

Dipolar Corrections to Spectral Densities in Predominantly Exchange-Coupled Systems

George Reiter

Department of Physics, City University of New York, New York, New York 10031

F. C. Barreto

Institute de Ciencias Exatas, Universidade Federal de Minas Gerais Belo Horizonte, M. G. Brazil

(Received 6 February 1973)

An exact expression for the spectral density in an exchange- and dipolar-coupled system in the presence of an external field is derived. A simplified form of this result is obtained when it is evaluated to lowest significant order in the ratio of dipolar to exchange energy ρ and at infinite temperature. The correction to the spectral densities of the system is linear in ρ at zero frequency for spins a fixed distance apart, and is the result of the introduction of a finite lifetime to the $q=0$ modes as a result of breaking the rotational symmetry. The exact expression is evaluated using a constant-relaxation-time approximation and the result applied to the interpretation of Myers and Narath's NMR experiments on GdP. Although there are significant corrections arising from the presence of the dipolar terms, they do not suffice to remove the discrepancy between the experimentally measured and the theoretically predicted spectral densities.

I. INTRODUCTION AND FORMAL EXPRESSION FOR SPECTRAL DENSITY

In this paper we present an approximate calculation of the effect of small dipole interactions on the spectral density in a Heisenberg paramagnet. This work was motivated in part by the experiment of Myers and Narath¹ (MN) on GdP, which was interpreted by them as a measurement of the correlation function;

$$F(z) \equiv \int_0^\infty e^{tzz^*} [\langle S_i^*(t) S_i^*(0) \rangle + \langle S_i^*(t) S_{i+1}^*(0) \rangle] dt$$

on a simple-cubic lattice. Their results are in significant disagreement with theoretical and numerical predictions for $F(z)$. An important feature of their interpretation is the neglect of the dipole interaction, since they assume that the Zeeman term in the Hamiltonian describing the GdP system in a magnetic field commutes with the remainder of the Hamiltonian. We will show that this neglect is not justified, and that there are significant ($\sim 14\%$) corrections to the spectral densities arising from the dipole terms, even though the ratio of nearest-neighbor dipole to exchange energy is only 0.02 in GdP. The corrections are a result of the large contribution to $F(0)$ from the long-wavelength diffusive modes in the system being reduced by the dipole interaction, which, by breaking the rotational symmetry of the Hamiltonian, introduces a finite lifetime to the modes as $\vec{q} \rightarrow 0$. They do not suffice to reconcile the theory and the experiment of MN.

In this section we derive an exact formal expression for the spectral density of the magnetization modes in a system described by the Hamiltonian

$$\mathcal{H} = -g\mu_B H \sum_i S_i^* - \frac{1}{2} \sum_{i,j} V_{i,j} \vec{S}_i \cdot \vec{S}_j - \frac{(g\mu_B)^2}{2} \times \sum_{i,j} \frac{\vec{S}_i \cdot \vec{S}_j}{(r_{ij})^3} - \frac{(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{(r_{ij})^5}. \quad (1.1)$$

We define $\hbar\omega_D$ as $(g\mu_B)^2/a^3$, where a is the lattice parameter, and where $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$. The derivation is based on standard methods that seem not to have been applied explicitly to this problem before, and leads to a result that is in a different form than that given by the treatment of Kubo and Tomita.² The expression obtained is valid for arbitrary temperatures. The limiting form of this expression, to the lowest significant order in $\rho = \omega_D/V$, and at infinite temperature is obtained ($V = |V_{i,i+1}|$).

In Sec. II, we introduce an approximation that has been shown by Reiter³ to yield reasonably accurate results for the spectral densities in the case that the dipole interaction is zero, in order to obtain an approximate result for the spectral density. We calculate the effect of varying the strength of the dipole term, and show that the corrections to the zero-frequency spectral density are proportional to ω_D/V . This has been pointed out also in the recent work of Myers and Narath.⁴ We will rewrite the Hamiltonian as

$$\mathcal{H} = -g\mu_B H \sum_i S_i^* - \frac{1}{2} \sum_{i,j} A_{ij} \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \sum_{i,j} B_{ij} S_i^* S_j^* - \frac{1}{2} \sum_{i,j} D_{ij} S_i^* S_j^* + D_{ij}^* S_i^* S_j^* - \frac{1}{2} \sum_{i,j} (C_{ij} S_i^* S_j^* + C_{ij}^* S_i^* S_j^*), \quad (1.2)$$

$$C_{i2} = C_{2i}^*, \quad D_{i2} = D_{2i}^*,$$

and the analysis will apply to this more general form. The Hamiltonian of (1.1) is recovered by choosing

$$A_{ij} = V_{ij} + \frac{1}{2} (1 - 3 \cos^2 \theta_{ij}) (g\mu_B)^2 r_{ij}^{-3},$$

$$B_{ij} = -\frac{3}{2} (1 - 3 \cos^2 \theta_{ij}) (g\mu_B)^2 r_{ij}^{-3},$$

$$C_{ij} = \frac{3}{2} \sin \theta_{ij} \cos \theta_{ij} e^{i\varphi_{ij}} (g\mu_B)^2 r_{ij}^{-3},$$

$$D_{ij} = \frac{3}{4} \sin^2 \theta_{ij} e^{-2i\varphi_{ij}} (g\mu_B)^2 r_{ij}^{-3}.$$

The linear response of a magnetization mode of wave vector \vec{q} is determined by

$$\Sigma^\alpha(\vec{q}, t) = \langle S^\alpha(\vec{q}, t) | S^\alpha(\vec{q}) \rangle, \quad \alpha = \pm, z \quad (1.3)$$

where $\langle A | B \rangle \equiv \langle \int_0^\beta e^{\tau \mathcal{H}} A^* e^{-\tau \mathcal{H}} B d\tau \rangle$ for any two operators A and B . As the symbol implies, $\langle | \rangle$ is actually an inner product on the vector space of all bounded linear operators in the Hilbert space of the spin system. The Liouville operator on this vector space for any Hamiltonian \mathcal{H} is defined by its action on any operator O as

$$\mathcal{L} \times O = (1/\hbar) [O, \mathcal{H}].$$

We will define \mathcal{L} , \mathcal{L}_z , \mathcal{L}_0 , \mathcal{L}_1 , and \mathcal{L}_2 , corresponding to the full Hamiltonian, the Zeeman term, \mathcal{H}_0 , \mathcal{H}_1 , and \mathcal{H}_2 , where

$$\mathcal{H}_0 = -\frac{1}{2} \sum_{i,j} A_{ij} S_i S_j - \frac{1}{2} \sum_{i,j} B_{ij} S_i^z S_j^z, \quad (1.4a)$$

$$\mathcal{H}_1 = -\frac{1}{2} \sum_{i,j} (C_{ij} S_i^+ S_j^z + C_{ij}^* S_i^z S_j^+), \quad (1.4b)$$

$$\mathcal{H}_2 = -\frac{1}{2} \sum_{i,j} (D_{ij} S_i^+ S_j^+ + D_{ij}^* S_i^- S_j^-). \quad (1.4c)$$

