this state whatever their number. There is no freedom in this number once the matter populations are given, because of conservation laws. Hence the photon entropy is always zero, and the above-mentioned equal matter-state population determines the equilibrium condition for the whole system. This is in agreement with the formal calculations of Sec. II.

The identification of equal matter populations with infinite temperature is inapplicable, because it assumes a canonical rather than the microcanonical ensemble. Similarly, the Planck law is not to be expected here for the photons. For the same reason the detailed-balance argument given above is not valid in this case. It is, however, possible within the formal framework of the master equation to show what the appropriate form of detailed balance is. Instead of Eq. (3.2), one may obtain directly from the master equation or from Eq. (2.4) for the generating function

$$\frac{d\bar{n}_\nu}{dt}=A\langle(n_\nu+1)n_2\rangle_{\mathrm{av}}-\langle n_\nu n_1\rangle_{\mathrm{av}}. \tag{3.6}$$

In the usual systems in contact with a heat reservoir it is justifiable to neglect correlations and take

$$\langle n_\nu n_1\rangle_{\mathrm{av}}=\bar{n}_\nu\bar{n}_1\,,\quad \text{etc.} \tag{3.7}$$

However, in our model the correlations produced by the conservation laws are so strong that this assumption is not justifiable. Indeed, one finds for our model that the difference between the right- and left-hand sides of Eq. (3.7) is not zero, but $N/4$.

In summary, all of the anomalies in this model can be understood physically as due to the constraints imposed on the system by the conservation laws.

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Nuclear Relaxation in Solid He^3 at Low Temperatures*†

E. R. Hunt,‡ R. C. Richardson,§ J. R. Thompson,‖ R. A. Guyer,** and Horst Meyer
Department of Physics, Duke University, Durham, North Carolina

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We have made measurements of the nuclear relaxation time τ in the bcc phase of solid He^3 for temperatures between 0.3 and 0.04°K. The relaxation times were found to decrease when the size of the sample chamber was reduced. In the range $0.2\gtrsim T\gtrsim 0.1$°K, τ is temperature-independent and inversely proportional to the exchange parameter J for our two smaller sample chambers. The relaxation is attributed to the single-phonon process occurring in the magnetically irregular region of the sample boundary; Zeeman and exchange energy in the bulk He^3 then diffuse to the boundary in the time τ. The diffusion, due to the exchange interaction, is temperature-independent. Below 0.1°K, τ increases mildly with temperature in the smallest chamber. The temperature dependence of τ below 0.1°K indicates a possible phonon bottleneck. An order-of-magnitude calculation shows that at about 0.2°K the rate at which the spin system puts energy into the lattice becomes comparable to the rate at which the lattice can transfer that energy to the bath. The results can be used to estimate the nuclear relaxation time in the millidegree region where the magnetic transition is expected.

I. INTRODUCTION

As a consequence of their large zero-point motion, the atoms in solid He^3 experience an unusually large exchange interaction. This interaction, which is described by the Hamiltonian $\mathcal{H}_{12}=-\hbar J\mathbf{I}_1\cdot\mathbf{I}_2$, gives rise to a manifold of energy levels called the exchange system. The properties of this system have been the subject of a great deal of experimental and theoretical attention.[1–7] The strength of the exchange interaction J characterizes the low-temperature thermal and magnetic properties of solid He^3. For example, magnetic ordering is expected to take place at a temperature of the order of $\hbar J/k_B$. In the bcc phase at the molar volume $v=24.0$ cm^3/mole, $J/2\pi=25$ MHz, which corresponds to a transition temperature T_N of about 1.8

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† Portions of this work have been reported elsewhere: E. R. Hunt, R. C. Richardson, J. Thompson, R. Guyer, and H. Meyer, Bull. Am. Phys. Soc. **12**, 95 (1967); Science **154**, 421 (1966).

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§ Present address: Cornell University, Ithaca, New York.

‖ U. S. Steel Fellow.

