

Density-Matrix Derivation of the Spin-Diffusion Equation*†

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A diffusion equation is derived for the spatial motion of spin magnetization that has an inhomogeneous distribution. The particles of the system are assumed to be fixed in space and have a spin of $\frac{1}{2}$. Only those terms in the interaction Hamiltonian are used that commute with the Zeeman Hamiltonian. A density-matrix calculational technique is used, and an assumption is made that the interaction Hamiltonian is small enough that the density matrix is diagonal to first order. The first-order results are similar to Bloembergen's, but have a different multiplying coefficient. An average diffusion constant is evaluated explicitly for a simple cubic lattice for cases of the applied magnetic field along the [100], [110], and [111] directions.

I. INTRODUCTION

IN 1949 Bloembergen¹ suggested that the magnetization of spins in a rigid lattice could be spatially transported by means of the mutual flipping of neighboring spins due to dipole-dipole interaction terms of type $I_{i+}I_{j-}$. Using first-order perturbation theory, he showed that the transport equation for magnetization was a diffusion equation, and he made an estimate of the diffusion constant D .

In 1959 Redfield² gave a prescription for testing whether the transport equation for magnetization could be approximated by a diffusion equation, and a prescription for deriving a diffusion constant D was given. His method depends upon the calculation of the higher-order moments of a resonance curve. This is a very laborious process, and the testing procedures and the evaluation of the diffusion constant D were not attempted.

In 1965 Buishvili and Zubarev³ derived a diffusion equation for spatial transport of magnetization by means of the statistical theory of irreversible processes. Their expression for D was similar to Bloembergen's.

In this paper we derive a diffusion equation for the spatial transport of magnetization, and find a formula for D by investigating the equation of motion of the density matrix $\rho(t)$ for the spin system. The fundamental *assumption* is made that the rate of transport of magnetization is *slow* enough that the diagonal part of the density matrix for the spin system can be closely approximated by a quasistatic equilibrium density matrix in which the *spin temperature* is spatially-dependent and time-dependent.

An inhomogeneous spatial distribution of magnetization can be produced in many ways. One way is to apply an inhomogeneous radiofrequency field to the spin system so that, after a given time, some nuclei have been

nutated further than others, and thus have a different value for the component of magnetization along the applied static magnetic field. Another possible way is the superposition of an inhomogeneous, static magnetic field upon a large homogeneous magnetic field for a period of time, and then turning it off. A third possible way could be that of the spins in different parts of the system having different spin lattice relaxation times (due to different motional spectra, or impurity spins, etc.), and thus having different components of magnetization along an applied static magnetic field following some saturation process. Whatever the reason for the inhomogeneous spatial distribution of magnetization, we shall assume that it has been turned off for the period of time treated by the calculation, and the source of the inhomogeneous spatial distribution of magnetization will not concern us.

II. DERIVATION OF THE DIFFUSION EQUATION

The system for which the calculation will be carried out is a set of N identical particles fixed in space. Each particle has spin I and magnetogyric ratio γ . There are both dipolar interaction and exchange interaction between the particles. The system is in an applied magnetic field $B_0\hat{z}$ that will be assumed to be very large in comparison to the internally produced magnetic fields denoted by B_{local} . For this case, the nonsecular terms of the interaction Hamiltonian (that is, those terms that do not commute with the Zeeman term of the Hamiltonian) can be dropped, because the probability of mutual flips of neighboring spins due to these terms will be smaller by approximately $(B_{\text{local}}/B_0)^2$ than the probability due to the $I_{i+}I_{j-}$ terms. The truncated Hamiltonian can be written as follows⁴:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_1 + \mathcal{H}_2, \quad (1)$$

$$\mathcal{H}_z = -\gamma\hbar B_0 \sum_{i=1}^N I_{iz}, \quad (2)$$

$$\mathcal{H}_1 = \hbar \sum_{i \neq j} B_{ij} I_{i2} I_{j2}, \quad (3)$$

$$\mathcal{H}_2 = -\sum_{i \neq j} \frac{\hbar}{2} A_{ij} (I_{i+} I_{j-} + I_{i-} I_{j+}). \quad (4)$$

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¹ N. Bloembergen, *Physica* **15**, 386 (1949).

² A. G. Redfield, *Phys. Rev.* **116**, 315 (1959).

³ L. L. Buishvili and D. N. Zubarev, *Fiz. Tverd. Tela* **7**, 722 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 580 (1965)].

⁴ Charles P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Inc., New York, 1963).

For pure dipolar interaction between the particles,

$$B_{ij} = -2A_{ij} = \frac{1}{2}\gamma^2\hbar r_{ij}^{-3}(1 - 3\cos^2\theta_{ij}). \quad (5)$$

r_{ij} is the distance between particles i and j . θ_{ij} is the angle between the vector \mathbf{r}_{ij} connecting particles i and j and the applied magnetic field $B_0\hat{z}$.

The equation of motion of the spin density matrix $\rho(t)$ is

$$\frac{\partial}{\partial t}\rho(t) = \frac{i}{\hbar}[\rho(t), \mathcal{H}]. \quad (6)$$

The expectation value for the z component of spin angular momentum for particle k is

$$\langle I_{kz}(t) \rangle = \text{Tr}\{\rho(t)I_{kz}\}. \quad (7)$$

Therefore,

$$\begin{aligned} \frac{\partial}{\partial t}\langle I_{kz}(t) \rangle &= \text{Tr}\left\{\frac{\partial\rho(t)}{\partial t}I_{kz}\right\} \\ &= \frac{i}{\hbar}\text{Tr}\{[\rho(t), \mathcal{H}]I_{kz}\}. \end{aligned} \quad (8)$$

Since $\text{Tr}\{AB\} = \text{Tr}\{BA\}$, Eq. (8) may be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t}\langle I_{kz}(t) \rangle &= \frac{i}{\hbar}\text{Tr}\{\rho(t)[\mathcal{H}, I_{kz}]\} \\ &= \frac{i}{\hbar}\text{Tr}\{\rho(t)[\mathcal{H}_2, I_{kz}]\} \\ &= i \sum_{i(i \neq k)} A_{ik} \text{Tr}\{\rho(t)(I_{i+}I_{k-} - I_{i-}I_{k+})\}. \end{aligned} \quad (9)$$

Equation (9) shows that \mathcal{H}_2 contributes directly to the spin-diffusion process, while \mathcal{H}_1 does not. The spin-diffusion process would vanish if \mathcal{H}_2 were zero.