The time dependence of the operators is then given by $O(t) = e^{-i\mathcal{L}t} \times O$, and hence the Laplace transform of the response function $\Sigma^\alpha(\vec{q}, t)$ can be written

$$\Sigma^\alpha(\vec{q}, z) = \int_0^\infty e^{izt} \Sigma^\alpha(\vec{q}, t) dt = i \langle S^\alpha(\vec{q}) | [z - \mathcal{L}]^{-1} | S^\alpha(\vec{q}) \rangle, \quad (1.5a)$$

i. e., it is a diagonal matrix element of the resolvent of the Liouville operator for the system. The expression (1.5a) may be reduced to a usable form by introducing a projection operator P^α onto the space of all single spin fluctuation states. P^α is defined as $\sum_a | S^\alpha(\vec{q}) \rangle \langle S^\alpha(\vec{q}) | / \chi^\alpha(\vec{q}, 0)$, where $\chi^\alpha(\vec{q}, 0) \equiv \langle S^\alpha(\vec{q}) | S^\alpha(\vec{q}) \rangle$. Let us define $D(z)$ as the diagonal part of $R(z) = (z - \mathcal{L})^{-1}$ in a basis that includes the states $| S^\alpha(\vec{q}) \rangle$, and $U(z)$ as the off-diagonal part.

Then from the identity $R(z)(z - \mathcal{L}) = I$ we have

$$P^\alpha R(z)(z - \mathcal{L}) P^\alpha = P^\alpha, \quad (1.5b)$$

$$P^\alpha R(z)(z - \mathcal{L})(I - P^\alpha) = 0. \quad (1.5c)$$

Since $R(z) = D(z) + U(z)$, we have

$$z P^\alpha D(z) P^\alpha - P^\alpha D(z) \mathcal{L} P^\alpha - P^\alpha U(z) \mathcal{L} P^\alpha = P^\alpha, \quad (1.6a)$$

$$z P^\alpha U(z)(I - P^\alpha) - P^\alpha D(z) \mathcal{L}(I - P^\alpha) - P^\alpha U(z) \mathcal{L}(I - P^\alpha) = 0 \quad (1.6b)$$

or

$$P^\alpha D(z) P^\alpha (z - P^\alpha \mathcal{L} P^\alpha) - [P^\alpha U(z)(I - P^\alpha)(I - P^\alpha \mathcal{L} P^\alpha) = P^\alpha, \quad (1.7a)$$

$$P^\alpha U(z)(I - P^\alpha)[z - (I - P^\alpha) \mathcal{L}(I - P^\alpha)] = P^\alpha D(z) P^\alpha \mathcal{L}(I - P^\alpha), \quad (1.7b)$$

where we have used the fact that $P^\alpha D(z)(I - P^\alpha) = P^\alpha U(z) P^\alpha = 0$ in going from (1.6) to (1.7). Solving (1.7b) for $P^\alpha U(z)(I - P^\alpha)$ and inserting the result in (1.7a) we obtain, upon solving the resultant equation for $P^\alpha D(z) P^\alpha$

$$P^\alpha D(z) P^\alpha = \{z - P^\alpha \mathcal{L} P^\alpha - P^\alpha \mathcal{L}(I - P^\alpha) \times [z - (I - P^\alpha) \mathcal{L}(I - P^\alpha)]^{-1} (I - P^\alpha) \mathcal{L} P^\alpha\}^{-1} P^\alpha. \quad (1.8)$$

Taking matrix elements of (1.8) we obtain

$$\langle S^\alpha(\vec{q}) | [z - \mathcal{L}]^{-1} | S^\alpha(\vec{q}) \rangle = \left(z - \frac{\langle S^\alpha(\vec{q}) | \mathcal{L} | S^\alpha(\vec{q}) \rangle}{\chi^\alpha(\vec{q}, 0)} - \phi^\alpha(\vec{q}, z) \right)^{-1} \chi^\alpha(\vec{q}, 0), \quad (1.9)$$

where

$$\phi^\alpha(\vec{q}, z) = \frac{\langle S^\alpha(\vec{q}) \mathcal{L}(I - P^\alpha) | [z - \mathcal{L}'] | (I - P^\alpha) \mathcal{L} S^\alpha(\vec{q}) \rangle}{\chi^\alpha(\vec{q}, 0)} \quad (1.10)$$

and $\mathcal{L}' = (I - P^\alpha) \mathcal{L}(I - P^\alpha)$. This may be simplified by observing that

$$\langle S^\alpha(\vec{q}) | \mathcal{L} | S^\alpha(\vec{q}) \rangle = (1/\hbar) \langle [S^\alpha(\vec{q}), S^{\alpha*}(-\vec{q})] \rangle \equiv \lambda^\alpha / \hbar,$$

where $\lambda^\alpha = \pm 2N^{-1/2} \langle S^\alpha(0) \rangle$, $\lambda^z = 0$. We have finally

$$\Sigma^\alpha(\vec{q}, z) = i \chi^\alpha(\vec{q}, 0) [z - \lambda^\alpha / \hbar \chi^\alpha(\vec{q}, 0) - \phi^\alpha(\vec{q}, z)]. \quad (1.11)$$

This is a general expression for the response function, valid at any temperature. We note that this result differs from the Kubo-Tomita expression for the magnetization-correlation function, $\Sigma^*(0, t)$ which is usually written in the time domain as

$$\Sigma^*(0, t) \equiv \langle M(t) | M(0) \rangle = \chi^*(0) \exp[i\omega_0 t + \omega_p^2 \int_0^t (t - \tau) \Psi(\tau) d\tau]. \quad (1.12)$$

In this form

$$\frac{d\Sigma^*(0, t)}{dt} = \left(i\omega_0 + \omega_p^2 \int_0^t \Psi(\tau) d\tau \right) \Sigma(0, t),$$

where ω_0 is the resonance frequency, whereas inverting (1.11) leads to the equation

$$\frac{d\Sigma^*(0, t)}{dt} = i\omega_+ \Sigma^*(0, t) + \int_0^t \bar{\Phi}(0, t - \tau) \Sigma^*(0, \tau) d\tau,$$

with $\omega_+ = \lambda^+ / \hbar \chi^+$, where $i\bar{\Phi}$ is the inverse of $\Phi(z)$. Therefore, it is only in the limit that $\bar{\Phi}(t)$ varies rapidly compared to $\Sigma(t)$ that there is any direct correspondence between $\Psi(t)$ and $\bar{\Phi}(t)$, in which case we have that $\omega_p^2 \int_0^\infty \Psi(\tau) d\tau = -i\Phi(0, 0)$. We

think that the expression (1.11) is more useful than (1.12) because the function Φ can be calculated directly as a diagonal matrix element of a propagator, whereas, Ψ is defined in terms of a cumulant expansion. (See noted added in proof).

