

## Magnetic Resonance with Strong Radio-Frequency Fields in Solids

I. SOLOMON\* AND J. EZRATY

*Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, Seine et Oise, France*

(Received February 5, 1962)

In order to explain nuclear magnetic resonance signals in solids, Redfield has proposed that, when a strong rf magnetic field is applied, the spin system can be described by the existence of a spin temperature in the rotating frame, that can be different from the lattice temperature. In the present work, we observe the fluorine resonance in a single crystal of  $\text{CaF}_2$ , with the dc field in the  $[111]$  direction. In our method of observation, the passage through the line is slow, but the modulation is fast, compared to the spin-lattice relaxation time. The signal is recorded after lock-in detection. It is shown that this technique permits one to study separately the behavior of the spin system when isolated from the lattice, and the effect of the spin-lattice relaxation.

Because the modulation period is fast compared to the spin-lattice relaxation time, the study of the corresponding fast variation of the magnetization gives the "response" of the spin system when isolated from the lattice. From this study, we have been able to verify Redfield's hypothesis independently of any relaxation theory and to measure the local field  $H_L = 0.90 \pm 0.025$  G, in good agreement with the theoretical value  $H_L = 0.884$  G calculated from first principles.

### I. INTRODUCTION

A CONSIDERABLE amount of both theoretical and experimental work has been performed on nuclear magnetic resonance in liquids, resulting in a justification and generalization of Bloch equations.<sup>1</sup>

In contrast very few studies have been made on solids, since the pioneer work of Redfield<sup>2</sup> who has fruitfully utilized the concept of spin temperature in the rotating frame to interpret the nuclear magnetic resonance signals in metals. This work has been extended, for the experimental part, to ionic crystals, by Goldburg.<sup>3</sup> These experiments have been performed under "slow passage" conditions, i.e., waiting long enough for the magnetization to reach its equilibrium value.

The interpretation of the results cannot separate the effect of the existence of a spin temperature from that of the relaxation, and a theory of the spin-lattice relaxation is required. For this reason, Slichter and Holton<sup>4</sup> have performed resonance experiments during times short compared to relaxation times. During such a short time, the spin system is effectively isolated from the lattice, giving the possibility to verify Redfield's hypothesis independently of any relaxation theory. The results so obtained confirm the existence of a spin temperature, but in the considered system (Na resonance in NaCl) a

In order to study the variation of the equilibrium magnetization as a function of the distance from resonance, we extend Redfield's theory to the case of relaxation by fixed paramagnetic impurities. We show that, although the relaxation field varies with the distance of the nuclear spin to a paramagnetic impurity, Redfield's formulas are still valid, with some modifications which take into account the correlation between the fields experienced by two neighboring spins, and the possibility of not being in the extreme narrowing situation. The comparison with the experimental results is complicated by the probable existence of several types of paramagnetic impurities with different relaxation times. However, it has been possible to demonstrate a strong correlation between the relaxation fields at two neighboring nuclear spins, as can be expected for this model.

A practical consequence of this study is to provide a method of obtaining usable signals in solids with large linewidths and very long relaxation times, where the ordinary absorption signal is practically undetectable.

quantitative interpretation of the results is complicated by the effect of the quadrupole interactions with the lattice defects, the magnitude of which is unknown.

In the present work, we observe the resonance of a system of spins  $I = \frac{1}{2}$ , for which there are no quadrupole interactions. In particular, we have studied the fluorine nuclei in cubic  $\text{CaF}_2$ . Most of the experiments have been performed on a single crystal with the magnetic field in the  $[111]$  direction. The method of observing the signals has all the advantages of lock-in detection: good signal-to-noise ratio and automatic recording, permitting a quantitative and precise comparison of experiment with theory. With this method, we have been able (a) to study the "response" of the spin system when isolated from the lattice, i.e., to verify the existence of a spin temperature in the rotating frame and to measure the value of the "local field"  $H_L$  which is an important parameter in the theory, verifying that we get the value calculated from first principles; (b) to study the relaxation of the spin system, and to measure the equilibrium value of the magnetization as a function of the rf field and of the distance from resonance.

In order to analyze the results and to explain the shape of the resonance signals in  $\text{CaF}_2$ , we must extend Redfield's relaxation theory in solids to the case of the relaxation by fixed paramagnetic impurities.<sup>5</sup> A practical result of this study is to give a method for obtaining and utilizing magnetic resonance signals having a good signal-to-noise ratio for samples in which the usual absorption signal is practically undetectable (solids with large linewidths and very long relaxation times).

\* Present address: Ecole Polytechnique, 17 Rue Descartes, Paris, France.

<sup>1</sup> F. Bloch, Phys. Rev. **70**, 460 (1946). The reader will find a complete exposition of the subject, as well as references in A. Abragam, *The Principles of Nuclear Magnetism* (The Clarendon Press, Oxford, 1961), Chap. VIII.

<sup>2</sup> A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

<sup>3</sup> W. I. Goldburg, Phys. Rev. **122**, 831 (1961).

<sup>4</sup> C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

<sup>5</sup> N. Bloembergen, Physica **15**, 386 (1949).

## II. SPIN SYSTEM ISOLATED FROM THE LATTICE

### Spin Interactions in the Rotating Frame

We consider a system of spins  $\mathbf{I}$ , in a magnetic field  $\mathbf{H}_0$  (along the  $z$  axis) and in a field  $\mathbf{H}_1$ , perpendicular to  $\mathbf{H}_0$  and rotating at the angular velocity  $\omega$  close to the Larmor frequency  $\omega_0 = \gamma H_0$  of the spins  $\mathbf{I}$ . In the rotating frame where  $\mathbf{H}_1$  (chosen to be along the  $y$  axis) is fixed, the effective<sup>2</sup> Hamiltonian of the spin system is

$$\mathcal{H} = Z + \mathcal{H}_d + \text{time-dependent terms.} \quad (1)$$

The Zeeman energy of the system  $Z$  is given by

$$Z = -\gamma \hbar \mathbf{H} \cdot \sum_i \mathbf{I}_i, \quad (2)$$

where  $\mathbf{H}$  is the effective external field in the rotating frame with coordinates

$$H_x = 0, \quad H_y = H_1, \quad H_z = H_0 - (\omega/\gamma) = \Delta.$$

The dipolar energy of the spins  $\mathcal{H}_d$  is given by

$$\mathcal{H}_d = \sum_{i>j} u_{ij} [\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz}I_{jz}], \quad (3)$$

where

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

Here,  $\theta_{ij}$  is the angle between the vector  $\mathbf{r}_{ij}$  joining two spins  $\mathbf{I}_i$  and  $\mathbf{I}_j$  and the  $z$  axis. We have supposed, for the sake of simplicity, that there are no pseudo-exchange interactions<sup>6</sup> between the spins. The time-dependent terms have a frequency of the order of  $\omega$  and  $2\omega$  and their effect will be neglected. This approximation is justified in references 2 and 4, and will not be discussed here.

### Spin Temperature in the Rotating Frame

We assume, following Redfield, that the spin system is described, in the rotating frame, by a density matrix  $\sigma$ :

$$\sigma = \frac{\exp(-\mathcal{H}/k\theta_s)}{\text{tr}[\exp(-\mathcal{H}/k\theta_s)]}, \quad (4)$$

where the parameter  $\theta_s$  is the spin temperature in the rotating frame, and can be quite different from the lattice temperature  $\theta_l$ . In the high-temperature approximation ( $\mathcal{H} \ll k\theta_s$ ), the expression for  $\sigma$  becomes

$$\sigma = \frac{[1] - \mathcal{H}/k\theta_s}{\text{tr}[1]}. \quad (5)$$

Although quite difficult to justify rigorously, the existence of a density matrix of this form, in the rotating frame seems quite reasonable; Abragam and Proctor<sup>7</sup> and Redfield<sup>2</sup> give a thorough discussion of its validity.