** A. P. Sloan Fellow.

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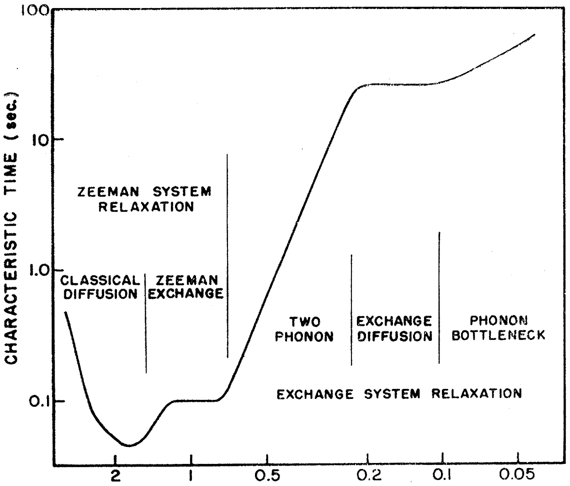

FIG. 1. Schematic behavior of the spin relaxation time τ as a function of temperature.

m°K.[8] At the smallest molar volume in the bcc phase, $v = 19.7$ cm^3/mole, $J/2\pi \approx 0.7$ MHz, one finds $T_N \approx 0.05$ m°K. The influence of the exchange interaction on the magnetic and thermal properties is very evident at sufficiently low temperatures and can be studied especially well employing nuclear magnetic resonance techniques.

This paper reports measurements of the exchange-lattice relaxation time τ over the temperature range $0.3 \gtrsim T \gtrsim 0.04$°K. The Zeeman system, which is in relatively good thermal contact with the exchange system in this temperature range, is used both as a heater and a thermometer for the exchange system. Our results suggest that below 0.2°K the relaxation takes place at a boundary of the sample and the relaxation time is the characteristic time for the energy to diffuse to that boundary. At temperatures less than 0.1°K, diffusion continues to transport energy to the boundary, but a phonon bottleneck inhibits the transfer of the energy out of the solid. The results permit us to estimate spin relaxation times down into the millidegree region.

II. EXPERIMENTAL

Relaxation measurements were carried out by means of pulse techniques on samples ranging in molar volume from 24.1 to 20.8 cm^3/mole in sample chambers of different sizes. After forming the He^3 sample in the chamber, the transverse relaxation time T_2 was measured to determine J and the density by comparison with previous results.[4] The exchange-lattice relaxation time was measured by partially saturating the spin system with several 90° pulses and then observing the recovery by means of recurring small angle pulses. A boxcar integrator made it possible to plot the recovery of the nuclear signal on a chart recorder. The Larmor frequency $\omega/2\pi$ was chosen to make the Zeeman specific heat $C_z = \frac{1}{4}[(\hbar\omega)^2/k_BT^2]$ approximately 20% of that of the exchange system $C_E = \frac{3}{4}[(\hbar J)^2/k_BT^2]$. Thus any effects due to the Zeeman system are small while still permitting us to heat the exchange system.

Sample chambers of three different sizes were employed in the experiment. Chamber I had a radius of 0.1 cm and a length of 1 cm. Chamber II was the annular region between two 1-cm-long concentric cylinders of radius 0.14 and 0.15 cm. Chamber III was the same as I but was filled with 200 No. 40 AWG Formex insulated copper wires. In this chamber, the solid He^3 crystals grew in the space between the wires and had a typical dimension of 10^{-3} cm. The He^3 had an impurity content of 200 ppm of He^4, as measured with a mass spectrometer.

The experiment was performed in a cryostat using adiabatic demagnetization of chromium methylammonium alum. A Speer 220-Ω resistor was calibrated against the susceptibility of solid He^3 ($v = 23$ cm^3/mole) which obeys Curie's law within our experimental error.

III. RESULTS AND DISCUSSION

Before presenting the results of this work, it will be useful to review what is already known about the relaxation mechanisms operating in solid He^3. Energy is put into the spin system by placing the sample in an

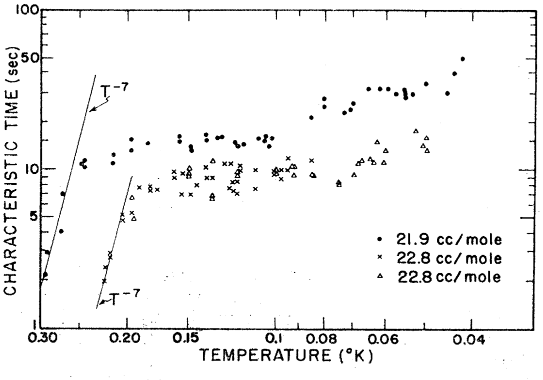

FIG. 2. Relaxation data for the two molar volumes 21.9 cm^3/mole ($J/2\pi = 5.5$ MHz) and 22.8 cm^3/mole ($J/2\pi = 10.3$ MHz). The data at 22.8 cm^3/mole were obtained in different runs.