A more restricted but explicit result can be obtained at infinite temperatures, where λ^a , $\chi^a \rightarrow 0$. For sufficiently high temperatures, $\lambda^{\pm} = \pm \chi^{\pm}(0, 0) \times g\mu_B H$, $\chi^{\pm}(0, 0) = \frac{1}{2}\chi^{\pm}(0, 0)$, and $\chi^{\pm}(q, 0)$ becomes independent of \vec{q} , so that we have

$$\begin{aligned}\Sigma^{\pm}(\vec{q}, 0) &= i\chi^{\pm}(\vec{q}, 0)[z \mp g\mu_B H/\hbar - \Phi^{\pm}(\vec{q}, z)]^{-1}, \\ \Sigma^{\pm}(\vec{q}, 0) &= i\chi^{\pm}(\vec{q}, 0)[z - \Phi^0(\vec{q}, z)]^{-1}.\end{aligned}\quad (1.13)$$

$\Phi^a(\vec{q}, z)$ can also be simplified. Using the hermiticity of \mathcal{L} , Φ^a can be written

$$\begin{aligned}\Phi^a(\vec{q}, z) &= \langle (I - P^a)\mathcal{L}S^a(q) | [z - \mathcal{L}']^{-1} \\ &\quad \times | (I - P^a)\mathcal{L}S^a(\vec{q}) \rangle / \chi^a(\vec{q}, 0).\end{aligned}$$

The Zeeman term does not contribute to $|I - P^a\mathcal{L}S^a(\vec{q})\rangle$ since $|S^a(\vec{q})\rangle$ is an eigenstate of \mathcal{L}_z with eigenvalues $\omega^a = \pm\omega_0, 0$, and this state is eliminated by the projection operator. It does affect the other terms. For instance, $|P^a\mathcal{L}_0S^a(q)\rangle \neq 0$, in general, in the presence of a magnetic field. However, this term and the others that enter, vanish at infinite temperature, so that we may write, in this limit

$$\Phi^a(q, z) = \sum_{i,j=0}^2 \frac{\langle \mathcal{L}_i S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_j S^a(\vec{q}) \rangle}{\chi^a(\vec{q}, 0)}.\quad (1.14)$$

We wish to calculate the change in the spectral density to lowest order in ρ . There are two sorts of terms in the summation in (1.14), those that vanish as q^2 when $q \rightarrow 0$ and those that approach a finite limit. In the absence of the dipole interaction, there are only the terms of the first sort, and the long-wavelength low-frequency ($\omega \ll V$) limit of $\Phi^a(\vec{q}, z)$ is $-iDq^2$, where the diffusion constant D is proportional to V . If the dipole terms are included, this limit becomes (almost, see Sec. II) $-i[D^a(\rho)q^2 + C^a(\rho)\omega_D^2/V]$, where C^a is a constant that depends upon ρ but is nonzero for

$\rho = 0$, and $D^a(\rho)$ is the diffusion constant with the effect of the dipole interaction included. Note that the ratio of the constant lifetime to the diffusion lifetime is proportional to $\rho^2 C^a(\rho)$ for fixed \vec{q} . This term will produce corrections to $\text{Re}\Sigma(\vec{q}, 0)$ that are proportional to ρ^2 and it might be thought that these could be neglected. However, in calculating correlation functions between spins that are a fixed distance apart, which requires the sums over all \vec{q} , this term leads to corrections that are proportional to $\omega_D[C^a(\rho)/D^a(\rho)V]^{1/2}$ and hence will be of order ρ if $C^a(\rho)$ and $D^a(\rho)$ are calculated to zeroth order. There will also, of course, be corrections of order ρ coming from the first-order change in $D^a(\rho)$. We must, therefore, keep terms up to first order in the dipole interaction if they vanish as $\vec{q} \rightarrow 0$, and second order if they do not. The terms $\langle \mathcal{L}_i S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_j S^a(\vec{q}) \rangle$, with $i, j \geq 1$ are all of the second sort. Since the operators $\mathcal{L}_i, \mathcal{L}_j$ are of order ρ in this case, these terms are at least of second order, and the propagator $[z - \mathcal{L}']^{-1}$ may be replaced by $[z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1}$, where \mathcal{L}_H is the Liouville operator corresponding to the Heisenberg interaction. Since this propagator conserves angular momentum about the z axis, terms for which $i \neq j$ will vanish. The terms $\langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_i S^a(\vec{q}) \rangle$, $i \geq 1$ are of the first sort, and appear to be of first order. However, if we write

$$[z - \mathcal{L}']^{-1} = [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} + [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} \mathcal{L}_D [z - \mathcal{L}']^{-1},\quad (1.15)$$

with \mathcal{L}_D the dipolar Liouville operator, then because of the conservation of angular momentum, the contribution from the first term in (1.15) will vanish and it can be seen that these terms are at least of second order. The only term that can be of the first sort, therefore, is $\langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle$. Since \mathcal{L}_0 contains terms from both the dipole and Heisenberg Hamiltonians, we will write it as $\mathcal{L}_{0,H} + \mathcal{L}_{0,D}$. Keeping terms to lowest significant order, as discussed above, we obtain

$$\begin{aligned}\langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle &= \langle \mathcal{L}_{0,H} S^a(\vec{q}) | [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} | \mathcal{L}_{0,H} S^a(\vec{q}) \rangle \\ &\quad + \langle \mathcal{L}_{0,H} S^a(\vec{q}) | [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} \mathcal{L}_{0,D} [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} | \mathcal{L}_{0,H} S^a(\vec{q}) \rangle \\ &\quad + \langle \mathcal{L}_{0,D} S^a(\vec{q}) | [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} | \mathcal{L}_{0,H} S^a(\vec{q}) \rangle \\ &\quad + \langle \mathcal{L}_{0,H} S^a(\vec{q}) | [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} | \mathcal{L}_{0,D} S^a(\vec{q}) \rangle + \langle \mathcal{L}_{0,D} S^a(\vec{q}) | [z - \mathcal{L}'_z - \mathcal{L}'_H]^{-1} | \mathcal{L}_{0,D} S^a(\vec{q}) \rangle.\end{aligned}\quad (1.16)$$

