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# Determination of the Spectral Density Function $J_1(\omega)$ in Solid He$^3$ from Nuclear-Relaxation Measurements*

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The transverse and longitudinal relaxation times are studied theoretically in a system of nuclear spins where the modulation of the dipolar Hamiltonian by an exchange interaction is the dominant relaxation mechanism. If the sample is a powder, it is shown that the nuclear-magnetic-resonance properties are entirely governed by the knowledge of one single spectral density function $J_1(\omega)$, which is determined experimentally for solid He$^3$, for both bcc and hcp phases. The shape of $J_1(\omega)$ depends strongly on the lattice structure and, in the case of a bcc lattice, does not have the Gaussian shape proposed in the existing literature. Attempts were made to measure the second order frequency shift associated with the nonadiabatic broadening (10/3 effect); however, the experimental error was too large for the predicted shift to be measured.

## I. INTRODUCTION

In a recent paper,[1] henceforth referred to as RHM, nuclear-magnetic-relaxation measurements in the bcc phase of solid He$^3$ were reported for the temperature range 0.35–2°K. Special emphasis was given to the study of the frequency dependence of the values of $T_1$ and $T_2$ in the region where they were temperature independent. In this region, called the plateau, the primary relaxation mechanism is the exchange modulation of the dipolar field. In solid He$^3$, the exchange interaction is unusually large because such a light atomic mass permits a large zero-point motion.

The 10/3 ratio between the values of $T_2$ in a high field and in a low field was experimentally checked by RHM.[2] It was also found that the plateau values of $T_1$ and $T_2$ for all densities in the bcc phase could be plotted on a common reduced curve as a function of $\omega/J$, where $\omega/2\pi$ is the Larmor frequency and $J$ is the exchange parameter. These curves deviated systematically from the relations derived for $T_2$ and for $T_1$ by Kubo and Tomita[3] and by Hartmann[4] who all assume the spectral density to be Gaussian.

On the other hand, it was found (see Ref. 1, *Note added in proof*) that for the hcp phase the frequency dependence of $T_2$ was in good agreement with the predictions of Kubo and Tomita. The conclusion that can be drawn from these observations is that the Gaussian approximation used by these authors[3–5] in evaluating the spectral densities in expressions for $T_1$ and $T_2$ is more valid in the hcp phase than in the bcc phase.

In that which follows, recent and more accurate data for $T_2$ in both phases at about the same molar volume, from 19.5 to 20.4 cm$^3$, and for $T_1$ in the hcp phase will be presented. A derivation for the plateau values of $T_1$ (called $T_{ZE}$) and $T_2$ will be given in terms of the spectral density function $J_1(\omega)$ without at first introducing the Gaussian approximation. The frequency dependence of $T_1$ and $T_2$ for both phases will then be analyzed to produce explicit experimental determinations of the function $J_1(\omega)$ for both phases. To our knowledge, this is the first time that such information has been obtained from NMR relaxation studies.

Finally, there is a description of an attempt to measure the second-order frequency shift[3,6] associated with the nonadiabatic linewidth in the presence of exchange coupling.

## II. THEORETICAL

There have been several papers[4,7,8] with theoretical treatment of the longitudinal and transverse relaxation processes in solid He$^3$, assuming a Gaussian approximation for the exchange correlation function. The fre-

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[1] R. C. Richardson, E. Hunt, and H. Meyer, Phys. Rev. **138**, A1326 (1965), henceforth referred to as RHM.

[2] Unpublished data by H. Reich and R. L. Garwin in the hcp phase ($V = 19.3$ cm$^3$) also showed this effect.

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

[4] S. R. Hartmann, Phys. Rev. **133**, A17 (1964).

[5] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 169 (1953); P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[6] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 446.

[7] R. L. Garwin and A. Landesman, Phys. Rev. **133**, A1503 (1964).

[8] M. G. Richards, J. Hatton, and R. P. Giffard, Phys. Rev. **139**, A91 (1965).

quency dependence of $T_2$ has been studied for solids with exchange by Kubo and Tomita.[3]

It appears useful at the present time to give a derivation for the two relaxation times using the same formalism, and where no assumptions are made on the form of the correlation functions. The purpose is then to obtain the relaxation times expressed in terms of the same functions, namely, the spectral densities.

After this derivation, the results obtained in the Gaussian approximation are discussed.

We will be interested in the case where the relaxation occurs by modulation of the dipolar field as a result of the exchange interaction only. For the calculation which follows, we will assume that the exchange bath is strongly coupled to the lattice so that $T_{EL} \ll T_{ZE}$ and the longitudinal relaxation time is given by $T_{ZE}$. After a derivation of $T_{ZE}$ analogous to that given by Hartmann,[4] the necessary relations for a parallel derivation of an expression for $T_2$ will be established.

We assume the nuclear spins, located at lattice sites $i$ and $j$ and joined by a vector $\mathbf{a}_{ij}$, to be coupled by

(1) a scalar exchange interaction, which will be eventually assumed to be nonvanishing only between spins $i$ and $j$ if they are first neighbors, and is given by

$$\hbar\mathcal{H}_{\mathrm{ex}}{}^{ij} = -\hbar J \mathbf{I}_i \cdot \mathbf{I}_j; \tag{1}$$

(2) a tensor interaction

$$\hbar\mathcal{H}_d{}^{ij} = \hbar b_{ij}\{\mathbf{I}_i \cdot \mathbf{I}_j - 3(\mathbf{I}_i \cdot \mathbf{a}_{ij})(\mathbf{I}_j \cdot \mathbf{a}_{ij})|a_{ij}|^{-2}\}. \tag{2}$$

If this interaction is purely dipolar magnetic, then

$$b_{ij} = \hbar\gamma^2 a_{ij}{}^{-3}, \tag{3}$$

$\gamma$ being the gyromagnetic ratio.

In an external field $\mathbf{H}$, the time-independent Hamiltonian is then written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_d, \tag{4}$$

where

$$\mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_{\mathrm{ex}}, \quad \mathcal{H}_Z = -\gamma \textstyle\sum_i \mathbf{I}_i \cdot \mathbf{H},$$

$\mathcal{H}_Z$, $\mathcal{H}_{\mathrm{ex}}$, and $\mathcal{H}_d$ being the Zeeman, exchange and dipolar Hamiltonians.

The most important terms in the Hamiltonian are the Zeeman and exchange energies. These terms commute with each other but not with the dipolar interaction. The dipolar Hamiltonian, however, is much smaller than the exchange energy so the problem of describing the nuclear magnetic relaxation of the system is formulated in terms of a model in which the Zeeman and the exchange interactions are treated as independent energy reservoirs, characterized by the temperatures $T_Z$ and $T_{\mathrm{ex}}$ which are weakly coupled by the dipolar interaction.

