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Longitudinal Spin Relaxation in Solid He^3†

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Calculations of the spin-lattice relaxation time, T_1, for He^3 nuclei in solid He^3 are made and the results are compared with experiment. A simple heuristic argument is first used which treats the two important relaxation mechanisms—diffusion and Zeeman-exchange coupling—as effectively independent and then a more precise calculation is made which takes into account interference effects. An expression for the exchange integral J is obtained as a function of molar volume which, compared with the experiment, indicates an effective, reduced dipolar coupling. The effect of zero point motion on the dipolar interaction is investigated and using a very simple lattice model, it is found to be an important (but not necessarily the major) factor.

I. INTRODUCTION

Nuclear magnetic resonance measurements on solid He^3 have recently been made[1–5] to determine (as a function of temperature and/or pressure) the nuclear magnetic susceptibility, self-diffusion constants, and spin-spin, T_2, and spin-lattice, T_1, relaxation times. The results of the spin-lattice relaxation measurements are of particular interest since they are characteristic of a nuclear spin system which relaxes to thermal equilibrium with the lattice by way of both self-diffusion and spin-spin interactions. For solid He^3 these relaxation mechanisms are not independent,[3] and a calculation of T_1 must include interference effects. This calculation is performed and an expression for T_1 is obtained which is in agreement with experimental data. Using the correlation time τ for self-diffusion obtained from self-diffusion measurements,[3] the exchange integral J is obtained by fitting the experimental values of T_1 to the theory in the region where T_1 is independent of temperature.

Before proceeding to a proper calculation of T_1, the available experimental data are reviewed and a simple calculation of T_1 is made, assuming that all interference effects can be neglected. This latter calculation is performed because it (1) results in a simple expression which gives the correct general behavior of T_1 as a function of the temperature T and the magnetic field H, and (2) gives insight into how the two relaxation mechanisms affect each other.

Solid He^3 exists at low temperatures $\approx 1°\text{K}$ and high pressures ≈ 30 atm in either an α phase (body-centered cubic), β phase (hexagonal close-packed), or γ phase (face-centered cubic). The nuclear spin of He^3 is $I=\frac{1}{2}$ and it has a relatively large gyromagnetic ratio, γ, of approximately 75% of the gyromagnetic ratio of the proton. As pointed out by Bernardes and Primakoff,[6] there is a sizeable overlap of the atom orbitals of nearest neighbors so that one can expect exchange effects to be important. The first measurements of the spin-lattice relaxation time T_1 in solid He^3 were made by Goodkind and Fairbank[1] (open circles in Fig. 1) who found that as the temperature was increased the relaxation rate T_1^{-1} increased to some maximum value and then decreased again. These measurements were made in the α phase at a molar volume of approximately 20.12 cm^3/mole, and the resultant behavior of T_1 was interpreted as being due to the diffusion relaxation mechanism investigated by Bloembergen, Purcell, and Pound (BPP),[7] which leads to an expression for T_1 (as corrected by Kubo and Tomita),[8] given by

$$\frac{1}{T_1}=\frac{2}{5}\frac{I(I+1)\mu_0^4}{\hbar}\sum_j r_{ij}^{-6}\left[\frac{\tau}{1+\omega^2\tau^2}+\frac{4\tau}{1+4\omega^2\tau^2}\right], \quad (1)$$

where μ_0 is the magnetic moment of the He^3 nucleus, r_{ij} is the distance between the ith and jth nucleus, $\omega=\gamma H$ (H is the applied dc magnetic field), and τ is the correlation time associated with the diffusion. The correlation time τ has the form

$$\tau=\tau_0\exp(W/T), \quad (2)$$

where τ_0 and W are constants, and this accounts for the linearity of $\ln T_1$ versus $(1/T)$ as plotted in Fig. 1 for large values of $1/T$. Equation (1) gives the correct general shape for T_1 (see upper solid line) but deviates from the data by approximately 15%. The solid curve used here was obtained by using the most probable values of W and τ_0 given by $W=13.6°\text{K}$ and $\tau_0=5.32\times10^{-12}$ sec^3. Because of the uncertainty in the value of τ_0, the solid curve can be shifted to the right until the left-hand side of the curve fits well with the data, and it can be shifted an equal distance to the left.

Shortly after the results of Goodkind and Fairbank

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[1] J. M. Goodkind and W. F. Fairbank, Phys. Rev. Letters 4, 458 (1960).

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

[3] H. A. Reich, Phys. Rev. **129**, 630 (1963), and *Proceedings of the Second Symposium on Liquid and Solid He*^{3} (Ohio State University Press, Columbus, Ohio, 1960).

[4] R. L. Garwin and A. Landesman, *Proceedings of the Eighth International Conference on Low-Temperature Physics* (Butterworths Scientific Publications Ltd., London, 1962).

[5] A. L. Thompson, H. Meyer, and P. N. Dheer, Phys. Rev. **132**, 1455 (1963).

[6] N. Bernardes and H. Primakoff, Phys. Rev. **119**, 968 (1960).

[7] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[8] R. Kubo and H. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

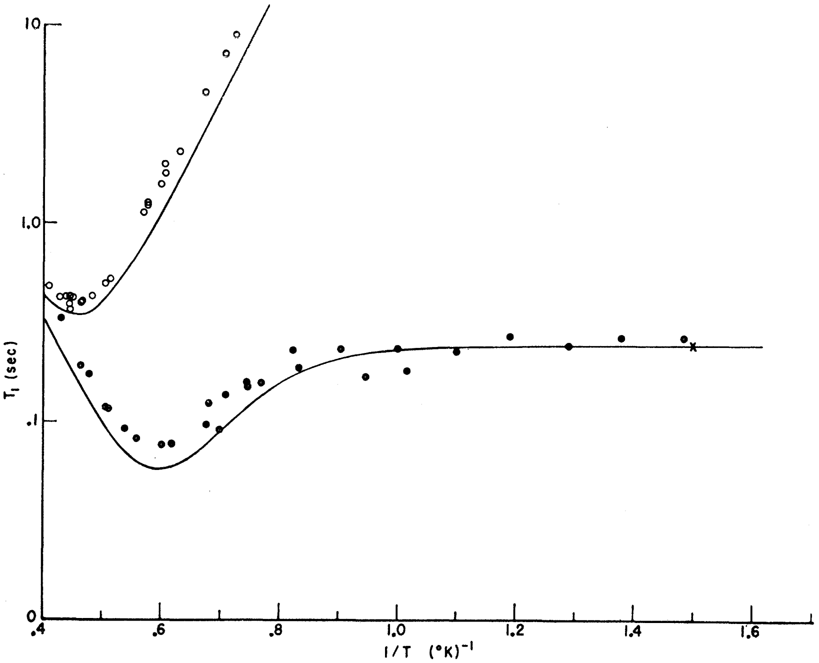

FIG. 1. Spin-lattice relaxation time T_1 versus $(1/T)$ for solid He^3 at 20.12 cm^3/mole. The open circles are the data of Goodkind and Fairbank at 30.4 Mc/sec, the solid circles are data of Reich at 5.224 Mc/sec. The solid lines are given by theory.