The first term is the result in the absence of dipole interaction, the second is the correction resulting from the effect of the dipole interaction in the intermediate states, and the last three

terms the effect of the dipole interaction on the initial decay rate of the state $|S^a(\vec{q})\rangle$. The second, third, and fourth terms lead to corrections to the diffusion constant of order ρ and the last term to

a contribution to $C^a(0)$, for the case that $\omega = \pm$, and a second-order, and hence negligible, correction to D^a if $a=0$. To summarize, if we define the functions

$$\Phi_1^a(\vec{q}, z) = \langle \mathcal{L}_I S^a(\vec{q}) | [z - \mathcal{L}'_I - \mathcal{L}'_H]^{-1} | \mathcal{L}_I S^a(\vec{q}) \rangle / \chi^a(\vec{q}, 0) \quad (1.17)$$

and define the second term in (1.16) divided by $\chi^a(\vec{q}, 0)$ as $\Delta\Phi_0^a(\vec{q}, z)$, we obtain

$$\Phi^a(\vec{q}, z) = \sum_0^2 \Phi_1^a(\vec{q}, z) + \Delta\Phi_0^a(\vec{q}, z). \quad (1.18)$$

The effect of the magnetic field can now be accounted for completely, since \mathcal{L}_I and \mathcal{L}_H commute and the states appearing in (1.16) are eigenstates of \mathcal{L}_I . For instance, since $\mathcal{L}_I | \mathcal{L}_0 S^a(\vec{q}) \rangle = \pm \omega_0 | \mathcal{L}_0 S^a(\vec{q}) \rangle \times \langle \vec{q} \rangle$, $\omega_0 = g\mu_B H/\hbar$, we will have

$$\Phi_0^a(\vec{q}, z) = \langle \mathcal{L}_0 S^a(\vec{q}) | [z \mp \omega_0 - \mathcal{L}'_H]^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle / \chi^a(\vec{q}, 0) \quad (1.19)$$

which can be written explicitly as

$$\begin{aligned} \Phi_0^a(\vec{q}, z) = & \sum_{a', a''} \left(A(\vec{q} - \vec{q}') - A(\vec{q}'') - B(\vec{q}') \right. \\ & \times [A(\vec{q} - \vec{q}'') - A(\vec{q}'') - B(\vec{q}'')] \\ & \times \frac{\langle S^a(\vec{q}') S^a(\vec{q} - \vec{q}') | [z \mp \omega_0 - \mathcal{L}'_H]^{-1} | S^a(\vec{q}'') S^a(\vec{q} - \vec{q}'') \rangle}{\chi^a(\vec{q}, 0)}. \end{aligned} \quad (1.20)$$

$A(\vec{q})$ and $B(\vec{q})$ are the Fourier transforms of the coefficients in (1.2). We shall not write down the remaining terms explicitly since we will not need them in this calculation.

For fields such that $\omega_0 \gg V$, $\Phi_{1,2}^a$ can be neglected in calculating the line shape of the main resonance line, which is at $z \approx \omega_0$, since they will be of order of magnitude ω_D^2/ω_0 and hence much smaller than Φ_0^a which is of order ω_D^2/V . The spectral density, in this limit is, therefore, when $z \approx \pm \omega_0$ and neglecting $\Delta\Phi_0^a$ [see discussion after (2.14)],

$$\Sigma^a(\vec{q}, z) = i\chi^a(\vec{q}, 0) [z \mp \omega_0 - \Phi_0^a(\vec{q}, z)]^{-1}. \quad (1.21)$$

The functions Φ_1^a , Φ_2^a are responsible for the satellite lines of the main resonance line. The appropriate expression for $\Sigma^a(\vec{q}, z)$, in the same limiting case, is

$$\Sigma^a(\vec{q}, z) = i\chi^a(\vec{q}, 0) [z - \Phi_0^a(\vec{q}, z)], \quad (1.22)$$

$$\Phi_0^a(\vec{q}, z) = \langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}'_H]^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle / \chi^a(\vec{q}, z). \quad (1.23)$$

In the event that $\omega_0 \lesssim V$, all terms contribute and the full expression (1.18) must be used.

II. APPLICATION TO MYERS-NARATH EXPERIMENT

MN measure the spectral density by measuring the linewidth of the P nuclear resonance as a func-

tion of field. The P nucleus is assumed to be coupled by means of an isotropic transferred hyperfine interaction to its six nearest neighbors on the fcc Gd lattice.⁵ Knight-shift data, treated in the mean-field approximation, is consistent with the exchange coupling to next-nearest neighbors being four times greater than the coupling to nearest neighbors,¹ and if treated within the spherical-model approximation, consistent with essentially zero nearest-neighbor coupling, which is assumed to be the case. Hence, the Gd lattice is treated as though it were three independent, interpenetrating simple-cubic lattices and the dipole terms neglected. These assumptions imply that the transverse relaxation time is

$$T_1^{-1} = 3(A/\hbar) \int_{-\infty}^{\infty} [\langle S_I^+(t) S_I^-(0) \rangle + \langle S_I^+(t) S_{I+1}^-(0) \rangle] dt \quad (2.1)$$

and the longitudinal relaxation time is

$$T_2^{-1} = \frac{1}{2} T_1^{-1} + 3(A/\hbar)^2 \int_{-\infty}^{\infty} \langle S_I^+(t) S_I^-(0) \rangle + \langle S_I^+(t) S_{I+1}^-(0) \rangle dt, \quad (2.2)$$

where A is the hyperfine constant, and $\langle AB \rangle = \text{Tr}AB$. Note that $\langle S^a(\vec{q}) | S^a(\vec{q}) \rangle = \beta \langle S^a(q) S^a(q) \rangle$ as $\beta \rightarrow 0$. In the absence of the dipolar terms we have

$$\langle S_I^+(t) S_I^-(0) \rangle = 2e^{i\omega_0 t} \langle S_I^+(t) S_I^-(0) \rangle, \quad (2.3)$$

where the time dependence of the longitudinal correlation function is determined solely by the exchange interaction.

By varying the field and measuring $T_1^{-1}(\omega_0)$ one is thus able to determine the spectral density $F(\omega)$, where

$$F(\omega_0) = \int_{-\infty}^{\infty} e^{i\omega_0 t} [\langle S_I^+(t) S_I^-(0) \rangle + \langle S_I^+(t) S_{I+1}^-(0) \rangle] dt, \quad (2.4)$$

as a function of frequency. Since the zero-frequency value cannot be obtained in this fashion, it is measured by measuring T_2^{-1} for large values of the field, where $T_1^{-1} \rightarrow 0$, so that only the second term in (2.2) contributes.