In determining the evolution of the spin-density matrix $\rho(t)$, the terms $\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_1$ of the Hamiltonian can be handled exactly. This will now be taken advantage of by going into the interaction representation that removes \mathcal{H}_0 from the Hamiltonian. The spin-density matrix $\tilde{\rho}(t)$ in this interaction representation is related to $\rho(t)$ by

$$\tilde{\rho}(t) = \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right)\rho(t)\exp\left(-\frac{i\mathcal{H}_0 t}{\hbar}\right). \quad (10)$$

The equation of motion for $\tilde{\rho}(t)$ is

$$\frac{\partial}{\partial t}\tilde{\rho}(t) = \frac{i}{\hbar}[\tilde{\rho}(t), \tilde{\mathcal{H}}_2(t)], \quad (11)$$

where

$$\tilde{\mathcal{H}}_2(t) = \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right)\mathcal{H}_2\exp\left(-\frac{i\mathcal{H}_0 t}{\hbar}\right). \quad (12)$$

Integrating Eq. (11) from 0 to t yields

$$\tilde{\rho}(t) = \rho(0) + \frac{i}{\hbar} \int_0^t [\tilde{\rho}(t'), \tilde{\mathcal{H}}_2(t')] dt', \quad (13)$$

$$\begin{aligned} \rho(t) &= \exp\left(-\frac{i\mathcal{H}_0 t}{\hbar}\right) \left(\rho(0) + \frac{i}{\hbar} \int_0^t [\tilde{\rho}(t'), \tilde{\mathcal{H}}_2(t')] dt' \right) \\ &\quad \times \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right). \end{aligned} \quad (14)$$

Using Eq. (14) in Eq. (9), and using $\text{Tr}\{AB\} = \text{Tr}\{BA\}$, yields

$$\begin{aligned} \frac{\partial}{\partial t}\langle I_{kz}(t) \rangle &= \frac{i}{\hbar} \text{Tr}\left\{\rho(0)\exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right)[\mathcal{H}_2, I_{kz}]\exp\left(-\frac{i\mathcal{H}_0 t}{\hbar}\right)\right\} \\ &\quad + \left(\frac{i}{\hbar}\right)^2 \int_0^t \text{Tr}\left\{[\rho(t'), \mathcal{H}_2]\exp\left(\frac{i(t-t')\mathcal{H}_0}{\hbar}\right)[\mathcal{H}_2, I_{kz}]\right. \\ &\quad \left.\times \exp\left(-\frac{i(t-t')\mathcal{H}_0}{\hbar}\right)\right\} dt'. \end{aligned} \quad (15)$$

Letting $t-t' = \tau$, and using the identity $\text{Tr}\{[A, B]C\} = \text{Tr}\{A[B, C]\}$, as well as the fact that \mathcal{H}_0 commutes with I_{kz} , yields

$$\begin{aligned} \frac{\partial}{\partial t}\langle I_{kz}(t) \rangle &= \frac{i}{\hbar} \text{Tr}\{\rho(0)[\tilde{\mathcal{H}}_2(t), I_{kz}]\} \\ &\quad + \left(\frac{i}{\hbar}\right)^2 \int_0^t \text{Tr}\{\rho(t-\tau)[\mathcal{H}_2, \tilde{\mathcal{H}}_2(\tau), I_{kz}]\} d\tau. \end{aligned} \quad (16)$$

The formulation of the problem of determining $(\partial/\partial t)\langle I_{kz}(t) \rangle$ is exact for large B_0 . We do not know the exact form of the spin-density matrix, so we shall have to make what we hope is an intelligent guess about it. Without any loss of generality we may assume that at time zero

$$\begin{aligned} \rho(t)_{t=0} = \rho(0) &= \exp\left(-\frac{\gamma\hbar B_0}{k} \sum_i \frac{I_{iz}}{T_i(0)}\right) / \\ &\quad \text{Tr}\left\{\exp\left(-\frac{\gamma\hbar B_0}{k} \sum_i \frac{I_{iz}}{T_i(0)}\right)\right\}, \end{aligned} \quad (17)$$

where $T_i(0)$ is the spin temperature for particle i at time zero. It will be assumed that as $t \rightarrow \infty$, the spin system eventually attains an equilibrium state where the spin temperature for all the particles is the same and is equal to T . Then the infinite time-density matrix, denoted by $\rho(\infty)$, is given by

$$\begin{aligned} \rho(\infty) &= \exp\left(-\frac{\gamma\hbar B_0}{k} \sum_i \frac{I_{iz}}{T}\right) / \\ &\quad \text{Tr}\left\{\exp\left(-\frac{\gamma\hbar B_0}{k} \sum_i \frac{I_{iz}}{T}\right)\right\}. \end{aligned} \quad (18)$$

Assuming $\mathfrak{C}_2=0$ for the moment, so that $\mathfrak{C}=\mathfrak{C}_0$, the spin-density matrix $\rho(t)$ would be time-independent since for this case

$$\rho(t) = \exp\left(\frac{i\mathfrak{C}_0}{\hbar}\right)\rho(0)\exp\left(-\frac{i\mathfrak{C}_0}{\hbar}\right) = \rho(0). \quad (19)$$

We may then argue that, by making \mathfrak{C}_2 small enough, the spin-density matrix can be made to evolve as slowly as we wish. It would be reasonable to assume that for \mathfrak{C}_2 small enough in comparison to \mathfrak{C}_1 the spin-density matrix *develops as a quasistatic density matrix* (that is, the spin system is very close to local equilibrium, and the local properties of the spin system are describable by a local spin temperature). The spin density matrix, denoted by $\rho_D(t)$, for these assumptions is given by

$$\rho_D(t) = \exp\left(-\frac{\gamma\hbar B_0}{k} \sum_j \frac{I_{iz}}{T_j}\right) / \text{Tr} \left\{ \exp\left(-\frac{\gamma\hbar B_0}{k} \sum_i \frac{I_{iz}}{T_i}\right) \right\}, \quad (20)$$

where T_i is the spin temperature for particle i and is time-dependent. $\rho_D(t)$ contains only diagonal terms, which seems to be a reasonable approximation for small enough \mathfrak{C}_2 . Since $\rho_D(t)$ commutes with \mathfrak{C}_0 , $\rho_D(t) = \bar{\rho}_D(t)$. Let us write $\bar{\rho}(t)$, the spin-density matrix in the interaction representation, as $\bar{\rho}_D(t) + \bar{\rho}_0(t)$, where $\bar{\rho}_0(t)$ generates only off-diagonal elements. Since $\bar{\rho}(t)$ satisfies Eq. (11), and since $[\bar{\rho}_D(t), \mathfrak{C}_2(t)]$ has only off-diagonal elements, then to *first* order in $\mathfrak{C}_2(t)$, the value of $\bar{\rho}_0(t)$ is given by

$$\frac{\partial \bar{\rho}_0(t)}{\partial t} = \frac{i}{\hbar} [\bar{\rho}_D(t), \mathfrak{C}_2(t)], \quad (21)$$

$$\bar{\rho}_0(t) = \bar{\rho}_0(0) + \frac{i}{\hbar} \int_0^t [\bar{\rho}_D(t'), \mathfrak{C}_2(t')] dt'. \quad (22)$$

$\bar{\rho}_0(0)$ may be set equal to zero without any loss of generality. Transforming back into the laboratory representation, the density matrix $\rho(t)$ reduces to

$$\rho(t) \cong \rho_D(t) + \frac{i}{\hbar} \int_0^t [\rho_D(t'), \mathfrak{C}_2(t'-t)] dt'. \quad (23)$$