were published, Haskell Reich[3] reported further measurements of T_1 as a function of $1/T$ at lower magnetic fields. The results of Reich show the same general diffusion relaxation behavior for small values of $1/T$ but were surprisingly independent of temperature for large values of $1/T$. Further measurements in agreement with these were made, and those data points corresponding to the molar volume of 20.12 cm^3/mole have been plotted as solid circles in Fig. 1. The theory of BPP[7] is again in good agreement with the data in the region before T_1 becomes independent of $1/T$, but some other mechanism is necessary to explain the behavior of T_1 at lower temperatures. Further experiments (in the β phase) in the temperature-independent region have shown that T_1 may be written approximately as

$$T_1 = (T_2)_0 \exp(H^2/2H_e^2), \tag{3}$$

where $(T_2)_0$ and H_e are both constants.[3] Relaxation of this character was first investigated by Kronig and Bouwkamp,[9] who considered the effect of the spin-spin coupling at low magnetic fields in relaxing the magnetization. Since $(T_2)_0$ is independent of temperature (as long as the molar volume remains constant), the resulting relaxation due to spin-spin coupling should be independent of temperature, and consequently the low-temperature region of Fig. 1 is identified as being dominated by this relaxation mechanism. The 1611-G magnetic field at which these experiments were performed is considered *low* because of the large effective exchange field present which is of the same order of magnitude.

II. APPROXIMATE CALCULATION

If two independent relaxation mechanisms are present, then there results a relaxation rate $1/T_1$, given by

$$1/T_1 = (1/T_1)_a + (1/T_1)_b, \tag{4}$$

and in our case (assuming for the moment that the diffusion and spin-spin relaxation mechanisms are independent) we might expect Eqs. (1) and (3) to be inserted above. This is too great a simplification, since in both the high- and low-temperature regions Eq. (3) would predict that the spin-spin relaxation would dominate, which is not observed experimentally. What appears to happen is that at high temperatures the diffusion mechanism dominates and at lower temperatures the spin-spin relaxation mechanism dominates. This comes about for two reasons: (1) At high temperatures the rapid diffusion of the atoms which gives rise to the diffusion relaxation process inhibits the spin-spin coupling mechanism by effectively averaging out the dipole-dipole interaction which is responsible for this coupling. (2) The large effective local field due to the exchange energy inhibits the diffusion relaxation mechanism at low temperatures and low-magnetic fields by providing a minimum polarizing (or stabilizing) field.

Let us consider how the relaxation equations should be modified to take into consideration the above-mentioned effects. The simplest case to consider is that of the diffusion relaxation, which can be given the required character by replacing ω^2 with $\omega^2 + \omega_e^2$ in Eq. (1)

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[9] R. Kronig and C. J. Bouwkamp, Physica 5, 521 (1938).

$$\left(\frac{1}{T_1}\right)_a=\frac{4}{5}\frac{I(I+1)\mu_0^4}{\hbar}\sum_i r_{ij}^{-6}\left[\frac{\tau}{1+(\omega^2+\omega_e^2)\tau^2}+\frac{4\tau}{1+4(\omega^2+\omega_e^2)\tau^2}\right], \quad (5)$$

where $\omega_e=\gamma H_e$, and H_e is the effective local field due to the exchange energy. The effect of including ω_e above prevents the maximum in the relaxation rate from appreciably increasing when ω becomes smaller than ω_e.

The model used to justify Eq. (5) is one in which the individual nuclei are polarized in both the applied dc magnetic field and the exchange field from near neighbors. This type of model is suggested by experiments performed in the demagnetized state[10] where nuclear magnetic resonance signals (both cw absorption and dispersion signals and pulsed free-induction decay signals) indicate that a nucleus effectively polarizes in whatever field it finds itself, independent of the origin of that field. The local fields due to neighbors are random, so the effective average polarizing field is obtained from

$$\omega_{\text{eff}}^2=\omega^2+\omega_e^2. \quad (6)$$

Equation (5) then states that a He^3 nucleus polarized in an effective field $\omega_{\text{eff}}/\gamma$ is relaxed by noise produced at that frequency and its second harmonic. In this model the noise is due to the modulated (or interrupted) magnetic dipole-dipole interaction only; the modulation of the exchange field gives rise to the exchange-lattice relaxation which, in this paper, is assumed to be very strong and serves to keep the exchange system in thermal equilibrium with the lattice.

The modification of the spin-spin relaxation mechanism is brought about because of the modulation of the interaction between the Zeeman system (characterized by the Zeeman energy) and the exchange system (characterized by the exchange energy). The dipole-dipole interaction which couples these two system is frequently interrupted because of the diffusion. We know from time-dependent perturbation theory that if a perturbation coupling two energy levels is suddenly turned on, then the rate at which transitions take place is proportional to t, where $t=0$ is the time at which the perturbation is turned on. If there are a continuum of levels, then the phases are soon randomized, and we obtain a time-independent transition rate. If the occupation number of a certain set of levels is observed, one can expect to find that its time dependence is given by a function of the form

$$N=N_0\exp\{-t^2/(2T_{2ab}^2+tT_2^*)\}, \quad (7)$$

where N is a number characteristic of the occupation number we are observing. For very short times $\Delta N=N-N_0$ is proportional to t^2, while for long times ΔN is directly proportional to t. The quantities T_{2ab} and T_2^* are related to each other by

$$1/T_2^*=[\pi g(\omega)/T_{2ab}^2], \quad (8)$$

where $g(\omega)$ is a normalized density-of-states function, i.e.,

$$\int_{-\infty}^{\infty} g(\omega)d\omega=1. \quad (9)$$

Equation (8) is obtained by noting the connection between the above expressions for ΔN for short and long times and the equivalent expressions as given by Schiff.[11]

