Rev. **127**, 787 (1962). J. Gruenebaum and P. Kusch, Columbia Radiation Laboratory Quarterly Report, 14 September 1960 (unpublished); their result is $\Delta\nu(2s) = 177\,556.842 \pm 0.010$ kc/sec for H^1 .

⁵ D. E. Zwanziger, Phys. Rev. **121**, 1128 (1961).

⁶ M. M. Sternheim, Phys. Rev. **130**, 211 (1963).