Inserting the above form for $\rho(t)$ into Eq. (16), letting $\tau' = t - \tau - t'$, and rearranging terms yields

$$(\partial/\partial t)\langle I_{kz}(t) \rangle = \xi_1 + \xi_2 + \xi_3, \quad (24)$$

where

$$\xi_1 = (i/\hbar) \text{Tr}\{\rho_D(0)C_1(t)\}, \quad (25)$$

$$\xi_2 = \left(\frac{i}{\hbar}\right)^2 \int_0^t \text{Tr}\{\rho_D(t-\tau)C_2(\tau)\} d\tau, \quad (26)$$

$$\xi_3 = \left(\frac{i}{\hbar}\right)^3 \int_{\tau=0}^t \int_{\tau'=0}^{t-\tau} \text{Tr}\{\rho_D(t-\tau-\tau')C_3(\tau',\tau)\} d\tau' d\tau, \quad (27)$$

$$C_1(t) = [\mathfrak{C}_2(t), I_{kz}], \quad (28)$$

$$C_2(\tau) = [\mathfrak{C}_2, [\mathfrak{C}_2(\tau), I_{kz}]] = [\mathfrak{C}_2, C_1(\tau)], \quad (29)$$

$$C_3(\tau, \tau') = \left[\mathfrak{C}_2, \exp\left(\frac{i\tau'\mathfrak{C}_0}{\hbar}\right) [\mathfrak{C}_2, [\mathfrak{C}_2(\tau), I_{kz}]] \times \exp\left(-\frac{i\tau'\mathfrak{C}_0}{\hbar}\right) \right] = \left[\mathfrak{C}_2, \exp\left(\frac{i\tau'\mathfrak{C}_0}{\hbar}\right) C_2(\tau) \exp\left(-\frac{i\tau'\mathfrak{C}_0}{\hbar}\right) \right]. \quad (30)$$

The terms $C_1(t)$, $C_2(\tau)$ and parts of $C_3(\tau, \tau')$ have been evaluated by us only for $I = \frac{1}{2}$ because the commutators are greatly simplified for this case. The calculations for $I > \frac{1}{2}$ should not yield a final result that differs greatly in form from the case of $I = \frac{1}{2}$. As an example of the technique used to evaluate the C 's, the evaluation of $C_1(t)$ is carried out in Appendix A. We have also carried out the evaluation of $C_2(\tau)$ completely and list the results below. Only those terms in $C_3(\tau', \tau)$ have been evaluated that make a nonzero contribution to ξ_3 . These are denoted by $C_{3D}(\tau, \tau')$ and are also listed below.

$$C_1(t) = \sum_{i(i \neq k)} A_{ik} \hbar I_{i+} I_{k-} \mathbf{L}_{k,i} (t) - \text{Hermitian conjugate}, \quad (31)$$

$$C_2(t) = C_2'(t) + C_2''(t) + C_2'''(t), \quad (32)$$

$$C_2'(t) = \sum_{i(i \neq k)} A_{ik} \hbar^2 (I_{kz} - I_{iz}) \mathbf{L}_{k,i} (t) + \text{Hermitian conjugate}, \quad (33)$$

$$C_2''(t) = \sum_{i(i \neq k)} A_{ik} \hbar^2 \left\{ \sum_{p(p \neq i, k)} (-A_{ip} I_{k-} I_{p+} [2I_{iz} \times \cos(B_{kp} - B_{ip})t + i \sin(B_{kp} - B_{ip})t] + A_{kp} I_{i+} I_{p-} [2I_{kz} \cos(B_{kp} - B_{ip})t + i \sin(B_{kp} - B_{ip})t]) \right\} \mathbf{L}_{k,i(i \neq p)} (t) + \text{Hermitian conjugate}, \quad (34)$$

$$C_2'''(t) = i \sum_{i(i \neq k)} A_{ik} \hbar^2 I_{i+} I_{k-} \times \left\{ \sum_{p, q(p \neq q \neq i \neq k)} A_{pq} (I_{p+} I_{q-} - I_{p-} I_{q+}) \times [\sin(B_{kq} + B_{ip} - B_{iq} - B_{kp})t] \right\} \mathbf{L}_{k,i(i \neq p, q)} (t) + \text{Hermitian conjugate}, \quad (35)$$

$$C_{3D}(\tau, \tau') = i \sum_{i(i \neq k)} \left[\sum_{p(p \neq i, k)} \hbar^3 A_{ik} A_{kp} A_{pi} \right. \\ \left. \times (U_{k,i,p}(\tau, \tau')(I_{pz} - I_{iz}) + V_{k,i,p}(\tau, \tau')(I_{pz} - I_{kz})) \right]. \quad (36)$$

In the above expressions

$$\mathbf{L}_{k,i(j \neq p, q, \dots)}(t) = \prod_{j \neq (k, i, p, q, \dots)} \exp[i(B_{kj} - B_{ij})I_{jz}t] \\ = \prod_{t \neq (k, i, p, q)} (\cos(B_{kj} - B_{ij})t + 2iI_{jz} \\ \times \sin(B_{kj} - B_{ij})t). \quad (37)$$

k and i appear as subscripts for the B 's, and j is a running subscript that covers all the particles except k and i and any others listed as subscripts to \mathbf{L} . Also

$$U_{k,i,p}(\tau, \tau') = \left(\mathbf{L}_{k,i(j \neq p)}(\tau) \mathbf{L}_{p,i}(\tau') + \mathbf{L}_{k,i(j \neq p)}(-\tau) \mathbf{L}_{p,i}(-\tau') \right) \\ \times \sin((B_{kp} - B_{ip})\tau), \quad (38)$$

$$V_{k,i,p}(\tau, \tau') = \left(\mathbf{L}_{k,i(j \neq p)}(\tau) \mathbf{L}_{k,p}(\tau') + \mathbf{L}_{k,i(j \neq p)}(-\tau) \mathbf{L}_{k,p}(-\tau') \right) \\ \times \sin((B_{kp} - B_{ip})\tau). \quad (39)$$

The evaluation of the traces listed in Eqs. (25), (26), and (27) is perfectly straightforward. The $\rho_D(t)$ listed in Eq. (20) may be written as

$$\rho_D(t) = \prod_{i=1}^N \rho_{Di}(t), \quad (40)$$

$$\rho_{Di}(t) = \exp\left(-\frac{\gamma \hbar B_0 I_{iz}}{kT_i}\right) / \text{Tr}_i \left\{ \exp\left(-\frac{\gamma \hbar B_0 I_{iz}}{kT_i}\right) \right\}, \quad (41)$$

where Tr_i means that the trace is only to be taken over spin-wave functions for particle i . Using Eq. (40) and wave functions for the system of particles that are products of spin-wave functions for each of the particles, the various traces can be written as the products of traces, each trace being over only the wave functions for a single particle. The only terms that end up having traces different from zero are those of terms $C_2'(t)$ and $C_{3D}(\tau, \tau')$. We thus find

$$\xi_1 = 0, \quad (42)$$

$$\xi_2 = 2 \sum_{i(i \neq k)} A_{ik}^2 \int_0^t \langle \langle I_{iz}(t-\tau) \rangle \rangle \\ - \langle I_{kz}(t-\tau) \rangle \langle G_{ki}(\tau) \rangle d\tau, \quad (43)$$