We now suppose that the perturbation is interrupted at $t=\tau$, at which time the atoms in the solid rearrange themselves, and then the solid remains fixed until τ seconds later, at which time the atoms jump again, and so on. Every time there is a rearrangment, we effectively start at $t=0$, and there is a slight Gaussian character to the relaxation. After n periods of time τ we have

$$M=M_0\exp\left(\frac{-n\tau^2}{2T_{2ab}^2+T_2^*\tau}\right), \quad (10)$$

or since $n\tau=\tau$, we write

$$M=M_0\exp(-t/T_1)_b, \quad (11)$$

where

$$\left(\frac{1}{T_1}\right)_b=\frac{\pi g(\omega)\tau}{T_{2ab}^2[2\pi g(\omega)+\tau]} \quad (12)$$

making use of Eq. (8). The relaxation function is now a simple exponential as observed experimentally. The function $g(\omega)$ is obtained by calculating the overlap between the Zeeman line

$$g_{\text{Ze}}(\omega)=\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{\omega_L}\exp\left[-\frac{(\omega-\omega_0)^2}{2\omega_L^2}\right], \quad (13)$$

and the line associated with zero magnetic field

$$g_{\text{ex}}(\omega)=\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{\omega_e}\exp\left[-\frac{\omega^2}{2\omega_e^2}\right]. \quad (14)$$

The quantities ω_L^2 and ω_e^2 are the second moments of the Zeeman and zero-field lines. In Eq. (13) we use $\omega_0=\gamma H_z$. We obtain for the overlap integral

$$g(\omega_0)=\int_{-\infty}^{\infty} g_{\text{ex}}(\omega)g_{\text{Ze}}(\omega)d\omega=\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{\omega_e^*}\exp\left[-\frac{\omega_0^2}{2\omega_e^{*2}}\right], \quad (15)$$

where $\omega_e^{*2}=\omega_e^2+\omega_L^2$. If we only consider the case in which $\omega_L\ll\omega_e$, then we can replace ω_e^* by ω_e in Eq.

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[10] A. G. Anderson and S. R. Hartmann, Phys. Rev. **128**, 2023 (1962).

[11] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), 1st ed., p. 193.

(15) to obtain (we again write $\omega=\gamma H$ instead of using ω_0)

$$(T_1^{-1})_b=\left\{T_{2ab}{}^2\left[\frac{2}{\tau}+\frac{\omega_e}{(2\pi)^{1/2}}\exp\left(\frac{\omega^2}{2\omega_e{}^2}\right)\right]\right\}^{-1}, \tag{16}$$

which, when τ is long reduces to

$$T_1=(T_2)_0\exp(\omega^2/2\omega_e{}^2), \tag{17}$$

the expression obtained by Kronig and Bouwkamp.[9]

Equations (6) and (16), when substituted into Eq. (4), give the correct general behavior for the spin-lattice relaxation. At high temperatures and/or high magnetic fields it reduces to Eq. (1) plus a small correction due to Eq. (16), and at low temperatures it reduces to Eq. (3).

The purpose of the preceding calculation was to show in a simple manner how the two relaxation processes compete with each other. In performing this calculation we have made strong simplifying approximations: (1) $\omega^2\rightarrow\omega^2+\omega_e{}^2$ when relaxation by diffusion is modified by the exchange energy. (2) It is permissible to regard the diffusion process in an extreme manner (all atoms jump together after a time interval τ). (3) The net relaxation rate is given by the sum of the individual relaxation rates. Since the same processes are responsible for both relaxation mechanisms, the third assumption is hardly valid and it is not legitimate to calculate the relaxation effects separately. The correct answers are obtained in the high- and low-temperature limits because then only one process is important and it does not matter if interference effects are ignored.

III. DENSITY MATRIX CALCULATION

We now proceed to a more realistic calculation of T_1. The spin Hamiltonian is written in the form

$$\mathcal{H}=\mathcal{H}_z+\mathcal{H}_{\mathrm{ex}}+\mathcal{H}_d, \tag{18}$$

where $\mathcal{H}_z$ is the Zeeman Hamiltonian:

$$\mathcal{H}_z=\gamma\hbar H_z\sum_n I_{z_n}. \tag{19}$$

$\mathcal{H}_{\mathrm{ex}}$ is the exchange Hamiltonian and the secular part of the dipole-dipole Hamiltonian

$$\mathcal{H}_{\mathrm{ex}}=\sum_{mn}(A_{mn}\mathbf{I}_m\cdot\mathbf{I}_n+B_{mn}I_{z_m}I_{z_n}), \tag{20}$$

and $\mathcal{H}_d$ is the nonsecular part of the dipole-dipole Hamiltonian.

$$\mathcal{H}_d\equiv G_{+1}+G_{-1}+G_{+2}+G_{-2} \tag{21}$$

with $[G_{+M},I_z]=MG_M$

$$\begin{aligned}A_{mn}&=J_{mn}+(\gamma^2\hbar/r_{mn}{}^3)(\tfrac{3}{2}\cos^2\theta_{mn}-\tfrac{1}{2})\\ B_{mn}&=(3\gamma^2\hbar/r_{mn}{}^3)(\tfrac{3}{2}\cos^2\theta_{mn}-\tfrac{1}{2}).\end{aligned} \tag{22}$$

r_{mn} is the distance between the nth and mth nuclei. θ_{mn} is the angle between $\mathbf{H}$ and $\mathbf{r}_{mn}$.