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[8] The transition temperature T_N can be estimated from the theory of Domb and Sykes [Proc. Roy. Soc. **A240**, 214 (1957)]. These authors show that for a Heisenberg ferromagnet with a spin $\frac{1}{2}$ in a bcc lattice (eight nearest neighbors) the Curie temperature T_c is given by $T_c = 0.66 \times 2(J\hbar/k_B)$. However there is some evidence that the coupling in solid He^3 is antiferromagnetic [A. L. Thomson, H. Meyer, and P. N. Dheer, Phys. Rev. **132**, 1455 (1963); D. H. Thouless, Proc. Phys. Soc. **86**, 893 (1965); L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters **14**, 133 (1965).] The relation between the Néel temperature T_N and the Curie temperature T_c is given by G. S. Rushbrooke and P. J. Wood [Mol. Phys. **6**, 409 (1963)] for the same $|J|$. For a system of spins $\frac{1}{2}$ and eight nearest neighbors, one then obtains $T_N = 1.11 T_c$. Unpublished calculations on the melting curve by two of us [J. R. T. and H. M., Cryogenics (to be published)] show that the highest molar volume of solid He^3, which is stable below about 2 m°K is 24.0 cm^3/mole. For this molar volume, one calculates $T_N = 1.8 \times 10^{-3}$°K.

externally applied steady magnetic field H_0 and saturating with rf pulses the resulting Zeeman system (the manifold of energy levels for the system which arise because of the coupling $\mathbf{I}\cdot\mathbf{H}_0$). Relaxation of the Zeeman energy may proceed either directly to the lattice or indirectly via the exchange system to the lattice. In the latter case the recovery is characterized by two time constants. A quantitative description of the different energy reservoirs and relaxation times is given in Refs. 2–4.

Region above 1.5°K. Above 1.5°K both the Zeeman system and the exchange system are strongly coupled to the lattice although relatively weakly to one another. Energy put into the Zeeman system is delivered directly to the lattice due to the modulation of the dipole-dipole interaction by classical diffusion.

Region between 1.5 and 0.6°K. In the neighborhood of 1°K, the Zeeman system becomes uncoupled from the lattice: the energy in the Zeeman system is delivered to the exchange system (which continues to be strongly coupled to the lattice) due to the modulation of the dipole-dipole interaction by exchange. This relaxation mechanism is temperature-independent for $T \gg T_N$.

Region between 0.6 and 0.2°K. Through this region, the coupling between the exchange system and the lattice becomes weaker than that between the Zeeman and exchange system. The latter two come into equilibrium with one another and relax collectively to the lattice. The mechanism of relaxation is the two-phonon (Raman) process which is due to the modulation of the exchange interaction by lattice vibrations. This process has a strong temperature dependence, T^{-m}, $6<m<10$.

Region between 0.2 and 0.1°K. At about 0.2°K, the exchange-lattice relaxation time becomes temperature-independent and the time dependence of the relaxation process becomes nonexponential. This behavior was first reported by Richards, Hatton, and Giffard.[3]

We have made a detailed investigation of the characteristic time in the temperature range $0.3 \gtrsim T \gtrsim 0.04$°K and over a wide range of molar volumes. The signal-to-noise ratio in the recovery curve was relatively poor because the rf pulses, used to measure the magnetization, were kept small. Also the departure of the recovery from a simple exponential (see below) made the analysis more involved in the region below 0.2°K. These circumstances accounted for most of the scatter in the data. In Fig. 2, data at molar volumes of 21.9 and 22.8 cm^3 are shown. Detailed studies showed three characteristic features of the relaxation process in the temperature range $0.2 \geqslant T \geqslant 0.1$°K.

(1) The relaxation rate depended on the size of the sample chamber. In three different sized chambers a variation of as much as a factor of 20 was observed, the smallest chamber having the shortest relaxation time.

(2) In all of the sample chambers, the characteristic time was temperature-independent: In the two smallest chambers it was inversely proportional to J (see Fig. 3).