We will make all of the assumptions of MN, but include the dipolar terms. The system cannot be thought of as three independent lattices then, but since we are interested only in an approximate calculation to estimate the size of the effect, we will include the fact that the Gd lattice is actually fcc in an approximate way described below. $\langle S_I^+ S_{I+j}^- \rangle$ depends upon the orientation of the lattice vector j with respect to the spin direction a when dipole terms are included. Since the experiment will sample equally nuclei with j along all three axes, the appropriate generalization of (2.1) and (2.2) will be

$$F^a(\omega_0, \omega) = [\pi \chi^a(0, 0)]^{-1} \sum_q \frac{\chi^{a''}(\vec{q}, \omega)}{\omega}$$

$$\times [1 + \frac{1}{3} (\cos q_x a + \cos q_y a + \cos q_z a)], \quad (2.5)$$

where $\chi^{a''}(q, \omega)/\omega = \text{Re}\Sigma^a(\vec{q}, \omega)$ is the spectral density appropriate to (1.1) and hence depends implicitly on ω_0 . Then we have

$$T_1^{-1}(\omega_0) = (A/\hbar)^2 4\pi S(S+1) F^-(\omega_0, 0),$$

$$T_2^{-1}(\omega_0) = T_1^{-1}(\omega_0) + (A/\hbar)^2 2\pi S(S+1) F^0(\omega_0, 0). \quad (2.6)$$

$F^a(\omega_0, \omega)$ has been normalized so that

$$\int_{-\infty}^{\infty} F^a(\omega_0, \omega) d\omega = 1. \quad (2.7)$$

It is not generally the case that (a) $F^{\pm}(\omega_0, \omega) = F^{\pm}(\omega_0 \pm \omega)$, or that (b) $F^{\pm}(0, \omega) = F^0(\omega_0, \omega)$. The condition (a) is necessary in the MN experiment in order to interpret the data as a measurement of $F^a(0, \omega)$, while the condition (b) is required to convert the T_2^{-1} measurement to a measurement of $T_1^{-1}(0)$. Let us consider first the case that $\omega_0 \gg V$.

Case I, $\omega_0 \gg V$

This spectral densities are given by Eqs. (1.20) and (1.21) and satisfy condition (a). To obtain an explicit expression for $\Phi^a(q, z)$, it is necessary to solve for the evolution of the two-spin correlation function that appears in $\langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}']^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle$. As we have seen it is only the \mathcal{L}'_0 part of \mathcal{L}' that contributes to lowest order in ρ . A kinetic theory for this operator has been developed by Barreto and Reiter⁶ and applied successfully to the calculation of the free-induction decay in CaF_2 , in which there are only dipole interactions. This theory is an extension of that developed by Reiter for the Heisenberg system and applied successfully to RbMnF_3 ³ and should, therefore, be adequate to describe the present case of weak dipole interactions. We will use the constant-relaxation-time approximation to the solution of the kinetic equations

$$\langle \mathcal{L}_0 S^a(\vec{q}) | [z - \mathcal{L}'_0]^{-1} | \mathcal{L}_0 S^a(\vec{q}) \rangle$$

$$= \langle S^a(\vec{q}) | \mathcal{L}'^2 | S^a(\vec{q}) \rangle / \nu_0^a(\vec{q}, \omega, \omega_0), \quad (2.8)$$

where $\nu^a(\vec{q}, \omega, \omega_0)$ is chosen so that the second and fourth moments of the spectral density are given correctly. It is given explicitly by ($\alpha = \pm, 0$)

$$\nu_0^a(\vec{q}, \omega, \omega_0) = \frac{1}{2} (\omega - a\omega_0)$$

$$+ i [\Omega_a^4(\vec{q})/\omega_a^2(\vec{q}) - \frac{1}{4} (\omega - a\omega_0)^2]^{1/2}, \quad (2.9)$$

where $\omega_a^2(\vec{q})$ is the second moment of the spectral density and $\Omega_a^4(\vec{q}) + \omega_a^2(\vec{q})^2$ the fourth moment. Explicitly

$$\omega_a^2(\vec{q}) = \langle S^a(\vec{q}) | \mathcal{L}'_0^2 | S^a(\vec{q}) \rangle / \chi^a(\vec{q}, 0),$$

$$\Omega_a^4(\vec{q}) = \langle S^a(\vec{q}) | \mathcal{L}'_0^4 | S^a(\vec{q}) \rangle / \chi^a(\vec{q}, 0). \quad (2.10)$$

With this approximation the spectral density is

$$\text{Re}\Sigma(\vec{q}, \omega, \omega_0) = \frac{1}{\omega_a^2(\vec{q})} \left(\frac{\Omega_a^4(\vec{q})}{\omega_a^2(\vec{q})} \right)^{1/2}$$

$$\times \left(1 - \frac{(\omega - a\omega_0)^2}{4} \frac{\omega_a^2(\vec{q})}{\Omega_a^4(\vec{q})} \right)^{1/2}$$

$$\times \left[1 + \frac{(\omega - a\omega_0)^2}{\omega_a^2(\vec{q})} \left(\frac{\Omega_a^4(\vec{q})}{\omega_a^2(\vec{q})^2} - 1 \right) \right]^{-1}. \quad (2.11)$$

It will be shown that as $\vec{q} \rightarrow 0$, $\omega_a^2(\vec{q}) \rightarrow aq^2 + b\omega_D^2$ while $\Omega_a^4(\vec{q})/\omega_a^2(\vec{q}) \rightarrow cV^2$, with a, b, c on the order of unity. In this limit the ratio $\Omega_a^4(\vec{q})/\omega_a^2(\vec{q})^2$ is large, the square-root factor in (2.11) is essentially unity for $\omega^2 \simeq \omega_a^2(\vec{q})$, and the spectral density has a Lorentzian line shape, with a cutoff far in the wings. The linewidth is of the form $Dq^2 + C\omega_D^2/V$, as mentioned in Sec. I, with D and C determined by the moments ω_a^2 and Ω_a^4 .

Thus the constant relaxation time approximation reduces the problem to a calculation of the moments. With this approximation the term

$$\Delta\Phi_0^a(\vec{q}, \omega) = -\frac{1}{2} \omega_a^2(\vec{q}) \omega_D \frac{d}{d\omega_D} \left(\frac{\Omega_a^4(\vec{q})}{\omega_a^2(\vec{q})} \right)$$

$$\times \left(\frac{\Omega_a^4(\vec{q})}{\omega_a^2(\vec{q})} - \frac{(\omega - \alpha\omega_0)^2}{4} \right)^{-1/2} / \nu_a(\vec{q}, \omega, \omega_0)^2. \quad (2.12)$$

The second moments are

$$\omega_x^2(\vec{q}) = \frac{2}{3} S(S+1) \times \left(V^2(0) - V^2(\vec{q}) \right)$$

$$+ \omega_D \sum_{q'} [a(\vec{q} - \vec{q}') - a(\vec{q}')] V(\vec{q}')$$

$$+ \omega_D^2 [5a^2(0) + 4a^2(\vec{q})], \quad (2.13a)$$

$$\omega_z^2(\vec{q}) = \frac{2}{3} S(S+1)$$

$$\times \left(V^2(0) - V^2(\vec{q}) - 2\omega_D \sum_{q'} [a(\vec{q} - \vec{q}') - a(\vec{q}')] V(\vec{q}') \right)$$

$$- \omega_D^2 [a^2(0) - a^2(\vec{q})], \quad (2.13b)$$

where

$$V^2(\vec{q}) = \sum_j e^{i\vec{q}\cdot\vec{r}_{ij}} V_{ij}^2, \quad a(q) = \sum_j e^{i\vec{q}\cdot\vec{r}_{ij}} (A_{ij} - V_{i2})^2$$