<sup>6</sup> N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

<sup>7</sup> A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

In any case, we shall see that this hypothesis is well justified by our experimental results.

With the density matrix  $\sigma$ , we are able to calculate the thermal average  $\langle Q \rangle$  of an operator  $Q$  by a trace calculation,  $\langle Q \rangle = \text{tr}(\sigma Q)$ . In particular, if we apply this relation to the energy operators  $Z$  and  $\mathcal{H}_d$ , we obtain

$$\frac{\langle Z \rangle}{H^2} = \frac{\langle \mathcal{H}_d \rangle}{H_L^2} = \frac{\langle \mathcal{H} \rangle}{H^2 + H_L^2} = -\frac{I(I+1)}{3} \frac{\gamma^2 \hbar^2}{k\theta_s} n, \quad (6)$$

where  $n$  is the number of spins,

$$H^2 = H_1^2 + \Delta^2,$$

$$H_L^2 = \frac{\text{tr}(\mathcal{H}_d^2)}{\text{tr}(\gamma^2 \hbar^2 \sum_i I_{iz}^2)}.$$

We have made use of the fact that

$$\text{tr} Z = \text{tr} \mathcal{H}_d = \text{tr} Z \mathcal{H}_d = 0.$$

We can verify, by direct comparison, that in the case of a single-spin species, the value of  $H_L^2$  is given by

$$H_L^2 = \frac{1}{3} \langle \Delta^2 \rangle, \quad (7)$$

where  $\langle \Delta^2 \rangle$  is the second moment of the unsaturated absorption line.<sup>8</sup> In the same manner, we find for the total magnetization operator  $\mathbf{M} = \gamma \hbar \sum_i \mathbf{I}_i$  that  $\langle \mathbf{M} \rangle$  is along  $\mathbf{H}$  and has the magnitude  $\langle M \rangle = -\langle Z \rangle / H$ , which follows directly from the definition of  $Z$ . In particular, it is to be remarked that the component of  $M$  orthogonal to  $\mathbf{H}_1$  in the  $xOy$  plane is zero. The absorption is completely "saturated." Thus, a necessary condition for the validity of the spin temperature hypothesis is that the rf field  $\mathbf{H}_1$  be large enough to saturate completely the absorption line.

### Adiabatic Fast Variation of the Magnetization

We wish to solve the problem of the variation of the magnetization  $\langle \mathbf{M} \rangle$ , when the field  $\mathbf{H}$  is changed adiabatically (in the thermodynamic sense) but fast enough for the spin system to be considered as *isolated* from the lattice (variation fast compared to the spin-lattice relaxation). For an isolated system, the variation  $d\langle \mathcal{H} \rangle$  of the internal energy of the system is equal to the work done by the applied forces

$$d\langle \mathcal{H} \rangle = -\langle \mathbf{M} \rangle \cdot d\mathbf{H}, \quad (8)$$

which, from (6) and the definition of  $\langle M \rangle$ , yields

$$\frac{d\langle M \rangle}{\langle M \rangle} = \frac{H_L^2}{H_L^2 + H^2} \frac{dH}{H}. \quad (9)$$

This is readily integrated to give

$$\langle M \rangle (H^2 + H_L^2)^{3/2} / H = \text{const.} \quad (10)$$

<sup>8</sup> J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

### Experimental Procedure

In the limits of validity of the existence of a spin temperature, the magnetization is along  $\mathbf{H}$  and the signal is in phase with  $H_1$ . It is then necessary to use a spectrometer tuned on the dispersion mode, resulting in a signal proportional to  $M_y$ . The use of high rf levels (up to  $H_1=1.5$  G, rotating component) requires a very stable compensation and the crossed-coil system is best suited. The utilization of a fast modulation of frequency  $\Omega$  allows a lock-in detection resulting in a signal-to-noise ratio much larger than that which can be obtained with transient methods.

However, it is to be remarked that, because of the very long spin-lattice relaxation times (between 5 and 30 sec), we are not in the usual slow passage conditions, where the magnetization has, at all times, its equilibrium value and the recorded signal, after coherent detection, is *not* the derivative of the signal obtained without modulation.<sup>9</sup> As usual, in the lock-in detection of a line, the passage through resonance has two components: (a) a slow passage ("slow scan") linear in time  $\Delta(t) = (H_1/\tau)t$  where the passing time  $\tau$ , defined as

$$\frac{1}{\tau} = \frac{1}{H_1} \frac{dH_0}{dt} = \frac{1}{H_1} \frac{d\Delta}{dt},$$

is typically of the order of several minutes, so that  $\tau \gg T_{sl}$  ( $T_{sl}$  is the spin-lattice relaxation time) and the magnetization reaches its equilibrium value  $M_{eq}$  determined by the relaxation mechanism in the sample; (b) a fast sinusoidal modulation of the form  $\delta(t) = H_m \sin(\Omega t)$  (we have used the values  $\Omega/2\pi = 20$  cps, 40 cps, and 80 cps) where  $1/\Omega \ll T_{sl}$ , so that during a modulation period, relaxation has no time to operate and the spin system is practically isolated from the lattice. Accordingly, for the fast modulation  $\delta$ , the variation of the magnetization around its equilibrium value  $M_{eq}$  is the adiabatic variation given by Eq. (10). We shall call this method, where  $\tau \gg T_{sl} \gg 1/\Omega$ , the "slow scan-fast modulation" technique. The analysis of the signal obtained by this method will give information both on the spin temperature model and on the relaxation process. Indeed, the study of the fast variation of the magnetization, corresponding to the fast modulation, shall give the response of the spin system when isolated from the lattice, resulting in the determination of  $H_L$  to be compared with the theoretical value (7). The measurement of the equilibrium value  $M_{eq}$  will permit a study of the spin-lattice relaxation of the system.

### Shape of the Signal. Determination of $H_L$

The signal, in the dispersion mode, is proportional to  $M_y = \langle M \rangle H_1/H$ . At a distance  $\Delta$  from resonance, and for a modulation  $\delta(t) = H_m \sin \Omega t$ , for which, as we have seen, we can apply Eq. (10), the variation of  $M_y$  is

given by

$$M_y(t) \{ [\Delta + \delta(t)]^2 + H_1^2 + H_L^2 \}^{\frac{1}{2}} = M_y(0) \{ \Delta^2 + H_1^2 + H_L^2 \}^{\frac{1}{2}}, \quad (11)$$

where  $M_y(0) = M_{y \text{ eq}}$  is, in fact, the equilibrium value of  $M_y$  in the absence of modulation, and is a function of the distance to resonance

$$M_{y \text{ eq}} = M_{\text{eq}} H_1/H. \quad (12)$$

We develop the expression (11) up to the second order in  $\delta$ ,

$$\frac{M_y(t) - M_{y \text{ eq}}}{M_{y \text{ eq}}} = - \frac{\Delta}{\Delta^2 + H_1^2 + H_L^2} \delta + \frac{1}{2} \frac{2\Delta^2 - (H_1^2 + H_L^2)}{(\Delta^2 + H_1^2 + H_L^2)^2} \delta^2 + \mathcal{O}(\delta^3). \quad (13)$$

The component at the frequency  $\Omega$ , which is the usual signal obtained by lock-in detection is then proportional to

$$S_1(\Delta) = - \frac{H_m}{H_1} \frac{\Delta H_1}{\Delta^2 + H_1^2 + H_L^2} M_{y \text{ eq}}. \quad (14)$$

In the absence of a relaxation theory which gives  $M_{y \text{ eq}}$  as a function of  $\Delta$ , one cannot predict the shape of the signal. Now, if we select the component at the frequency  $2\Omega$ , we obtain

$$S_2(\Delta) = - \left( \frac{H_m}{H_1} \right)^2 \frac{H_1^2 [2\Delta^2 - (H_1^2 + H_L^2)]}{(\Delta^2 + H_1^2 + H_L^2)^2} M_{y \text{ eq}}. \quad (15)$$