$$\xi_3 = \sum_{i(i \neq k)} \left(\sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{pi} \int_{\tau=0}^t \int_{\tau'=0}^{t-\tau} [\langle \langle I_{pz}(t-\tau-\tau') \rangle \rangle \right. \\ \left. - \langle I_{iz}(t-\tau-\tau') \rangle \right] \times \langle U_{k,i,p}(\tau, \tau') \rangle + \langle \langle I_{pz}(t-\tau-\tau') \rangle \rangle \\ \left. - \langle I_{kz}(t-\tau-\tau') \rangle \langle V_{k,i,p}(\tau, \tau') \rangle \right] d\tau d\tau', \quad (44)$$

where

$$\langle I_{iz}(t) \rangle = \text{Tr} \{ \rho_{Di}(t) I_{iz} \}, \quad (45)$$

$$\langle G_{k,i}(\tau) \rangle = \frac{1}{2} (\langle \mathbf{L}_{k,i}(\tau) \rangle + \langle \mathbf{L}_{k,i}(\tau) \rangle^*), \quad (46)$$

$$\langle \mathbf{L}_{k,i}(\tau) \rangle = \text{Tr} \{ \prod_j \rho_{Dj}(t-\tau) \mathbf{L}_{k,i}(\tau) \} \\ = \prod_{j \neq k, i} (\cos(B_{kj} - B_{ij})\tau \\ + 2i \langle I_{jz}(t-\tau) \rangle \sin(B_{kj} - B_{ij})\tau), \quad (47)$$

$$\langle U_{k,i,p}(\tau, \tau') \rangle = \text{Tr} \{ \prod_j \rho_{Dj}(t-\tau-\tau') U_{k,i,p}(\tau, \tau') \}, \quad (48)$$

$$\langle V_{k,i,p}(\tau, \tau') \rangle = \text{Tr} \{ \prod_j \rho_{Dj}(t-\tau-\tau') V_{k,i,p}(\tau, \tau') \}. \quad (49)$$

Let us examine the behavior of $\langle \mathbf{L}_{k,i}(\tau) \rangle$ in Eq. (47) for the temperature T_j high enough for all j that $\langle I_{jz}(t-\tau) \rangle \ll \frac{1}{2}$. Each term in the product in Eq. (47) has a maximum value of 1 and a minimum absolute value of $2 \langle I_{jz}(t-\tau) \rangle \ll 1$. For $\tau=0$, $\langle \mathbf{L}_{k,i}(\tau) \rangle$ equals one. Because the B 's have an infinite range of values for an infinite size crystal, very few of the terms in the product in Eq. (47) are 1 for $\tau > 0$ and $\langle \mathbf{L}_{k,i}(\tau) \rangle < 1$ for $\tau > 0$. In particular, for τ on the order of several T_2 's (where T_2 is a crude measure of the transverse relaxation time of the absorption line), many of the terms of the product are quite close to zero and $\langle \mathbf{L}_{k,i}(\tau) \rangle$ is very small. Thus, $\langle \mathbf{L}_{k,i}(\tau) \rangle \rightarrow 0$ as $\tau \rightarrow \infty$, becoming negligible for τ on the order of several T_2 's. Thus, from Eq. (46), we see that $\langle G_{k,i}(\tau) \rangle$ is a function that has a value of 1 for $\tau=0$ and falls to zero rapidly for τ on the order of several T_2 's. The same arguments hold for $\langle U_{k,i,p}(\tau, \tau') \rangle$ and $\langle V_{k,i,p}(\tau, \tau') \rangle$ except that, because of the sine term, they have a value of 0 for $\tau=0$ and fall to zero rapidly for either τ or τ' on the order of several T_2 's.

The assumption will now be made that $\langle I_{iz}(t-\tau) \rangle - \langle I_{kz}(t-\tau) \rangle$ varies slowly in comparison to $\langle G_{ki}(\tau) \rangle$ in the region where $\langle G_{ki}(\tau) \rangle$ is large (the region near $\tau=0$). This assumption is equivalent to assuming that the z component of magnetization for spins i and k does not change appreciably in time T_2 . For such an assumption,

$$\xi_2 \cong 2 \sum_{i(i \neq k)} A_{ik}^2 [\langle I_{iz}(t) \rangle - \langle I_{kz}(t) \rangle] \int_0^t \langle G_{ki}(\tau) \rangle d\tau \quad (50)$$

for $t \gg T_2$. The value of the integral is almost independent of t because $\langle G_{ki}(\tau) \rangle$ has fallen to such a small fraction of its original value by the time $t \gg T_2$. Then the upper limit may be replaced by infinity without changing the value of the integral very much, and

$$\xi_2 \cong 2 \sum_{i(i \neq k)} A_{ik}^2 F_{ki} [\langle I_{iz}(t) \rangle - \langle I_{kz}(t) \rangle], \quad (51)$$

where

$$F_{ki} = \int_0^\infty \langle G_{ki}(\tau) \rangle d\tau. \quad (52)$$

The same arguments may be used to evaluate ξ_3 . The terms $\langle U_{k,i,p}(\tau,\tau') \rangle$ and $\langle V_{k,i,p}(\tau,\tau') \rangle$ are not as sharply peaked as $\langle G_{k,i}(\tau) \rangle$ and have a sine function in them that ensures their being zero for $\tau=0$. However, these two functions do peak within the region of $0 \leq \tau, \tau' < T_2$, so that for the case where $\langle I_p(t-\tau-\tau') \rangle$ varies only by a small amount over the time interval T_2 , and for $t \gg T_2$

$$\xi_3 \cong \sum_{i(i \neq k)} \sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{pi} [\langle I_{pz}(t) \rangle - \langle I_{iz}(t) \rangle] Y_{k,i,p} + \langle \langle I_{pz}(t) \rangle - \langle I_{kz}(t) \rangle \rangle Z_{k,i,p}, \quad (53)$$

where

$$Y_{k,i,p} = \int_{\tau=0}^{\infty} \int_{\tau'=0}^{\infty} \langle U_{k,i,p}(\tau,\tau') \rangle d\tau d\tau', \quad (54)$$

$$Z_{k,i,p} = \int_{\tau=0}^{\infty} \int_{\tau'=0}^{\infty} \langle V_{k,i,p}(\tau,\tau') \rangle d\tau d\tau'. \quad (55)$$

