likely comes from the center with the largest magnetic concentration.

Our experience indicates that the rapid-passage signal level is proportional to F-center concentration. No anisotropy has been found. The shape of the resonance is as expected when the principal broadening arises from interactions of an F-center electron with six nearest-neighbor nuclei. It seems likely that only a center with the symmetry of the F center could have a spin-lattice relaxation time long enough at room temperature to put it into the rapid-passage region. We concluded that the F center gives rise to the rapid-passage response.

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APPENDIX. OPTICAL ABSORPTION OF IRRADIATED LiF

It seems desirable to summarize our experience in coloring of LiF crystals with Co^{60}. The number of F centers was determined using the Smakula[13] formula as quoted in Landolt-Börnstein[19] and assuming an oscillator strength of unity. The numbers of F centers we have found produced in Harshaw LiF for various irradiation doses are:

dose (rep)	N_F/cm^3
1.1×10^5	6.7×10^{16}
1.6×10^5	1.5×10^{17}
4.4×10^5	2.1×10^{17}
9.6×10^5	5.2×10^{17}
5.3×10^6	1.0×10^{18}
4.0×10^7	3.4×10^{18}

The data show that coloration is more efficiently accomplished at low levels than at high levels, as is well known.

Typical absorption spectra for four levels of coloration, obtained using a Cary Recording Spectrophotometer, are shown in Fig. 11. Several interesting observations can be made. The broad band on the long-wavelength side is very pronounced relative to the F band at low coloration; at intermediate levels this band can barely be detected; at highest levels other bands begin to appear in this region.

The absorption curve for heaviest irradiation is of interest. To our knowledge, absorption peaks have not previously been reported at 4050 and at 3700 A. Delbecq and Pringsheim[20] do list bands at 3400 and 3800 A, which can be seen in the figure (Fig. 11).

[19] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1955), Vol. 1, Part 4, p. 981.

[20] C. J. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953).

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Saturation of the Magnetic Resonance Absorption in Dilute Inhomogeneously Broadened Systems*

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The existing theory due to Portis for the saturation of inhomogeneously broadened resonances is discussed and a new theoretical formulation of the problem is developed using an expression for the transition probability first given by Rabi. For γH_1 greater than both T_1^{-1} and T_2^{-1}, the rf field interacts with spins precessing in the frequency interval γH_1; this expression permits explicit calculation of the resulting magnetic loss. No assumption is made of the shape of the individual (homogeneously broadened) spin packets in weak exciting fields. For F centers in alkali halides, the results are identical with those of Portis, but the underlying physical reasons differ.

SPIN systems that give rise to magnetic resonance absorption may be classified as homogeneous or inhomogeneous. A homogeneous resonance arises from unpaired spins placed in identical local magnetic fields and precessing at the same characteristic frequency except for a bandwidth due to mutual coupling. An inhomogeneous resonance is caused by spins spread over a continuous distribution of local fields and precessing at a variety of Larmor frequencies. The responses of these two types of systems to a large rf field (H_1) are quite different. The loss part of the rf susceptibility, χ'', for a homogeneous line saturates as $1/H_1^2$ with an accompanying change of line shape, but for a dilute, inhomogeneous line, as $1/H_1$ with no change in line shape.[1]

Bloch[2] and Bloembergen, Purcell, and Pound[3] have

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[1] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[2] F. Bloch, Phys. Rev. **70**, 460 (1946).

[3] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

given expressions for the saturation behavior of a homogeneous resonance,[4]

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega_0\frac{\pi g(\omega-\omega_0)}{1+\pi\gamma^2H_1^2g(\omega-\omega_0)T_1}. \quad (1)$$

χ_0 is the usual temperature-dependent dc susceptibility, T_1 the spin-lattice relaxation time, and $g(\omega-\omega_0)$ the normalized shape factor for the transition. Usually $g(\omega-\omega_0)$ is determined by spin-spin interaction and is described by the Lorentzian function: $g(\omega-\omega_0)=(T_2/\pi)/[1+T_2^2(\omega-\omega_0)^2]$, where T_2 is the spin-spin relaxation time.

Portis[1] has developed a theory which accounts for the observed saturation behavior of dilute inhomogeneously broadened resonances. Let the distribution in resonant frequencies be given by $h(\omega-\omega_0)$, which is normalized so that $\int_0^\infty h(\omega-\omega_0)d\omega=1$. Portis visualizes the rf susceptibility at a point ω as being determined by an integration of the contribution from overlapping spin packets. Each spin packet arises from a group of spins in nearly the same local field which therefore obeys the equation describing homogeneous resonance absorption. He then writes:

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{\omega'\pi g(\omega-\omega')h(\omega'-\omega_0)d\omega'}{1+\pi\gamma^2H_1^2T_1g(\omega-\omega)'}. \quad (2)$$

If the system is dilute, which implies that $h(\omega-\omega_0)$ is much broader than $g(\omega-\omega_0')$, and if $g(\omega-\omega')$ is Lorentzian, this expression may be evaluated

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\frac{\pi}{(1+\gamma^2H_1^2T_1T_2)^{\frac{1}{2}}}. \quad (3)$$

Thus as H_1 becomes large, $\chi''(\omega)$ varies as $1/H_1$ and the line shape $h(\omega-\omega_0)$ is preserved.