Let us first treat the case in which there is no diffusion. Define the operators Q and $\mathcal{H}_0$ by

$$Q=a\mathcal{H}_z+b\mathcal{H}_{\mathrm{ex}},\quad \mathcal{H}_0=\mathcal{H}_z+\mathcal{H}_{\mathrm{ex}}. \tag{23}$$

Since we are interested in the Zeeman and exchange energies as a function of time, we calculate

$$\frac{d\langle Q\rangle}{dt}=\mathrm{Tr}\left(Q\frac{d\rho}{dt}\right)=\mathrm{Tr}\left(Q\frac{d\rho^*}{dt}\right), \tag{24}$$

where ρ is the density matrix,[12] and

$$\rho=\exp[-(i/\hbar)\mathcal{H}_0t]\rho^*\exp[(i/\hbar)\mathcal{H}_0t]. \tag{25}$$

If we define

$$\mathcal{H}^*(t)=\exp[(i/\hbar)\mathcal{H}_0t]\mathcal{H}_d\exp[-(i/\hbar)\mathcal{H}_0t], \tag{26}$$

then $d\rho^*/dt=-(i/\hbar)[\mathcal{H}^*(t),\rho^*]$ and $\rho^*(t)$ can be approximated by

$$\rho^*(t)=-\frac{i}{\hbar}\int_0^t[\mathcal{H}^*(\tau),\rho_0]d\tau-\frac{1}{\hbar^2}\int_0^t d\tau\int_0^\tau d\tau'[\mathcal{H}^*(\tau),\mathcal{H}^*(\tau');\rho_0] \tag{27}$$

so that

$$\frac{d\langle Q\rangle}{dt}=-\frac{i}{\hbar}\mathrm{Tr}\{Q[\mathcal{H}^*(t),\rho_0]\}-\frac{1}{\hbar^2}\int_0^t d\tau\,\mathrm{Tr}\{Q[\mathcal{H}^*(t),\mathcal{H}^*(\tau);\rho_0]\}. \tag{28}$$

We now assume that the Zeeman and exchange systems can each be characterized by spin temperatures (not necessarily equal), i.e.,

$$\begin{aligned}\rho(t)&=\exp(-\mathcal{H}_z/kT_z)\exp(-\mathcal{H}_{\mathrm{ex}}/kT_{\mathrm{ex}})\\ &\cong1-(\mathcal{H}_z/kT_z)-(\mathcal{H}_{\mathrm{ex}}/kT_{\mathrm{ex}})\\ &=1-(\mathcal{H}_0/kT_{\mathrm{ex}})-(1/k)(1/T_z-1/T_{\mathrm{ex}})\mathcal{H}_z,\end{aligned} \tag{29}$$

so that on using the relation

$$\begin{aligned}\int_0^t d\tau\,\mathrm{Tr}\{Q[\mathcal{H}^*(t),\mathcal{H}^*(\tau);\mathcal{H}_0]\}&=-\int_t^0 d\tau\,\mathrm{Tr}\{Q[\mathcal{H}^*(0),\mathcal{H}^*(-\tau);\mathcal{H}_0]\}\\ &=-i\hbar\,\mathrm{Tr}\{Q[\mathcal{H}^*(t),\mathcal{H}^*(0)]\},\end{aligned} \tag{30}$$

we obtain

$$\frac{d\langle Q\rangle}{dt}=-\frac{i}{\hbar kT_{\mathrm{ex}}}\mathrm{Tr}\{Q[\mathcal{H}^*(t),\mathcal{H}^*(0)]\}+\frac{1}{\hbar^2k}\left(\frac{1}{T_z}-\frac{1}{T_{\mathrm{ex}}}\right)\times\int_0^t d\tau\,\mathrm{Tr}\{Q[\mathcal{H}^*(t),\mathcal{H}^*(\tau);\mathcal{H}_z]\}. \tag{31}$$

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[12] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938); A. Abragram, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

When $Q=\mathcal{H}_{\text{ex}}=\mathcal{H}_0-\mathcal{H}_z$, then since

$$\int_0^t d\tau\, \mathrm{Tr}\{\mathcal{H}_0[\mathcal{H}^*(t),\mathcal{H}^*(\tau);\mathcal{H}_z]\} = i\hbar\, \mathrm{Tr}\{\mathcal{H}_z[\mathcal{H}^*(0),\mathcal{H}^*(t)]\}\,, \tag{32}$$

and

$$\lim_{t\to\infty} \mathrm{Tr}\left\{\begin{pmatrix}\mathcal{H}_{\text{ex}}\\ \mathcal{H}_z\end{pmatrix}[\mathcal{H}^*(t),\mathcal{H}^*(0)]\right\}=0\,, \tag{33}$$

we find that

$$\frac{d\langle\mathcal{H}_z\rangle}{dt}=\frac{1}{\hbar^2 k}\left(\frac{1}{T_z}-\frac{1}{T_{\text{ex}}}\right) \times\int_0^\infty d\tau\, \mathrm{Tr}\{\mathcal{H}_z[\mathcal{H}^*(\tau),\mathcal{H}^*(0);\mathcal{H}_z]\} \tag{34}$$

and

$$(d/dt)\langle\mathcal{H}_{\text{ex}}\rangle=-(d/dt)\langle\mathcal{H}_z\rangle\,. \tag{35}$$

Equation (34) is equivalent to an expression obtained by Kubo and Tomita[8] in studying the energy exchange between two modes of a spin system. Equation (33) was obtained by expanding $\mathcal{H}^*$ in terms of the $G_{\pm M}$ operators, so that for the term involving $\mathcal{H}_z$ we find

$$\begin{aligned}\mathrm{Tr}\{\mathcal{H}_z[\mathcal{H}^*(t),\mathcal{H}^*(0)]\} &=\mathrm{Tr}\{-G_{+1}(t)G_{-1}e^{i\omega t}+G_{-1}(t)G_{+1}e^{-i\omega t}\\ &\quad -2G_{+2}(t)G_{-2}e^{2i\omega t}+2G_{-2}(t)G_{+2}e^{-2i\omega t}\}\end{aligned} \tag{36}$$

where

$$G_M(t)=\exp[(i/\hbar)\mathcal{H}_{\text{ex}}t]G_M\exp[-(i/\hbar)\mathcal{H}_{\text{ex}}t]\,. \tag{37}$$

In the limit of large t all terms average out except those for which

$$\mathrm{Tr}G_M(t)G_{-M}=\exp(-i\omega t)$$

and

$$\mathrm{Tr}G_{-M}(t)G_M=\exp(i\omega t)\,,$$

and inserting these terms above we find

$$\lim_{t\to\infty}\mathrm{Tr}\{\mathcal{H}_z[\mathcal{H}^*(t),\mathcal{H}^*(0)]\}=0\,. \tag{38}$$