We use the unitary transformation

$$U(t) = \exp(i\mathcal{H}_0 t) \tag{5}$$

to define an interaction representation, where the density matrix $\sigma^*$ is related to the density matrix $\sigma$ in the Schrödinger representation by

$$\sigma^*(t) = U(t)\sigma U(-t). \tag{6}$$

The interaction representation of the perturbation Hamiltonian is

$$\mathcal{H}^*(t) = U(t)\mathcal{H}_d U(-t). \tag{7}$$

The equation of motion for $\sigma^*$, developed in the text by Abragam[9] is

$$\dot{\sigma}^*(t) = -i[\mathcal{H}^*(t), \sigma(0)] - \int_0^\infty d\tau \{\mathcal{H}(t), [\mathcal{H}^*(t-\tau), \sigma^*(t)]\}, \tag{8}$$

valid if the time $t$ is not too short ($t > J^{-1}$).

### A. Longitudinal Relaxation

The density matrix of our spin system is assumed to be given by

$$\sigma = \exp(-\beta_Z\mathcal{H}_Z)\exp(-\beta_{\mathrm{ex}}\mathcal{H}_{\mathrm{ex}}) / \mathrm{Tr}\{\exp(-\beta_Z\mathcal{H}_Z)\exp(-\beta_{\mathrm{ex}}\mathcal{H}_{\mathrm{ex}})\}, \tag{9}$$

where $\beta_Z = \hbar/kT_Z$ and $\beta_{\mathrm{ex}} = \hbar/kT_{\mathrm{ex}}$.

When using Eq. (8), the expectation value of the rate of change of the Zeeman energy is given by

$$\left\langle \frac{d\mathcal{H}_Z}{dt} \right\rangle = \mathrm{Tr}\{\mathcal{H}_Z \dot{\sigma}^*\} = \int_0^\infty d\tau\, \mathrm{Tr}\{\mathcal{H}_Z[\mathcal{H}^*(t), [\mathcal{H}^*(t-\tau), \sigma^*(t)]]\}. \tag{10}$$

If we use the high-temperature approximation for the density matrix, we have

$$\begin{aligned}\sigma &= (1 - \beta_Z\mathcal{H}_Z - \beta_{\mathrm{ex}}\mathcal{H}_{\mathrm{ex}})(\mathrm{Tr}1)^{-1} \\ &= \{1 - (\beta_Z - \beta_{\mathrm{ex}})\mathcal{H}_Z - \beta_{\mathrm{ex}}(\mathcal{H}_Z + \mathcal{H}_{\mathrm{ex}})\}(\mathrm{Tr}1)^{-1}.\end{aligned} \tag{11}$$

Equation (10) then becomes

$$\begin{aligned}(\mathrm{Tr}1)\cdot\left\langle \frac{d\mathcal{H}_Z}{dt} \right\rangle &= (\beta_Z - \beta_{\mathrm{ex}}) \int_0^\infty d\tau\, \mathrm{Tr}\{\mathcal{H}_Z[\mathcal{H}^*(t), [\mathcal{H}^*(t-\tau), \mathcal{H}_Z]]\} \\ &\quad + \beta_{\mathrm{ex}} \int_0^\infty d\tau\, \mathrm{Tr}\{\mathcal{H}_Z[\mathcal{H}^*(t)[\mathcal{H}^*(t-\tau), \mathcal{H}_Z + \mathcal{H}_{\mathrm{ex}}]]\}.\end{aligned} \tag{12}$$

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[9] See Ref. 6, Chap. VIII.

Hartmann[4] has shown that the second term on the right-hand side vanishes. As a consequence of the invariance properties of the trace, the integral in Eq. (12) must be independent of $t$. Therefore, Eq. (12) now becomes

$$\left\langle\frac{d\mathcal{H}_Z}{dt}\right\rangle=(\beta_Z-\beta_{\text{ex}})(\text{Tr}1)^{-1}\int_0^\infty d\tau \times\text{Tr}\{\mathcal{H}_Z[\mathcal{H}^*(0),[\mathcal{H}^*(-\tau),\mathcal{H}_Z]]\}. \tag{13}$$

We can also obtain the average energy of the Zeeman system directly from the high-temperature approximation of $\sigma$:

$$\langle\mathcal{H}_Z\rangle=\text{Tr}\{\mathcal{H}_Z(1-\beta_Z\mathcal{H}_Z-\beta_{\text{ex}}\mathcal{H}_{\text{ex}})(\text{Tr}1)^{-1}\} =-\beta_Z\,\text{Tr}\{\mathcal{H}_Z{}^2\}(\text{Tr}1)^{-1}. \tag{14}$$

Differentiation of both sides produces

$$\langle d\mathcal{H}_Z/dt\rangle=-\dot{\beta}_Z\,\text{Tr}\{\mathcal{H}_Z{}^2\}(\text{Tr}1)^{-1}. \tag{15}$$

If the Zeeman-exchange relaxation time $T_{ZE}$ is defined by the relation

$$-\dot{\beta}_Z=(1/T_{ZE})(\beta_Z-\beta_{\text{ex}}), \tag{16}$$

we obtain, using Eqs. (4) and (12)

$$\frac{1}{T_{ZE}}=\int_0^\infty d\tau\,\text{Tr}\{[I_z,\mathcal{H}_d][\mathcal{H}^*(-\tau),I_z]\}\Big/\text{Tr}I_z{}^2, \tag{17}$$

$$\frac{1}{T_{ZE}}=\int_0^\infty d\tau\,\text{Tr}\{[I_z,\mathcal{H}_d]\exp(-i\mathcal{H}_0\tau)[\mathcal{H}_d,I_z]\exp(i\mathcal{H}_0\tau)\}\Big/\text{Tr}I_z{}^2, \tag{18}$$

$I_z$ being the component of the total spin $\mathbf{I}=\sum_i\mathbf{I}_i$ parallel to $\mathbf{H}$. As usual, let us decompose the dipolar Hamiltonian:

$$\mathcal{H}_d=\sum_{q=-2}^{+2}G_q \qquad G_q=(G_{-q})^+=\sum_{i<j}F_q{}^{ij}A_q{}^{ij}, \tag{19}$$

where the $A_q{}^{ij}$ are the spin operators given by

$$A_0{}^{ij}=\tfrac{3}{2}I_z{}^iI_z{}^j-\tfrac{1}{2}\mathbf{I}^i\cdot\mathbf{I}^j, \qquad A_{\pm1}{}^{ij}=I_\pm{}^iI_z{}^j+I_z{}^iI_\pm{}^j, \qquad A_{\pm2}{}^{ij}=I_\pm{}^i\cdot I_\pm{}^j, \tag{20}$$