It is essential, in this treatment, that the spin-packet line shape, $g(\omega-\omega')$, be Lorentzian. If one studies the integral, it becomes apparent that any shape other than Lorentzian will give the wrong dependence of $\chi''(\omega)$ at large values of H_1.

Although Portis initially assumed that spin-spin processes determined $g(\omega-\omega')$, giving rise to the appearance of T_2 in Eq. (3), he subsequently pointed out that this was in error.[5] In dilute inhomogeneous systems spin-spin interaction is very weak and the characteristic width and shape of $g(\omega-\omega')$ is determined by spin-lattice relaxation. T_2 is then replaced by T_1 in Eq. (3).

The approach used by Portis has caused us concern for the following qualitative reason: It is well known that in a dilute inhomogeneous system a strong rf field H_1 will interact with spins in the frequency interval γH_1 and will in fact "eat a hole" of width γH_1 in the distribution. It was difficult to understand how the Portis treatment took this into account, and why in such a process it should be essential that $g(\omega-\omega')$ (as determined by either spin-lattice or spin-spin processes) be precisely Lorentzian.

We have developed another approach to the problem of magnetic resonance absorption in magnetically dilute inhomogeneous systems. In this calculation it is assumed that the natural line width, $1/\gamma T_2$, arising from direct spin-spin interaction, is negligible, and that the spin-packet width for weak excitation is determined by spin-lattice interaction. In large rf fields the effective width is determined by the rf field strength itself.

Analysis of the situation is made, using the time-dependent Schrödinger equation. Rabi[6] solved a similar problem; the expression for the transition probability derived by him can be taken over with only slight modification. Johnson and Strandberg[7] have also applied the technique to collision broadening in gases. We assume that the intial probability of a particle being in (+) state is $|a_+^0|^2$ and in (−) state $|a_-^0|^2$. Then the probability $|a_-|^2$ that the particle is in (−) state at time t is given by

$$|a_-|^2-|a_-^0|^2=\left[\frac{(\gamma H_1)^2(|a_+^0|^2-|a_-^0|^2)}{(\gamma H_1)^2+(\omega-\omega')^2}\right]\times\sin^2t/2[(\omega-\omega')^2+(\gamma H_1)^2]^{\frac{1}{2}}. \quad (4)$$

An equivalent expression for $|a_+|^2$ is obtained by interchanging the (−) and (+) signs in this equation. It is assumed that the radiation is in a narrow frequency band centered about ω. This expression tells us there is a probability that a spin rotating at a Larmor frequency ω', where $\omega'\neq\omega$, will undergo a transition. The half-width of the time-independent term in the above expression occurs when $(\omega'-\omega)=\gamma H_1$.

We proceed to find the resonance-signal levels. There are two methods of dealing with the problem, giving identical results, each however providing new physical insight into the matter.

Method 1

From Eq. (4) we can derive an expression for the number of transitions that have occurred at a given value of time and frequency $\eta(\omega',t)$ if the rf field is turned on at time $t=0$ and the system is initially in thermal equilibrium:

$$\eta(\omega',t)=Nh(\omega'-\omega_0)\Delta\omega'(|a_-^0|^2-|a_+^0|^2)\times\frac{(\gamma H_1)^2\sin^2(t/2)[(\omega-\omega')^2+(\gamma H_1)^2]^{\frac{1}{2}}}{(\gamma H_1)^2+(\omega-\omega')^2}. \quad (5)$$

[4] Throughout, the rf field is assumed to be linearly polarized of amplitude $2H_1$ and resolved into two oppositely rotating circularly polarized fields of amplitude H_1.

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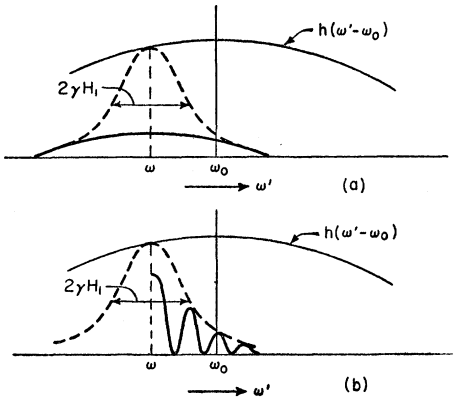

FIG. 1. Number of transitions as a function of the spin-packet resonance frequency ω' near the excitation frequency ω: (a) $\gamma H_1 t \approx 1$, (b) $\gamma H_1 t \simeq 9\pi$.