A similar argument holds when H_z replaces $\mathcal{H}_{\text{ex}}$ in Eq. (36). The expressions for the relaxation of Zeeman and exchange energy, Eqs. (34) and (35), can be evaluated by expanding the integrand in powers of τ. If the expansion is carried out to terms involving τ^2 we find that since the coefficient of the term involving the first power of τ is zero we can replace the power expansion by a Gaussian function. The Gaussian function is uniquely determined by expanding it in powers of τ up to the τ^2 term and equating it to the series expansion of the integrand of Eq. (34). We find[13]

$$\frac{d}{dt}\left(\frac{1}{T_z}\right)=\frac{1}{\tau_z}\left(\frac{1}{T_z}-\frac{1}{T_{\text{ex}}}\right) \tag{39}$$

$$\frac{d}{dt}\left(\frac{1}{T_{\text{ex}}}\right)=\frac{1}{\tau_{\text{ex}}}\left(\frac{1}{T_{\text{ex}}}-\frac{1}{T_z}\right), \tag{40}$$

where

$$\frac{1}{\tau_z}=\frac{(2\pi)^{1/2}}{\hbar^2\,\mathrm{Tr}I_z^2}\sum_{M=1}^{2}\left[\frac{M^2\,\mathrm{Tr}G_{+1}G_{-1}}{\langle\Delta\omega_M\rangle^{1/2}} \times\exp\left(-\frac{M^2\Omega^2}{2\langle\omega_M^2\rangle}\right)\right], \tag{41}$$

$$\langle\Delta\omega_M^2\rangle=\frac{\mathrm{Tr}[G_{-M},\mathcal{H}_{\text{ex}}][\mathcal{H}_{\text{ex}},G_{+M}]}{\hbar^2\,\mathrm{Tr}G_{+M}G_{-M}}, \tag{42}$$

$$\tau_{\text{ex}}=\tau_z\frac{\mathrm{Tr}\mathcal{H}_{\text{ex}}^2}{\mathrm{Tr}\mathcal{H}_z^2}\,. \tag{43}$$

For relaxation in solid He³ it has been shown experimentally,[3] at least in the region $T>0.5$°K, that the exchange system is tightly coupled to the lattice so that the exchange temperature T_{ex} is equal to the lattice temperature T and $T_1=\tau_z$. The above result is similar to the Kronig-Bouwkamp result but differs in that there are two exponential terms. Yokota has also considered this relaxation mechanism and has obtained an equivalent result.[14]

Now consider the effects of diffusion. If the atoms diffuse, then the terms containing r_{mn} and θ_{mn} will fluctuate. We assume that the major effect of the diffusion is to make $\mathcal{H}_d$ depend on time. The only effect of the fluctuation of $\mathcal{H}_{\text{ex}}$ is to couple the exchange system with the lattice so that we can put $T_{\text{ex}}=T$. On this basis we are led to Eq. (28) in which $\mathcal{H}^*(t)$ also includes the time because of diffusion. We argue that in taking the trace we are effecting an average, and so we can separate out the effect of the diffusion by including some correlation function $f(t-\tau)$ into Eq. (28) and then treating the problem as we did before. If this is done we are led to the result given by Eq. (34) except that the function $f(t)$ must be included inside the integral. If this is correct, then the problem is one of determining the correct form of $f(t)$. If we choose

$$f(t)=\exp(-t/\tau)\,, \tag{44}$$

where τ is the correlation time, then on performing the integration and using the expression obtained previously for the integrand in Eq. (36), we find that $1/T_1$ is given by

$$\frac{1}{T_1}=\frac{(2\pi)^{1/2}}{\hbar^2\,\mathrm{Tr}I_x^2}\sum_{M=1}^{2}\frac{M^2\,\mathrm{Tr}G_{+M}G_{-M}}{\langle\Delta\omega_M^2\rangle^{1/2}}\,\mathrm{Re}W(z_M)\,, \tag{45}$$

where

$$\begin{aligned}z_M&=x_M+iy_M\,,\\ x_M&=-\frac{M\omega}{\sqrt{2}\langle\Delta\omega_M^2\rangle^{1/2}}\,,\\ y_M&=\frac{1}{\sqrt{2}\langle\Delta\omega_M^2\rangle^{(1/2)}\tau}\end{aligned} \tag{46}$$

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[13] S. R. Hartmann and A. G. Anderson, in *Magnetic and Electric Resonance and Relaxation, Proceedings of the Colloque Ampère, Eindhoven, July 1962,* edited by J. Smidt (Interscience Publishers, Inc., New York, 1963).

[14] M. Yokota, J. Phys. Soc. Japan **10**, 762 (1955).

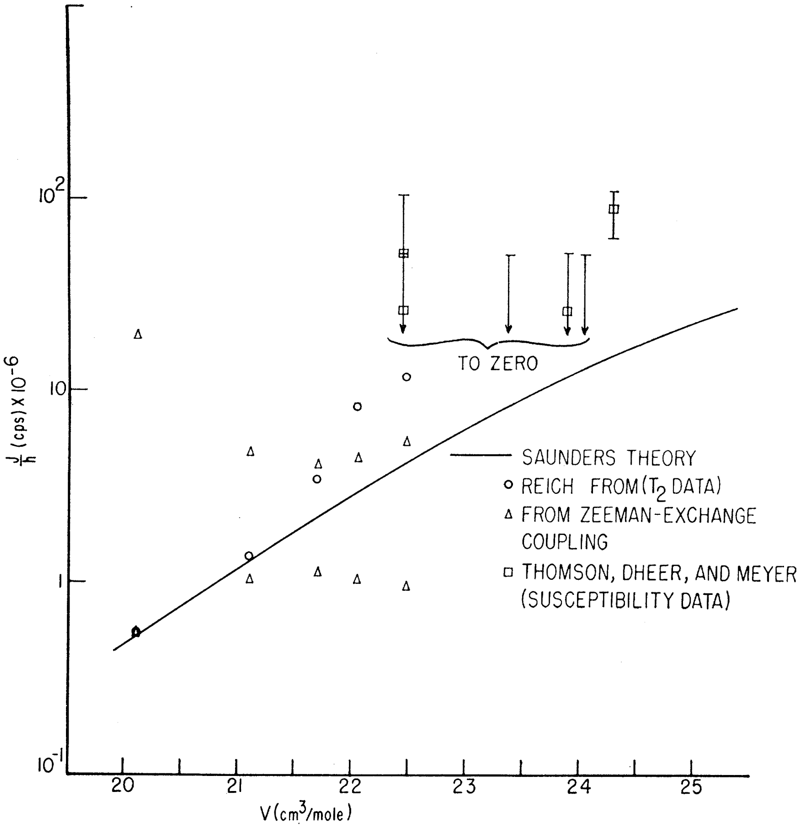

FIG. 2. The exchange integral J as a function of molar volume.

$$W(z)=\exp(-z^2)\left\{1+\frac{2i}{\sqrt{\pi}}\int_0^z e^{+t^2}dt\right\} \qquad (47)$$

and $\langle\Delta\omega_M^2\rangle$ is given as before.