and the $F_q{}^{ij}$ are the lattice variables given by

$$F_0{}^{ij}=b_{ij}(1-3\cos^2\theta_{ij}), \quad F_{\pm1}{}^{ij}=-\tfrac{3}{2}b_{ij}\sin\theta_{ij}\cos\theta_{ij}\exp(\mp i\phi_{ij}), \quad F_{\pm2}{}^{ij}=-\tfrac{3}{4}b_{ij}\sin^2\theta_{ij}\exp(\mp2i\phi_{ij}), \tag{21}$$

where $\theta_{ij}$ and $\phi_{ij}$ specify the direction of the vector $\mathbf{a}_{ij}$ with respect to a coordinate system in which the axis $Oz$ is along the external field $\mathbf{H}$. $G_0$ is the adiabatic part of the dipolar Hamiltonian, producing no longitudinal relaxation. We note that

$$[G_q,\mathcal{H}_Z]=q\omega G_q, \tag{22}$$

where $\omega=-\gamma H$ and

$$\exp(i\mathcal{H}_Zt)G_q\exp(-i\mathcal{H}_Zt)=\exp(iq\omega t)G_q. \tag{23}$$

Then Eq. (18) yields

$$1/T_{ZE}=J_1(\omega)+J_2(2\omega), \tag{24}$$

where

$$J_q(\omega)=\int_{-\infty}^{+\infty}\mathcal{G}_q(\tau)\exp(-i\omega\tau)d\tau \tag{25}$$

and

$$\mathcal{G}_q(\tau)=q^2\sum_{i<j}\frac{|F_q{}^{ij}|^2\,\text{Tr}\{A_q{}^{ij}\exp(i\mathcal{H}_{\text{ex}}\tau)A_{-q}{}^{ij}\exp(-i\mathcal{H}_{\text{ex}}\tau)\}}{\text{Tr}\{I_z{}^2\}}. \tag{26}$$

The $J_q(\omega)$ are the spectral densities which are Fourier transforms of the correlation functions $\mathcal{G}_q(\tau)$. Further discussion of the evaluation of $\mathcal{G}_q(\tau)$ will be postponed until after a similar expression has been developed for $T_2$.

### B. Transverse Relaxation and Exchange Narrowing

The calculation of $T_2$ can proceed by essentially the same method. The precessing magnetization in the plane perpendicular to the $z$ axis is given by

$$\tilde{I}_x=I_x\cos\omega t+I_y\sin\omega t=U^{-1}(t)I_xU(t) \tag{27}$$

and has the expectation value

$$\langle\tilde{I}_x\rangle=\text{Tr}\{\tilde{I}_x\sigma\}=\text{Tr}\{I_x\sigma^*\}. \tag{28}$$

To study the dynamical behavior of $\langle\tilde{I}_x\rangle$, let us prepare the system so that it has a nonvanishing precessing magnetization at some given time

$$\sigma=(1-\beta_Z\mathcal{H}_Z-\beta_{\text{ex}}\mathcal{H}_{\text{ex}}-\alpha\omega\tilde{I}_x)(\text{Tr}1)^{-1}. \tag{29}$$

We need not specify $\alpha$, $\beta_Z$, and $\beta_{\text{ex}}$ any further. To give an example, once the system has come in equilibrium with the lattice at a temperature $T$, a 90° pulse will make $\beta_Z=0$, $\beta_{\text{ex}}=\alpha=\hbar(kT)^{-1}$.

The expectation value of the transverse magnetization in the high-temperature approximation becomes

$$\langle\tilde{I}_x\rangle\cong-\alpha\omega\,\text{Tr}\{I_x{}^2\}(\text{Tr}1)^{-1}, \tag{30}$$

and if we define the transverse relaxation rate by the relation

$$d\alpha/dt=-\alpha/T_2, \tag{31}$$

we obtain for $T_2$ an expression analogous to Eq. (17), $I_z$ being replaced by $I_x$:

$$\frac{1}{T_2}=\int_0^\infty d\tau\,\text{Tr}\{[I_x,\mathcal{H}_d][\mathcal{H}^*(-\tau),I_x]\}(\text{Tr}I_x{}^2)^{-1}, \tag{32}$$

$$\frac{1}{T_2}=\int_0^\infty d\tau\,\text{Tr}\{[I_x,\mathcal{H}_d]\exp(-i\mathcal{H}_{\text{ex}}\tau)[\exp(-i\mathcal{H}_Z\tau)\mathcal{H}_d\exp(i\mathcal{H}_Z\tau),I_x]\exp(i\mathcal{H}_{\text{ex}}\tau)\}\Big/\text{Tr}I_x{}^2. \tag{33}$$

In this case, since $[I_x,G_0]\neq0$, there will be a contribution to the transverse relaxation rate from the secular part of the dipolar Hamiltonian; when $\gamma\mathcal{H}\gg|J|$ the adiabatic contribution is predominant. Using standard commutation rules, one can obtain

$$[I_x,G_0]=\tfrac{3}{4}\sum_{i<j}F_0{}^{ij}(A_{-1}{}^{ij}-A_{+1}{}^{ij}),\quad[I_x,G_{\pm1}]=\sum_{i<j}F_{\pm1}{}^{ij}(\mp2A_0{}^{ij}-A_{\pm2}{}^{ij}),\quad[I_x,G_{\pm2}]=\mp\sum_{i<j}F_{\pm2}{}^{ij}I_z{}^iI_\pm{}^j. \tag{34}$$

(i) We now compute the adiabatic contribution $T_2'$ of the transverse relaxation time, obtained when $\mathcal{H}_d$ is replaced by $G_0$ in Eq. (33):

$$\frac{1}{T_2'}=\int_0^\infty d\tau\,\text{Tr}\{[I_x,G_0]\exp(-i\mathcal{H}_{\text{ex}}\tau)[G_0,I_x]\exp(i\mathcal{H}_{\text{ex}}\tau)\}\Big/\text{Tr}I_x{}^2. \tag{35}$$

The trace in the numerator on the right-hand side of this equation is obviously real, and the adiabatic linewidth can be written as

$$\frac{1}{T_2'}=\frac{1}{2}\int_{-\infty}^{+\infty}G_\omega(\tau)d\tau, \tag{36}$$

the correlation function $G_\omega(\tau)$[10] being defined as

$$G_\omega(\tau)=\frac{\text{Tr}\{[I_x,G_0]\exp(-i\mathcal{H}_{\text{ex}}\tau)[G_0,I_x]\exp(i\mathcal{H}_{\text{ex}}\tau)\}}{\text{Tr}I_x{}^2}. \tag{37}$$

Making use of the commutation rules previously given, $G_\omega(\tau)$ can take the following form:

$$G_\omega(\tau)=(9/8)\sum_{i<j}|F_0{}^{ij}|^2\frac{\text{Tr}\{A_1{}^{ij}\exp(i\mathcal{H}_{\text{ex}}\tau)A_{-1}{}^{ij}\exp(-i\mathcal{H}_{\text{ex}}\tau)\}}{\text{Tr}I_x{}^2}. \tag{38}$$