Here again the shape of  $S_2$  depends upon  $M_{y \text{ eq}}$ . But, quite independently of this shape, one can see that  $S_2$  becomes zero for a value  $\Delta_0$  of  $\Delta$  such that

$$\Delta_0^2 = \frac{1}{2} (H_1^2 + H_L^2). \quad (16)$$

Thus, if  $M_{y \text{ eq}} \neq 0$  (and we shall see that  $M_{y \text{ eq}}$  becomes zero only for  $\Delta = 0$ ), the values of  $\Delta$  for which  $S_2 = 0$  permit a measurement of  $H_L^2$  independently of any relaxation theory. Figure 1 shows the shape of  $S_2(\Delta)$ , and Fig. 2 shows the linear dependence between  $\Delta_0^2$  and  $H_1^2$ , confirming Eq. (16). From this curve, we measure the value of  $H_L$  for the fluorine spins in  $\text{CaF}_2$  in the [111] direction

$$H_L \sqrt{3} = 1.56 \pm 0.04 \text{ G},$$

whereas the calculated value of the second moment of the absorption line is

$$\langle \Delta^2 \rangle_{\text{th}}^{\frac{1}{2}} = 1.53 \text{ G},$$

and the measured value is

$$\langle \Delta^2 \rangle_{\text{ex}}^{\frac{1}{2}} = 1.52 \pm 0.03 \text{ G},$$

in good agreement with Bruce's measurements.<sup>10</sup> This

<sup>9</sup> K. Halbach, *Helv. Phys. Acta* **27**, 259 (1954).

<sup>10</sup> C. R. Bruce, *Phys. Rev.* **107**, 43 (1957).

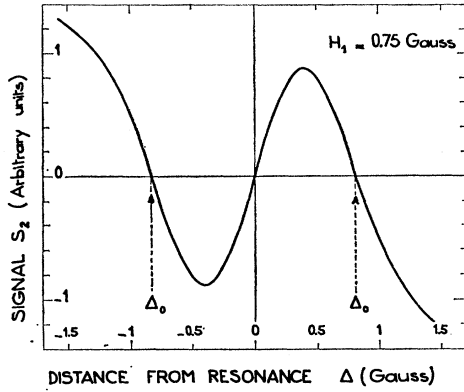


FIG. 1. Shape of the signal  $S_2(\Delta)$  obtained at double the modulation frequency. The value  $\Delta_0$  for which  $S_2=0$  does not depend on the relaxation and permits the measurement of  $H_L$ .

result seems a good experimental justification of Eqs. (6), which are a direct consequence of the spin temperature hypothesis.

### III. THEORY OF RELAXATION

#### Equilibrium Magnetization in the Rotating Frame

The shapes of the signals  $S_1$  and  $S_2$  [Eqs. (14) and (15)] are determined by the value of the equilibrium magnetization  $M_{eq}$  which results from the interaction of the spin system with the lattice and can only be given a relaxation theory. We characterize the interactions responsible for the relaxation by a fluctuating Hamiltonian  $\mathcal{H}'(t)$  considered as a perturbation. We consider the case where  $\mathcal{H}'(t)$  has the form

$$\mathcal{H}'(t) = \sum_i \mathcal{H}'_i(t), \quad (17)$$

where each  $\mathcal{H}'_i(t)$  applies to a single spin  $I_i$ . This includes a large class of relaxation processes, excluding, however, the case of relaxation by the modulation of the dipole-dipole interactions between the spins by lattice vibrations.<sup>11</sup> In any case, this mechanism is very ineffective for relaxation in solids. The motion of a spin operator will then have two components, one arising from the static Hamiltonian  $\mathcal{H} = Z + \mathcal{H}_a$  and the other from the relaxation  $\mathcal{H}'(t)$ . Now, we have already supposed, in Sec. II, that the effect of the static Hamiltonian  $\mathcal{H}$  is to establish among the spins a temperature  $\theta_s$ . The time of establishment of such a temperature is of the order of  $1/\gamma H_L \approx 50 \mu\text{sec}$ , much shorter than the relaxation times which are of the order of a few seconds. Thus, if one is interested only in times long compared to  $1/\gamma H_L$ , the effect of the static interactions  $\mathcal{H} = Z + \mathcal{H}_a$  is simply to maintain at all times a spin temperature  $\theta_s$  in the rotating frame, this temperature having a slow variation caused by the relaxation. This slow variation is, in particular, that of the total energy  $\langle \mathcal{H} \rangle$  which, in the absence of the perturbing Hamiltonian  $\mathcal{H}'(t)$ , would

<sup>11</sup> I. Waller, Z. Physik **79**, 370 (1932).

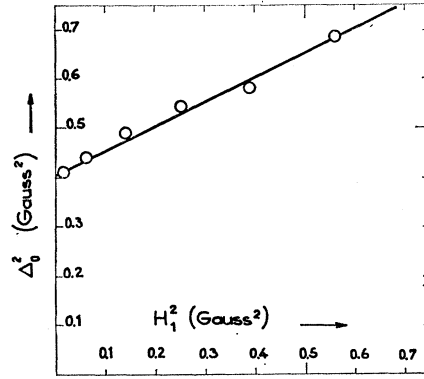


FIG. 2. Measurement of  $\Delta_0^2$  as a function of  $H_1^2$ . The straight line through the experimental points has the equation  $2\Delta_0^2 = H_1^2 + H_L^2$ , with  $H_L = 0.90$  G, in good agreement with the theoretical value  $H_L = 0.884$  for the fluorine nuclei in  $\text{CaF}_2$  (field in the [111] direction).

be constant. The principles of the reasoning are then the following: in order to study the relaxation of  $\langle \mathcal{H} \rangle$ , we shall consider only the slow variation [arising from  $\mathcal{H}'(t)$ ] of the two components  $\langle Z \rangle$  and  $\langle \mathcal{H}_a \rangle$  of  $\langle \mathcal{H} \rangle$ ; in order to take into account the much faster effect due to the static interaction  $\mathcal{H}$ , we shall simply write that the spin system is all the time in a state described by a temperature, i.e., by a density matrix  $\sigma$  of the form (4) or (5). Accordingly,  $\langle Z \rangle$  and  $\langle \mathcal{H}_a \rangle$  are not independent but have to satisfy Eqs. (6) during their slow motion caused by the relaxation  $\mathcal{H}'(t)$ .

We shall see in the following paragraphs that in the case of the existence of a spin temperature, the effect of  $\mathcal{H}'(t)$  is to relax the average value of the magnetization  $\langle \mathbf{M} \rangle$  according to the equations<sup>12</sup>:

$$\frac{\partial}{\partial t} \langle M_z \rangle = -\frac{1}{T_1} [\langle M_z \rangle - M_0] \quad (18)$$

and

$$\frac{\partial}{\partial t} \langle M_y \rangle = -\frac{1}{T_2} \langle M_y \rangle,$$

where  $M_0$  is the magnetization at thermal equilibrium in the absence of the rf field  $H_1$ . The partial differentials in the equations indicate that only the effect of the relaxation is considered. If the effect of the static Hamiltonian  $\mathcal{H}$  was absent, and in particular without the interactions between the spins, these equations would be independent and would define the motion of the magnetization; indeed, they are the equations of motion that one obtains for liquids where precisely the interactions between spins are decoupled by the fast Brownian motion. In fact, the static interactions  $\mathcal{H}$  maintain a density matrix  $\sigma$  of the form (5) causing

<sup>12</sup> The quantity  $T_2$  of the equations has no relation with the inverse linewidth of the unsaturated line in the solid. It is, in fact, in the limit of large rf field  $H_1$ , a transverse relaxation time, a quantity for which Redfield uses the notation  $T_{2e}$  in reference 2 (p. 1792).