When $y_M\rightarrow 0$ we obtain the familiar expression for relaxation by diffusion.

$$\frac{1}{T_1}=\frac{2}{\hbar^2\,\mathrm{Tr}I_x^2}\sum_{M=1}^{2} M^2\,\mathrm{Tr}G_{+M}G_{-M}\frac{\tau}{1+M^2\omega^2\tau^2}, \qquad (48)$$

while for $\langle\omega_M^2\rangle\rightarrow 0$ we find that Eq. (41) is again the correct expression for $1/T_1$. The expressions for T_1 are given in terms of quantities which are susceptible to independent measurement, so that only within the uncertainty of outside measurements of such quantities as the exchange integral, correlation time, lattice constant, temperature, etc., can one adjust the parameters to obtain a best fit. On the other hand, one can use Eq. (41) to determine, say, J, if all other parameters are known.

In order to compare the above theory with experiment it is necessary to evaluate the various lattice sums in Eq. (41). Using the results of related lattice sum calculations[15,16] we find that for a cubic lattice powder

$$\left.\begin{array}{c}\mathrm{Tr}G_{+1}G_{-1}=\mathrm{Tr}G_{+2}G_{-2}\\ \text{and}\\ \langle\Delta\omega_1^2\rangle=\langle\Delta\omega_2^2\rangle\end{array}\right\}, \qquad (49)$$

and for a body-centered cubic lattice

$$\frac{1}{T_1}=\frac{14.5\hbar^2\gamma^4 I(I+1)}{a^6\langle\Delta\omega_1^2\rangle^{1/2}}\left[\mathrm{Re}W(x+iy)+4\,\mathrm{Re}W(2x+iy)\right], \qquad (50)$$

with

$$\langle\Delta\omega_1^2\rangle=(7.59)(J/\hbar)^2 I(I+1) \qquad (51)$$

and a is the lattice constant, assuming $J\neq 0$ for nearest neighbors only.[17]

The data in Fig. 1 correspond to: $a=4.05\times10^{-8}$ cm; $\tau=\tau_0\exp(W/T)$; $\tau_0=5.3\times10^{-12}$ sec; $W=13.6$°K. The value for J was also determined from T_2 measurements but because of the approximations made it will be regarded as determined by fitting Eq. (50) to the data. The criterion for fitting the data was to adjust the value of J so that the experiment and theory agree in the region where the theory predicts that T_1 is independent of temperature. The small cross at $1/T=1.5(°\mathrm{K})^{-1}$ was chosen as the reference point in this region and the value of J so determined together with the above data then determines the whole theoretical curve. A surprising result of this fit is that J is determined to be (in units of cps)

$$(J/\hbar)=1.1\times10^6\ \mathrm{cps},$$

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[15] R. L. Strombotne, thesis, University of California, Berkeley, 1961 (unpublished).

[16] H. Cheng, Phys. Rev. **124**, 1359 (1961).

[17] The expression for $W(z)$ was evaluated on an IBM-7090 computer using program C3 BS WOFZ of the SHARE catalog.

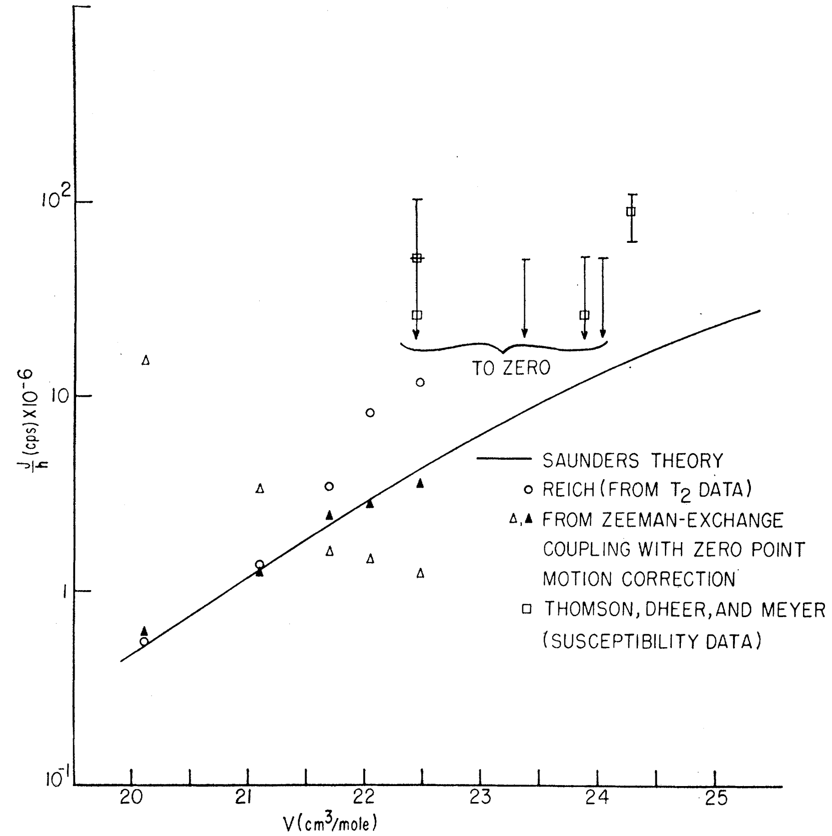

FIG. 3. The exchange integral J as a function of molar volume after correcting for a modified dipolar interaction.

which was (to an accuracy of two significant figures) just what was obtained by the T_2 data.