It is worth pointing out that this correlation function is not identical to either of the functions $\mathcal{G}_q(\tau)$ defined by Eq. (26). The Taylor expansion of $G_\omega(\tau)$ for small times $\tau$ is easily written in terms of the moments of the resonance line:

$$G_\omega(\tau)=M_2-\tfrac{1}{2}M_4\tau^2+(1/24)M_6\tau^4+\cdots. \tag{39}$$

(ii) We now concentrate on the real part $1/T_2{}^{na}$ of the nonadiabatic linewidth. Replacing $\mathcal{H}_d$ by $\sum_{q\neq0}G_q$ in

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[10] The notation $G_\omega(\tau)$ is that of Ref. 6. A normalized correlation function $G_\omega(\tau)/M_2$ is defined as $f_0(\tau)$, $\varphi_{\Delta\omega}(\tau)$, or $g_\omega(\tau)$ in Refs. 3, 5, or 6.

Eq. (33), one obtains using commutation rules [Eq. (34)]:

$$\frac{1}{T_2{}^{na}}=\int_{-\infty}^{+\infty}\{\exp(-i\omega\tau)k_0(\tau)+\tfrac{1}{4}\exp(-i\omega\tau)h_2(\tau)+\exp(-2i\omega\tau)h_1(\tau)\}d\tau, \tag{40}$$

where we define three new correlation functions:

$$k_0(\tau)=\frac{4\sum_{i<j}|F_1{}^{ij}|^2\,\mathrm{Tr}\{A_0{}^{ij}(\exp i\mathcal{H}_{\mathrm{ex}}\tau)A_0{}^{ij}(\exp -i\mathcal{H}_{\mathrm{ex}}\tau)\}}{\mathrm{Tr}I_z{}^2}, \tag{41}$$

$$h_q(\tau)=q^2\sum_{i<j}|F_{q-3}{}^{ij}|^2\frac{\mathrm{Tr}\{A_q{}^{ij}\exp(i\mathcal{H}_{\mathrm{ex}}\tau)A_{-q}{}^{ij}\exp(-i\mathcal{H}_{\mathrm{ex}}\tau)\}}{\mathrm{Tr}I_z{}^2}, \tag{42}$$

$$q=1,\ 2.$$

Altogether we have thus introduced six correlation functions [$\mathcal{G}_q(\tau)$ and $h_q(\tau)$ for $q=1$ or 2, $G_\omega(\tau)$ and $k_0(\tau)$] to calculate both relaxation times in the most general case. To proceed in spite of this complication we must take more restrictive assumptions.

### C. Powder Assumption

We assume that we are dealing with a powder and observe angular averages of the relaxation rates previously calculated. In the case of He$^3$, this assumption is in conflict with the deductions from studies by x-ray diffraction,[11] where it was possible only to grow single crystals. From the point of view of magnetic resonance, our assumption is feasible if the relaxation times of various crystallites are not too different, i.e., if they do not vary very much with the orientation of the magnetic field, which seems reasonable. Besides, as we will see, this assumption seems to be justified by the results.

For a powder, the averages over the lattice coordinates become:

$$\begin{aligned}|\bar{F}_0{}^{ij}|^2&=(\tfrac{4}{5})(b^{ij})^2,\\ |\bar{F}_1{}^{ij}|^2=|\bar{F}_2{}^{ij}|^2&=(3/10)(b^{ij})^2.\end{aligned} \tag{43}$$

The number of useful correlation functions is reduced, since one now has

$$\begin{aligned}h_q(\tau)&=\mathcal{G}_q(\tau), \quad q=1,\ 2\\ G_\omega(\tau)&=3\mathcal{G}_1(\tau),\end{aligned} \tag{44}$$

so that the adiabatic linewidth becomes

$$1/T_2{}'=\tfrac{3}{2}J_1(0). \tag{45}$$

In fact, the simplification is even greater because the correlation functions $\mathcal{G}_q(\tau)$ and $k_0(\tau)$ are isotropic for a powder.

In Eq. (41) we can perfectly well replace the operator $A_0{}^{ij}$ by the operator

$$\begin{aligned}X^{ij}&=\tfrac{3}{2}I_x{}^iI_x{}^j-\tfrac{1}{2}\mathbf{I}^i\cdot\mathbf{I}^j\\ &=-\tfrac{1}{2}A_0{}^{ij}+\tfrac{3}{8}(A_2{}^{ij}+A_{-2}{}^{ij}),\end{aligned}$$

which leads to

$$k_0(\tau)=\tfrac{3}{8}\mathcal{G}_2(\tau). \tag{46a}$$

For $\mathcal{G}_2(\tau)$ we can also replace in Eq. (26) the operator

$$A_2{}^{ij}=(I_x{}^i+iI_y{}^i)(I_x{}^j+iI_y{}^j),$$

by the operator

$$\begin{aligned}W^{ij}&=(I_z{}^i+iI_x{}^j)(I_z{}^j+iI_x{}^j)\\ &=A_0{}^{ij}-\tfrac{1}{4}(A_2{}^{ij}+A_{-2}{}^{ij})+\tfrac{1}{2}i(A_1{}^{ij}+A_{-1}{}^{ij}),\end{aligned}$$

which leads to

$$\tfrac{7}{8}\mathcal{G}_2(\tau)=k_0(\tau)+2\mathcal{G}_1(\tau),$$

or (46b)

$$\tfrac{1}{2}\mathcal{G}_2(\tau)=2\mathcal{G}_1(\tau).$$

We are thus left with only one independent correlation function, which we shall choose to be $\mathcal{G}_1(\tau)$. Making use of both Eqs. (46a) and (46b), Eq. (24) becomes

$$1/T_{ZE}=J_1(\omega)+4J_1(2\omega), \tag{47a}$$

and Eq. (40) becomes

$$\frac{1}{T_2}=\frac{1}{T_2{}'}+\frac{1}{T_2{}^{na}}=\tfrac{3}{2}J_1(0)+\tfrac{5}{2}J_1(\omega)+J_1(2\omega). \tag{47b}$$

One notes that at low magnetic fields (extreme narrowing case[9]) both transverse and longitudinal relaxation rates are now equal to $(10/3)(1/T_2{}')$. We have thus demonstrated once more the celebrated 10/3 ratio between the linewidths in the adiabatic and in the extreme narrowing case.

As long as the mathematical form of the spectral density $J_1(\omega)$ is unspecified, the Eqs. (47a) and (47b) are valid in the case of motion modulation of the dipolar field (see BPP equations[9]), provided the lattice Hamiltonian is isotropic, as well as in the case of exchange modulation of the dipolar field.

