Classical Microscopic Model for Magnetic Resonance Including Relaxation Effects

R. K. WARING, JR.
Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware
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A classical theoretical model for magnetic resonance is suggested, and several of its implications are developed. The solution to Bloch's equations for magnetic resonance, without relaxation, is assumed for each incremental portion of the total magnetization of a system. With a suitably rotating coordinate system, an investigation is then made of the steady-state angular distribution of magnetization that results from the random relaxation process to which each element of magnetization is subject. When the longitudinal relaxation time, T_1, is taken to equal the transverse relaxation time, T_2, this procedure leads to the same results as the direct solution of Bloch's equations with relaxation. In addition, the model yields a general description of the saturated dispersion signal for sinusoidal modulation of the external field, for both homogeneous and inhomogeneous broadening of the resonance line. A method for measuring T_1 based on this description is presented. For $T_1 \neq T_2$, the model reveals on classical, geometrical grounds an inconsistency in Bloch's implicit assumption that the transverse relaxation effects are independent of the applied radio-frequency field.

I. INTRODUCTION

THE model described in this article grew out of an effort to form a reasonably clear intuitive picture of the classical behavior of the individual elements of a paramagnetic system under the conditions of ordinary magnetic resonance experiments. In such experiments the system is placed in a magnetic field, H_0, and a radio or microwave frequency (rf) magnetic field, $2H_1 \cos\omega t$, is applied in a direction perpendicular to H_0. Also, as a rule, $H_0 \gg H_1$. Since the magnetic moment of the system has associated with it a definite amount of angular momentum, the torque resulting from the action of the applied field, H_0, causes the moment to precess around the applied static field at the Larmor frequency, $2\pi\gamma H_0$, where γ is the gyromagnetic ratio. As the frequency of the applied alternating field approaches the Larmor frequency, the alternating field will have an increasing effect on the orientation of the magnetic moment and various resonance phenomena can be observed.

Also affecting the orientation and magnitude of the magnetic moment will be those fields that, in the absence of the alternating field, would relax the system to a state of equilibrium within itself and with its surroundings. In his now-classic paper on nuclear induction, Bloch[1] wrote phenomenological differential equations in which he added the gyroscopic terms, which describe the time dependence of the total macroscopic magnetization of the system in the absence of the relaxation fields, to relaxation terms, which describe the time dependence of the macroscopic magnetization in the absence of the alternating field. Simply adding these terms is tantamount to assuming that the presence of the alternating field does not affect the relaxation process. This assumption has been examined by a number of authors, notably Redfield.[2]

The approach here is to assume that the macroscopic magnetization is divisible into incremental elements of constant amplitude, each of which obeys the gyroscopic part of Bloch's equations, precessing about the external static field and nutating in response to the alternating field. For brevity, these elements are referred to as spins even though no attention is given to the quantum mechanical implications of the model. It is arbitrarily stated that each spin is subject to a simple relaxation event in which it discontinuously changes its orientation from whatever that may be to alignment along H_0. This is a randomly occurring event with a probability per unit time of $1/T_1$.[3] As a result of the simultaneous, and presumably independent, action of the two effects, the magnetization of the system assumes a steady state distribution in a phase space whose variables describe the orientation of the magnetization elements. With this distribution known, the signal can be predicted under several sets of conditions commonly encountered in magnetic resonance experiments. Wangsness and Bloch[4] have achieved a similar objective on a quantum-statistical basis. However, the present approach is justified by its intuitive transparency, and by certain new results to which it leads.

This paper is divided into several sections. In Sec. II, the basic model is developed for $T_1 = T_2$. Next, the model is used to obtain expressions for the saturated dispersion signal when the external field is changing with time. This is done for a single adiabatic sweep and for adiabatic sinusoidal modulation of the external field. Included in this section is an explanation of the dependence upon reference signal phase of the line shape recorded by the phase-sensitive detector employed in field modulation spectrometers. A method for using this dependence to measure T_1 is also described. In Sec. IV the model is used in an examination of Bloch's assumption that the spin-spin relaxation process is independent of the strength of the applied radio frequency field. The discussion section includes a

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).
[2] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[3] Quantum mechanically, for spin $\frac{1}{2}$, the probability per unit time is given by $1/2T_1$. This arises because each transition changes the difference in occupation of the two available states by two.
[4] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

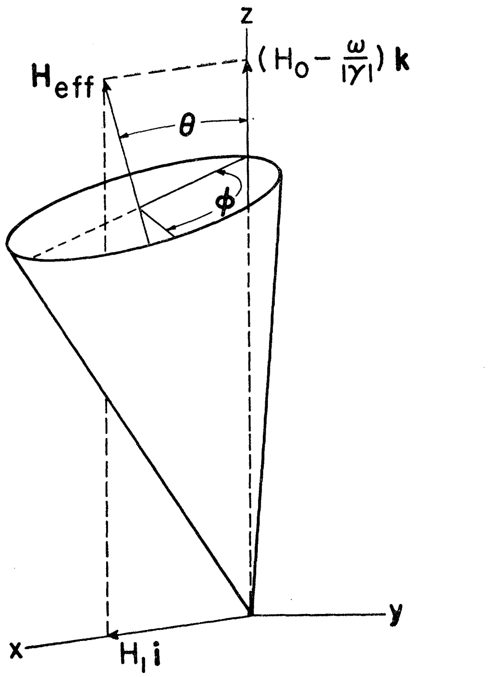

FIG. 1. Cone of precession in a rotating coordinate system. The external field, H_0, is static. The angle ϕ is measured here in the direction of precession for positive γ.

consideration of the physical reality of the model. An appendix discusses the relationship between the methods of this article and Chamber's solution to the classical Boltzmann transport equation.