Let us define $\langle I_z(t) \rangle$ as a continuous function of spatial variables such that when evaluated at lattice site j , it is equal to $\langle I_{jz}(t) \rangle$. Carrying out a Taylor series expansion of $\langle I_z(t) \rangle$ about the k th lattice site and then evaluating the results at position j yields

$$\langle I_{jz}(t) \rangle \cong \langle I_{kz}(t) \rangle + \sum_{\alpha=1}^3 \frac{\partial}{\partial x^\alpha} \langle I_z(t) \rangle |_{kx_{kj}^\alpha} + \frac{1}{2} \sum_{\alpha, \beta=1}^3 \frac{\partial^2}{\partial x^\alpha \partial x^\beta} \langle I_z(t) \rangle |_{kx_{kj}^\alpha x_{kj}^\beta} + \dots, \quad (56)$$

where x_{kj}^α is the α coordinate ($\alpha=1, 2, 3$) in an arbitrary Cartesian coordinate system for \mathbf{r}_{kj} , and

$$\frac{\partial}{\partial x^\alpha} \langle I_z(t) \rangle |_{kx^\alpha}$$

is the partial derivative of $\langle I_z(t) \rangle$ with respect to x^α , evaluated at lattice site k . Substituting Eq. (56) into Eq. (51), and dropping third- and higher-order derivatives, yields

$$\xi_2 = 2 \sum_{i(i \neq k)} A_{ik}^2 F_{ki} \left(\sum_{\alpha=1}^3 \frac{\partial}{\partial x^\alpha} \langle I_z(t) \rangle |_{kx_{ki}^\alpha} + \frac{1}{2} \sum_{\alpha, \beta=1}^3 \frac{\partial^2}{\partial x^\alpha \partial x^\beta} \langle I_z(t) \rangle |_{kx_{ki}^\alpha x_{ki}^\beta} \right). \quad (57)$$

It will now be assumed that the particles are located in a lattice that has inversion symmetry. Then, for every i there exists a j such that $A_{ik} = A_{jk}$, $F_{ik} = F_{jk}$, and $x_{ki}^\alpha = -x_{kj}^\alpha$. For such a lattice, the summation over i of the first term on the right-hand side of Eq. (57) vanishes. Substituting Eq. (56) into Eq. (53) and

dropping third- and higher-order derivatives yields

$$\xi_3 = \sum_{i(i \neq k)} \sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{pi} \left(Y_{k,i,p} \left(\sum_{\alpha=1}^3 \frac{\partial}{\partial x^\alpha} \langle I_z(t) \rangle |_{kx_{kp}^\alpha} \right) \times (x_{kp}^\alpha - x_{ki}^\alpha) + \frac{1}{2} \sum_{\alpha, \beta=1}^3 \frac{\partial^2}{\partial x^\alpha \partial x^\beta} \langle I_z(t) \rangle |_{kx_{kp}^\alpha x_{kp}^\beta} - x_{ki}^\alpha x_{ki}^\beta \right) + Z_{k,i,p} \left(\sum_{\alpha=1}^3 \frac{\partial}{\partial x^\alpha} \langle I_z(t) \rangle |_{kx_{kp}^\alpha} + \frac{1}{2} \sum_{\alpha, \beta=1}^3 \frac{\partial^2}{\partial x^\alpha \partial x^\beta} \langle I_z(t) \rangle |_{kx_{kp}^\alpha x_{kp}^\beta} \right). \quad (58)$$

For a lattice that has inversion symmetry, there exists a j and an l for every i and p such that $A_{jk} A_{kl} A_{lj} = A_{ik} A_{kp} A_{pi}$, $Y_{kjl} = Y_{kip}$, and $Z_{kjl} = Z_{kip}$, while $x_{kj}^\alpha = -x_{ki}^\alpha$ and $x_{kl}^\alpha = -x_{kp}^\alpha$. For such a lattice, the summation over i and p of the first term on the right-hand side of Eq. (58) vanishes. Substituting Eqs. (42), (57), and (58) into Eq. (24) and taking

$$\frac{\partial}{\partial x^\alpha} \frac{\partial}{\partial x^\beta} \langle I_z(t) \rangle |_{kx^\alpha x^\beta}$$

outside the summations over i and p yields

$$\frac{\partial}{\partial t} \langle I_z(t) \rangle |_{kx^\alpha x^\beta} = \sum_{\alpha, \beta} D^{\alpha\beta} \frac{\partial^2}{\partial x^\alpha \partial x^\beta} \langle I_z(t) \rangle |_{kx^\alpha x^\beta}, \quad (59)$$

where

$$D^{\alpha\beta} = D_2^{\alpha\beta} + D_3^{\alpha\beta}, \quad (60)$$

$$D_2^{\alpha\beta} = \sum_{i(i \neq k)} A_{ik}^2 F_{ki} x_{ki}^\alpha x_{ki}^\beta, \quad (61)$$

$$D_3^{\alpha\beta} = \frac{1}{2} \sum_{i(i \neq k)} \sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{pi} \times [Y_{kip} (x_{kp}^\alpha x_{kp}^\beta - x_{ki}^\alpha x_{ki}^\beta) + Z_{kip} x_{kp}^\alpha x_{kp}^\beta]. \quad (62)$$

Equation (59) is the desired equation for spatial diffusion of spin magnetization. $D_2^{\alpha\beta}$ is the contribution to the diffusion constant from the ξ_2 term, and $D_3^{\alpha\beta}$ is the contribution to the diffusion constant from the ξ_3 term.

III. EVALUATION OF THE DIFFUSION CONSTANT

To evaluate $D_2^{\alpha\beta}$, we first need to evaluate F_{ki} listed in Eq. (52). As mentioned in the previous section, for $\langle I_{jz}(\tau) \rangle \ll \frac{1}{2}$, the function $\langle G_{k,i}(\tau) \rangle$ is a very rapidly decreasing function of time, falling to a small fraction of its initial value for τ on the order of T_2 . The main contribution to the integral comes in the region of small τ where the sine terms do not change the value of

$\langle G_{ik}(\tau) \rangle$ very much for $\langle I_{jz}(\tau) \rangle \ll \frac{1}{2}$. Thus we may approximate F_{ki} by

$$F_{ki} = \int_0^\infty \prod_{j(j \neq i, k)} \cos[(B_{kj} - B_{ij})\tau] d\tau. \quad (63)$$

For a lattice with inversion symmetry, there exists an l for every j such that $B_{kl} = B_{ji}$ and $B_{il} = B_{jk}$. Thus, the product of cosines is always positive. One would expect that any function that approximated $\langle G_{ki}(\tau) \rangle$ for small τ and went to zero rapidly enough that the contribution to its time integral was small in the region of large τ would give a fairly accurate value of F_{ki} . One possible and convenient function is the Gaussian $\exp(-\Delta_{ki}\tau^2)$, where

$$\Delta_{k,i} = \frac{1}{2} \sum_{j(j \neq i, k)} (B_{kj} - B_{ij})^2. \quad (64)$$

Both the Gaussian and $\langle G_{ki}(\tau) \rangle$ have a value of 1 for $\tau=0$. Both are quadratic in τ , and have the same coefficient for τ^2 , and thus the same behavior for small τ . The contribution to the integral of the Gaussian function for large τ is very small. The value of F_{ki} using the Gaussian approximation is

$$F_{ki} = \frac{1}{2} \left(\frac{\pi}{\Delta_{ki}} \right)^{1/2} \\ = \left(\frac{2}{\pi} \sum_{j(j \neq i, k)} (B_{kj} - B_{ij})^2 \right)^{-1/2}; \quad (65)$$

$$\sum_{j(j \neq i, k)} (B_{kj} - B_{ij})^2 = \sum_{j(j \neq i, k)} (B_{kj}^2 + B_{ij}^2) - 2 \sum_{j(j \neq i, k)} B_{kj} B_{ij} \\ \cong \sum_{j(j \neq i, k)} B_{kj}^2 + \sum_{j(j \neq i, k)} B_{ij}^2. \quad (66)$$