The consequence of the powder assumption which have obviously been observed in RHM are that (1) there is only one observed transverse relaxation time; (2) at low fields $T_{ZE}=T_2$ and (3) the asymptotic value of the $T_2$ ratio in high and low fields is 10/3. It is worth

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[11] A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. **110**, 775 (1958).

pointing out that nothing has yet been assumed about the range of the exchange interaction.

### D. Gaussian Assumption

So far we have shown that all the magnetic resonance properties are governed, in the powder assumption, by the knowledge of a single correlation function $\mathcal{G}_1(\tau)$. To compute $\mathcal{G}_1(\tau)$ for all values of $\tau$ is a very difficult problem, even when using a modern computer.[12]

Following the model Anderson and Weiss[5] used for the adiabatic linewidth, one usually assumes $\mathcal{G}_1(\tau)$ to be a Gaussian with a curvature at origin given by Eqs. (39) and (44):

$$\mathcal{G}_1(\tau)=(M_2/3)\exp(-\tfrac{1}{2}\omega_e^2\tau^2)\,, \qquad (48)$$

where

$$\omega_e^2=M_4/M_2\,. \qquad (49)$$

The exchange modulation frequency $\omega_e$ can be calculated for both phases of solid He$^3$, assuming now that the exchange interaction is nonvanishing only for first neighbors and knowing $M_2$ and $M_4$ as a function of $J$[13]:

$$\begin{aligned}\omega_e&=2.387\ J\ \text{(bcc phase)}\,,\\&=3.24\ \ J\ \text{(hcp phase)}\,.\end{aligned} \qquad (50)$$

The Gaussian assumption being made,[14] it is easy to calculate the adiabatic linewidth by means of Eq. (45):

$$J_1(\omega)=(M_2/3\omega_e)(2\pi)^{1/2}\exp(-\omega^2/2\omega_e^2)\,, \qquad (51)$$

$$\frac{1}{T_2'}=\left(\frac{\pi}{2}\right)^{1/2}\left(\frac{M_2}{\omega_e}\right) \qquad (52)$$

and then relate it to the exchange interaction. To emphasize that the value so obtained for the exchange $J$ is based on the Gaussian assumption and, strictly speaking, should not be taken for granted before that assumption is checked, we will call it $J_G$:

$$(J_G/2\pi)=18.98\times10^3(T_2'/V^2)\ \text{for the bcc phase}\,, \qquad (53a)$$

$$(J_G/2\pi)=13.926\times10^3(T_2'/V^2)\ \text{for the hcp phase}\,, \qquad (53b)$$

where the molar volume $V$ is in cm$^3$, $T_2'$ in sec and $J_G/2\pi$ in Mc/sec. For intermediate frequencies, we have

$$T_{ZE}^{-1}=\frac{1.89\times10^{11}}{\omega_eV^2}\left\{\exp\left(-\frac{\omega^2}{2\omega_e^2}\right)+4\exp\left(-\frac{2\omega^2}{\omega_e^2}\right)\right\}\ \text{sec}^{-1}\,, \qquad (54a)$$

$$T_2^{-1}=\frac{1.89\times10^{11}}{\omega_eV^2}\left\{\tfrac{3}{2}+\tfrac{5}{2}\exp\left(-\frac{\omega^2}{2\omega_e^2}\right)+\exp\left(-\frac{2\omega^2}{\omega_e^2}\right)\right\}\ \text{sec}^{-1}\,. \qquad (54b)$$

These equations are a special case of Eqs. (47) under the Gaussian assumption. Within less than 1%, the numerical factor in front of the parentheses is the same for both hcp and bcc phases.

### E. The Line Shift

The calculations we made so far treated the traceless dipolar Hamiltonian $\mathcal{H}_d$ as a perturbing operator. It is a standard result of quantum mechanics that some average displacement of the energy levels will appear only in the second order with respect to the perturbing term and will be due only to the nonsecular part of $\mathcal{H}_d$. This means that the nonadiabatic linewidth $1/T_2^{na}$ must be associated with an imaginary part $i\delta\omega$, a mathematical representation of a shift $\delta\omega$ easily related[3] to the correlation function $\mathcal{G}_1(\tau)$ and given, in the powder assumption, by

$$-\delta\omega=(\tfrac{1}{3})M_2\tau_1''+(\tfrac{2}{3})M_2\tau_2''\,, \qquad (55)$$

$$\left(\frac{M_2}{3}\right)\tau_q''=\mathcal{I}m\int_0^\infty\exp(-iq\omega\tau)\mathcal{G}_1(\tau)d\tau\,. \qquad (56)$$

This shift vanishes at zero and at high magnetic fields. It has a maximum for a Larmor frequency which is, *a priori*, of the order of $\omega_e$ (or $J$) and is then equal to $1/T_2$ within a factor of the order of unity.

It is found that in the Gaussian approximation

$$-\delta\omega=\frac{0.76\times10^{11}}{\omega_eV^2}\left\{\exp\left(-\frac{\omega^2}{2\omega_e^2}\right)\phi\left(\frac{\omega}{\omega_e}\right)+2\exp\left(-\frac{2\omega_e^2}{\omega_e^2}\right)\phi\left(\frac{2\omega}{\omega_e}\right)\right\}\,, \qquad (57)$$

where

$$\phi(u)=\int_0^u\exp\left(\frac{x^2}{2}\right)dx\,.$$

This formula is again valid for both hcp and bcc phases.

## III. EXPERIMENTAL APPARATUS AND PROCEDURE

The method used for the relaxation time measurements was the same as that described in RHM. The temperature during the measurements was kept between

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[13] The value of $M_2$ for both the bcc and hcp phases is given by Eq. (3) of Ref. 7; for given nuclear species and given molar volumes, the second moments in the two phases happen to differ by less than 1%. As for $M_4$, Eqs. (4) of Ref. 7 are, in the case of a spin $\frac{1}{2}$, correct for the hcp phase but erroneous for the bcc phase for which we calculated the correct value to be

$$M_4^{\alpha}=31.456(\gamma^4\hbar^2J^2/a^6),$$

smaller by 17% than the value of Ref. 7. Consequently, exchange interactions obtained in Refs. 1 and 7 from relaxation measurements in the bcc phase should be increased by 9%.

[14] One way to justify Eq. (48) would be to compare the fourth derivative of its right-hand side at $\tau=0$ with the Taylor expansion of Eq. (39), i.e., to evaluate the ratio

$$\rho=3\omega_e^4(M_2/M_6)=3M_4^2/(M_6M_2),$$

which should be equal to unity were $\mathcal{G}_1$ a Gaussian. A very crude estimate is to see what it is when the resonance line is taken to be a truncated Lorentzian (see Ref. 6, p. 107); $\rho$ is then equal to 5/3, thus is not much larger than unity.