II. BASIC MODEL

The description of magnetic resonance phenomena will be referred to a rotating, right-handed coordinate system.[5,6] The z axis is taken to lie along the direction of the applied static field, H_0, in the positive sense, and rotation occurs about this axis at the frequency of the applied radio-frequency field in the positive or negative sense for negative or positive gyromagnetic ratios, respectively. The applied rf field, $2H_1\cos\omega t$, is resolved into contra-rotating components of amplitude H_1; and, at high static fields, only the component that is stationary in the rotating system has a significant physical effect. It is taken to lie along the x axis in the positive sense, and it forms the x component of the effective field in the rotating coordinate system.

The z component of this effective field is given by

$$\hat{k}\cdot\mathbf{H}_{\text{eff}}=H_0-\omega/|\gamma|.$$

If relaxation effects are neglected, the total magnetization of a system characterized by the gyromagnetic ratio γ may be thought of as precessing about the effective field with an angular velocity given by

$$\Omega=|\gamma|[H_1^2+(H_0-\omega/|\gamma|)^2]^{\frac{1}{2}}=[\gamma^2H_1^2+(\omega_0-\omega)^2]^{\frac{1}{2}}. \quad (1)$$

If we consider only a single resonance line, uncomplicated by structure, the magnetization will lie on a cone centered on the effective field as shown in Fig. 1.

To inject the concept of relaxation into this picture, the total magnetization is taken to be made up of independent spins. The term "independent" here implies that the spins have a negligible average effect upon each other in times comparable to T_1, the spin-lattice or longitudinal relaxation time, and thus that $T_1=T_2$, where T_2 is the transverse relaxation time. Each such spin will precess about the effective field. For the present, only the spin-lattice relaxation process, characterized by a probability per unit time of $1/T_1$, will be considered. As indicated in Sec. I, the relaxation event is pictured as the disappearance of a spin and its immediate reappearance at the z axis. The physical reality of this assumption is examined in Sec. V. After relaxation, a spin will begin to precess again around the effective field.

The resultant distribution of magnetization around the cone of precession can be determined by noting that in the steady state the amount of magnetization arriving at any position on the cone per unit time must equal the amount leaving per unit time. Thus

$$M/T_1-\int_0^\phi M(\phi)d\phi/T_1=M(\phi)\Omega, \quad (2)$$

where M is the total magnetization, $M(\phi)$ is the distribution function sought, and ϕ is measured in the direction of precession, as shown on Fig. 1. The first term gives the rate of injection of magnetization at the z axis. The second gives the rate of relaxation in the range of azimuthal angle from zero to ϕ. $M(\phi)\Omega$ is the rate at which magnetization passes the position at ϕ because of precession in the rotating system.

Differentiating (2), one has

$$-M(\phi)/\Omega T_1=dM(\phi)/d\phi. \quad (3)$$

The solution for (3) that also satisfies (2) is

$$M(\phi)=(M/\Omega T_1)e^{-\phi/\Omega T_1}. \quad (4)$$

The same result could have been obtained by subjecting the solution of (3) to the requirement that the total magnetization be M.

The dispersion signal (u, in Bloch's notation[1]) in the laboratory coordinate system is in phase with the applied radio-frequency field and is thus proportional to M_x, the projection of the distribution of magnetization on the x axis of the rotating frame.

$$M_x=\int_0^\infty M(\phi)(1-\cos\phi)\sin\theta\cos\theta d\theta, \quad (5)$$

[5] R. K. Wangsness, Am. J. Phys. **21**, 279 (1953).
[6] I. I. Rabi, N. F. Ramsey, and J. Schwinger, Rev. Modern Phys. **26**, 167 (1954).

where the integration is carried to infinity to account for the possibility that many precession periods will pass before a given increment relaxes. Similarly, the absorption signal ($-v$, in Bloch's notation, for positive γ) is given by

$$M_y=\int_0^\infty M(\phi)\sin\phi\,\sin\theta d\phi. \tag{6}$$

Also[7]

$$M_z=\int_0^\infty M(\phi)(\cos^2\theta+\sin^2\theta\cos\phi)d\phi. \tag{7}$$

The trigonometric terms are the projections on the appropriate axes of unit vectors on the cone of precession. It should be noted that these expressions automatically take into account the fact that the cone of precession will be in the $-x$, $+z$ quadrant when the effective field is in the $+x$, $-z$ quadrant, since $\cos\theta$ will be negative for that case. Equations (5)–(7), together with (4) and (1), yield:

$$M_x=\gamma H_1 M T_1^2(\omega_0-\omega)(1+\Omega^2T_1^2)^{-1}, \tag{8}$$

$$M_y=\gamma H_1 M T_1(1+\Omega^2T_1^2)^{-1}, \tag{9}$$

$$M_z=M[1+(\omega_0-\omega)^2T_1^2](1+\Omega^2T_1^2)^{-1}. \tag{10}$$

But $M=\chi_0 H_0$; thus

$$M_x=\chi_0\omega_0 H_1\frac{T_1^2(\omega_0-\omega)}{1+\gamma^2H_1^2T_1^2+(\omega_0-\omega)^2T_1^2}, \tag{11}$$

$$M_y=\chi_0\omega_0 H_1\frac{T_1}{1+\gamma^2H_1^2T_1^2+(\omega_0-\omega)^2T_1^2}, \tag{12}$$

$$M_z=\chi_0 H_0\frac{1+(\omega_0-\omega)^2T_1^2}{1+\gamma^2H_1^2T_1^2+(\omega_0-\omega)^2T_1^2}. \tag{13}$$

These will be recognized as the steady-state solutions to Bloch's[1] equations for $T_1=T_2$ in the rotating coordinate system, where the total radio-frequency field is taken to be $2H_1\cos\omega t$ along the x axis in the laboratory frame of reference.