It should be noted that the size of the dip in T_1 was not an adjustable parameter but was fixed once the reference point cross was chosen. In fact, if we had chosen a reference point which was greater (i.e., a larger value of T_1) than that actually chosen, the theoretical dip would have been greater, so that the reference point in the temperature-independent limit does not affect the fit to the data in the diffusion-limited region very much. The fit to the open circles of Fig. 1 is, of course, also determined by Eq. (50) and is given by the solid curve of Fig. 1. This curve was discussed in the beginning of this paper when relaxation by diffusion was considered. Several other T_1 measurements with solid He^3 in the α phase have been made and by fitting the theory with the data in the temperature-independent region, values for J have been obtained at several molar volumes. The values for τ_0 and W have been taken from Reich's diffusion measurements.[3] A plot of J versus molar volume is given in Fig. 2 where the triangles indicate the value of J obtained by the foregoing procedure. It is to be noted that for each molar volume we determine two values of J. (When $\langle\Delta\omega_M{}^2\rangle<\omega^2$ and increase in J increases the Zeeman-exchange coupling as more transitions are possible which can conserve energy, whereas when $\langle\Delta\omega_M{}^2\rangle>\omega^2$ the Zeeman-exchange coupling is essentially proportional to $T_2{}^{-1}$, which being exchange narrowed, means that a decrease in J will also increase the Zeeman-exchange coupling.) In the case of $V=20.12$ cm³/mole, the lower value for J is clearly the correct value since the larger value of J would not produce any dip in the relaxation curve as given in Fig. 1. The other sets of J values cannot be·differentiated from the T_1 versus $1/T$ data because of the slight disagreement between theory and experiment in the region of the T_1 minimum as evidenced in Fig. 1. If we assume that J is continuous then we are led to the conclusion that J increases to a maximum value at about 21.6 cm³/mole and then decreases again. The results of Reich[3] and Thompson, Dheer, and Meyer[5] have been plotted in Fig. 2, together with a curved line predicted by Saunders' theory.[18] At 20.12 cm³/mole the results of Reich,[3] Saunders,[18] and this calculation are in excellent agreement. At lower densities the agreement between our results and those of Saunders and Reich is less satisfactory, but there is reason to be suspicious of our results in the region about 21.6 cm³/mole and 1611 G, because at this molar volume and field, the behavior of J versus molar volume is very sensitive to the absolute value of T_1 in the temperature-independent

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[18] E. M. Saunders, Phys. Rev. **126**, 1724 (1962).

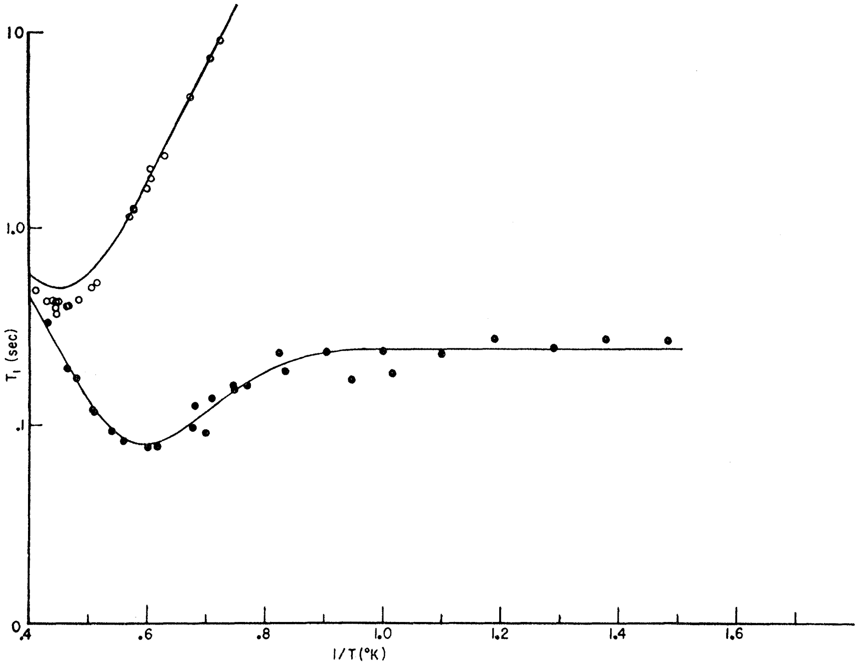

FIG. 4. Spin-lattice relaxation time T_1 versus $(1/T)$ for solid He^3 at 20.12 cm^3/mole. The open circles are the data of Goodkind and Fairbank at 30.4 Mc/sec, the solid circles are data of Reich at 5.224 Mc/sec. The solid lines are given by theory after correcting for a modified dipolar interaction.

region. We are further handicapped because, for values of $J/\hbar$ greater than 1.5×10^6 cps at 1611 G, only a very small diffusion dip in the relaxation curve is predicted which prevents one from distinguishing unambiguously between the two possible values of J. If data had been taken at higher molar volumes, we could have again been able to distinguish between the two values of J and would know whether or not we remained on the same branch in Fig. 2.

Since the theoretical preduction[18] of J versus V and the experimental determination of J from T_2 data both yield a monotonic curve for J, it is informative to inquire what modifications in the spin-lattice relaxation calculation (Sec. III) are necessary to achieve this monotonic behavior for J when determined from T_1 data. One can question the assumption that the character of the relaxation function for the spin-spin relaxation is Gaussian, but we prefer to accept this simplifying assumption and look elsewhere for the discrepancy. According to Reich, his sample of solid He^3 was a powder (polycrystalline), but there is the possibility that it consists of only a few crystals randomly oriented. Grilly and Mills[19] have reported that they found it difficult to avoid making single crystals because of the large diffusion which is present. Reich's sample volume is an order of magnitude larger than that of Grilly and Mills, and it therefore would have been more difficult to have grown a single crystal. If the sample differs substantially from a powder, then the values for $\langle\Delta\omega_M{}^2\rangle$ and $\mathrm{Tr}G_{+M}G_{-M}$ will differ accordingly. A change in $\mathrm{Tr}G_{+1}G_{-1}$ of only 25% is enough to produce a monotonic J versus V curve when J is determined from T_1 data. The quantity $\langle\Delta\omega_M{}^2\rangle$ is not as sensitive as $\mathrm{Tr}G_{+M}G_{-M}$ to deviations of the sample from being a perfect powder.