TABLE I. Values of $T_1$ and $T_2$ obtained with the double cavity. All values are ±5% unless otherwise noted. $J_G$ are the values obtained for the exchange interactions by Eqs. (53).

| hcp phase | | | | | bcc phase | |
|---|---|---|---|---|---|---|
| $V=19.50$ cm$^3$/mole | | $V=19.55$ cm$^3$/mole | | | $V=20.40$ cm$^3$/mole | |
| $\omega/2\pi$ Mc/sec | $T_2$ msec | $\omega/2\pi$ Mc/sec | $T_1$ msec | $T_2$ msec | $\omega/2\pi$ Mc/sec | $T_2$ msec |
| 4.64 | 7.1 | 2.10 | 107 | | 7.40 | 20.6 |
| 4.22 | 7.3 | 2.04 | 96 | | 6.80 | 20.2 |
| 3.54 | 7.3 | 1.80 | 57 | 6.1 | 6.30 | 20.2 |
| 2.92 | 7.1 | 1.45 | 34.4 | 5.7 | 5.50 | 19.4 |
| 2.44 | 7.1 | 1.20 | 19.6 | 5.2 | 5.00 | 17.7 |
| 2.19 | 7.1 | 0.890 | 10.0 | 3.7±0.3 | 4.10 | 15.9 |
| 1.92 | 6.9 | 0.670 | 6.8±0.7 | 3.0±0.3 | 3.30 | 15.3 |
| 1.41 | 5.9 | 0.540 | 4.9±0.5 | | 2.65 | 13.0 |
| 1.12 | 4.8 | 0.470 | 4.6±0.5 | | 2.00 | 11.1 |
| 0.925 | 4.4 | 0.400 | 3.5±0.4 | | 1.36 | 10.6 |
| 0.713 | 3.7 | | | | 1.10 | 8.7 |
| 0.574 | 3.4±0.3 | | | | 0.580 | 7.8±0.7 |
| 0.500 | 2.9±0.3 | | | | 0.375 | 6.6±0.7 |
| 0.360 | 2.6±0.3 | | | | | |
| $J_G/2\pi=0.267$ Mc/sec | | $J_G/2\pi=0.32$ Mc/sec | | | $J_G/2\pi=0.94$ Mc/sec | |

about 1.3 and 0.7°K, where the plateau in $T_1$ and $T_2$ occurred. The data for a given density were taken at up to 12 different frequencies and both phases were investigated during the same series of experiments, in order to avoid any systematic differences in procedure.

For the measurements of the frequency shift between samples having different densities, the method of differential frequency measurement was chosen. Two identical high-pressure cavities were constructed in the same block of brass. Care was taken to avoid any magnetic metal or superconducting solder. One cavity was filled with solid He$^3$ with a molar volume of about 24 cm$^3$. This sample was then used as the reference. For this sample $\omega_e/2\pi$ was greater than 50 Mc/sec so that the shift of the resonance predicted by Eq. (57) was negligible at the frequency used, about 1 Mc/sec. The other cavity was filled with solid He$^3$ of various densities. During an experiment, the magnetic field was first stabilized and then the cryostat temperature was lowered from 4°K to about 0.7°K, the solid He$^3$ in the two cavities having different densities. The center of the resonance for one rf cavity was determined by observing the tail in the NMR signal following a 90° pulse and adjusting the frequency until no beats could be observed. Then the pulse system was immediately switched to the other sample cavity and the period of the beats following the 90° pulse was measured. The beat frequency observed for the second sample was then the difference in the resonant frequencies of the two samples.

In order to obtain the amount the line shifted as the density was changed, the frequency difference between the two samples cavities was first measured with a low-density solid in both cavities and then with a high-density solid (~20 cm$^3$/mole) in the second cavity.[15] The magnitude of the shift due to the change in density was then the difference between the two values of the relative frequency difference of the cavities.

The chief error in this procedure was in setting the reference sample on resonance. The precision in setting the first cavity on resonance and in measuring the beat frequency of the second cavity depends on the length of time that the tail following a 90° pulse can be observed. By trying to reproduce the measurements of the frequency difference between the cavities many times with different field gradients between the cavities, it was found experimentally that the minimum possible error $\Delta\delta\omega/2\pi$ in the frequency difference measurement was approximately $20\times10^{-3}/T_2^*$ cps, where $T_2^*$ is the characteristic decay time after the 90° pulse. If the external field were ideally homogeneous, $T_2^*$ would be the same as $T_2$. Using the value of the shift given by Eq. (57) and with $T_2^*=T_2$, it is found that the most favorable ratio of the shift $\delta\omega$ to the error in the shift measurement $\Delta\delta\omega$ will be of the order of 3. In practice, we were unable to approach such a favorable ratio in the measurements because of the inhomogeneity in our magnetic field. It is possible that there were parts of the cryostat containing magnetic or superconducting impurities. At the highest frequencies the absolute frequency shift measured was the most accurate, but then the magnitude of the frequency shift as calculated from Eq. (57) was no longer favorable.

## IV. RESULTS AND DISCUSSION

### A. Nuclear Relaxation Times and the Spectral-Density Function

(1) From the consideration of Sec. II, it appears advantageous to present the results for $T_{ZE}$ and $T_2$

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[15] It was thought impractical to go to appreciably higher densities because, then, the frequency for observing the maximum in the shift is lowered to about 100 kc/sec. There the signal-to-noise ratio would not permit any precise measurements. Also, as is developed in Sec. III, the most favorable ratio of the frequency shift to the error in the shift measurement is independent of frequency.

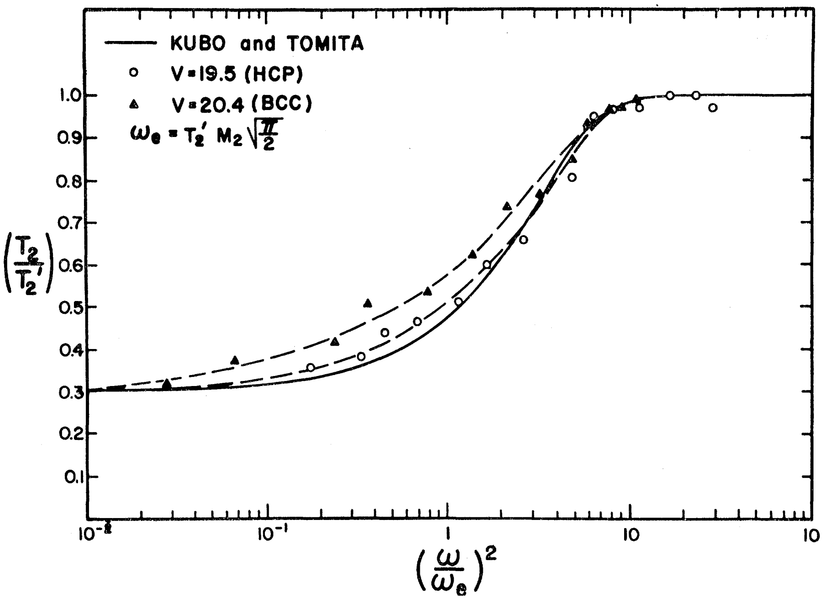

FIG. 1. The reduced transverse relaxation time $(T_2/T_2')$ versus the square reduced frequency $(\omega/\omega_e)^2$ for two molar volumes, one in the hcp phase and one in the bcc phase. The figure makes use of data given by Table I. The solid line is calculated by using Eq. (54b).

together. The raw data are tabulated in Table I and reduced plots similar to those described in RHM are presented in Figs. 1 and 2 for the two phases. The value of $J_G$ has been determined from the $T_2$ data [by using Eq. (53)] for each density at higher frequencies where $T_2'$ was measured. As can be seen in Fig. 2, the results for the hcp phase agree with the theoretical prediction based upon the Gaussian approximation for the correlation function.