The model permits a simple intuitive interpretation of various relaxation phenomena. To give an example, if $\gamma H_1\gg 1/T_1$, the average spin precesses many times around the effective field between relaxations. Thus, the distribution of magnetization around the cone shown in Fig. 1 becomes uniform because of the random nature of the relaxation process. (See Appendix.) Then there will be no projection of the distribution of magnetization on the y axis, and the absorption signal will be saturated. On the other hand, a projection on the x axis persists until H_1 is so large that the effective field lies essentially along the x axis, in which case the magnetization all lies in the y-z plane, as it does at resonance for any value of H_1. Thus, the dispersion signal saturates in a different manner than does the absorption signal. This last statement requires elaboration, since (11) and (12) have the same denominator.

In many experiments, ω is held constant and H_0 is slowly varied, the signal being plotted as a function of H_0. When the signal is plotted as a function of δ,

$$M_x+M\delta/(1+\delta^2+\alpha^2), \tag{14}$$

$$M_y=M\alpha/(1+\delta^2+\alpha^2), \tag{15}$$

where

$$\delta=(H_0-H^*)/H_1=\cot\theta,\quad H^*=\omega/|\gamma|,$$

and

$$\alpha=1/|\gamma|H_1T_1.$$

Bloch obtained expressions analogous to (14) and (15) by direct solution of the equations of motion for the slow-passage case. Note that the absorption signal, for constant δ, can be entirely eradicated at sufficiently high rf fields, whereas the dispersion signal cannot. In the model this corresponds to the fact that, for constant δ, a uniformly occupied cone of precession at $\theta=\cot^{-1}\delta$ has a zero projection on the y axis and a finite, constant projection on the x axis. Perhaps one can say that, in systems obeying Bloch's equations for $T_1=T_2$, large rf fields "kill" the absorption signal, whereas they only "push aside" the dispersion signal.

This distinction is important in the common type of experiment where H_0 is modulated sinusoidally with an amplitude much less than the line width and with a frequency low enough to ensure equilibrium throughout a modulation cycle. The resultant modulation of the components of magnetization is translated into a signal proportional to the first derivative of the appropriate magnetization component with respect to H_0. But from (14) and (15) it may be shown that, for $\alpha\ll 1$:

$$(dM_x/dH_0)_{\max}\approx M_0/H_1, \tag{16}$$

$$(dM_y/dH_0)_{\max}\approx\pm(\tfrac{3}{4})^{\frac{3}{2}}M_0/\gamma T_1H_1^2. \tag{17}$$

To obtain the actual signal detected as a function of the radio-frequency susceptibility, (16) and (17) must be multiplied by H_m/H_1, where H_m is the modulation amplitude. Thus, the peak dispersion and absorption derivatives saturate in substantially differing manners; even though, for systems obeying Bloch's equations, the dispersion and absorption saturate according to the same function for constant field.[8]

III. PASSAGE EFFECTS

A. Single Sweep

This section treats the case for which H_1 is large enough to ensure uniform distribution of magnetization around the effective field in the rotating coordinate system and for which the external field is changing.

[7] These expressions are reminiscent of those obtained by Garstens (reference 18), who treated gases and averaged the components of magnetization resulting from gyroscopic motion over the time since the last collision. See also reference 17, p. 109.

[8] Equation (17) is an extrapolation of case 1 of reference 16. The more complicated cases will not be treated here.

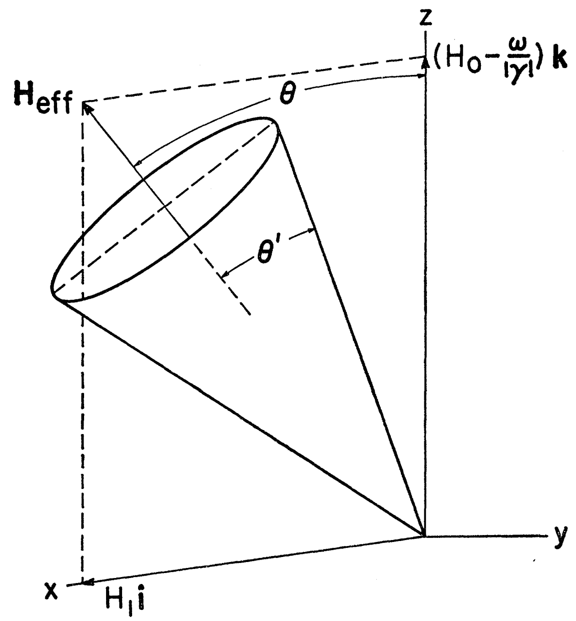

FIG. 2. Representative cone of precession in a rotating coordinate system. The external field, H_0, is changing.

We limit the discussion to changes that are slow relative to the precession rate, Ω. Specifically:

$$(dH_0/dt)/H_1 \ll \gamma H_1. \tag{18}$$

Under this "adiabatic" condition, each spin continues to precess around the effective field at a constant angle, until it relaxes to the z axis.[9] It then precesses around the effective field at a new angle equal to the angle between the z axis and the effective field at the instant of relaxation. If the precession rate, Ω, is sufficiently large, the distribution of magnetization in a differential range of cones characterized by $d\theta'$ will be uniform around the effective field. (See Fig. 2.)