$\langle \mathbf{M} \rangle$  to lie along the effective field  $\mathbf{H}$ . The values of  $\langle M_z \rangle$  and  $\langle M_y \rangle$  are not independent, but must satisfy at all times the condition

$$\frac{\langle M_z \rangle}{\Delta} = \frac{\langle M_y \rangle}{H_1} = \frac{|\langle \mathbf{M} \rangle|}{(H_1^2 + \Delta^2)^{\frac{1}{2}}}. \quad (19)$$

From Eqs. (18) and (19), one obtains the effect of relaxation on the motion of  $\langle Z \rangle = -\langle \mathbf{M} \rangle \cdot \mathbf{H}$ :

$$\frac{\partial}{\partial t} \langle Z \rangle = -\frac{1}{T_z} (\langle Z \rangle - Z_0), \quad (20)$$

with

$$\frac{1}{T_z} = \left( \frac{\Delta^2}{T_1} + \frac{H_1^2}{T_2} \right) \frac{1}{\Delta^2 + H_1^2}$$

and

$$Z_0 = M_0 \frac{\Delta(\Delta^2 + H_1^2)}{\Delta^2 + (T_1/T_2)H_1^2}.$$

Similarly, it is shown in the Appendix that, in the case of the existence of a spin temperature, the effect of the relaxation  $\mathcal{H}'(t)$  on the dipole-dipole energy  $\langle \mathcal{H}_d \rangle$  is given by

$$(\partial/\partial t) \langle \mathcal{H}_d \rangle = -(\alpha/T_1) \langle \mathcal{H}_d \rangle, \quad (21)$$

where the quantity  $\alpha$  has the values

$$\alpha = 3 \quad \text{if } \mathcal{H}'_i(t) = \mathcal{H}'_j(t) \quad \text{for two neighboring spins } I_i \text{ and } I_j, \quad (21')$$

and

$$\alpha = \frac{2}{3}(2 + T_1/T_2) \quad \text{if there is no correlation between } \mathcal{H}'_i(t) \text{ and } \mathcal{H}'_j(t) \text{ for } i \neq j.$$

In addition to the motion arising from the relaxation which is given by Eqs. (20) and (21), there is the motion caused by the static Hamiltonian  $\mathcal{H}$ . But, as was discussed previously, we take its effect into account by imposing a spin temperature to the system; i.e., the quantities  $\langle Z \rangle$  and  $\langle \mathcal{H}_d \rangle$  are not independent but must satisfy, at all times, Eqs. (6). We then obtain the final equation of the motion of the total energy  $\langle \mathcal{H} \rangle$ , by combining Eqs. (20), (21), and (6) to give

$$\frac{d}{dt} \langle \mathcal{H} \rangle = -\frac{1}{T} [\langle \mathcal{H} \rangle - \mathcal{H}_0], \quad (22)$$

where

$$\frac{1}{T} = \frac{1}{T_1} \frac{\Delta^2 + (T_1/T_2)H_1^2 + \alpha H_L^2}{\Delta^2 + H_1^2 + H_L^2}$$

and

$$\mathcal{H}_0 = M_0 \frac{\Delta(\Delta^2 + H_1^2 + H_L^2)}{\Delta^2 + (T_1/T_2)H_1^2 + \alpha H_L^2}.$$

In this equation, the derivation is not a partial derivation but a total one, since the static interaction  $\mathcal{H}$  has no effect on the motion of  $\langle \mathcal{H} \rangle$  (the Hamiltonian  $\mathcal{H}$  commutes with itself). The magnetization  $\langle \mathbf{M} \rangle$ , which remains along the effective field  $\mathbf{H}$ , and which is simply

proportional to  $\langle \mathcal{H} \rangle$  is from Eqs. (6)

$$\langle M \rangle = -\frac{\langle Z \rangle}{H} = \frac{H}{H^2 + H_L^2} \langle \mathcal{H} \rangle.$$

Therefore, its total motion is given by

$$\frac{d}{dt} \langle M \rangle = -\frac{1}{T} [\langle M \rangle - M_{\text{eq}}], \quad (23)$$

where

$$M_{\text{eq}} = \frac{H}{H^2 + H_L^2} \mathcal{H}_0 = M_0 \frac{\Delta H}{\Delta^2 + (T_1/T_2)H_1^2 + \alpha H_L^2},$$

and  $\alpha$  is given by Eqs. (21').

This is the result obtained by Redfield,<sup>2</sup> when the intensity of relaxation is the same for each spin  $I_i$ . This is the case for relaxation (a) by conduction electrons in a metal or a semiconductor, (b) by quadrupolar interactions with the lattice vibrations for spins larger than  $\frac{1}{2}$ . For both cases, the correlation time  $\tau$  of  $\mathcal{H}'(t)$  is very short ( $\omega\tau \ll 1$ ), so that we have  $T_1 = T_2$ , and Redfield has given the explicit value of  $M_{\text{eq}}$  only in this case. For  $\text{CaF}_2$ , where the fluorine spins are relaxed by dipole-dipole interaction with fixed paramagnetic impurities,<sup>5</sup> the intensity of the relaxing field varies with the distance of the nuclear spin to a paramagnetic impurity and consequently is very different from one spin to another. Also, the correlation time  $\tau$  of the relaxing Hamiltonian  $\mathcal{H}'(t)$  is, in this case, the spin-lattice relaxation time of the paramagnetic impurity and we do not always have the condition  $\omega\tau \ll 1$ . Therefore, we must generalize Redfield's analysis to situations where (a) the intensity of the relaxing field varies from one spin to another, and (b) we have  $T_1 \neq T_2$  in Eqs. (18).

### Existence of a Spin Temperature in the Case of Relaxation by Fixed Paramagnetic Impurities

We consider a nuclear spin  $\mathbf{I}_i$  relaxed by dipole-dipole interaction with a fixed paramagnetic impurity  $\mathbf{S}$ :

$$\mathcal{H}'_i(t) = \frac{\hbar\gamma_i\gamma}{r_i^3} \left[ \mathbf{S}(t) \cdot \mathbf{I}_i - \frac{3}{r_i^2} (\mathbf{S}(t) \cdot \mathbf{r}_i)(\mathbf{I}_i \cdot \mathbf{r}_i) \right], \quad (24)$$

where  $\mathbf{r}_i$  is the vector joining the impurity  $\mathbf{S}$  to the nucleus  $\mathbf{I}_i$ , and where the spin  $\mathbf{S}(t)$ , which is strongly bound to the lattice, is considered as a classical stochastic variable. The transition probability of  $I_z$ , due to this interaction, has the value

$$W_1 = C_1(\theta_i)/r_i^6, \quad (25)$$

where  $C_1$  is derived in the Appendix, and  $\theta_i$  is the angle between  $\mathbf{r}_i$  and the  $z$  axis. This process, where the intensity of the relaxation varies from one spin to the other, tends to produce different spin temperatures in the sample. However, Bloembergen<sup>5</sup> has shown that spin diffusion is an efficient mechanism to equalize these

temperatures. In fact, De Gennes<sup>13</sup> has found for this model that, in the case of very diluted impurities, there is a single spin temperature for the great majority of the spins of the system.