The ratio $\Omega_a^4(\vec{q})/\omega_a^2(\vec{q})$, in the absence of dipole interactions is given approximately by³

$$\Omega_a^4(\vec{q})/\omega_a^2(\vec{q}) = \frac{2}{3} S(S+1) \{ 2V^2(0) + \frac{1}{2} [V^2(0) - V^2(\vec{q})] \}. \quad (2.14)$$

The corrections to the fourth moment that are linear in ω_D can be calculated diagrammatically.⁷ The exact result is rather complicated. If, however, the terms A_{ij} are taken to be zero except for nearest neighbors on the simple-cubic lattice, the result is obtained by replacing $V^2(\vec{q})$ by $V^2(\vec{q}) + 2\omega_D \sum_q a(\vec{q} - \vec{q}') V(\vec{q}')$ in (2.14). The remain-

ing terms are comparable to the terms that couple together the three lattices, and will be neglected. Since, as will be shown below, $\sum a(\vec{q}') \times V(\vec{q}') = 0$, these corrections vanish as $\vec{q} \rightarrow 0$, and hence, in the present approximation, $\Delta\Phi_0^a$ can be taken as zero. The last term in (2.13a) may be evaluated at $\vec{q} = 0$, and the last term in (2.13b) omitted.

The experiments are done on powder samples, which should be accounted for by calculating $F^a(\omega_0, \omega)$ and then averaging it over all orientations of the crystal axis. However, to lowest order in ρ , this is equivalent to averaging Φ^a instead. We shall use for the last term in (2.13a) the averaged value for the second moment of the dipole Hamiltonian, calculated for the fcc lattice in order to account partially for the interactions between the simple-cubic lattice provided by the dipole terms. We have from a simple calculation, that to lowest order in \vec{q} ,

$$\left\langle \sum_{q'} a(\vec{q} - \vec{q}') V(\vec{q}') \right\rangle = \mp \frac{4}{3} V q^2 a^2 (1 - 3q_x^2/q^2), \quad (2.15)$$

where the bracket denotes an average over the orientation of the simple-cubic lattice. Since these terms contribute to the correction of order ρ for all values of q , we will approximate the result for larger values of q by

$$\omega_D \left\langle \sum_{q'} a(\vec{q} - \vec{q}') V(\vec{q}') \right\rangle \approx \mp \frac{4}{15} \rho [V^2(0) - V^2(\vec{q})] (1 - 3q_x^2/q^2),$$

where the + sign holds for the antiferromagnet. This may be thought of as the first term in a Fourier-series expansion in terms having the symmetry of the lattice, of the exact result. With these further approximations, the moments that we will use to calculate the spectral density are, for the antiferromagnet GdP,

$$\langle \omega_x^2(\vec{q}) \rangle = \frac{2}{3} S(S+1) \times \{ [V^2(0) - V^2(\vec{q})] [1 + \frac{2}{15} \rho (1 - 3q_x^2/q^2)] + \omega_D^2 100.5 \}, \quad (2.16a)$$

$$\langle \omega_z^2(\vec{q}) \rangle = \frac{2}{3} S(S+1) [V^2(0) - V^2(\vec{q})] [1 - \frac{4}{15} \rho (1 - 3q_x^2/q^2)]. \quad (2.16b)$$

To summarize, the spectral densities will be calculated from (2.11), using the approximation (2.8), with (2.16) and (2.14) used for the values of the moments. It should be noted that the spectral density calculated in this way does not satisfy condition (b).

Case II, $\omega_0 \ll V$

In this situation, all of the terms in (1.18) must

be kept. The constant-relaxation-time approximation may also be used for $\Phi_{1,2}^a$, but $\nu_1^a(\vec{q}, \omega, \omega_0)$ will not depend simply on $\omega - a\omega_0$, but will contain terms that depend on $\omega, \omega \pm 2\omega_0$. The spectral density will not satisfy condition (a). However, for the range ω, ω_0 , for which the corrections to $F(\omega)$ are significant, $\nu_1^a(\vec{q}, \omega, \omega_0) \approx i[\Omega_a^4(\vec{q})/\omega_a^2(\vec{q})]^{1/2}$, so that the violation of condition (a) has little effect. Since these terms do not change the diffusion coefficient, their affect at values of ω, ω_0 , such that $(\omega - a\omega_0) \ll V$ can be obtained by changing the last term in (2.16a) to the value one would obtain by calculating the second moment with the full, rather than the truncated dipole Hamiltonian. The value is $\frac{10}{3}$ the value shown in (2.16a). The same term must be added also to (2.16b), since the longitudinal spin components are no longer conserved. The moments that should be used in this case are, therefore,

$$\langle \omega_x^2(\vec{q}) \rangle = \frac{2}{3} S(S+1) \{ [V^2(0) - V^2(\vec{q})] \times [1 + \frac{2}{15} \rho (1 - 3q_x^2/q^2)] + \omega_D^2 335 \}, \quad (2.17a)$$

$$\langle \omega_z^2(\vec{q}) \rangle = \frac{2}{3} S(S+1) \{ [V^2(0) - V^2(\vec{q})] \times [1 - \frac{4}{15} \rho (1 - 3q_x^2/q^2)] + \omega_D^2 335 \}. \quad (2.17b)$$

It should be noted that the diffusion coefficient is not isotropic when the dipole terms are included. The diffusion constant for spin components parallel to \vec{q} is different from that for spin components perpendicular to \vec{q} , and depends also on the orientation of the \vec{q} vector with respect to the crystal axis. It is also the case that the spin direction can change in time, since $\langle S^\alpha(\vec{q}, t) S^\beta(-\vec{q}) \rangle \neq 0$ when $\alpha \neq \beta$, as it must be when the system is invariant under rotations of the spin operators. The long-wavelength behavior is most generally described by a diffusion tensor $D_{ij}^{\alpha\beta}$ and a "relaxation frequency" tensor $\Gamma^{\alpha\beta}$ such that

$$\frac{\partial S^\alpha(\vec{q})}{\partial t} = -q_i D_{ij}^{\alpha\beta} q_j S^\beta(q) - \Gamma^{\alpha\beta} S^\beta(q).$$

The present analysis, by making use of the constant relaxation time approximation for $\omega_0 \ll V$, implicitly neglects the effect of the off-diagonal terms in Γ and D on the spectral density.