It is of interest to find the distribution, $M(\theta')$, of magnetization in the various cones centered on the effective field. A given differential cone can receive magnetization only while it is in contact with the z axis. Subsequently its magnetization is assumed to decay exponentially at a rate determined by T_1. Thus, to first order,

$$dM(\theta') = \frac{M}{T_1} \frac{\exp(-[t(\theta)-t(\theta')]/T_1)}{(d\theta/dt)'} d\theta'. \tag{19}$$

Here $t(\theta)$ is the present time; $t(\theta')$ is the time at which the cone at θ' touched the z axis. The rate of change of θ, $(d\theta/dt)'$, is evaluated at $t(\theta')$. Strictly speaking, M is not a constant, since the external field is varying. M will not even have its equilibrium value at any given time, so it is complicated to evaluate exactly. The signal will be determined by the projection of the total distribution of magnetization on the x axis. Since the distribution is uniform around the effective field, the x projection of the magnetization in a differential cone is given by

$$dM_x = dM(\theta') \cos\theta' \sin\theta d\theta'.$$

Thus, the total x projection is

$$M_x(t) = (1/T_1) \int_\tau^t M(t') e^{-(t-t')/T_1} \cos\theta(t') \sin\theta(t) dt' + M(\tau) e^{-(t-\tau)/T_1} \cos\theta(\tau) \sin\theta(t), \tag{20}$$

where the variable has been changed from cone angle to time. The time at which the sweep started is τ, and $\theta(\tau)$ is the angle at which the system was allowed to come to equilibrium before the field sweep started. The second term accounts for the magnetization still in the cone at $\theta(\tau)$ at the time t. If $\tau = -\infty$, (20) reduces to Bloch's solution of his equations for

$$T_2 = T_1, \quad \gamma H_1 \gg 1/T_1, \quad dH_0/dt \ll \gamma H_1^2. \tag{21}$$

Equation (20) applies for all rates of passage, providing only that (21) is obeyed.

This approach provides a useful picture of the adiabatic rapid-passage phenomenon.[1] If the sweep of the external field from above resonance to below resonance is sufficiently rapid relative to the relaxation rate, most of the magnetization will remain in the initial cone at $\theta(\tau)$ during the entire passage. Thus the contribution of the integral in (20) to M_x will be small, and the second term will dominate.

$$M_x(t) \approx M(\tau) \cos\theta(\tau) \sin\theta(t).$$

If the sweep is started sufficiently far off resonance, $\theta(\tau) \approx 0$ or π. Thus, $\cos\theta(\tau) \approx \pm 1$, where the plus sign applies for a sweep starting at a field above that for resonance, and the minus sign applies for a sweep from below resonance. Thus:

$$M_x(t) \approx \pm M(\tau) \sin\theta(t) = \pm M(\tau)/[1+\delta(t)^2]^{\frac{1}{2}}. \tag{22}$$

This is the usual expression for the rapid-passage signal.

It is generally stated that, for rapid passage, the field sweep must obey the condition:

$$dH_0/dt \gg H_1/T_1. \tag{23}$$

The model indicates that a further restriction should be applied. This is that

$$d\theta/dt \gg \pi/T_1. \tag{24}$$

Unless this condition is met, the distribution of magnetization in cones around the effective field will change during the passage, tending to relax into cones close to the z axis, and (22) will not apply. But $\theta = \cot^{-1}\delta$, and thus

$$d\theta/dt = -H_1^{-1}(1+\delta^2)^{-1}(dH_0/dt).$$

Hence, in addition to indicating the well-known condition that passage through a line must occur in a

[9] An intuitive picture of adiabatic passage without relaxation is given by J. G. Powles, Proc. Phys. Soc. (London) **71**, 497 (1958).

time less than T_1; (24) implies that, in a sweep over a portion of the wing of a line, dH_0/dt must be larger than at the center of the line. This fact has application in the summation of rapid passage signals from several lines.[15]

B. Sinusoidal Field Modulation

If the external field H_0 is modulated sinusoidally[10] so that $H_0(t)=H_0+H_m\cos\omega_m t$, differential cones that touch the z-axis at fields within the modulation range, H_0+H_m to H_0-H_m, will do so twice during a modulation cycle. In the steady state, the occupation of each such cone will be a periodic function of time, and the total amount of magnetization entering the cone per cycle must equal that leaving the cone per cycle. It is assumed that the sweep through resonance of the external field on which the modulation is superimposed in most experiments is sufficiently slow so that the steady state prevails at all times. Again, only the saturated case is considered; i.e., H_1 is assumed large enough to ensure uniform distribution of magnetization in each differential cone. As in equation (20), time is used as the variable. Thus, the differential cones correspond to intervals of time, dt', spent in contact with the z axis. The total magnetization, M, is taken to be constant over the modulation range, $2H_m$. In the steady state:

$$2Mdt'/T_1=\Delta M_a(1-e^{-(T-2t')/T_1})+(\Delta M_a e^{-(T-2t')/T_1}+Mdt'/T_1)(1-e^{-2t'/T_1}). \quad (25)$$

Here $T=2\pi/\omega_m$, the modulation period, and t' is the first time during a cycle of the modulation field that a given differential cone touches the z axis. The cycle is assumed to start at $t=0$. Essentially, t' is the variable that defines the differential cone of interest. Thus, Eq. (25) applies to that cone making its first contact with the z axis at time t' after the start of the modulation cycle. ΔM_a is the occupation of the cone immediately after its first contact. Equation (25) may be solved to yield

$$\Delta M_a=(M/T_1)(1+e^{-2t'/T_1})(1-e^{-T/T_1})^{-1}dt'. \quad (26)$$

Similarly

$$\Delta M_b=(M/T_1)(1+e^{-(T-2t')/T_1})(1-e^{-T/T_1})^{-1}dt', \quad (27)$$

where ΔM_b is the occupation of the cone *first* touching the z axis at t' immediately after its *second* contact with the z axis.

M_x at any instant, t, is given by the integral of the contributions from all cones. The calculation is straightforward and only the results under certain approximations will be given here. If $\omega_m T_1 \ll 1$, the saturated dispersion signal is obtained as expected. If one considers a line lying within the modulation range and takes $H_m \gg H_1$ and $\omega_m H_m \gg H_1/T_1$ (ensuring that the modulation range is much greater than the linewidth, H_1, and that the rate of field change is sufficient to give a rapid-passage signal), M_x may be evaluated at the times during the cycle when the field has the value for resonance. This procedure yields the formula employed by Drain[11] in his method for determining T_1.

