

ionized halogen ions and n conduction electrons per unit volume. We assume that the density of the centers is sufficiently small for interactions between them to be neglected, and that the mobility of an electron is much larger than that of an ionized center. Since a doubly ionized halogen ion has an effective charge $+2e$, it exerts a Coulomb attraction on the surrounding electrons. The lifetime of a center is (a) the time that an electron takes to reach the center, plus (b) the time that an electron takes, once in the immediate neighborhood of a center, to be captured. A lower limit is obtained if we neglect the latter. The average time for an electron to reach a center may be estimated very simply. At the time $t=0$, the closest electron to a given center is about $[(4\pi/3)n]^{-3}$ cm away. This electron will be attracted toward the center with a force $2e^2/Kr^2$ and move toward it with a velocity $\mu E = 2\mu e/Kr^2$.

Here K is a dielectric constant and μ is the mobility of an electron. The time for the electron to reach the center is

$$\tau = \int_0^{\bar{r}} \frac{K\tau^2}{2\mu e} dr = \frac{K}{8\pi e\mu n},$$

where $\bar{r} = [(4\pi/3)n]^{-3}$.

For NaCl at 200°K, the high-frequency dielectric constant $K \sim 2$, and $\mu = 40$ cm²/v-sec,⁹ which gives $\tau \simeq 10^5/n$ sec. If $n \lesssim 10^{17}$ /cm³, then $\tau > 10^{-12}$ sec, and it is thus very likely that a doubly ionized halogen has time to escape into an interstitial position. It should be possible to estimate n by measuring the electrical conductivity of a crystal during irradiation. Such measurements are now in progress.

⁹ A. G. Redfield, Phys. Rev. **91**, 753 (1953).

Spatial Diffusion of Spin Energy

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A procedure is outlined for evaluating the spatial diffusion coefficient of magnetization of spins on a rigid lattice. The temporal recession of a spatially sinusoidally varying magnetization is analyzed, and is reduced to the problem of finding a function whose moments are known. An unambiguous value of diffusion coefficient can be obtained but the possibility of a complete lack of diffusion cannot be ruled out.

SOME years ago Bloembergen¹ pointed out that certain spin relaxation phenomena could be explained if it was assumed that energy can be spatially transported in the spin system of a rigid lattice via mutual spin flips of near neighbors, brought about by the dipole-dipole interaction. He was able to make a rough estimate of the diffusion coefficient, but efforts to improve on his theory have failed because of the inapplicability of perturbation theory to this problem.

In many cases it is difficult, if not impossible, to prove theoretically whether or not such spin diffusion actually occurs,² but if we assume that it does, then it is possible in principle to find a unique value for the diffusion coefficient D . We consider for simplicity the high-field case, for which total M_z is conserved, and for which the Hamiltonian can be suitably truncated.³ It suffices to consider a single spatial Fourier component of the spin magnetization. At time $t=0$, we assume $M_z = M_0 + C(0) \sin kx$. Such a nonuniform magnetization could be produced by adding a nonuniform field to the uniform high field for $t < 0$ and switching this added field off at $t=0$. According to the usual diffusion equa-

tion, $C(t)$ will decay exponentially for $t > 0$ with time constant $\tau^{-1} = Dk^2$. We assume that this is the case, and find that the consequences of this assumption are consistent with a certain rigorous quantum calculation provided k^{-1} is large compared to the interspin distance. The resulting diffusion coefficient D can be regarded as an upper limit and is probably the true one for those cases in which spin diffusion actually does occur.

We consider the time derivatives of $C(t)$ at $t=0$; these can be calculated assuming that the system is described for $t=0$ by the density matrix

$$\rho \simeq A(1 - \mathcal{H}C/kT + BU), \quad (1)$$

where

$$U = \sum_j \sin kx_j S_{zj}. \quad (2)$$

Here A and B are suitable constants, \mathcal{H} is the Hamiltonian³ of the spin system for $t > 0$, S_{zj} is the z component of spin angular momentum operator for the j th spin, and x_j is its x coordinate. The fact that (1) is written as a series rather than an exponential form implies that we are considering the high-temperature limit only.

The expectation value of U , $\text{Tr}U\rho(t)$, is proportional to $C(t)$; thus the derivatives of C at $t=0$ can be calcu-

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

² P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

³ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

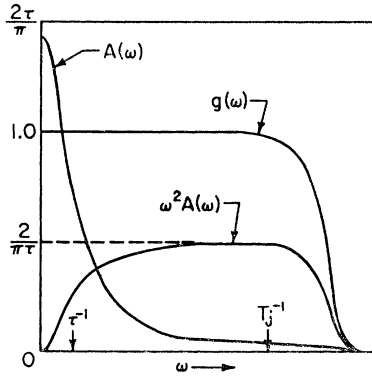


FIG. 1. Behavior of various functions discussed in the text.

lated.⁴ Odd derivatives vanish and the even derivatives $M_{2n} \equiv (d^{2n}C/dt^{2n})/C(0)$ will be discussed below. We immediately see that $C(t)$ cannot be exponential; instead we may hope that its behavior is exponential for time greater than some time $T_j \ll \tau$; for time less than T_j , $C(t)$ must depart from exponential behavior to have zero first derivative at $t=0$.