The system is perturbed only in the vicinity of an impurity, but outside of a sphere of radius  $a_1$  diffusion insures the existence of a spin temperature. The length  $a_1$  is given by<sup>13,14</sup>

$$a_1 = 0.7 \left( \frac{\langle C_1 \rangle}{D} \right)^{\frac{1}{2}}, \quad (26)$$

where  $D$  is the spin diffusion coefficient, assumed to be isotropic, and  $\langle C_1 \rangle$  is the angular average of  $C_1(\theta_i)$ . The radius  $a_1$  is typically of the order of a few interatomic distances. Blumberg<sup>15</sup> has given a very physical analysis of this model, with a few experimental justifications. He shows that the relaxation tends to produce two regions with different spin temperatures approximately separated by a sphere of radius  $r_0(t)$  around an impurity  $S$ . This sphere spreads from an initial time  $t=0$  according to the relation  $r_0(t) \approx (\langle C_1 \rangle t)^{1/6}$ . On the other hand, spin diffusion tends to equalize temperatures according to the diffusion law  $r_D(t) \approx (Dt)^{\frac{1}{2}}$ . The two effects balance out at the distance  $a_1$  given by Eq. (26), and for  $r > a_1$ , the diffusion is dominant and insures the existence of a single spin temperature in the system. Blumberg's and De Gennes' analysis are relative to relaxation along the  $z$  axis, but they can be readily extended to relaxation along the effective field  $\mathbf{H}$  in the rotating frame. One has, then, to replace the coefficient  $C_1$  of Eq. (25) by another coefficient  $C_H$  representing relaxation along  $\mathbf{H}$ . The value of  $C_H$ , as well as the value of the diffusion  $D$  depends, in general, upon the magnitude and direction of  $H$ , and the corresponding variation of the radius  $a_H$  is very complicated and cannot be studied without a theory of spin diffusion, which is so far nonexistent. Fortunately, we shall see that the equilibrium magnetization  $M_{eq}$ , at least in the case of a single type of paramagnetic impurity, is independent of  $a_H$ , so that we are able to avoid the difficult question of the dynamics of spin diffusion.

### Relaxation Theory

In a general theory of relaxation,<sup>1,16</sup> it is shown that the motion of the density matrix in the rotating frame arising from the effect of a fluctuating perturbing Hamiltonian  $\mathcal{H}'(t)$  is given by

$$\frac{\partial}{\partial t} \sigma(t) = - \int_0^\infty \langle [\mathcal{H}'(t), [\mathcal{H}'(t-\tau'), \sigma(t) - \sigma_0]] \rangle_{av} d\tau', \quad (27)$$

where  $[A, B]$  is the commutator of  $A$  with  $B$ , and the

$\langle \rangle_{av}$  around the integrand indicates that one averages over the random components of  $\mathcal{H}'(t)$ . The perturbing Hamiltonian  $\mathcal{H}'(t)$  is expressed in the rotating coordinate system and is related to the expression  $\mathcal{H}_{lab}'(t)$  in the laboratory frame of reference by

$$\mathcal{H}'(t) = e^{+iH_0 M_z t} \mathcal{H}_{lab}'(t) e^{-iH_0 M_z t}. \quad (28)$$

Equation (27), which, in fact, expresses the relaxation in the absence of rf field and spin-spin interactions, is still valid in the presence of these interactions,<sup>17</sup> provided that the fluctuations of  $\mathcal{H}'(t)$  are rapid compared to the frequency corresponding to these interactions, i.e., when

$$\gamma H_1 \tau \ll 1 \quad \text{and} \quad \gamma H_L \tau \ll 1, \quad (29)$$

where  $\tau$  is the correlation time of  $\mathcal{H}'(t)$ .

We have not assumed the case of extreme narrowing here, which would be expressed by the condition  $\omega \tau \ll 1$ . The relaxation of an observable represented by an operator  $Q$ , is then given from the density matrix by

$$\langle Q(t) \rangle = \text{tr}[Q \sigma(t)]. \quad (30)$$

With the special form (17) of the Hamiltonian  $\mathcal{H}'(t)$ , we can obtain relaxation equations for a single spin operator. For example, applied to the operators  $I_{iy}$  and  $I_{iz}$ , Eqs. (27) and (30) yield

$$\begin{aligned} \frac{\partial}{\partial t} \langle I_{iz} \rangle &= -W_{1i} (\langle I_{iz} \rangle - I_0), \\ \frac{\partial}{\partial t} \langle I_{iy} \rangle &= -W_{2i} \langle I_{iy} \rangle, \end{aligned} \quad (31)$$

as is shown in detail in the Appendix.

In the situation considered by Redfield,<sup>2</sup> all the  $W$ 's are equal and a simple summation gives Eqs. (18) with  $1/T_1 = W_1$  and  $1/T_2 = W_2$ . But in the case of relaxation by fixed paramagnetic impurities, we have

$$W_{1i} = C_1(\theta_i)/r_i^6, \quad W_{2i} = C_2(\theta_i)/r_i^6, \quad (32)$$

where  $C_1$  and  $C_2$  are calculated in the Appendix. The values of the  $W$ 's vary from one spin to another and we have not, *a priori*, equations of the form (18) for the total magnetization  $\langle M \rangle$ . But, if there is a spin temperature in the rotating frame, then Eqs. (31) give again the expressions (18). This is caused by the particular form (5) of the density matrix  $\sigma$ . For this form, it is easy to see that all the average values  $\langle \mathbf{I}_i \rangle$  relative to a particular spin  $\mathbf{I}_i$  are proportional to  $\langle \mathbf{M} \rangle$ . We have seen that there is a spin temperature in the rotating frame for all the spins outside of a sphere of radius  $a_H$  around each impurity. Then, if we limit the summation to these spins, which are practically the

<sup>13</sup> P. G. De Gennes, J. Phys. Chem. Solids **7**, 345 (1958).

<sup>14</sup> G. R. Khontsichvili, Proc. Georgian Acad. Sci. (U.S.S.R.) **4**, 3 (1956).

<sup>15</sup> W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

<sup>16</sup> A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

<sup>17</sup> F. Bloch, Phys. Rev. **105**, 1206 (1957). The reader will also find in the book of reference 1 (Chap. XII, pp. 511-517) the detailed justification of Eqs. (27) and (28) in the presence of an rf field  $H_1$  when  $\gamma H_1 \tau \ll 1$ . The argument can be readily extended in the presence of  $\mathcal{H}_A$  with  $\gamma H_L \tau \ll 1$ .

only ones observed, the trace calculation gives Eqs. (18) with

$$\frac{1}{T_1} = \frac{1}{n} \sum_{r_i > a_H} \frac{C_1(\theta_i)}{r_i^6}, \quad \frac{1}{T_2} = \frac{1}{n} \sum_{r_i > a_H} \frac{C_2(\theta_i)}{r_i^6}, \quad (33)$$

where  $n$  is the number of spins which are in the summation, i.e., practically the total number of nuclei. If  $a_H$  is large enough, we may replace the sum by an integration to obtain

$$\frac{1}{T_1} = \frac{4\pi}{3} N \frac{\langle C_1 \rangle}{a_H^3}, \quad \frac{1}{T_2} = \frac{4\pi}{3} N \frac{\langle C_2 \rangle}{a_H^3}, \quad (34)$$

where  $N$  is the number of impurities per  $\text{cm}^3$  and  $\langle C_1 \rangle$  and  $\langle C_2 \rangle$  are the angular averages given in the Appendix.

The same calculation applied to the operator  $\mathcal{H}_d$ , where we limit the summations to the spins located outside of the spheres of radius  $a_H$  gives Eq. (21) with the same expressions (34) for  $T_1$  and  $T_2$ . This is again due essentially to the form (5) of the density matrix  $\sigma$ . Because of this form, the average value of any bilinear combination of operators relative to two spins  $I_i$  and  $I_j$ , such as  $\langle I_{iz} I_{jz} \rangle$  or  $\langle I_{ix} I_{jx} \rangle$ , is proportional to  $\langle \mathcal{H}_d \rangle$ . It is to be remarked that in the relaxation by a fixed paramagnetic impurity, the fields "seen" by two neighboring spins are strongly correlated. One can then predict, in Eq. (21), a value of  $\alpha$  close to 3, or, if  $T_1 \gg T_2$ , an intermediate value between 3 and  $\frac{2}{3}(2 + T_1/T_2)$ , if the correlation is not complete.

We have, thus, extended the validity of Eq. (23), which gives the value  $M_{\text{eq}}$  of the equilibrium magnetization in the rotating frame, to the situation of relaxation by fixed paramagnetic impurities.