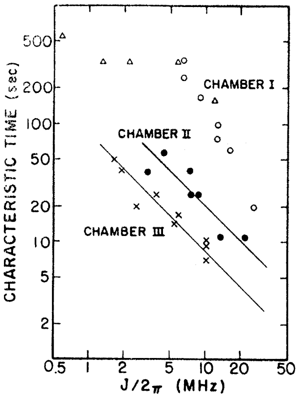

FIG. 3. The temperature-independent values of the characteristic relaxation time τ for our three chambers. The smaller chambers have the shorter times. The lines drawn show the slope for $\tau \propto J^{-1}$. The triangular points represent the data of Richards, Hatton, and Giffard (Ref. 3), and are plotted using values of J obtained in Ref. 4.

(3) The time dependence of the relaxation process was not exponential in the usual sense and was qualitatively the same for the various densities and sample chamber sizes. The extensive data were analyzed by plotting the logarithm of the fractional change in magnetization versus time and then measuring the slope at times long after the saturating pulses. These resulting times τ were empirically found to be approximately $3\tau_D$ where τ_D was obtained by a more exact analysis according to Eq. 3 derived below.

These observations suggest the following interpretation. The energy put initially into the Zeeman system is rapidly transferred between it and the exchange system bringing the two into equilibrium with one another. Relaxation of the coupled system proceeds by diffusion of the energy to the boundary of the sample where the exchange system and He^3 lattice interact strongly. At the boundary, energy is delivered from the Zeeman-exchange systems to the lattice and then from the lattice to the surrounding reservoir (bath). This latter process (lattice)-(bath) takes place very rapidly so that the characteristic time for the over-all relaxation is the time required for the energy, mainly exchange energy to diffuse to the boundary. The diffusion process is exchange diffusion and its characteristic time is

$$\tau_D = R^2/4D_E, \qquad (1)$$

where R is the distance the energy must diffuse and D_E is the exchange diffusion constant which is proportional to J and temperature-independent[9] for $T \gg T_N$. A temperature-independent diffusion constant has been observed in solid He^3 below 1°K by Reich[1,10] using NMR techniques. He attributed this result to exchange. If we associate Reich's value of the diffusion constant, 2×10^{-8} cm^2/sec at $V=22$ cc/mole, with D_E and using $R=10^{-3}$ cm for sample chamber III we find $\tau_D = 8$ sec. The relaxation time observed for these conditions was 5 sec. Thus the observed relaxation time is of the same

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[9] See for instance, P. G. de Gennes, J. Phys. Chem. Solids **4**, 223 (1958); H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962); H. S. Bennett and P. C. Martin, Phys. Rev. **138**, A608 (1965).

[10] *Note added in proof.* More recent measurements have been reported by Hunt, Thompson and Meyer, Phys. Letters **25A**, 313 (1967).

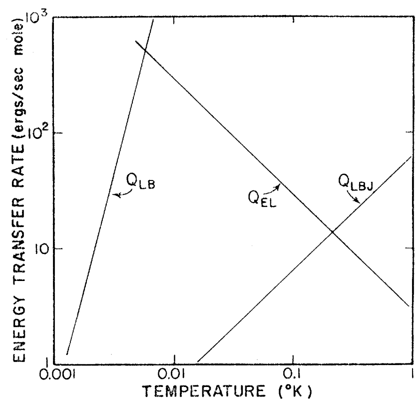

FIG. 4. The energy transfer rates ($\Delta T=0.1T$) for the (lattice)–(bath), (lattice)–(bath) at frequency J within a range J and (exchange)–(lattice) processes. The intersection of the lines labeled Q_{EL} and Q_{LBJ} define the bottleneck temperature T_b.

order as the diffusion time τ_D, depends correctly on J, and is temperature-independent.

As seen in Fig. 3, the dependence of the relaxation time on the sample chamber size is in qualitative agreement with the expectation for the diffusion mechanism. However, the quantitative agreement is poor. We suspect that this is due to the conditions under which the samples were formed. The various size sample chambers can only set upper limits on the size of the crystallites.

The time dependence of the relaxation process can be estimated for the diffusion mechanism by solving the diffusion equation

$$\dot{\beta}_E=D_E\nabla^2\beta_E\,, \tag{2}$$

where $k_B\beta_E=T_E^{-1}$ and T_E is the temperature of the exchange system. For computational purposes we use the following model: (a) The geometry of the sample in the space between the copper wires is approximated by a long cylinder whose radius R is the typical distance to the boundary of the space; (b) the speed of the relaxation process operating in the boundary region is taken into account by assuming that all of the energy in the exchange system which reaches the boundary is taken away; and (c) the time dependence of the decay of the energy at the center of the cylinder is taken to be typical of the time dependence of the decay of its average energy. If at $t=0$ the temperature of the cylinder is uniformly $T_E(0)$, then at time t later one has

$$\beta_E(t)-\beta_E(0)=[\beta_E(\infty)-\beta_E(0)]\times\exp[-R^2/(4D_Et)]\,. \tag{3}$$

This equation describes the time dependence of the observed relaxation process accurately for times greater than τ_D.