Another way of reducing the data is to use Eqs. (47a) and (47b). If, for a given Larmor frequency, we measure $T_{ZE}$ and $T_2$, those two linear equations are a system with two unknowns $J_1(\omega)$ and $J_1(2\omega)$ which we may determine simultaneously. This procedure was used to analyze the reduced plots in Figs. 5 and 6 of RHM together with the new data presented in Table I for an ensemble of molar volumes in the bcc phase. We thus obtained the ratio $J_1(\omega)/J_1(0)$ plotted in Fig. 3 of this

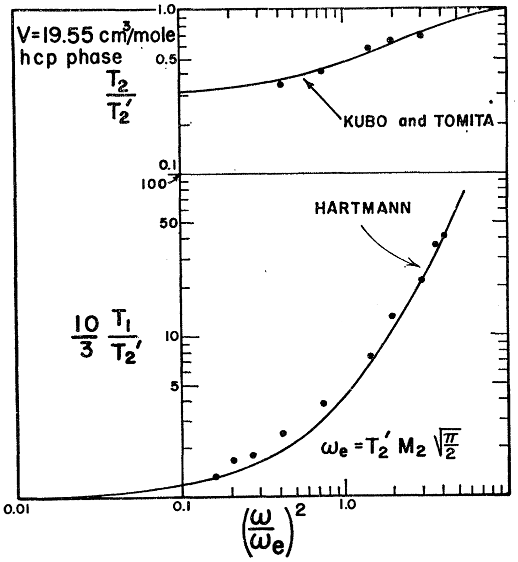

FIG. 2. The reduced relaxation times, transverse $(T_2/T_2')$ and longitudinal $(10/3)(T_1/T_2')$, versus the square reduced frequency $(\omega/\omega_e)^2$, in the hcp phase. The figure makes use of data given by Table I. The solid lines are calculated by using Eqs. (54a) and (54b).

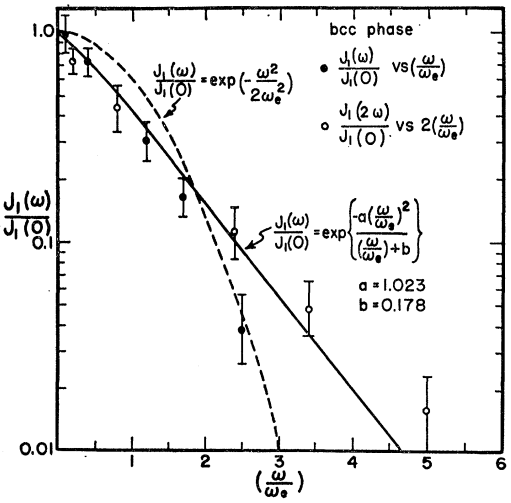

FIG. 3. The reduced spectral density $J_1(\omega)/J_1(0)$ versus the reduced frequency $(\omega/\omega_e)$, in the bcc phase for several molar volumes. The figure makes use of data given in RHM and by Table I. The exchange modulation frequency is obtained by Eq. (52). The ratio $J_1(\omega)/J_1(0)$ is obtained by solving the system of Eqs. (47a) and (47b). The dashed line is the reduced spectral density in the Gaussian assumption. The solid line has been obtained by a least-squares fitting of the experimental points to the empirical expression given by Eq. (58).

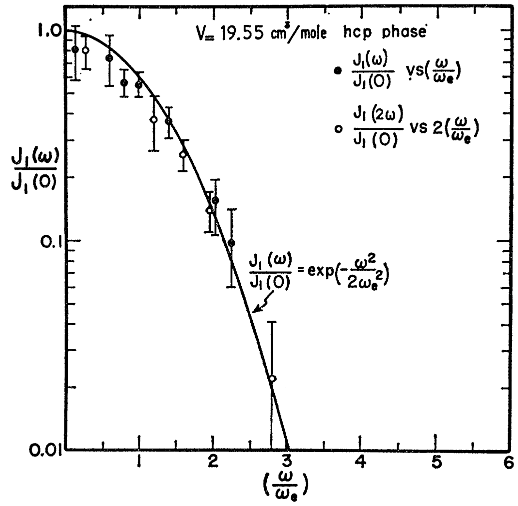

FIG. 4. The reduced spectral density $J_1(\omega)/J_1(0)$ versus the reduced frequency $(\omega/\omega_e)$, in the hcp phase ($V=19.55$ cm$^3$). The figure makes use of data given by Table I. The exchange modulation frequency is obtained by Eq. (52). The ratio $J_1(\omega)/J_1(0)$ is obtained by solving the system of Eqs. (47a) and (47b). The solid line is calculated by using Eq. (51).

article versus $x=\omega/\omega_e$, where $\omega_e$ is a value for the exchange modulation frequency obtained by Eq. (52).

To find an analytical expression for this spectral density, a least-squares fit to the expression

$$J_1(\omega)/J(0)=\exp[-ax^2/(x+b)] \tag{58}$$

was made. This empirical expression can fit a Gaussian ($b$ very large) as well as a plain exponential ($b=0$). Such a fitting gave values for $a$ and $b$ for the bcc phase with a reasonably small mean deviation, as shown in Fig. 3. The fitting corresponds to a curve which is almost an exponential in the range of the frequencies used in the experiments. The spectral density appears to decrease less rapidly in the wings than a Gaussian.

The same procedure was used for the hcp phase ($V=19.55$ cm$^3$) as is shown in Fig. 4. For this phase it is evident that a spectral density based upon a Gaussian correlation function fits the calculated points well.