### Equilibrium Magnetization in the Case of Relaxation by Fixed Paramagnetic Impurities

We have seen that  $a_H$  varies in a complicated manner with the magnitude and direction of  $\mathbf{H}$  and the expressions (34) show that, in general, it is not possible to make quantitative predictions on  $T_1$  and  $T_2$  separately. But, as for the equilibrium magnetization  $M_{\text{eq}}$  which depends only on the ratio  $T_1/T_2$ , the situation can be more favorable, and we distinguish two cases:

(1) There is only one type of impurity. In this case, we have

$$\frac{T_1}{T_2} = \frac{\langle C_2 \rangle}{\langle C_1 \rangle} = \frac{7}{6} + \frac{2}{3} \omega^2 \tau^2 \quad (35)$$

from the values of  $C_1$  and  $C_2$  (see Appendix).

The correlation time  $\tau$  is simply the spin-lattice relaxation time of the impurities. The ratio  $T_1/T_2$  is independent of  $a_H$  and the signal, at a given frequency  $\omega$ , will be determined by Eqs. (14) and (23), where  $T_1/T_2$  is independent of  $\Delta$  and  $H_1$ . In fact, if we take into account the fact that the diffusion as well as

relaxation are anisotropic, the perturbed region around each impurity is not rigorously a sphere of radius  $a_H$ , but a volume of a more complicated shape. However, one can expect that the ratio  $T_1/T_2$  will vary only very slightly with  $\Delta$  and  $H_1$ .

(2) If there are several types of impurities with different relaxation times  $\tau_k$ , then

$$\frac{T_1}{T_2} = \frac{\sum_k \langle C_{2k} \rangle N_k / a_{Hk}^3}{\sum_k \langle C_{1k} \rangle N_k / a_{Hk}^3}. \quad (36)$$

This ratio will depend, in general, on the radii  $a_{Hk}$  relative to the different impurities, and the ratio  $T_1/T_2$  is not independent of  $\mathbf{H}$ . It is only in the case where all the relaxation times  $\tau_k$  are short enough, so that  $\omega\tau_k \ll 1$  (extreme narrowing case), that the ratio  $T_1/T_2$  is constant. In this situation, all the values of  $\langle C_{1k} \rangle$  and  $\langle C_{2k} \rangle$  are equal and we have (see Appendix)  $T_1/T_2 = 7/6$ . This again is a case where the equilibrium magnetization is independent of  $a_H$  and of the diffusion.

### Comparison with Experiment

From Eqs. (12), (14), and (23), the expression of the signal  $S_1(\Delta)$  obtained by coherent detection at the modulation frequency is:

$$S_1(\Delta) = -M_0 \frac{H_m}{H_1} \times \frac{\Delta^2 H_1^2}{(\Delta^2 + H_1^2 + H_L^2) [\Delta^2 + (T_1/T_2) H_1^2 + \alpha H_L^2]}. \quad (37)$$

Figure 3 (top) shows the theoretical shape of the signal, when  $T_1/T_2$  and  $\alpha$  are constant, independent of  $\Delta$ . With the values  $T_1/T_2 = 9$  and  $\alpha = 5$ , we have a very good agreement with an actual recording (Fig. 3 bottom) obtained at 2 Mc/sec. The slight dissymmetry of the curve arises from the fact that the passage through the line is a little too fast for the magnetization to reach its equilibrium value. The condition to have a line rigorously symmetrical for long relaxation times ( $T_1 \approx 22$  sec at 2 Mc/sec) leads to scanning speeds prohibitively slow. A whole set of such curves obtained at 2 Mc/sec for different values of  $H_1$  give, within our experimental errors, a constant value of  $T_1/T_2 = 9 \pm 1$  and  $\alpha = 5 \pm 1$ . We remark that the value of  $\alpha$  falls in between the values  $\alpha = \frac{2}{3}(2 + T_1/T_2) = 7.3$  (field completely uncorrelated at two spins locations) and  $\alpha = 3$  (complete correlation).

At higher frequencies (8 Mc/sec and 16 Mc/sec) the signals obtained are not compatible with the shape given by Eq. (37) with  $T_1/T_2$  independent of  $\Delta$  and  $H_1$ , as can be seen, for example, on the recording of Fig. 4 obtained at 16 Mc/sec. This indicates that there is certainly more than one type of paramagnetic impurities responsible for the relaxation in our sample of  $\text{CaF}_2$ . In the absence of a detailed knowledge of the nature of the impurities contained in the natural crystal that we have

used, it is difficult to discuss quantitatively the experimental results. We can, however, make the following qualitative remarks: (a) Although the value of  $T_1/T_2$  varies in a complicated manner with  $\Delta$  and  $H_1$ , we have found that it remains within limits. It stays between 60 to 85 at 8 Mc/sec and between 230 to 290 at 16 Mc/sec, which seems to indicate, along with the value 9 at 2 Mc/sec, a rough variation in  $\omega^3$  as a function of frequency, which is slightly less rapid than the variation as  $\omega^2$  given by Eq. (35), in the case of a single type of impurity. (b) The value of  $\alpha$  deduced from the experimental curves varies very little with frequency,  $\alpha=8\pm 3$ . We can attempt to give a qualitative explanation of these results. At low frequency (2 Mc/sec) the different values of  $\omega^2\tau^2$ , corresponding to the different impurities, are not very large, thus, attenuating the differences between the paramagnetic impurities (we are close to the extreme narrowing case) and explaining the approximate constancy of  $T_1/T_2$ . At higher frequencies, the differences become larger, and the ratio  $T_1/T_2$  cannot be considered as a constant any more. In addition, the impurities with the longest relaxation times, with the corresponding very large values of  $\omega^2\tau^2$ , are less and less efficient for the nuclear relaxation, explaining a variation of  $T_1/T_2$  less rapid than  $\omega^2$  as a function of the resonance frequency. The value of  $\alpha$  which stays, at least for the high fields, much smaller than the value  $\alpha=\frac{2}{3}(2+T_1/T_2)$ , corroborates our model, where one predicts an important correlation between the fluctuating field seen by two neighboring spins.

#### Signal-to-Noise Ratio in the "Slow Scan-Fast Modulation" Method

One of the practical consequences of Eq. (23) is that the signal-to-noise ratio, obtained with a strong rf field  $H_1$  in a solid, can be much larger than the optimum

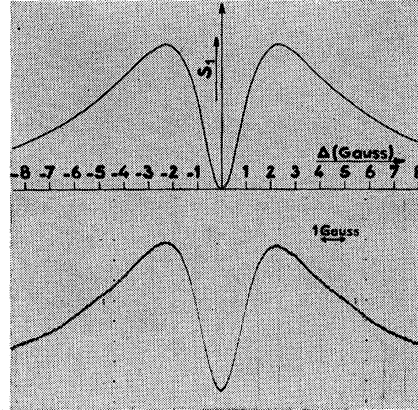


FIG. 3. Signal  $S_1$  obtained in the "slow scan-fast modulation" condition with lock-in detection. ( $\text{CaF}_2$ ,  $[111]$  direction.)  $H_1=1.06$  G. Top: Theoretical curve [Eq. (37)] with  $T_1/T_2=9$  and  $\alpha=5$ . The signal is in arbitrary units. Bottom: Actual recording obtained at 2 Mc/sec, with an integrating time of 0.65 sec,  $H_m=0.25$  G,  $\Omega/2\pi=20$  cps. Scanning speed: 0.215 G per min.