The value of ρ appropriate to the MN experiment will be calculated using the value of the exchange constant MN obtained by fitting the high-field portion of their data with a phenomenological theory, $V = 0.71^\circ \text{K}$, and the value of the lattice parameter for the fcc lattice of 5.7286⁸ and is $\rho = 0.02$. The spectral densities for case II are displayed in Fig. 1, where we have displayed the autocorrelation function and averaged nearest-neighbor correlation function at low frequencies for $\alpha = \pm$, as well as their sum. The scale has been set by as-

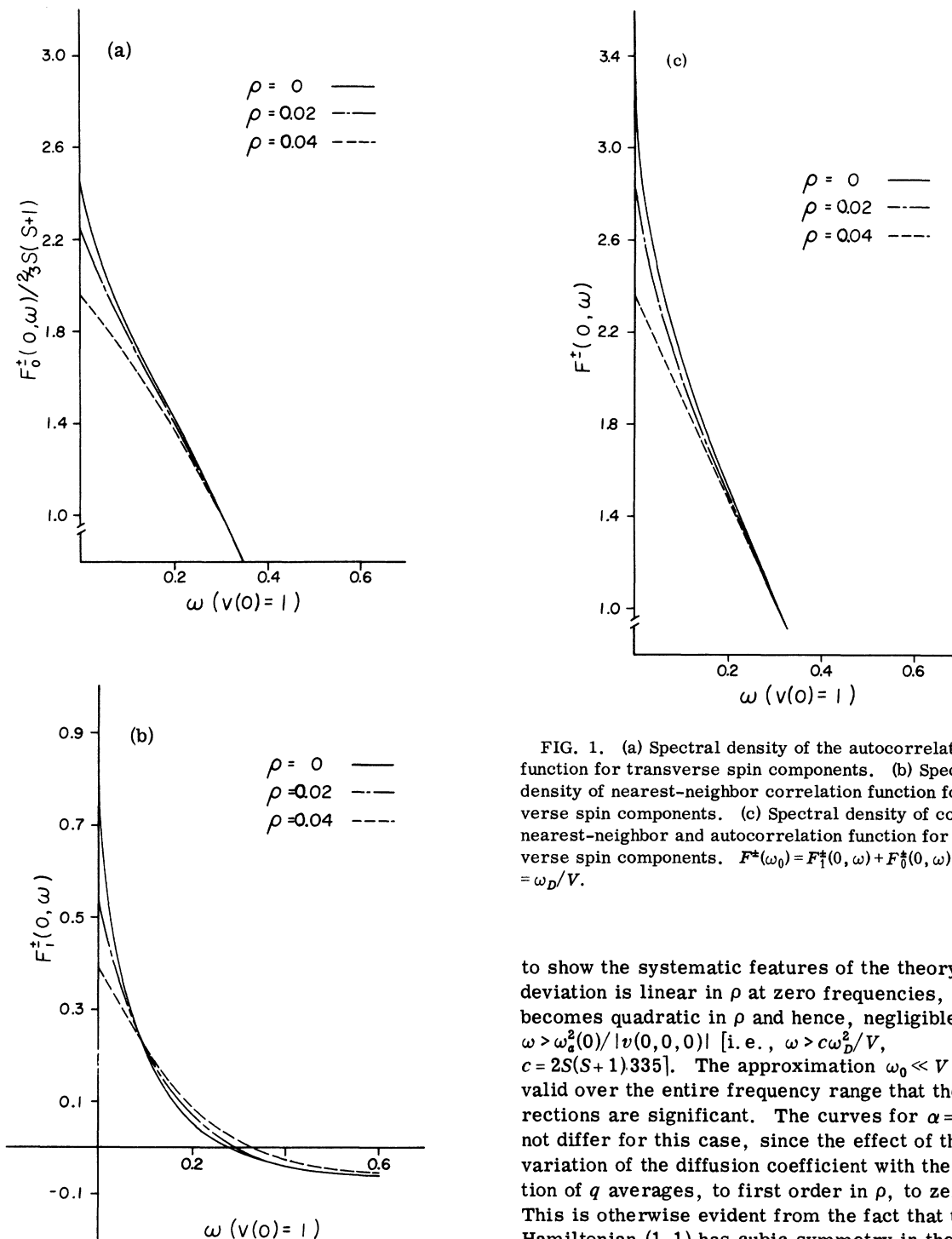


FIG. 1. (a) Spectral density of the autocorrelation function for transverse spin components. (b) Spectral density of nearest-neighbor correlation function for transverse spin components. (c) Spectral density of combined nearest-neighbor and autocorrelation function for transverse spin components. $F^*(\omega_0) = F_1^*(0, \omega) + F_0^*(0, \omega)$; $\rho = \omega_D/V$.

to show the systematic features of the theory. The deviation is linear in ρ at zero frequencies, but becomes quadratic in ρ and hence, negligible, for $\omega > \omega_a^2(0)/|v(0, 0, 0)|$ [i. e., $\omega > c\omega_D^2/V$, $c = 2S(S+1)335$]. The approximation $\omega_0 \ll V$ is valid over the entire frequency range that the corrections are significant. The curves for $\alpha=0$ do not differ for this case, since the effect of the variation of the diffusion coefficient with the direction of q averages, to first order in ρ , to zero. This is otherwise evident from the fact that the Hamiltonian (1.1) has cubic symmetry in the absence of a magnetic field. The corrections of higher order in ρ do not average to zero, but this is not significant, as they have not been treated consistently in the present discussion. Since $F^\alpha(\omega_0, \omega) \cong F^\alpha(\omega_0 - \omega)$ for the frequency range that the corrections are significant, the curves of Fig. 1 may be used in interpreting the data of MN.

In Fig. 2 we have shown the fractional change

suming $\frac{1}{3}S(S+1)=1$, and $V(0)=1$, i. e., $V=\frac{1}{8}$. To convert the curves to experimental frequencies, the abscissa should be multiplied by, and the ordinate divided by, $[\frac{1}{3}S(S+1)]^{1/2}6V$. We have displayed also the result for $\rho=0$, $\rho=0.04$ in order

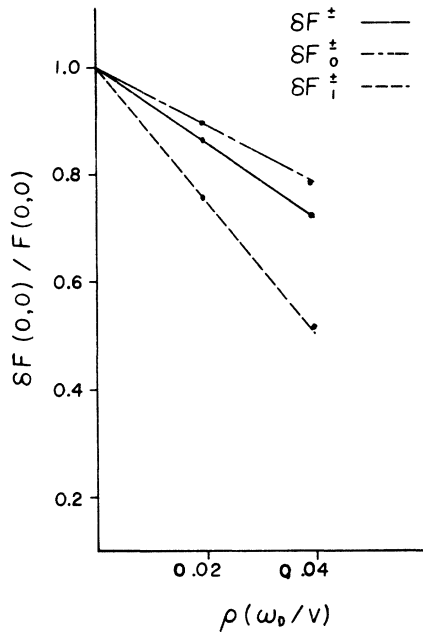


FIG. 2. Variation of zero-frequency value of spectral density with magnitude of dipole interaction.

in the zero-frequency spectral density as a function of ρ , exhibiting the linear behavior explicitly. The accuracy of the calculated slopes obtained in the present fashion, is expected to be comparable to the accuracy of the diffusion constant, which is smaller than the observed value by about 30%.