$C(t)$ is analytic and has a normalized Fourier transform $A(\omega)$:

$$C(t) = C(0) \int_0^\infty A(\omega) \cos \omega t d\omega. \quad (3)$$

The $2n$ th moment of $A(\omega)$ is $(-1)^n M_{2n}$. If one assumes that $C(t)$ is nearly exponential, $A(\omega)$ will be nearly Lorentzian, except for $\omega > T_j^{-1}$, where it will be cut off (Fig. 1). Thus we can write

$$A(\omega) = \frac{2\tau/\pi}{1 + \omega^2 \tau^2} g(\omega), \quad (4)$$

where $g(\omega)$ equals unity for $\omega=0$ and is a function which approaches zero for $\omega \geq T_j$ (see Fig. 1). Since $\omega^2 A(\omega) \simeq (2/\pi\tau)g(\omega)$ for $\omega > \tau^{-1}$, we have

$$M_2 \simeq (2/\pi\tau) \int g(\omega) d\omega, \quad (5)$$

for $\tau \gg T_j$; therefore τ and thus D can be determined if the shape of $g(\omega)$ is known. But the $2n$ th moment of g is approximately given by $|M_{2n+2}/M_2|$, and the shape of g can in principle be determined from its moments.

In order to be consistent, D must be independent of k , so τ^{-1} and all the M_{2n} must be proportional to k^2 . We have

$$(i\hbar)^{2n} M_{2n} \sum_j (\sin kx_j)^2 \text{Tr} S_{zj}^2 = \sum_{ij} \sin kx_i \sin kx_j \text{Tr} [\mathcal{H}, S_{zi}]_n [\mathcal{H}, S_{zj}]_n, \quad (6)$$

⁴ The reasoning used here is similar to that used in treating free-induction decays in magnetic resonance. See, for example, I. J. Lowe and R. E. Norberg, *Phys. Rev.* **107**, 46 (1957); R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

where $[A, B]_1 \equiv [A, B]$; $[A, B]_2 \equiv [A, [A, B]]$, etc. Using the fact that the truncated \mathcal{H} commutes with total S_z and that the trace on the right-hand side is, on the average, an even function of $x_i - x_j$, and assuming that the spin system is macroscopically homogeneous, we can reduce (6) to

$$-(i\hbar)^{2n} M_{2n} \sum_j \text{Tr} S_{zj}^2 = 2 \sum_{ij} [\sin \frac{1}{2} k(x_i - x_j)]^2 \text{Tr} [\mathcal{H}, S_{zi}]_n [\mathcal{H}, S_{zj}]_n. \quad (7)$$

For the usual dipole-dipole and exchange interactions, the trace on the right-hand side decreases rapidly with increasing $x_i - x_j$, so that only nearby spins i and j need be included in the double sum. Thus (7) is proportional to k^2 for k^{-1} much larger than the spacing between spins. This condition also leads to $\tau \gg T_j$ (T_j is of the order of the nearest neighbor interaction T_2), so that the assumption of spin diffusion is indeed consistent with the calculated M_{2n} .

The theory can be applied to the low-field case and to spectral diffusion^{2,5,6} by suitable modifications of \mathcal{H} and U . The low-field case appears to be straightforward, but the results of the spectral-diffusion calculation are complex and the interpretation obscure.

When applied to an electronic spin system with static microscopic inhomogeneous (hyperfine) broadening, this theory predicts spatial diffusion even for spin-spin interaction much smaller than the hyperfine broadening, in disagreement with the natural interpretation of experiments⁵ on spectral diffusion and with other more sophisticated theoretical work.² A partial or complete lack of diffusion means $C(\infty) \neq 0$, $A(0)$ singular. A true singularity appearing in $A(0)$ at $\omega=0$ would be virtually impossible to distinguish from a Lorentzian peak at $\omega < \tau^{-1}$ by means of a moment calculation.

Nevertheless, we may hope that in cases where diffusion does occur, the present formalism would apply. The best quantitative experimental comparison would be with angular⁷ and field⁸ dependence of T_1 in ionic crystals. The actual calculation of the M_{2n} and $g(\omega)$ would be difficult but does not appear to be out of the question.

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⁵ G. Feher (to be published).

⁶ A. Portis, *Phys. Rev.* **104**, 584 (1956).

⁷ G. D. Watkins, thesis, Harvard University (unpublished).

⁸ N. F. Ramsey and R. V. Pound, *Phys. Rev.* **81**, 278 (1950).