### B. The Frequency-Shift Experiment

Our data for the frequency shift at several densities are presented in Table II, which gives also the frequency shift $\delta\omega_{\text{th}}$ calculated by means of Eq. (57). For the bcc phase, that theoretical shift is calculated in the Gaussian approximation, only for the sake of comparison. Since this approximation has just been shown not to be verified in that phase. As can be seen, the scatter of the results is too large to allow any quantitative comparison with the theory. The only conclusion that can be drawn from our measurements is that the frequency shift, if it exists, is not larger than about two or three times the shift Kubo and Tomita have predicted. In order to obtain a more precise result, in particular, to detect any deviations from the curve calculated from Kubo and Tomita's theory, an improvement of the differential-frequency measurement by a factor of 10 must be made. The difficulty in obtaining such an accuracy has already been mentioned. By eliminating the inhomogeneities present in the magnetic field in the cryostat, and by improving the signal-to-noise ratio at the low frequencies that are used our accuracy would perhaps improve by a factor of 5.

TABLE II. The measured frequency shift ($\delta\omega_{\text{exp}}/2\pi$) for several samples. The molar volume of the reference sample is 24 cm$^3$/mole. The exchange modulation frequency $\omega_e$ is obtained by Eq. (52). $\delta\omega_{\text{th}}$ is the frequency shift calculated in the Gaussian approximation by means of Eq. (57).

| Phase | $V_{\text{test}}$ cm$^3$/mole | $T_2'$ msec | $\omega/\omega_e$ | $-\delta\omega_{\text{exp}}/2\pi$ cps | $-\delta\omega_{\text{th}}/2\pi$ cps |
|---|---|---|---|---|---|
| hcp | 19.3 | 6.2 | 0.76 | $0\pm50$ | 13.7 |
| bcc | 19.83 | 11 | 0.47 | $0\pm20$ | 6.8 |
| bcc | 20.2 | 16.5 | 1.65 | $15\pm30$ | 3.8 |
| bcc | 20.6 | 26 | 1.10 | $0\pm20$ | 3.2 |

## V. CONCLUSION

It has been possible to determine the spectral-density ratio $J_1(\omega)/J_1(0)$ for solid He$^3$ in the bcc and hcp phases from relaxation time measurements. The spectral densities reflect what the reduced plot of the relaxation times has already shown: that there is a surprising difference in the shape of the correlation function for the two phases, which have very different structures.

For the bcc lattice, a given atom has its first neighbors at a distance $a$ and its second neighbors at a distance $2a/\sqrt{3}$, thus not very much larger than $a$. Consequently, in view of the existing theories for the exchange interactions in solid He$^3$, the exchange for second neighbors in the bcc lattice may still be larger than the dipolar interaction. This is indeed a complication for the problem of the spectral density.

In principle, the shape of $\mathcal{G}_1(\tau)$ has a direct bearing on the experimental determination of an exchange interaction by measurements of the relaxation time. The real interaction $J$ is equal to $J_G$ multiplied by a factor which differs from unity if $\mathcal{G}_1(\tau)$ differs from a Gaussian. In practice the precision on that factor would be very poor if we had to use an experimental spectral density, given, for instance, by our Fig. 3. That means that any determination of $J$ based on relaxation-time measurement and on assumptions made on the correlation function is not absolute but relative.

On the other hand, measurements of $J$ from spin-lattice relaxation in the bcc phase at 20.15 cm$^3$ were carried out by RHM. These measurements depend on the ratio[16] $C_Z/C_E$, where $C_Z$ and $C_E$ are the specific heats of the Zeeman and exchange reservoirs, and therefore do not depend on any assumption regarding the correlation function. The $J$ derived from this measure-

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[16] See Ref. 1, Eqs. (17) and (18).

ment (~800 kc/sec) is in good agreement with that obtained from $T_2$ and $T_{ZE}$ data in the plateau region (780 kc/sec). Therefore, the deviation of $J_G$ from $J$ is shown to be small, certainly within the experimental error of the determination of the exchange integral.

The frequency shift experiment has given an upper limit one might expect for the shift predicted by Kubo and Tomita,[3] and our results are consistent with their calculations. In view of the errors inherent to shift measurements, it is improbable that much quantitative information will be obtained even under the best conditions.

## ACKNOWLEDGMENTS

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# Electronic Structure of $MgF_2:Co^{++}$

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The $F^{19}$ superhyperfine structure of the EPR spectra of $Co^{++}$ in $MgF_2$ is interpreted with simple molecular-orbital theory. A necessary preliminary analysis is made of the $g$ tensor and of the spacing of the six Kramers doublets derived from the $^4T_1$ ground manifold. The ligand-field parameters of the rhombic field, $\Delta \cong 510$ cm$^{-1}$ and $\Gamma \cong -390$ cm$^{-1}$, and the spin-orbit coupling, $\lambda \cong -157$ cm$^{-1}$, are significantly different from values derived from less complete data. The reported superhyperfine interactions provide sufficient data to determine, without recourse to much less certain orbital-reduction factors, the $s$-, sigma-, and pi-bonding fractions: $f_s = (0.61 \pm 0.02)\%$, $f_\sigma = (3.9 \pm 0.3)\%$, and $f_\pi = (0.9 \pm 0.3)\%$ for the two equivalent fluorine ions along [110]. For the other four fluorine ions similar estimates are obtained. These results are at variance with the suggestion, made for octahedral $Co^{++}$, that sigma and pi bonding are of comparable magnitude.

## INTRODUCTION

A PREVIOUS paper[1] describes the EPR spectra of cobalt as a dilute substitutional impurity in magnesium fluoride, and presents a complete analysis of the complex $F^{19}$ superhyperfine structure (shfs). It is the purpose of the present paper to interpret the measured superhyperfine tensors at the simplest possible level of phenomenological molecular-orbital (MO) theory.

$MgF_2:Co^{++}$ and closely related materials provide an unusually complete set of data to be correlated and interpreted.

(1) The EPR spectra are fit by a spin-Hamiltonian with completely anisotropic spectroscopic splitting and cobalt hyperfine tensors. The superhyperfine tensors of two nonequivalent $F^{19}$ ligand-nuclei are also anisotropic. The principal-axis directions of one of these tensors are not symmetry-determined, and do not coincide with the bond direction. The nearly identical spectra of $ZnF_2:Co^{++}$ have not been completely analyzed.[2,3]

(2) The infrared (IR) absorption spectrum of $CoF_2$ at low temperature[4] has several peaks near 1000 cm$^{-1}$.

(3) Fluorescence spectra[5] provide remarkably precise information of the energies of the lowest set of excited states.

(4) EPR[6,7] and optical[8] spectra are known for the corresponding octahedral complex $KMgF_3:Co^{++}$.

Besides these researches, there have been studies of the static susceptibility and antiferromagnetic resonance of[9–15] $CoF_2$ and of the NMR of fluorine[15] and cobalt.[16]

Simple MO theory of superhyperfine interactions has been described for similar systems,[7,17,18] but not for an orbitally unquenched octahedral ground state which is

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