It is also possible to use (26) and (27) for determining the phase of the first harmonic of $M_x(t)$ relative to the modulation field. Since this result appears to be in part new, the calculation will be described in more detail.

The signal from one differential cone, characterized by t', is given by

$$dM_x(t',t)=dM(t',t)\cos\theta(t')\sin\theta(t), \quad (28)$$

where

$$dM(t',t)=\Delta M_b e^{-(t'+t)/T_1}, \quad 0\le t\le t',$$
$$dM(t',t)=\Delta M_a e^{-(t-t')/T_1}, \quad t'\le t\le T-t',$$
$$dM(t',t)=\Delta M_b e^{-(t-T+t')/T_1}, \quad t-t'\le t\le T.$$

Equation (28) is the product of two periodic functions of time; thus

$$dM_x(t)=(M_0'a_1+a_0M_{a1}')\cos\omega_m t+(M_0'b_1+a_0M_{b1}')\sin\omega_m t+\cdots,$$

where M_0', M_{a1}', M_{b1}', and a_0, a_1, b_1 are the appropriate coefficients for the Fourier analysis of $dM(t',t)\cos\theta(t')$ and $\sin\theta(t)$, respectively. Higher order terms will henceforth be neglected. Thus

$$M_0'=M(\pi)^{-1}\cos\theta(t')d(\omega_m t'), \quad (29)$$

$$M_{a1}'=2(\pi)^{-1}(1+\omega_m^2T_1^2)^{-1}M\cos\omega_m t' \times\cos\theta(\omega_m t')d(\omega_m t'), \quad (30)$$

$$M_{b1}'=2(\pi)^{-1}\omega_m T_1(1+\omega_m^2T_1^2)^{-1}M\cos\omega_m t' \times\cos\theta(\omega_m t')d(\omega_m t'). \quad (31)$$

Note that

$$\cos\theta(t')=[\delta_0+H_m(H_1)^{-1}\cos\omega_m t'] \times\{1+[\delta_0+H_m(H_1)^{-1}\cos\omega_m t']^2\}^{-\frac{1}{2}}, \quad (32)$$

where $\delta_0=(H_0-\omega_{rf}/|\gamma|)/H_1$.

The phase lag β' of the projection on the effective field of the magnetization in a single cone is given by

$$\tan\beta'=M_{b1}'/M_{a1}'.$$

From (30) and (31) we see that all such phases are the same, and the projections of all cones on the effective field may be added algebraically. Thus, the net signal from a single line may be regarded as the projection on the x axis of a time dependent magnetization directed along the effective field and having the phase of any individual cone. That is,

$$M_x(t)=(M_0a_1+a_0M_{a1})\cos\omega_m t+(M_0b_1+a_0M_{b1})\sin\omega_m t. \quad (33)$$

[10] A number of authors have treated modulation effects by direct integration of Bloch's equations. See, for instance, R. Gabillard, Compt. rend. **232**, 1477 (1951); K. Halbach, Helv. Phys. Acta **27**, 259 (1954).

[11] L. E. Drain, Proc. Phys. Soc. (London) **A62**, 301 (1949).

The constants here cannot be evaluated so readily as M_0', M_{a1}', and M_{b1}', but certain qualitative comments can be made regarding them.

1. a_0 is positive, since $0 \leqq \theta(t) \leqq \pi$.

2. a_1 is positive for lines resonating above H_0, and negative for lines resonating below H_0. This can be appreciated by examining an appropriate plot of $\sin\theta(t)$ in each case.

3. $b_1=0$, since $\sin\theta(t)$ is symmetric about $t=0$.

4. M_0 is positive for lines below H_0, and negative for lines above H_0; because, when $\theta<\pi/2$ for a greater portion of a cycle, the net magnetization in the steady state will spend a larger amount of time directed along the positive sense of the effective field, and vice versa.

5. M_{a1} and M_{b1} are positive, since $\cos\omega_m t'$ and $\cos\theta(\omega_m t')$ in (30) and (31) have the same sign for all cones. Also

$$M_{b1}=\omega_m T_1(1+\omega_m^2 T_1^2)^{-1}A, \quad M_{a1}=(1+\omega_m^2 T_1^2)^{-1}A,$$

where A is a constant, independent of frequency, obtained by integrating (30) or (31) over all cones.[12] Thus

$$M_x(t)=[(1+\omega_m^2T_1^2)^{-1}a_0A-|M_0a_1|]\cos\omega_m t \\ +\omega_m T_1(1+\omega_m^2T_1^2)^{-1}a_0A\sin\omega_m t. \quad (34)$$

Note that M_0a_1 is always negative from 2 and 4 above. At low frequencies ($\omega_m T_1 \ll 1$),

$$M_x(t)\approx(a_0A-|M_0a_1|)\cos\omega_m t=D\cos\omega_m t,$$

or

$$a_0A=D+|M_0a_1|. \quad (35)$$

At intermediate frequencies

$$M_x(t)=-|M_0a_1|\cos\omega_m t \\ +(1+\omega_m^2T_1^2)^{-\frac{1}{2}}|M_0a_1|\cos(\omega_m t-\tan^{-1}\omega_m T_1) \\ +(1+\omega_m^2T_1^2)^{-\frac{1}{2}}D\cos(\omega_m t-\tan^{-1}\omega_m T_1). \quad (36)$$

At high frequencies ($\omega_m T_1 \gg 1$)

$$M_x(t)=-|M_0a_1|\cos\omega_m t. \quad (37)$$

Equation (36) is shown vectorially in Fig. 3. Note that the first and second terms of (36) combine to give a signal at a phase lag of $\pi/2$ with the second term. The third term is either in phase with or at 180° to the second term. Hence, a phase-sensitive detector set in quadrature with the combination of the first and second terms would detect only the third term.