Region below 0.1°K. For temperatures below 0.1°K the relaxation times increase with decreasing temperature for chamber III, the smallest one, and are proportional to J^{-1} (see Fig. 2). We believe that the (lattice)–(bath) process which operates rapidly at $T>0.1$°K has slowed sufficiently so that at $T<0.1$°K a lattice-to-bath bottleneck is observed.

We suggest the following explanation for this bottleneck. The coupling of the exchange system to the lattice in the magnetically irregular region near the boundary of the sample gives rise to a one- or two-phonon process much faster than that which occurs in the bulk of the sample. At all temperatures this process is sufficiently fast so that energy delivered to the boundary region by the exchange diffusion process is immediately transferred to the lattice. The bottleneck occurs in the (lattice)–(bath) relaxation process. Although the process at the boundary is very fast and therefore its characteristic time does not enter into the present considerations, the qualitative nature of this process is of great importance. If it is a two-phonon process, the energy in the exchange system is delivered to all of the phonons which in turn transfer it to the bath at the rate[11]

$$Q_{\mathrm{LB}}=\Gamma(Ac/V)\tfrac{1}{4}[E(T_L)-E(T)]\,, \tag{4}$$

where A is the area of contact between the lattice and bath, V the volume of the sample, c the velocity of sound of the He^3 and Γ a measure of the acoustic mismatch between the He^3 and bath material (in this case the insulated copper wires). $E(T)$ is the energy in the He^3 lattice at temperature T. Whereas, if the process is a one-phonon process, the energy in the exchange system is delivered to a small band of phonons with energy range $\Delta J=\alpha J$ at frequency J, which in turn delivers it to the bath at the much slower rate[12]

$$Q_{\mathrm{LBJ}}=\frac{9\alpha N}{\tau_{\mathrm{LB}}}\left(\frac{\hbar J}{k_B\Theta}\right)^3 k_B\Delta T\,, \tag{5}$$

where $\tau_{\mathrm{LB}}=V/(\Gamma Ac)$. N is the number of He^3 atoms, and Θ is the Debye temperature of the He^3. A bottleneck will occur if the rate at which the exchange system delivers energy to the lattice

$$Q_{\mathrm{EL}}=\frac{3}{4}\,\frac{N}{\tau}\,\frac{(\hbar J)^2}{k_B}\,\frac{\Delta T}{T^2} \tag{6}$$

exceeds the rate at which the lattice can transfer this energy to the bath. We have calculated the energy transfer rates for $\Delta T=0.1T$ given by Eqs. (4), (5), and (6) for the solid He^3 sample at $v=24$ cm^3/mole and using the following values of the various constants: $(J/2\pi)=25$ MHz, $\Theta=20$°K,[13] $c=2\times10^4$ cm/sec, $V/A=(1/2)\times10^{-3}$cm, $\Gamma=10^{-1}$, $\alpha=1$, $\tau_{\mathrm{LB}}=(1/4)\times10^{-6}$ sec, and $\tau=3$ sec.

The results are shown in Fig. 4. We note that if the exchange to lattice process is a one-phonon process, the bottleneck occurs at temperature T_b for which

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[11] W. A. Little, Can. J. Phys. **37**, 334 (1959).

[12] See, for example, J. A. Giordmaine and E. R. Nash, Phys. Rev. **138**, A1510 (1965).

[13] H. H. Sample and C. A. Swenson, Phys. Rev. **158**, 188 (1967).

$Q_{\mathrm{EL}}=Q_{\mathrm{LBJ}}$, which is given by

$$T_b^2=\frac{\Theta^2}{12\alpha}\left(\frac{k_B\Theta}{\hbar J}\right)\frac{\tau_{\mathrm{LB}}}{\tau}. \tag{7}$$

Since $\tau_{\mathrm{LB}}\propto\Theta^{-1}$ and $\tau\propto J^{-1}$, then $T_b\propto\Theta$, the temperature at which the bottleneck occurs, is a mild function of molar volume. The value $T_b=0.2$°K is consistent with our observations, and leads us to assume that such a process operates rapidly in the region of the sample boundary. The two-phonon process would not form a bottleneck until $Q_{\mathrm{LB}}\simeq Q_{\mathrm{EL}}$, which occurs at about 5m°K.