$Nh(\omega'-\omega_0)\Delta\omega'$ is the number of spins in the interval $\Delta\omega'$.

If we are at a particular point $h(\omega'-\omega_0)$ and the radiation frequency ω is held constant, $(\omega-\omega')$ is constant, and the time-dependent term oscillates between zero and unity. If on the other hand we consider the behavior at a specified time t, but change ω progressively, we again find oscillatory behavior under a Lorentzian envelope of width $2\gamma H$. Figure 1 shows the behavior of the transition probability for $\gamma H_1 t \approx 1$ (a) and also for $\gamma H_1 t > 1$ (b). As t continues to increase, the oscillations as a function of ω become increasingly rapid.

Begin by writing the integral of $\eta(\omega' t)$ over ω';

$$\eta(t) = N(|a_-^0|^2 - |a_+^0|^2)\int_0^\infty \frac{h(\omega'-\omega_0)(\gamma H_1)^2}{(\gamma H_1)^2+(\omega-\omega')^2} \times \sin^2(t/2)[(\omega-\omega')^2+(\gamma H_1)^2 d\omega']. \quad (6)$$

We differentiate to obtain

$$\frac{d\eta(t)}{dt} = N\frac{(|a_-^0|^2 - |a_+^0|^2)}{2} h(\omega-\omega_0) \times \int_0^\infty \frac{(\gamma H_1)^2}{[(\gamma H_1)^2+(\omega-\omega')^2]^{\frac{1}{2}}} \times \sin t[(\omega-\omega')^2+(\gamma H_1)^2]^{\frac{1}{2}} d\omega', \quad (7)$$

which gives the instantaneous rate at which the population changes if the rf field is suddenly turned on at time $t=0$. Let the average lifetime of a spin state due to lattice interaction be given by

$$T_1 \int_0^\infty t f(t) dt, \quad (8)$$

where $f(t) = 1/T_1 e^{-t/T_1}$. This is consistent with the assumption of exponential relaxation in formulations of Bloch[2] and Bloembergen *et al.*[3] Then the number of transitions per unit time which occur is

$$N(|a_-^0|^2 - |a_+^0|^2)\frac{h(\omega-\omega_0)}{2T_1}\int_0^\infty \left(\frac{(\gamma H_1)^2}{[(\gamma H_1)^2+(\omega-\omega')^2]^{\frac{1}{2}}} \times \int_0^\infty e^{-t/T_1} \sin t[(\omega-\omega')^2+(\gamma H_1)^2]^{\frac{1}{2}} dt \right) d\omega'$$

$$= N(|a_-^0|^2 - |a_+^0|^2)\frac{h(\omega-\omega_0)}{2T_1} \times \int_0^\infty \frac{(\gamma H_1)^2 d\omega'}{(1/T_1)^2+(\omega'-\omega)^2+(\gamma H_1)^2}. \quad (9)$$

This agrees exactly with the integral calculated by Portis if in his calculation $g(\omega-\omega')$ is assumed to be given by $(T_1/\pi)/[1+T_1^2(\omega-\omega')^2]$. Thus

$$\chi''(\omega) = \tfrac{1}{2}\chi_0 \omega h(\omega-\omega_0)\frac{\pi}{(1+\gamma^2 H_1^2 T_1^2)^{\frac{1}{2}}}. \quad (10)$$

Method 2

In the above derivation, the shape of individual spin packets was assumed Lorentzian in weaker excitation by introducing a specific relaxation formula. The high field dependence of the loss $\chi''(\omega)$ is in fact insensitive to this assumption. To see this more clearly we return to Eq. (6). In the absence of any spin-spin or spin-lattice relaxation, we can immediately integrate over ω' and show that as $t \to \infty$, $\eta(t)$ becomes independent of t. Assume that $h(\omega'-\omega_0)$ is slowly varying and use the identity $\sin^2 x = \frac{1}{2}(1-\cos 2x)$. Then

$$\eta(t) = N(|a_-^0|^2 - |a_+^0|^2)h(\omega-\omega_0) \times \frac{1}{2}\left(\int_0^\infty \frac{(\gamma H_1)^2 d\omega'}{(\gamma H_1)^2+(\omega-\omega')^2} - \int_0^\infty \frac{(\gamma H_1)^2 \cos t[(\omega-\omega')^2+(\gamma H_1)^2]^{\frac{1}{2}} d\omega'}{(\gamma H_1)^2+(\omega-\omega')^2} \right). \quad (11)$$