absorption signal. From Eq. (23), we obtain

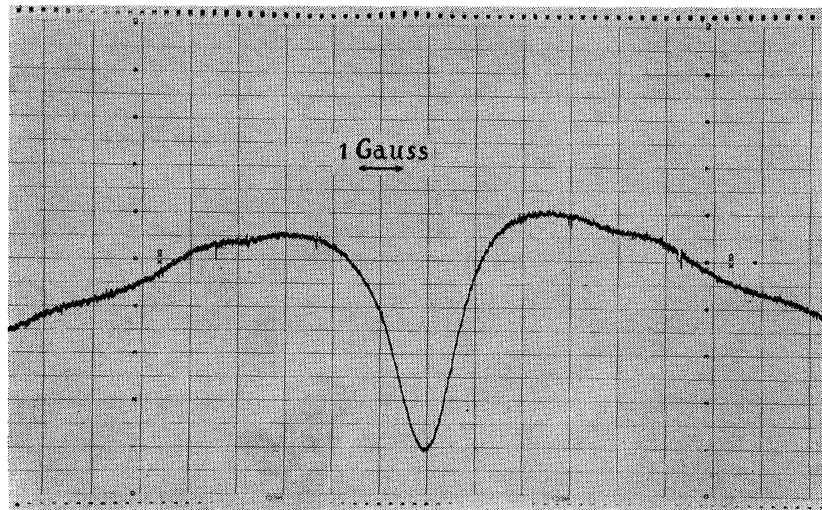
$$M_{y \text{ eq}} = \frac{H_1}{H} M_{\text{eq}} = M_0 \frac{\Delta H_1}{\Delta^2 + (T_1/T_2)H_1^2 + \alpha H_L^2}. \quad (38)$$

The maximum signal obtained in optimizing expression (38) is then

$$(M_y)_{\text{max}} = \frac{1}{2} M_0 \left[ \frac{H_1^2}{(T_1/T_2)H_1^2 + \alpha H_L^2} \right]^{\frac{1}{2}}. \quad (39)$$

An absorption signal is obtained for a weak  $H_1$ , the case in which the theory of Bloembergen, Purcell, and Pound<sup>18</sup> is applicable, at least to an order of magnitude. The maximum absorption signal corresponds to a

FIG. 4. Signal  $S_1$  obtained at 16 Mc/sec in the same sample as Fig. 3 (bottom).  $H_1=0.52$  G,  $H_m=0.13$  G. Notice "bumps" in the curve, which indicate that  $T_1/T_2$  varies with the distance from resonance  $\Delta$ .



<sup>18</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).



component in quadrature with  $H_1$  of magnitude

$$(M_x)_{\max} = \frac{1}{2} M_0 [\gamma T_1 \Delta H]^{-\frac{1}{2}}, \quad (40)$$

where  $\Delta H$  is the half-width of the line, defined by  $\Delta H = (2/\pi) \int_0^\infty f(H) dH$ , and where  $f(H)$  is the equation of the unsaturated absorption line such that  $f(H_0) = 1$  at resonance. This optimum is obtained for a field,  $(H_1)_{\text{sat}}$ , which saturates the line at half its value,

$$(H_1)_{\text{sat}} = (\Delta H / \gamma T_1)^{\frac{1}{2}}. \quad (41)$$

Equation (40) can then be written

$$(M_x)_{\max} = \frac{1}{2} M_0 (H_1)_{\text{sat}} / \Delta H. \quad (42)$$

The ratio of the maximum signals obtained by the two methods is then

$$\rho = \frac{(M_y)_{\max}}{(M_x)_{\max}} = \frac{H_1}{(H_1)_{\text{sat}}} \frac{\Delta H}{[(T_1/T_2)H_1^2 + \alpha H_L^2]^{\frac{1}{2}}}. \quad (43)$$

As  $H_1$  and  $H_L$  are, in general, of the same order of magnitude, and if  $T_1/T_2$  is not too large, the gain  $\rho$  is of the order of  $\rho \approx H_1 / (H_1)_{\text{sat}}$ . For protons (or fluorine) with  $T_1 = 10$  sec,  $\Delta H = 1$  G we have  $(H_1)_{\text{sat}} = 2 \times 10^{-3}$  G and the dispersion signal obtained with a rf field  $H_1$  of 1 G is three orders of magnitude larger than the optimum absorption signal.

### Rotary Saturation in the Rotating Frame

In calculating the expression for the signal (Eqs. 14 and 15), we have assumed that the only effect of the modulation is to vary, adiabatically, the magnitude and direction of the magnetization. In fact, Redfield<sup>2</sup> shows that a field modulation along  $H_0$  "heats up" the spin system in the rotating frame, i.e., decreases the magnetization (rotary saturation). The equation of motion of the magnetization along  $H$  in the rotating

frame is, indeed,

$$\frac{dM}{dt} = -\frac{1}{T}(M - M_{\text{eq}}) - WM, \quad (44)$$

where  $T$  is the relaxation time of the magnetization along  $H$  [Eq. (23)];  $W$  is the effect of the modulation and has the value<sup>2</sup>

$$W = -\frac{1}{8} \frac{H_m^2 \sin^2 \theta}{(H_1^2 + \Delta^2 + H_L^2)} \Omega f(\Omega) \quad (45)$$

for a modulation  $\delta(t) = H_m \sin \Omega t$ ; and  $\theta$  is the angle of  $\mathbf{H}$  with the  $z$  axis. The normalized function  $f(\Omega)$  defines the shape of the absorption curve in the rotating frame.<sup>19</sup> From Eq. (44) the magnetization reaches a decreased value  $M_{\text{eq}} / (1 + WT)$  with a time constant  $T'$  given by

$$1/T' = 1/T + W. \quad (46)$$

If the modulation frequency  $\Omega$  is small

$$\Omega \ll \gamma(H^2 + H_L^2)^{\frac{1}{2}},$$

we have practically  $f(\Omega) \approx f(0)$ , and for fixed values of  $\Delta$  and  $H_1$ ,  $W$  is proportional to  $H_m^2 \Omega^2$ . Fig. 5 shows that this is well verified by the measurements. We have used these results to make sure that our experimental conditions were such that rotary saturation had a negligible effect when recording  $S_1$  and  $S_2$  signals, in order to compare with the theoretical expressions.

### ACKNOWLEDGMENTS

We wish to thank Dr. A. G. Redfield, Dr. P. G. De Gennes, and Dr. M. Goldman for many discussions and comments. The direction and guidance of Professor A. Abragam, his constant interest in problems concerning spin temperature, and his many suggestions have permitted the completion of the present work.

### APPENDIX

Multiplying both sides of Eq. (27) by the operator  $Q$  and taking the trace, we obtain

$$\frac{\partial}{\partial t} \langle Q \rangle = -(a - a_0), \quad (A1)$$

where  $a = \text{tr}(\sigma A)$ ,  $a_0 = \text{tr}(\sigma_0 A)$ , and

$$A = \int_0^\infty \langle [\mathcal{I}c'(t), [\mathcal{I}c'(t - \tau'), Q]] \rangle_{\text{av}} d\tau'.$$

We apply this equation to the operators  $I_z$  and  $I_y$  with

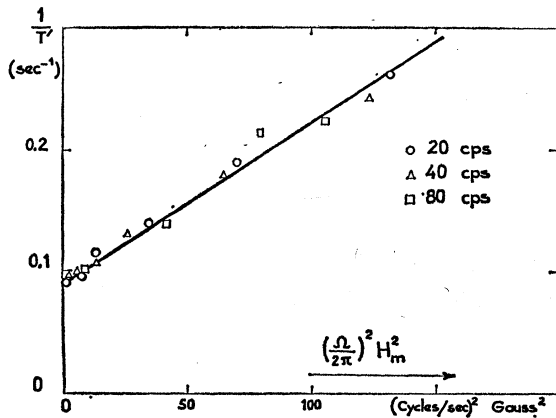


FIG. 5. Time constant  $T'$  of the return of the magnetization to its equilibrium value in presence of modulation.  $H_1 = 0.65$  G,  $\Delta = 0.5$  G,  $\omega/2\pi = 8$  Mc/sec. The transition probability caused by the modulation (rotary saturation) is proportional to  $\Omega^2 H_m^2$ .