Another effect which should be considered is that due to the very large zero-point motion. Since the interacting atoms are vibrating with large excursions and at very high frequencies, the effective interaction between the atoms is altered.[20] In order to estimate the effect, we assume that the relaxation is altered according to the equation

$$\mathrm{Tr}G_{+1}G_{-1}=(\mathrm{Tr}G_{+1}G_{-1})_0[1+A\langle\xi_x{}^2\rangle_{\mathrm{av}}/(R^0)^2], \quad (52)$$

where A is a constant, R^0 is the distance between nearest neighbors, $R_\alpha=R_\alpha{}^0+\xi_\alpha$, $R_\alpha{}^0$ is the equilibrium αth component of the position vector to an atom, and ξ_α is the deviation from $R_\alpha{}^0$. The variation in $\langle\Delta\omega_M{}^2\rangle$ with V has been assumed to be very small, since it is independent of R^0. Saunders[18] has calculated $\langle\xi_x{}^2\rangle_{\mathrm{av}}$ as a function of molar volume, and we find that if we choose $A=-14$, then we obtain the J versus V plot shown in Fig. 3.

In Fig. 3, the upper and lower branches come together and the solid triangles give a good fit to Saunders' theory. As a further check, the T_1 versus $1/T$ curves have been recalculated using $A=-14$, and we find in Fig. 4 that the agreement between the theory and the experiment has improved. In fact, the fit in the region of the relaxation dip is good enough to enable us to distinguish between the two possible values of J at 22.6 cm^3/mole. The higher value of J is found to be the

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

[20] D. E. O'Reilly and Tung Tsang, Phys. Rev. **128**, 2639 (1962).

correct one indicating that at higher molar volumes J lies on the upper branch. The values of J as obtained from relaxation data in the β phase have recently been compared[4] with the theoretical predictions of Saunders[18] and, as we find in the α phase, the agreement is rather good.[21]

The results of Figs. 3 and 4 remain essentially the same if we postulate a constant correction factor to $\mathrm{Tr}G_{+1}G_{-1}$ of $\approx -25\%$ due to not having a perfect powder since $\langle\xi_x^2\rangle_{\mathrm{av}}$ is essentially constant (there is $\approx 25\%$ variation) over this range of molar volumes.

We now consider the validity of Eq. (52). In the simplest model of two atoms vibrating along the line joining their centers, the sign of A is positive and not negative resulting in a correction factor of the wrong sign. The next approximation is that of considering one atom fixed and its neighbor oscillating about its equilibrium position with oscillations of spherical symmetry, i.e., $\langle\xi_x^2\rangle_{\mathrm{av}}=\langle\xi_y^2\rangle_{\mathrm{av}}=\langle\xi_z^2\rangle_{\mathrm{av}}$. In this model we find that A is zero. The transverse oscillations, therefore, tend to decrease the dipole-dipole interaction, while the longitudinal oscillations have the opposite effect. In order to make a more realistic estimate of the effect of zero-point vibrations, we expand $\mathrm{Tr}G_{+1}G_{-1}$ to the second order in its displacements and we find that

$$\mathrm{Tr}G_{+1}G_{-1}=(\mathrm{Tr}G_{+1}G_{-1})\times\left[1+\frac{27}{2}\sum_{NN}\frac{R_x^0R_y^0\xi_{nn'x}\xi_{nn'y}}{(R^0)^4}\right], \tag{53}$$

where $\xi_{nn'x}=\xi_{nx}-\xi_{n'x}$, and the subscripts n, n' refer to the nth and n'th atoms. In obtaining Eq. (53) we only considered nearest neighbor interactions and a single crystal oriented with the cube axes along the x, y, and z axes. The symbol $\sum_{NN}$ means a sum over nearest neighbors. For the case considered it is readily shown that

$$\textstyle\sum_{NN} R_\alpha^0R_\beta^0\xi_{nn'\alpha}\xi_{nn'\beta}$$

is independent of α and β as long as $\alpha\neq\beta$. In order to get agreement with experiment it is necessary to show that Eqs. (52) and (53) are equivalent, i.e.,

$$\sum_{NN}\frac{R_x^0R_y^0\langle\xi_{nn'x}\xi_{nn'y}\rangle_{\mathrm{av}}}{(R^0)^2}\approx-\langle\xi_{nx}^2\rangle_{\mathrm{av}}. \tag{54}$$

As a crude approximation it was assumed that

$$\begin{aligned}\omega_{kl}&=c_lk\,,\\ \omega_{kt}&=c_tk\,,\\ e_\alpha{}^l(k)&=k_\alpha/k\,,\end{aligned} \tag{55}$$

where k is the wave vector, c_l and c_t are the velocities of longitudinal and transverse waves, respectively, and $e_\alpha{}^l(k)$ is the αth component of the polarization vector for a longitudinal wave whose wave vector is k. If a square Brillouin zone is chosen and if $c_l=\sqrt{3}c_t$ (as given in Kittel[22] when the forces are central and each atom is at a center of symmetry), then we find that the sign in Eq. (54) is indeed negative but the expression on the left-hand side is about a factor of ten too small. Because of the gross oversimplifications made above, this result does not rule out the possibility of the 25% T_1 correction factor being due to zero-point motion, but it does indicate that the zero-point motion does have a sizeable effect of a few percent and consequently must be taken into consideration in any precise calculation involving magnetic interactions between the nuclei.

CONCLUSION

An expression has been obtained for the relaxation of magnetization in a solid where the principal relaxation mechanisms are due to diffusion and Zeeman-exchange coupling, and where the exchange system is tightly coupled to the lattice. It is found that the resulting expression for the relaxation rate T_1^{-1} when plotted as a function of T^{-1} is in excellent agreement with experiments performed on solid He^3. When the above theory is used to determine the exchange integral J it is found that there is reasonable agreement with the theoretical calculations of Saunders[18] and the measurements of Reich.[3] The resulting determination of J indicates an effective reduced dipolar interaction which can arise from either a nonperfect powder or zero-point motion, and a simple calculation of the effect of zero-point motion indicates a contribution of possibly 10% to the effect.

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[21] A more detailed paper concerned with the relaxation of solid He^3 in the β phase is in preparation by R. L. Garwin and A. Landesman.

[22] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1962).