An experimental procedure for determining the relaxation time, T_1, is to observe the *shape* of D as H_0 is swept through the line at low modulation frequency. The spectrometer must be tuned to reject higher harmonics of the modulation frequency. Then, at an intermediate frequency and the same modulation amplitude and radio frequency power, the phase lag of the reference signal to the detector for which a spectrum of the same shape is obtained will be given by

$$\tan\Theta=\omega_m T_1. \quad (38)$$

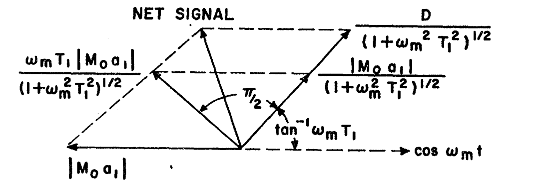

FIG. 3. Components of the signal at intermediate modulation frequencies. Here ω_m is the modulation frequency, D is the signal obtained for $\omega_m T_1 \ll 1$, and $|M_0a_1|$ is the signal obtained for $\omega_m T_1 \gg 1$.

This will be true without regard for the values of H_m or H_1 as long as $T_1=T_2$ and the adiabatic passage condition (18) is obeyed throughout a modulation cycle. At sufficiently low modulation amplitudes, D will simply be the saturated dispersion derivative. At other phases of the reference signal a combination of the high-frequency and low-frequency signal shapes will be observed, except at a phase lag given by $\tan\Theta=-(\omega_m T_1)^{-1}$, where a pure high-frequency shape will be recorded. If the modulation amplitude is kept sufficiently small so that the dispersion derivative is not distorted, there is no need to keep the amplitude constant as the frequency is changed.

A related result has been obtained from Bloch's equations by Halbach[10] and discussed further by Redfield.[2] The approach here has the advantages that it applies for any modulation amplitude whether or not the line shape is distorted, and it gives a complete description of the line shape for any reference phase. It has the disadvantage that it is limited to conditions at complete saturation.

The present treatment extends to the case of a spectrum of partially or totally unresolved lines, all having the same relaxation time. At any point in the spectrum, the phase of the signal from the first two terms of (36) will be the same for all lines. The third term for each line will be either in phase or 180° out of phase with that for other lines. Thus the high-frequency and low-frequency components of all lines will add algebraically and the experimental method described above can be applied.

Of particular interest in this regard is the case of an inhomogeneously broadened line. From the work of Portis, and of Feher[13] we can identify the high-frequency term at a phase lag of 180° relative to the modulation field, $-|M_0a_1|\cos\omega_m t$, as very nearly equal to the absorption envelope, providing H_m is sufficiently less than the total linewidth and sufficiently greater than H_1.

[12] It is interesting to note that this result implies that an observer in a frame of reference having its z axis along the effective field would see an oscillating z component of magnetization that conforms to the Debye function and obeys the Kramers-Kronig relations. See C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947), p. 22.

[13] A. M. Portis, Technical Note No. 1, Sarah Mellon Scaife Radiation Laboratory, University of Pittsburgh, 1955, Air Research and Development Command (unpublished). See also G. Feher, Phys. Rev. **114**, 1219 (1959).

Under the same circumstance the low-frequency term, $D\cos\omega_m t$, will be the derivative of the dispersion envelope. At intermediate frequencies different combinations of the two will be recorded depending upon the phase of the reference signal. That such combinations occur in electron magnetic resonance is confirmed by the experience of Hyde[14] and of Weger.[15] It is also confirmed by observations of the author on F centers in KCl, on paramagnetic radiation damage sites in fused quartz, and on free radicals in a large variety of irradiated organic solids.

The ratio of the amplitude of the absorption, recorded at a reference signal phase of $\tan^{-1}[(\omega_m T_1)^{-1}]$, to the amplitude of the dispersion derivative recorded at a phase of $\tan^{-1}(\omega_m T_1)$ may be computed from the theory:

$$R=(|M_0 a_1|/D)\omega_m T_1. \qquad (39)$$

Equation (39) applies only for constant H_m and H_1. The linear dependence on modulation frequency has been confirmed by the author for F centers in KCl.

One further point should be made about the phase method of measuring T_1. Redfield[2] has shown that at sufficiently high radio-frequency fields, $T_2=T_1$. Thus the method applies for determining T_1 even if $T_2\neq T_1$ providing sufficiently high values of H_1 are employed. This point will be reinforced in a qualitative manner in the following section.

IV. INTRODUCTION OF T_2

In the preceding sections the steady-state angular distribution of magnetization under the combined-effects of a radio-frequency field and spin-lattice relaxation has been determined. The question naturally arises whether the effect of additional processes that tend to cause dephasing of spins around the external field can be treated. This should have the effect of injecting T_2 into the solutions for various experimental conditions.