For a lattice where all the sites for the particles are equivalent, the sums in Eq. (66) are independent of i and k and

$$F_{ki} = \left(\frac{4}{\pi} \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right) \right)^{-1/2}. \quad (67)$$

F_{ki} as given in Eq. (63) has been evaluated exactly for a simple cubic lattice, using a computer to evaluate the integrand and then integrate it. The computer results differed by only a few percent from the value of F_{ki} obtained from Eq. (67). From Eqs. (61) and (69), we find

$$D_2^{\alpha\beta} = \frac{\pi^{1/2}}{2} \sum_{i(i \neq k)} A_{ik}^2 x_{ki}^\alpha x_{ki}^\beta \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2}. \quad (68)$$

Summing over k and dividing by N (the number of particles in the system) yields the symmetric form

$$D_2^{\alpha\beta} = \frac{\pi^{1/2}}{2N} \sum_{i \neq k} A_{ik}^2 x_{ki}^\alpha x_{ki}^\beta \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2}. \quad (69)$$

The evaluation of $D_3^{\alpha\beta}$ is similar in technique to that just carried out for $D_2^{\alpha\beta}$, but the details are much more messy. Again using $\langle I_{jz}(t-\tau-\tau') \rangle \ll \frac{1}{2}$, and dropping all sine terms that add to cosine terms,

$$\langle U_{k,i,p}(\tau, \tau') \rangle = 2 \sin((B_{kp} - B_{ip})\tau) \cos((B_{kp} - B_{ik})\tau') \\ \times \prod_{j(j \neq i, k, p)} \cos((B_{kj} - B_{ij})\tau + (B_{pj} - B_{ij})\tau'). \quad (70)$$

Approximating the cosine part of Eq. (70) by a Gaussian function,

$$\langle U_{k,i,p}(\tau, \tau') \rangle \cong 2 \sin[(B_{kp} - B_{ip})\tau] \\ \times \exp[-(\epsilon\tau^2 + \zeta\tau\tau' + \phi\tau'^2)], \quad (71)$$

where

$$\epsilon = \frac{1}{2} \sum_{j \neq (k, i, p)} (B_{kj} - B_{ij})^2, \quad (72)$$

$$\zeta = \sum_{j \neq (k, i, p)} (B_{ij} - B_{kj})(B_{ij} - B_{pj}), \quad (73)$$

$$\phi = \frac{1}{2} \sum_{j \neq (k, i, p)} (B_{pj} - B_{ij})^2 + \frac{1}{2} (B_{pk} - B_{ik})^2. \quad (74)$$

The Gaussian function has decayed to a very small fraction of its initial value by the time the argument of the sine function is near $\pi/2$. Thus, in evaluating $Y_{k,i,p}$ listed in Eq. (54), we may replace the sine function by its linear approximation, and

$$Y_{k,i,p} \cong 2(B_{kp} - B_{ip}) \int_0^\infty \int_0^\infty \tau \\ \times \exp(-(\epsilon\tau^2 + \zeta\tau\tau' + \phi\tau'^2)) d\tau d\tau', \quad (75)$$

$$Y_{k,i,p} = \frac{\pi^{1/2}}{\epsilon^{1/2}(4(\epsilon\phi)^{1/2} + 2\zeta)}. \quad (76)$$

If one now assumes that $\sum_{j \neq (k, i, p)} B_{kj} B_{ij} \cong 0$, and that all lattice sites for particles are equivalent, $Y_{k,i,p}$ may be reduced to the approximate form

$$Y_{k,i,p} \cong \pi^{1/2} (B_{kp} - B_{ip}) \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2} \\ \times (-B_{ip}^2 + 3 \sum_{j(j \neq i, k)} B_{kj}^2)^{-1}. \quad (77)$$

The same evaluation procedure, when applied to $Z_{k,i,p}$, shows it to be equal to $Y_{k,i,p}$.

Inserting the results of Eq. (77) into Eq. (62) yields

$$D_3^{\alpha\beta} = \frac{\pi^{1/2}}{2} \sum_{i(i \neq k)} \sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{ip} (B_{kp} - B_{ip}) \\ \times (2x_{kp}^\alpha x_{kp}^\beta - x_{ki}^\alpha x_{ki}^\beta) \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2} \\ \times (-B_{ip}^2 + 2B_{ki}^2 + 3 \sum_{j(j \neq i, k)} B_{kj}^2)^{-1}. \quad (78)$$

For the case where all the particles are equivalent, one may sum Eq. (78) over all particles by summing over

all k and then dividing by N to get a more symmetric form of $D_3^{\alpha\beta}$. Dropping B_{ip}^2 from the last product in Eq. (78) and averaging this result with $D_3^{\alpha\beta}$ for i and k interchanged yields

$$D_3^{\alpha\beta} = \frac{\pi^{1/2}}{2N} \sum_{i \neq k} \sum_{p(p \neq i, k)} A_{ik} A_{kp} A_{ip} (B_{kp} - B_{ip}) \\ \times (x_{kp}^\alpha x_{kp}^\beta - x_{ip}^\alpha x_{ip}^\beta) \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2} \\ \times (2B_{ki}^2 + 3 \sum_{j(j \neq i, k)} B_{kj}^2)^{-1}. \quad (79)$$

IV. COMPARISON OF $D_2^{\alpha\beta}$ WITH $D_3^{\alpha\beta}$

To compare $D_3^{\alpha\beta}$ with $D_2^{\alpha\beta}$, some crude approximations to simplify $D_3^{\alpha\beta}$ will be made. Both A_{jl} and B_{jl} decrease very rapidly for increasing r_{jl} . For dipolar interactions, for instance, they are both proportional to r_{jl}^{-3} . Therefore, in Eq. (79), the main contribution to the summation over i, k , and p should come from those sets of particles, taken three at a time, that are close together. Further, in summing over p for a given pair i and k , the particle p must be much closer to k than to i , or vice versa, in order to have that term of the sum make an appreciable contribution, because of the multiplying factor $(B_{kp} - B_{ip})(x_{kp}^\alpha x_{kp}^\beta - x_{ip}^\alpha x_{ip}^\beta)$ in Eq. (79). For particle p much closer to i than it is to k ,

$$A_{kp} \approx A_{ki}, \\ B_{kp} - B_{ip} \approx -B_{ip}, \\ x_{kp}^\alpha x_{kp}^\beta - x_{ip}^\alpha x_{ip}^\beta \approx x_{ki}^\alpha x_{ki}^\beta.$$

For particle p much closer to k than it is to i ,

$$A_{ip} \approx A_{ik}, \\ B_{kp} - B_{ip} \approx B_{kp}, \\ x_{kp}^\alpha x_{kp}^\beta - x_{ip}^\alpha x_{ip}^\beta \approx -x_{ik}^\alpha x_{ik}^\beta.$$