At temperatures above T_b the restricted band of phonons is able to transfer the energy delivered to it (by the exchange system) to the bath without being overdriven and heated. At temperatures below T_b this is not the case and in the limit where the (lattice)–(bath) process determines the observed relaxation time we have $T_E\simeq T_L$ and

$$\frac{dE_E}{dt}=\frac{3}{4}\left(\frac{\hbar J}{k_B}\right)^2\frac{k_Bd\beta_E}{dt}=Q_{\mathrm{LBJ}}. \tag{8}$$

When $T_E\approx T$, Q_{LBJ} can be written

$$Q_{\mathrm{LBJ}}\approx 9\alpha N\left(\frac{\hbar J}{k_B}\right)^3\frac{k_BT^2}{\tau_{\mathrm{LB}}}(\beta_E-\beta). \tag{9}$$

Equations (8) and (9) combine to give the relaxation time associated with the bottleneck

$$\tau_b=\frac{1}{12\alpha}\left(\frac{k_B\Theta}{\hbar J}\right)\left(\frac{\Theta}{T}\right)^2\tau_{\mathrm{LB}}=\tau\left(\frac{T_b}{T}\right)^2. \tag{10}$$

The actual shape of the recovery is, of course, nonexponential.[14]

Since the (exchange)–(lattice) and (lattice)–(bath) relaxation processes are in series, we expect the over-all relaxation time to have the form

$$\tau(\mathrm{total})=\tau+\tau_b=\tau[1+(T_b/T)^2]. \tag{11}$$

As remarked above, $T_b\propto\Theta$; hence the dominant molar volume dependence of this combined relaxation time at all temperatures is the J dependence in τ. For the data given in Fig. 2 for the volume 21.9 cm^3/mole, we obtain $T_b=0.06\pm0.02$°K using Eq. (11). The value given by Eq. (7) for this volume is 0.2°K and hence the calculated and observed bottleneck temperatures are in order of magnitude agreement.

It should be pointed out that the mild temperature dependence below about 0.1°K may be influenced by the isotopic phase separation[15] in our samples. At pressures close to the melting curve, the temperature of the phase separation is about 0.08°K for a sample with 200 ppm He^4, which is the region where the temperature dependence of τ is observable. Therefore the observed characteristic temperature T_b may differ from that for pure He^3.

It is interesting to compare the present work to the recent results of Osgood and Goodkind.[16] They estimated the spin relaxation time of solid He^3 at 7.5 m°K, to be less than 10 min for pressure of 36 atm. Part of their sample chamber was also packed with copper wires with about the same surface to volume ratio as our chamber III. If we assume the relaxation mechanism at the boundary does form a bottleneck, we can use Eq. (11) to estimate their time. Using $\tau=3$ sec and $T_b=0.05$°K appropriate to $v=24$ cm^3/mole, we find a characteristic time of 2 min. However, according to their Fig. 1, Osgood and Goodkind did not have the copper wires in the He^3 where the measurements was taken and, therefore, their time probably was limited by the diffusion through He^3 to their auxiliary chamber.

IV. SUMMARY

Below 0.2°K it is found that diffusion due to exchange is transporting nuclear spin energy to a boundary where relaxation occurs. The relaxation process at the boundary is predominantly a one-phonon process. The emitted phonons are in good contact with the "bath" (copper wires) above 0.1°K. Below that temperature, the contact lessens and results in a bottleneck for the over-all relaxation process.

These experiments permit us to estimate the optimum conditions and the corresponding times for cooling He^3 nuclei to the millidegree regions by means of heat conduction. The best conditions for heat transfer are to have He^3 with a large exchange and in the form of very small crystals packed between copper wires. The time estimates for He^3 at about 24 cm^3/mole ($P=35$ atm) are consistent with the time constants recently observed by Osgood and Goodkind.[16]

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[14] A very similar relaxation process (spin-lattice-bath) has been considered by B. W. Faughan and M. W. P. Strandberg, J. Phys. Chem. Solids **19**, 155 (1961).

[15] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Letters **1**, 218 (1962).

[16] E. B. Osgood and J. M. Goodkind, Phys. Rev. Letters **18**, 894 (1967).