<sup>19</sup> This is the equivalent of the definition given in the laboratory frame for absorption in low fields by L. J. F. Broer, *Physica* **10**, 801 (1943).

a relaxation Hamiltonian  $\mathcal{H}'(t)$  given by

$$\mathcal{H}'(t) = -\gamma\hbar\mathbf{h}(t) \cdot \mathbf{I}. \quad (\text{A2})$$

Because all the operators apply only to a single spin  $I_i$ , we have dropped the subscript  $i$  from the formulas. From Eq. (24) the fluctuating field  $\mathbf{h}(t)$  has the expression

$$\mathbf{h}(t) = -\frac{\gamma_s}{r^3} \{ \mathbf{S}(t) - (3/r^2) [\mathbf{S}(t) \cdot \mathbf{r}] \mathbf{r} \}. \quad (\text{A3})$$

If the relaxation time  $\tau$  of the paramagnetic impurity is not too short, i.e., if  $\omega_s\tau \gg 1$ , where  $\omega_s$  is the Larmor frequency of the electron, only those terms containing  $S_z$  which do not involve an electronic flip will be efficient for nuclear relaxation. Accordingly, the effective components of  $\mathbf{h}(t)$  are

$$\begin{aligned} h_x(t) &= (\gamma_s/r^3) S_z(t) 3 \cos\theta \sin\theta \cos(\varphi - \omega t), \\ h_y(t) &= (\gamma_s/r^3) S_z(t) 3 \cos\theta \sin\theta \sin(\varphi - \omega t), \\ h_z(t) &= (\gamma_s/r^3) S_z(t) (1 - 3 \cos^2\theta), \end{aligned} \quad (\text{A4})$$

where  $\theta$  and  $\varphi - \omega t$  are, respectively, the polar and azimuthal angles of  $\mathbf{r}$  in the rotating frame. The only nonvanishing averages of bilinear products of these components are

$$\begin{aligned} \langle h_x(t) h_x(t-t') \rangle_{\text{av}} &= \langle h_y(t) h_y(t-t') \rangle_{\text{av}} \\ &= \frac{1}{3} S(S+1) \frac{\gamma_s^2}{r^6} (3 \cos\theta \sin\theta)^2 \\ &\quad \times \cos(\omega t'/2) e^{-t'/\tau}, \end{aligned} \quad (\text{A5})$$

$$\langle h_z(t) h_z(t-t') \rangle_{\text{av}} = \frac{1}{3} S(S+1) \frac{\gamma_s^2}{r^6} (1 - 3 \cos^2\theta)^2 e^{-t'/\tau},$$

where we have used

$$\langle S_z(t) S_z(t-t') \rangle_{\text{av}} = \frac{1}{3} S(S+1) e^{-t'/\tau}. \quad (\text{A6})$$

Applying these formulas to Eq. (A1) we obtain Eq. (18) with

$$\begin{aligned} C_1(\theta) &= \frac{1}{3} S(S+1) \hbar^2 \gamma_s^2 \gamma^2 (3 \cos\theta \sin\theta)^2 \tau (1 + \omega^2 \tau^2)^{-1}, \\ C_2(\theta) &= \frac{1}{3} S(S+1) \hbar^2 \gamma_s^2 \gamma^2 \\ &\quad \times \left[ (1 - 3 \cos^2\theta)^2 \tau + \frac{1}{2} (3 \cos\theta \sin\theta)^2 \tau (1 + \omega^2 \tau^2)^{-1} \right]. \end{aligned} \quad (\text{A7})$$

The angular averages are

$$\begin{aligned} \langle C_1 \rangle &= \frac{1}{3} S(S+1) \hbar^2 \gamma_s^2 \gamma^2 2\tau (1 + \omega^2 \tau^2)^{-1}, \\ \langle C_2 \rangle &= \frac{1}{3} S(S+1) \hbar^2 \gamma_s^2 \gamma^2 \left[ \frac{4}{3} \tau + \tau (1 + \omega^2 \tau^2)^{-1} \right]. \end{aligned} \quad (\text{A8})$$

In order to apply the same calculation to the operator  $\mathcal{H}_d$  given by (3), we must distinguish two cases:

(1) The fields  $\mathbf{h}_i(t)$  and  $\mathbf{h}_j(t)$  experienced by two spins  $\mathbf{I}_i$  and  $\mathbf{I}_j$  are identical. In this case, the relaxation Hamiltonian relative to the two spins,  $\mathcal{H}'_i + \mathcal{H}'_j = -\gamma\hbar\mathbf{h}_i(t) \cdot (\mathbf{I}_i + \mathbf{I}_j)$  commutes with  $\mathbf{I}_i \cdot \mathbf{I}_j$  and it is sufficient to take in  $\mathcal{H}_d$  only the term  $I_{iz}I_{jz}$ . We find, using the formulas (A5),

$$\frac{\partial}{\partial t} \langle I_{iz}I_{jz} \rangle = -W_{1i} [2 \langle I_{iz}I_{jz} \rangle - \langle I_{ix}I_{jx} + I_{iy}I_{jy} \rangle], \quad (\text{A9})$$

where  $W_{1i}$  is the value given by (32) and (A7).

By performing the trace calculations with the density matrix  $\sigma$  given by (5), we find

$$\frac{\partial}{\partial t} \langle \mathcal{H}_d \rangle = -\frac{3}{T_1} \langle \mathcal{H}_d \rangle, \quad (\text{A10})$$

where  $T_1$  is given by (33).

(2) The fields  $\mathbf{h}_i(t)$  and  $\mathbf{h}_j(t)$  at the two spins are completely uncorrelated, i.e.,

$$\langle h_{ix}(t) h_{jz}(t) \rangle_{\text{av}} = \langle h_{iy} h_{jy} \rangle_{\text{av}} = \langle h_{iz} h_{jz} \rangle_{\text{av}} = 0. \quad (\text{57})$$

In this case, we find

$$\begin{aligned} \frac{\partial}{\partial t} \langle I_{iz}I_{jz} \rangle &= -(W_{1i} + W_{1j}) \langle I_{iz}I_{jz} \rangle, \\ \frac{\partial}{\partial t} \langle I_{ix}I_{jz} \rangle &= -(W_{2i} + W_{2j}) \langle I_{ix}I_{jz} \rangle, \\ \frac{\partial}{\partial t} \langle I_{iy}I_{jy} \rangle &= -(W_{2i} + W_{2j}) \langle I_{iy}I_{jy} \rangle. \end{aligned} \quad (\text{A11})$$

Taking the trace with the density matrix (5), we obtain

$$\frac{\partial}{\partial t} \langle \mathcal{H}_d \rangle = -\frac{2}{3} (2/T_1 + 1/T_2) \langle \mathcal{H}_d \rangle, \quad (\text{A12})$$

where  $T_1$  and  $T_2$  are again given by (33).

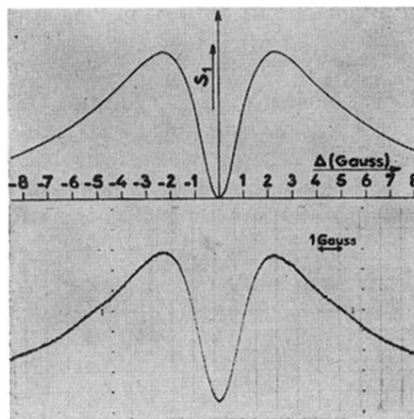


FIG. 3. Signal  $S_1$  obtained in the "slow scan-fast modulation" condition with lock-in detection. ( $\text{CaF}_2$ ,  $[111]$  direction.)  $H_1 = 1.06$  G. Top: Theoretical curve [Eq. (37)] with  $T_1/T_2 = 9$  and  $\alpha = 5$ . The signal is in arbitrary units. Bottom: Actual recording obtained at 2 Mc/sec, with an integrating time of 0.65 sec,  $H_m = 0.25$  G,  $\Omega/2\pi = 20$  cps. Scanning speed: 0.215 G per min.

FIG. 4. Signal  $S_1$  obtained at 16 Mc/sec in the same sample as Fig. 3 (bottom).  $H_1=0.52$  G,  $H_m=0.13$  G. Notice "bumps" in the curve, which indicate that  $T_1/T_2$  varies with the distance from resonance  $\Delta$ .