Using the above approximations, and replacing $-B_{ki}^2 + 3 \sum_{j(j \neq k)} B_{kj}^2$ by $3 \sum_{j(j \neq k)} B_{kj}^2$, reduces the formula for $D_3^{\alpha\beta}$ listed in Eq. (79) to

$$D_3^{\alpha\beta} \approx \frac{-\pi^{1/2}}{2N} \sum_{i, k(i \neq k)} \left[\frac{A_{ik}^2 x_{ki}^\alpha x_{ki}^\beta}{(-B_{ki}^2 + \sum_{j(j \neq k)} B_{kj}^2)^{1/2}} \right. \\ \left. \times \frac{\sum_{\substack{p \neq i, k; \\ p \text{ near } i, \\ \text{and not near } k}} A_{ip} B_{ip} + \sum_{\substack{p \neq i, k; \\ p \text{ near } k \\ \text{and not near } i}} A_{k, B_{kp}}}{3 \sum_{j(j \neq k)} B_{kj}^2} \right]. \quad (80)$$

The main contribution to the summation over i and k will come for particles i and k close together, because of the factor $A_{ik}^2 x_{ki}^\alpha x_{ki}^\beta$. For particles i and k close

together, there are very few particles *between* particles i and k that are near i and not near k , or near k and not near i . Thus, assuming that all the particles are equivalent, one has

$$\sum_{\substack{p \neq i, k \\ (p \text{ near } i \text{ and} \\ \text{not near } k)}} A_{ip} B_{ip} + \sum_{\substack{p \neq i, k \\ (p \text{ near } k \text{ and} \\ \text{not near } i)}} A_{kp} B_{kp} \\ \approx \sum_{\substack{p(p \neq i) \\ (p \text{ near } i)}} A_{ip} B_{ip}, \quad (81)$$

and independent of i . Recognizing the first term in Eq. (80) as $D_2^{\alpha\beta}$, we find

$$D_3^{\alpha\beta} \approx D_2^{\alpha\beta} \left[\frac{\sum_{\substack{j(j \neq k \text{ but} \\ \text{near } k)}} A_{kj} B_{kj}}{3 \sum_{j(j \neq k)} B_{kj}^2} \right]. \quad (82)$$

$D_3^{\alpha\beta}$ is much less than $D_2^{\alpha\beta}$ for two cases. The first is where A_{kp} is larger than or equal to B_{kp} for p near k , but, because A_{kp} has a much shorter range than B_{kp} , the fraction in Eq. (82) is still much less than 1. The second case occurs for $|A_{kp}/B_{kp}| = \eta \ll 1$. Then $|D_3^{\alpha\beta}/D_2^{\alpha\beta}| < \eta \ll 1$. For dipolar interaction, $A_{ij} = -\frac{1}{2}B_{ij}$, and

$$\left(\frac{D_3^{\alpha\beta}}{D_2^{\alpha\beta}} \right)_{\text{dipolar}} \approx \frac{\sum_{\substack{j(j \neq k \text{ but} \\ \text{near } k)}} B_{kj}^2}{6 \sum_{j(j \neq k)} B_{kj}^2} < \frac{1}{6}. \quad (83)$$

Thus, for dipolar interaction, the $D_3^{\alpha\beta}$ term contributes something like 15% of the $D_2^{\alpha\beta}$ term to the diffusion constant D . Considering the crude approximations made in evaluating $D_3^{\alpha\beta}$ in this section, this estimate might be off by a factor of 2 in either direction.

V. EVALUATION OF D FOR A SIMPLE CUBIC LATTICE

Considering the status of experiments where spin diffusion is involved, a knowledge of the diffusion constant to 50% is more than adequate. Thus, only $D_2^{\alpha\beta}$ will be evaluated here since we have shown that for dipolar interaction, $D_3^{\alpha\beta} < D_2^{\alpha\beta}$. The evaluation of $D_3^{\alpha\beta}$ is also straightforward, but somewhat tedious.

Equation (69) shows $D_2^{\alpha\beta}$ to be a symmetric second-rank tensor and to thus have six different terms. It is obvious that $D_2^{\alpha\beta}$, for $\alpha \neq \beta$, will be much smaller than $D_2^{\alpha\beta}$ for $\alpha = \beta$ regardless of the orientation of the x_1, x_2, x_3 Cartesian coordinate system relative to the crystal axes. For a simple cubic lattice, the case for which the calculation will be carried out here, if the x_1, x_2, x_3 coordinate system is chosen to be the cubic axes system, $D_2^{\alpha\beta} = 0$ for $\alpha \neq \beta$ when the applied magnetic field \mathbf{B}_0 is parallel to a cubic axis. The case of $\alpha \neq \beta$ will not be considered any further. Also, we shall define an average diffusion constant \bar{D}_2 as $\frac{1}{3}(D_2^{11} + D_2^{22} + D_2^{33})$. Thus,

TABLE I. Average diffusion constant \bar{D}_2 for a simple cubic lattice for three different directions of the applied magnetic field. a is the distance between nearest neighbors.

Direction of \mathbf{B}_0	\bar{D}_2
[100]	$0.16\gamma^2\hbar a^{-1}$
[110]	$0.14\gamma^2\hbar a^{-1}$
[111]	$0.14\gamma^2\hbar a^{-1}$

from Eq. (68)

$$\bar{D}_2 = \frac{\pi^{1/2}}{6} \sum_{i(i \neq k)} A_{ik}^2 r_{ki}^2 \left(\sum_{j(j \neq i, k)} B_{kj}^2 \right)^{-1/2}. \quad (84)$$

Using the above formula, \bar{D}_2 was evaluated for a simple cubic lattice for three different directions of applied magnetic field, and the results are listed in Table I. Using the numbers in the table, we find for instance that for calcium fluoride, where for the fluorine nuclei, $a = 2.725 \text{ \AA}$ and $\gamma = 2.51 \times 10^4 \text{ rad/Oe sec}$, the computed value of \bar{D}_2 for \mathbf{B}_0 in the [111] direction is $3.4 \times 10^{-12} \text{ cm}^2/\text{sec}$.

VI. DISCUSSION

The expression for \bar{D}_2 , listed in Eq. (84), is similar in form to Bloembergen's¹ diffusion constant, but has a slightly different value. The difference arises because Bloembergen, in carrying out a first-order perturbation calculation of \bar{D} , used the full second moment of the resonance line shape to compute his transition probabilities. Since he used the \mathcal{H}_2 listed in Eq. (4) as his perturbing Hamiltonian, he should have used the \mathcal{H}_1 in Eq. (3) as his zeroth-order Hamiltonian. By using the second moment of the resonance line shape, however, he actually used a zeroth-order Hamiltonian of

$$\hbar \sum_{i \neq j} (B_{ij} - A_{ij}) I_{iz} I_{jz}.$$

For dipolar interaction, this zeroth-order Hamiltonian is 1.5 times larger than the one he should have used to carry out a consistent first-order perturbation calculation. An additional correction factor appears in Eq. (84) because the term B_{ik}^2 does not appear in the term $\sum_{j(j \neq i, k)} B_{kj}^2$. This just corresponds to the fact that,

for spin- $\frac{1}{2}$ particles, $[I_{iz} I_{kz}, I_{i+} I_{k-} + I_{i-} I_{k+}] = 0$ and the $I_{iz} I_{kz}$ term of the interaction Hamiltonian does not affect the $\uparrow \downarrow$ to $\downarrow \uparrow$ transitions for particles i and k , produced by the $I_{i+} I_{k-} + I_{i-} I_{k+}$ term of the interaction Hamiltonian. Comparing our results with first-order perturbation theory, one can add the additional insight that the source of the difference of B_{kj} and B_{ij} in Eq. (65) in computing a line shape is that it is not the value of the local field at sites k or i that affects the transition probability, but the *difference* in values at sites k and i , averaged over all *differences*, that should be taken into account. Only when the cross term in Eq. (65) is zero, can one really ignore this fact.