By analogy with (3) the differential equation for the steady-state distribution of magnetization over an entire sphere, instead of only around a cone, is

$$RM(\theta,\phi)=-\nabla\cdot\mathbf{V}. \qquad (40)$$

Here R is a general relaxation function that may be dependent on θ, ϕ, and on any external parameter such as H_1. $\mathbf{V}$ is the flux vector on the surface of the sphere of the tips of the spin vectors. Equation (40) contains the assumption that the relaxation rate from any surface element of the sphere is proportional to the amount of magnetization associated with that element. The additional dephasing processes require the presence of static and of certain fluctuating local variations in the z component of the net field to which spins are subjected.[16] When it is proper to use a single effective field, $\mathbf{V}=M(\theta,\phi)\mathbf{\Omega}\times\mathbf{r}$ where $\mathbf{r}$ is the radius of the reference sphere. This radius is unity, since $M(\theta,\phi)$ is normalized to give a total magnetization M. Further, if there is no local field variation, $R=1/T_1$, and (40) reduces to (3), in a left-handed coordinate system having its z axis along the effective field. If there is a local field variation, (40) becomes difficult to use. Under appropriate conditions, however, and by making certain assumptions, it is possible to derive the solution to Bloch's equations for $T_1\neq T_2$. The conditions are

$$\gamma H_1 \gg 1/T_2 \quad\text{and}\quad dH_0/dt \ll \gamma H_1^2. \qquad (41)$$

Since $T_2\approx 1/|\gamma|H'$, where H' is the spread of local z field components, the first condition means that H_1 will greatly exceed the range of local field variation and, thus, that the use of a single effective field for all spins will be appropriate. Further, the distribution of magnetization will be uniform around this effective field. The assumption that turns out to be necessary is that R in (40) is a function such that the projection on the effective field of the magnetization in a cone characterized by t', $\Delta M(t,t')$, will obey the following equation:

$$\frac{d\Delta M(t,t')}{dt}=-\left[\frac{\cos^2\theta(t)}{T_1}+\frac{\sin^2\theta(t)}{T_2}\right]\Delta M(t,t'). \qquad (42)$$

The elliptical relaxation term in (42) reduces to the spherical term, $1/T_1$, when $T_1=T_2$. Then, by direct analogy with the method of deriving (20):

$$\Delta M(t,t')=\Delta M(t',t')\exp\left\{-\int_{t'}^{t}[\cos^2\theta(t'')/T_1+\sin^2\theta(t'')/T_2]dt''\right\}. \qquad (43)$$

On the assumption that each cone receives magnetization only while it is in contact with the z axis,

$$M(t)=(1/T_1)\int_{-\infty}^{t}dt'\,M(t')\cos\theta(t')\times\exp\left\{-\int_{t'}^{t}[\cos^2\theta(t'')/T_1+\sin^2\theta(t'')/T_2]dt''\right\}, \qquad (44)$$

where $M(t)$ is the projection of all of the magnetization on the effective field in the rotating coordinate system. Note that, since the distribution of magnetization around the effective field is uniform,

$$M_x(t)=M(t)\sin\theta(t).$$

Equation (44) can be reduced to give

$$M(t)=\int_{-\infty}^{t'}dt'\frac{M_0(t')\delta(t')}{T_1(1+\delta^2(t'))^{\frac{1}{2}}}\times\exp\left[\int_{t}^{t'}\frac{\delta^2(t'')+T_1/T_2}{T_1[1+\delta^2(t'')]}dt''\right], \qquad (45)$$

[14] J. S. Hyde, Phys. Rev. **119**, 1483 (1960).
[15] M. Weger, Bell System Tech. J. **39**, 1013 (1960).
[16] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

which is the appropriate solution to Bloch's equations.

However, the development of (45) contains an inconsistency. It was assumed that each cone received an amount of magnetization $M_0(t')dt'/T_1$ while in contact with the z axis. Subsequently this magnetization decayed at a rate dependent on T_1 and T_2. Thus, (45) fails to take into account the signal from magnetization leaving each cone by means of the dephasing process between the time it leaves and the time it relaxes to the z axis. This can only be proper if, during that intermediate time, the magnetization goes into a distribution having no projection on the x axis. But it was assumed that the rf field is sufficiently large to ensure that all spins see nearly the same effective field, and thus they are prevented from relaxing into the necessary temporary distribution but are held very nearly in their original cones until lattice relaxation occurs. Thus, even though $T_1 \neq T_2$, Eq. (20) should be used under conditions (41).

These arguments lead, on purely classical, geometrical grounds, to the conclusion that the effects of the rf field and the spin-spin relaxation processes are not independent. In fact, the distribution of effective fields, both static and fluctuating, in the rotating coordinate system is a function of H_1 under any circumstances.

Certain qualitative considerations can be made on the basis of the model. For instance, the spin-spin interaction that rapidly transfers the energy absorbed at one frequency in a dipolar broadened line to all of the spins[17] is seen to break down at high rf fields. Classically, this interaction requires for its occurrence between two spins that they be precessing around the external field, H_0, out of phase with each other. They must continue to do so for a time sufficient that each spin will experience a significant change in its orientation as a result of the oscillating field induced by the precession of the other spin. The maximum effect will occur when they are in quadrature. Near resonance a relatively large rf field will tend to prevent the spins from precessing in the proper phase since they will all be nearly in the y-z plane of the rotating frame. Off resonance, the conical distribution of magnetization allows the proper phase relation to prevail for some spins, but, since H_1 greatly exceeds the range of local fields, this phase relation will not last long enough for a change in orientation to occur. In fact, for a given pair of spins, the effect during one-half of the period, $1/\Omega$, will cancel that during the other half. Since $T_1 \gg 1/\Omega$, the net effect will average to zero.

V. DISCUSSION

Some discussion of the physical reality of the model is in order. Its most obvious deficit is that the relaxation event described does not conform to the true state of affairs. To a first approximation relaxation in a classical picture must take place into a Boltzmann distribution around the external field, not to alignment with the external field as in the present model. However, this will have no effect on the result, since a group of spins existing at a given moment in a Boltzmann distribution symmetrical around the applied static field will subsequently move in the rotating coordinate system in such a way as to remain symmetrically disposed around the direction of a spin starting out aligned with the z axis. This group of spins can thus be replaced, for the purposes of the theory, by an increment of magnetization moving in the cones of Figs. 1 and 2. Such a group gradually would be attenuated by relaxation, an effect replaced in the theory by a single, statistically equivalent event.