Case I is appropriate for treating the measurement T_2^{-1} at high fields, since T_2^{-1} is proportional to $\lim_{\omega \rightarrow 0} F^*(\omega, 0)$. Since the linear contribution to this term from the modification of the diffusion coefficient vanishes, the value for this term is the same as that in the absence of dipole interactions. If MN could extend their measurements of T_1^{-1} to zero frequency, the theoretically predicted result would differ from the result inferred from the T_2^{-1} measurement by the amount shown in Fig. 1(a) for the difference of $F^*(0, \omega)$ for $\rho = 0$ and $\rho = 0.02$, i. e., 14%. However, their data for T_1^{-1} does not extend into the region in which the dipole corrections are significant, so that one may reasonably regard the combined set of data points obtained from the T_2^{-1} and T_1^{-1} measurements as a measurement of $F^*(0, \omega)$ in the absence of dipole interactions, as they have assumed.

In Fig. 3, we have compared our theoretical expression for $F^*(0, \omega)$, calculated in the presence of dipole interaction, with their data and with the results of Blume and Hubbard,⁹ again using the value of the exchange constant measured by MN.

The Blume and Hubbard results do not include the effect of the nearest-neighbor correlation func-

tion, which has not been published. There would be significant corrections, from including this term, to the spectral density shown at zero frequency, but, as may be seen from Fig. 1(b), the corrections in the range of frequencies where T_1^{-1} data exists are small, and do not significantly improve the fit to the data. We have normalized the data by forcing agreement with our theoretical curve at $\omega = 0$, an arbitrary procedure. It should be noted, however, that the fit is very poor to either theory, no matter how the normalization, which is determined by the hyperfine constants, is chosen. Nor can a fit be obtained by varying the value of the exchange parameter within the limits given by the Knight-shift data.¹⁰

The difference in the theoretical curves is due to the different approximations made and is discussed in Ref. 3, where we also discuss improvements of the constant relaxation time approximation. The theory presented here tends to underestimate the diffusion coefficient by about 30%,

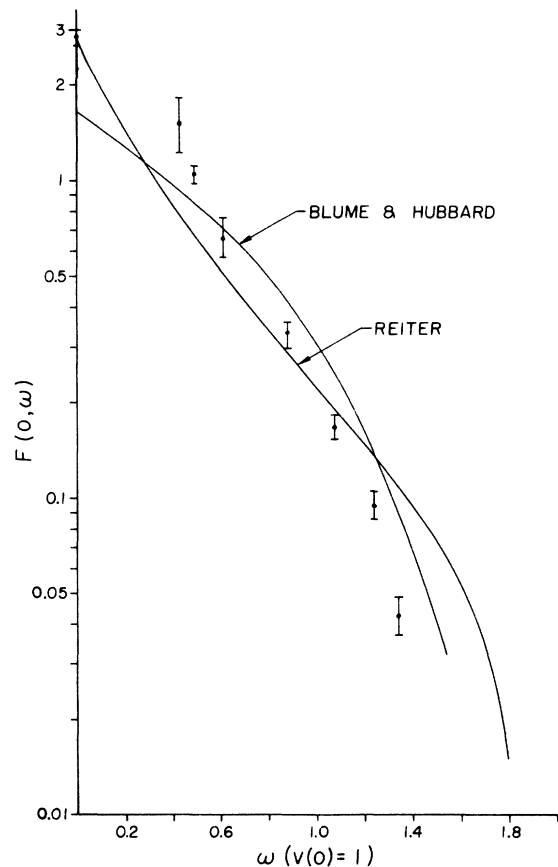


FIG. 3. Comparison of theoretical predictions for spectral densities by Reiter, and Blume and Hubbard, with the experimental results of MN. The experimental data have been arbitrarily normalized by forcing agreement with Reiter's theory at $\omega = 0$.

and hence overestimates the zero-frequency value of the autocorrelation function

It is conceivable that some of the discrepancy could be due to longer-range hyperfine interactions, which would contribute preferentially at low frequencies.

III. CONCLUSION

The effect of the inclusion of small dipole interactions on the spectral densities in a Heisenberg paramagnet are threefold: The diffusion constant must be replaced by a diffusion tensor with diffusion along and perpendicular to the direction of the wave vector being determined by different diffusion constants, there is a finite lifetime for the fluctuations introduced at $\vec{q}=0$ by the breaking of the rotational symmetry, and the longitudinal and transverse fluctuations are coupled. The anisotropy of the diffusion tensor is first order in ρ , the relative magnitude of the dipole energy, but gives no first-order correction to correlation functions that retain the cubic symmetry of the lattice. The $\vec{q}=0$ lifetime of the fluctuations is second order in ρ , but yields a first-order correction to the spectral densities for spins a fixed distance apart. The off-diagonal (in the spin indices) components of the diffusion and lifetime tensor, that produce

the coupling of longitudinal and transverse fluctuation are first order in ρ but give a second-order correction to the spectral density for either transverse or longitudinal modes; for fixed q their effect has been neglected. Although there are significant (14%) dipolar corrections to the theoretical value of $T_1^{-1}(0)$ for the GdP, arising from the second effect, Myers and Narath's procedure of inferring the zero-field value $T_1^{-1}(0)$ from the high-field value of $T_2^{-1}(\omega_0)$ is justified if the combined data is taken as a measure of the spectral density in the absence of dipolar interactions. As such, it remains in strong disagreement with the theoretical predictions at low frequencies.

Note added in proof. In one- and two-dimensional systems, where $\vec{\phi}(t)$ has a significant "slow" component, the Kubo-Tomita theory leads to incorrect results, and the perturbation approach of this work must be replaced by a self-consistent treatment.

ACKNOWLEDGMENTS

We would like to thank Sam Myers and Pete Richards for useful informative conversations, and Steve Ostrow, M. Block, and Joan Limbird for their assistance in preparing the manuscript.

¹S. Myers and A. Narath, Phys. Rev. Lett. **27**, 641 (1971).

²R. Kubo and H. Tomita, J. Phys. Soc. Jap. **9**, 888 (1954).

³G. Reiter, Phys. Rev. B **7**, 3325 (1973).

⁴S. Myers and A. Narath, Phys. Rev. B (to be published).

⁵In subsequent work, MN have shown that there is significant longer-range and anisotropic hyperfine interactions. We will neglect these effects in the present work as they do not affect

our conclusions.

⁶F. C. Barreto and G. Freiter, Phys. Rev. B **6**, 2555 (1972).

⁷F. C. Barreto and G. Reiter (unpublished).

⁸E. D. Jones, Phys. Rev. **160**, 451 (1971).

⁹M. Blume and J. Hubbard, Phys. Rev. B **1**, 3815 (1970).

¹⁰E. D. Jones and B. Morosin, Phys. Rev. **160**, 451 (1967).