At the present time, experiments carried out on substances where spin diffusion exists have so many sources of inaccuracy that their results cannot be thought to check the value of \bar{D} to better than a factor of 2 to 3. Within this limitation, the results for \bar{D}_2 computed in the previous section is consistent with experimental results.

APPENDIX A: EVALUATION OF $C_1(t)$

$C_1(t)$ is defined as Eq. (28). Using the facts that $[\mathcal{H}_2, \mathcal{H}_1] = [\mathcal{H}_2, \mathcal{H}_2] = [\mathcal{H}_1, I_{kz}] = 0$, we find that

$$\begin{aligned} C_1(t) &= [\tilde{\mathcal{H}}_2(t), I_{kz}] \\ &= \exp\left(\frac{it\mathcal{H}_0}{\hbar}\right) [\mathcal{H}_2, I_{kz}] \exp\left(\frac{-it\mathcal{H}_0}{\hbar}\right); \quad (A1) \end{aligned}$$

$$\begin{aligned} [\mathcal{H}_2, I_{kz}] &= \sum_{i \neq j} \frac{A_{ij}\hbar}{2} [I_{i+} I_{j-} + I_{i-} I_{j+}, I_{kz}] \\ &= \hbar \sum_{i(i \neq k)} A_{ik} (I_{k-} I_{i+} - I_{k+} I_{i-}). \quad (A2) \end{aligned}$$

Since all terms in \mathcal{H}_1 commute,

$$\exp\left(\frac{it\mathcal{H}_1}{\hbar}\right) = \prod_{j \neq l} \exp(itB_{jl} I_{jz} I_{lz}). \quad (A3)$$

Inserting Eq. (A2) and Eq. (A3) into Eq. (A1) and using the fact that all the exponential factors that do not contain particle indices i and k may be passed through $(I_{k-} I_{i+} - I_{k+} I_{i-})$ and combined with their inverse, we find

$$\begin{aligned} C_1(t) &= \hbar \sum_{i(i \neq k)} A_{ik} \exp[2it(I_{iz} \sum_{j(j \neq i, k)} B_{ij} I_{jz} + I_{kz} \sum_{j(j \neq i, k)} B_{jk} I_{jz} + B_{ik} I_{iz} I_{kz})] (I_{k-} I_{i+} - I_{k+} I_{i-}) \\ &\quad \times \exp[-2it(I_{iz} \sum_{j(j \neq i, k)} B_{ij} I_{jz} + I_{kz} \sum_{j(j \neq i, k)} B_{jk} I_{jz} + B_{ik} I_{iz} I_{kz})]. \quad (A4) \end{aligned}$$

Using the identities

$$\exp(i\phi I_z) I_+ \exp(-i\phi I_z) = I_+ \exp(i\phi), \quad \exp(i\phi I_z) I_- \exp(-i\phi I_z) = I_- \exp(-i\phi), \quad (A5)$$

Eq. (A4) may be reduced to

$$C_1(t) = \hbar \sum_{i(i \neq k)} A_{ik} I_{i+} \exp[2itB_{ik}(I_{kz} - I_{iz})] I_{k-} \prod_{j(j \neq i, k)} \exp(2iI_{jz}(B_{ij} - B_{kj})) - \text{Hermitian conjugate.} \quad (\text{A6})$$

For $I = \frac{1}{2}$, the only case considered from now on, one may use the identity in Eq. (A7) to simplify Eq. (A6).

$$\exp(i\phi I_{jz}) = \cos(\phi/2) + 2iI_{jz} \sin(\phi/2). \quad (\text{A7})$$

The final result is that

$$C_1(t) = \hbar \sum_{i(i \neq k)} A_{ik} I_{i+} I_{k-} \prod_{j(j \neq i, k)} \exp[i(B_{kj} - B_{ij})I_{jz}] - \text{Hermitian conjugate.} \quad (\text{A8})$$

Optical Properties of Zinc Telluride*

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The optical absorption of ZnTe single crystals grown by the Bridgeman method has been studied from visible wavelengths to 50 μ , at temperatures from 1.4 to 300°K. Lattice combination bands are observed from which assignments of zone-boundary phonon energies are made: LO = TO = 22, LA = 16, TA = 7×10^{-3} eV. The temperature dependence of the absorption is discussed. Absorption due to inter-valence-band transitions has been observed, which indicates the presence of two bands degenerate at $k=0$ and a split-off band lying 1 eV below. Infrared absorption is observed for As impurity in the range 0.05 to 0.1 eV and for a residual impurity in undoped material, probably a zinc vacancy, in the range 0.1 to 0.9 eV. For each impurity, absorption due to transitions to the split-off valence band is also observed near 1 eV. Sharp excitation lines are seen in the spectrum of the residual impurity. The lines are repeated with emission of optical phonons of energy 0.026 eV, from which the electron-phonon coupling coefficient is estimated. Some structure is observed also in the spectrum of As impurity. The intrinsic absorption edge has been measured at 1.7, 80, and 300°K. The energy gap is determined to be 2.385, 2.37, and 2.25 eV, respectively. A tail is observed at the absorption edge which shows the effect of various impurity levels in the undoped material and in the samples doped with As, In, or Fe. In two samples grown from the vapor phase, some sharp absorption lines are present in the range 2.2 to 2.35 eV. These lines are apparently due to exciton-impurity complexes.

I. INTRODUCTION

ZINC telluride is a II-VI compound semiconductor with zinc-blende structure. Undoped ZnTe turns out to be p type. n -type material with very low carrier concentration has been obtained in highly compensated form, in particular with In doping. It has been suggested that zinc vacancies acting as double acceptors give rise to self-compensation.^{1,2}

The energy gap of ZnTe has been estimated to be ~ 2.1 – 2.3 eV from room-temperature optical measurements.^{3–6} From low-temperature studies of oscillating

photoconductivity and optical behavior near the absorption edge, we have obtained values of the carrier effective masses and the energy gap at 4.2°K: $m_e = 0.09m$, $m_{hh} = 0.6m$, $E_g = 2.385$ eV.⁷ The structure of the valence band is expected to be similar to that of the III-V compounds. Piezoresistance data⁸ are consistent with such a model. Absorption bands have been observed near 1 eV in crystals doped with various impurities,^{9,10} and these bands were attributed to transitions between the impurity level and the split-off valence band.

We report, in this paper, studies of optical absorption over a range from the visible region to 50 μ . The measurements were made at temperatures between 1.4°K and room temperature. Absorption bands of lattice combination modes were observed in the region between

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