As $t \to \infty$, the second integral approaches zero since the numerator oscillates rapidly as a function of ω', and the denominator increases slowly compared with the oscillation frequency but fast enough for convergence of the integral. If the average lifetime of a spin state is T_1, and if $T_1 \gg 1/\gamma H_1$, t may be regarded as infinite. The first integral equals $\gamma H_1 \pi$. Thus for $\gamma H_1 T_1 \gg 1$,

$$\eta(t) = N(|a_-^0|^2 - |a_+^0|^2)\pi\tfrac{1}{2}h(\omega-\omega_0)\gamma H_1. \quad (12)$$

The average lifetime T_1 is defined from Eq. (8), except that the only restriction placed on $f(t)$ is that it does not differ greatly from $1/T_1$ for values of t of the order of $1/\gamma H_1$. Then the average power absorbed by the

crystal is by definition

$$P\triangleq\tfrac{1}{2}\omega(2H_1)^2\chi'', \tag{13}$$

$$P=N(|a_-^0|^2-|a_+^0|^2)\pi\gamma H_1 h(\omega-\omega_0)\hbar\omega/2T_1. \tag{14}$$

From the Boltzmann distribution

$$(|a_-^0|^2-|a_+^0|^2)=\hbar\omega/2kT, \tag{15}$$

while the low-field susceptibility for a two-level system is

$$\chi_0=Ng^2\mu_B^2/4kT. \tag{16}$$

Thus

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\pi/\gamma T_1 H_1, \tag{17}$$

in agreement with the high field limit of Eq. (10).

We pointed out, in reviewing Portis' calculations, that the assumption of a Lorentzian line shape is very critical if the integral is to be proportional to $1/H_1$ at high rf fields. Portis remarks that the observed independence of $\chi''H_1$ on the rf field is proof of a Lorentzian line shape. In this section, on the other hand, the assumptions concerning T_1, at least for $\gamma H_1 T_1\gg 1$, are very weak. It would seem that for $\gamma H_1 T_1<1$ the Portis approach is correct, while for $\gamma H_1 T_1>1$, our approach is correct; in other words, the rf field interacts with a portion of the spectrum either $1/\gamma T_1$ or H_1 wide, whichever is greater.

One wonders if a case could be found where the two formulations predict different results. If $T_2<T_1$ but the interaction of the spins is still weak, so that complications of spin diffusion[5] need not concern us, our formulation predicts that for $\gamma H_1 T_2\gg 1$ the susceptibility will be proportional to $1/T_1$, whereas the Portis formulation predicts it to be proportional to $1/(T_1T_2)^{\frac{1}{2}}$. In this limit we can find no reason to believe that the signal level is related to T_2. Only the rapidity with which the excited spins in the interval H_1 can return to the ground state by excitation of phonons should determine the power absorption. (This inconsistency is essentially that pointed out by Bloembergen and treated by Redfield[8] in a modified Bloch description of nuclear resonance saturation.) We interpret the line width H_1 as arising from the uncertainty principle because the lifetime of a spin state is limited by the rf field. In other words, the change in populations of the levels occurs in a time $t\simeq 1/\gamma H_1$, accompanied by an uncertainty in energy $\gamma H_1\hbar$. As H_1 becomes small, the lifetime will be limited by T_2 or T_1 processes.

[8] B. Redfield, Phys. Rev. **98**, 1787 (1955).

SUMMARY

This study considered the resonance absorption of a magnetically dilute, inhomogeneously broadened spin system. It was assumed that interaction between spins is very weak, that diffusion of spin excitation or cross relaxation may be ignored, and that instrumental broadening, such as caused by magnetic-field inhomogeneity or nonmonochromatic rf radiation, is negligible. We have not considered the complications which arise if the radio-frequency or dc magnetic field is modulated, whether deliberately or because of noise, at a frequency of the order of a reciprocal characteristic relaxation time.

Nevertheless, the calculation is believed to be sufficient to describe the saturation behavior of electron-surplus centers in many ionic crystals. For alkali halides, the over-all line width ranges between 50 and 400 gauss and concentrations are normally between 10^{16} and 10^{18} per cm^3. For these materials, $T_2>T_1$ at room temperature, and the calculations presented here and those of Portis predict the same result. At lower temperatures or somewhat narrower lines and higher concentrations, T_2 is expected to be $<T_1$. Then we expect that the signal level for $T_2<T_1<1/\gamma H_1$ will be

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\pi, \tag{18}$$

i.e., only the density of spins per unit frequency interval is important. For $1/\gamma H_1<T_2<T_1$, the signal level becomes

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\pi/\gamma H_1 T_1. \tag{19}$$

The unambiguous dependence of the signal level on T_1 in this expression suggests that the temperature dependence of T_1 might be found by a single measurement at each temperature.

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