Even relaxation into a distribution around the applied static field is not strictly correct, since the susceptibility of the paramagnetic system can be reduced to the proper Debye formula for low static fields only by assuming an event in which the magnetization relaxes into a Boltzmann distribution relative to the instantaneous net field[18–20] in the laboratory coordinate system. However for $H_0 \gg H_1$ the simpler picture of the relaxation event employed in this paper will be adequate. For another method of introducing relaxation effects into the rotating coordinate system, see papers by Bonera and co-workers.[21]

With regard to the quantum mechanical implications of the model, Rabi *et al.*[6] have shown that, if relaxation effects are neglected, the correct quantum mechanical expectation values of M_x, M_y, and M_z are given by the classical description of the resonance phenomenon in a rotating coordinate system. Thus, in the model, the description of the behavior of each element of magnetization between spin-lattice relaxation events leads to the correct value of the observables for that element. It has not been shown that the expectation values for the entire assembly of elements are correctly given by the averaging process used here. However, presumably they are correctly given for those conditions under which Bloch's equations have been shown to be quantum mechanically correct.[4]

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[17] N. Bloembergen, thesis, Leiden (unpublished), p. 49.

[18] M. A. Garstens, Phys. Rev. **93**, 1228 (1954).

[19] R. S. Cordrington, J. D. Olds, and H. C. Torrey, Phys. Rev. **95**, 607 (1954).

[20] R. K. Wangsness, Phys. Rev. **98**, 927 (1955).

[21] G. Bonera and P. De Stefano, Nuovo cimento **20**, 316 (1961).

APPENDIX

Kittel[22] has pointed out that the methods employed in this article bear a resemblance to Chambers'[23] solution to the classical Boltzmann transport equation. Investigation of this point has revealed the following very simple derivation of the solutions to Bloch's equation for $T_1=T_2$. By accounting for all magnetization entering the cone at times previous to the time being considered, the rate of arrival of magnetization elements at an angle ϕ, where ϕ is measured only once around the cone, may be determined:

[22] C. Kittel (private communication).

[23] R. G. Chambers, Proc. Phys. Soc. (London) **A65**, 458 (1952), see also V. Heine, Phys. Rev. **107**, 436 (1957).

$$\text{Rate}=\sum_{n=0}^{\infty} M(T_1)^{-1}\exp[-(\phi+2\pi n)/(\Omega T_1)]$$
$$=M(T_1)^{-1}\exp[-(\phi/\Omega T_1)]/[1-\exp(-2\pi/\Omega T_1)].$$

But this must equal $M(\phi)\Omega$, the flow rate by the position, ϕ. Thus

$$M(\phi)=M(\Omega T_1)^{-1}\exp(-\phi/\Omega T_1)[1-\exp(-2\pi/\Omega T_1)]^{-1}.$$

This expression substituted into (5), (6), and (7) with a range of integration from 0 to 2π yields (11), (12), and (13). Note that as $\Omega T_1\rightarrow\infty$, $M(\phi)\rightarrow M/2\pi$, which explains the uniform distribution of magnetization in the cone at high radio frequency fields.

It may be possible to extend this approach to account for all magnetization scattered by various relaxation processes into each trajectory passing through a point on the reference sphere, and thus to obtain a completely general classical description of magnetic resonance.

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De Haas-van Alphen Effect in Bismuth-Tellurium Alloys*†

DANIEL WEINER‡
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

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De Haas-van Alphen measurements have been made on pure bismuth and several bismuth-tellurium alloys. It is found that the observed variation of external cross section and cyclotron effective mass with tellurium concentration and magnetic field orientation can be interpreted using a special case of Cohen's nonellipsoidal model of bismuth. The results indicate that there is a thermal energy gap between the conduction and valence band of about 0.046 ev in agreement with various optical experiments and that there are six electron "ellipsoids." The results also agree with a model for the hole band involving one light-hole ellipsoid and one heavy-hole ellipsoid and are used as evidence against some other possible models for the hole band.

I. INTRODUCTION

RECENT experiments[1] indicate that the Fermi surface of bismuth may not be parabolic-ellipsoidal, so that both the absolute and relative size of its effective mass components depend on the Fermi energy. The details of this dependence, if known, would establish many of the parameters in Cohen's[2] nonellipsoidal theory of the bismuth band structure.

The Fermi level in bismuth may be conveniently changed without appreciably affecting the crystal potential by addition of an electron donor such as tellurium. Each tellurium atom presumably contributes one electron to the Fermi sea. Since the instrinsic number of conduction electrons in bismuth is small (about 10^{-5}/atom), very little tellurium is needed to increase it appreciably.

A powerful method of studying the band structure of these alloys is provided by the de Haas-van Alphen effect.[3] It measures the extreme cross-sectional areas of the Fermi surface and their energy derivative. Furthermore, the interpretation of the effect is unaffected by the changes in collision times on alloying. Also, as we shall see later, we can find the number of equivalent ellipsoid-like pieces of the electron Fermi surface with our de Haas-van Alphen data and a knowledge of the amount of tellurium present in those alloys in which we have filled the hole band. In alloys where we have not filled the hole band, a knowledge of the tellurium concentration helps give us an average density of states.

Indeed, Shoenberg and Uddin[4] have already explored

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‡ Now at Hughes Research Laboratories, Malibu, California.

[1] B. Lax, Bull. Am. Phys. Soc. **5**, 167 (1960).

[2] M. H. Cohen, Phys. Rev. **121**, 387 (1961).

[3] D. Shoenberg, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. 2, Chap. 8.

[4] D. Shoenberg and M. Z. Uddin, Proc. Roy. Soc. (London) **A156**, 701 (1936).