

Thermodynamics of Spin Systems in Solids*

J. JEENER, H. EISENDRATH, AND R. VAN STEENWINKEL†

Université Libre de Bruxelles, Bruxelles, Belgium

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Quasiequilibrium states of the spin system in a solid are described in terms of one "Zeeman" temperature for each spin species plus one "dipole-dipole" temperature, T_D . Energy and entropy are calculated and used to predict the steady state of processes such as cross relaxation. It is predicted and demonstrated by an experiment on the nuclear spins in LiF that the state of the "dipole-dipole" system has a strong influence on such steady states. Continuous wave (cw) and pulse spectroscopy are discussed for systems with low T_D . Techniques are proposed (and have been used) to measure T_D and one Zeeman temperature simultaneously, using coherent pulse instrumentation, and for preparing a state of low T_D in a large magnetic field by complete adiabatic demagnetization followed by sudden magnetization. A density matrix formalism is proposed for the description of quasiequilibrium situations in the case of "spins" with unequally spaced energy levels. Finally the influence of the "nonsecular" part of the spin-spin Hamiltonian on the quasiequilibrium states is estimated by a perturbation calculation, and the resulting description includes the cases of low- or zero-magnetic field and partly or completely overlapping absorption lines.

1. INTRODUCTION

THERMODYNAMICS is a very powerful technique for correlating various properties of complex systems, because its use does not depend upon a detailed knowledge of the structure of the system, or of the exact mechanism of the rate processes involved.¹ The second law of thermodynamics has been used by a number of authors²⁻⁴ to obtain quantitative information about reversible processes in spin systems, such as slow magnetization or demagnetization. In the present paper, we use the second law to discuss irreversible spin-spin processes (spin-lattice relaxation will be neglected for simplicity): These always take place in the direction of increasing entropy and the steady state corresponds to a maximum of entropy. Our method is quite analogous to ordinary chemical thermodynamics.⁵

We shall first consider a spin system in a large magnetic field, in which each spin species gives rise to a single ordinary NMR absorption line, the width of which is mainly due to dipole-dipole couplings. (A more general case will be discussed in Sec. 7.) Following Anderson and Hartmann⁶ and Provotorov,^{7,8} such a

spin system can be described as a superposition of a number of subsystems: One "Zeeman" subsystem for each spin species and one "dipole-dipole" subsystem. A weak applied rf field can be considered as an additional subsystem. The coupling inside each subsystem is strong whereas the couplings between subsystems are weak. As a consequence, the subsystems reach internal thermal equilibrium independently of each other and one can ascribe a temperature, an energy, an entropy . . . , to each of them (Sec. 2). Further theoretical discussion and justification of these ideas is given by J. Philippot in the preceding paper.⁹

The usual prediction of statistical mechanics that the temperatures of interacting subsystems become equal in equilibrium is a direct consequence of the hypothesis that the total energy is the only analytic constant of the motion. In the case of spin systems, this hypothesis is always valid for two interacting subsystems, but it very often breaks down when spin processes couple together three or more subsystems because of the very peculiar property of many spin processes of causing changes in the energies of the subsystems which are proportional to each other with fixed proportionality constants. In this latter case, a steady state can result in which the temperatures of the various subsystems are different from each other, as shown by the following simplified example. Consider three different spin species a, b, c , in a solid subjected to a large magnetic field, such that the following relation holds between their Larmor frequencies: $\omega^a = \omega^b + \omega^c$. The cross relaxation process¹⁰ in which one a -spin flips down while one b -spin and one c -spin flip up conserves energy exactly, and will thus have a fast rate. If this process alone is taken into account, the changes of the Zeeman energies E^a, E^b ,

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† Present address: Euratom, Ispra, Italy.

¹ The reader will find an exposition of most of the subject of nuclear magnetism, as well as references, in A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961); and in C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

² A. G. Redfield, *Phys. Rev.* **98**, 1787 (1955).

³ A. Abragam and W. G. Proctor, *Phys. Rev.* **109**, 1441 (1958).

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

⁵ See for instance, I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans Green and Company, Inc., New York, 1954).

⁶ A. G. Anderson and S. R. Hartmann, *Phys. Rev.* **128**, 2023 (1962). See also, A. G. Anderson and S. R. Hartmann, *Bull. Am. Phys. Soc.* **6**, 507 (1961); S. R. Hartmann and A. G. Anderson, *ibid.* **6**, 507 (1961); S. R. Hartmann and A. G. Anderson, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963), p. 157.

⁷ B. N. Provotorov, *Zh. Eksperim. i Teor. Fiz.* **41**, 1582 (1961)

[translation: *Soviet Phys.—JETP* **14**, 1126 (1962)]. See also B. N. Provotorov, *Phys. Rev.* **128**, 75 (1962).

⁸ B. N. Provotorov, *Zh. Eksperim. i Teor. Fiz.* **42**, 882 (1962) [translation: *Soviet Phys.—JETP* **15**, 611 (1962)].

⁹ J. Philippot, preceding paper, *Phys. Rev.* **133**, A471 (1964).

¹⁰ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.* **114**, 445 (1959).

and E^c after ξ "processes" will be $\Delta E^a = \xi \hbar \omega^a$, $\Delta E^b = -\xi \hbar \omega^b$, and $\Delta E^c = -\xi \hbar \omega^c$, and the two following independent quantities will be constants of the motion: $E^a + E^b + E^c$ (total energy) and $E^a/\omega^a + E^b/\omega^b$. Starting with $E^a = E^b = 0$ and $E^c \neq 0$, cross relaxation will lead to a state in which E^a and E^b , and also the corresponding Zeeman temperatures, have opposite signs.

In Secs. 3 and 4, two examples in which the dipole-dipole subsystem plays the role of the c system in the above example, are worked out in detail by the proposed thermodynamical method: the effects of a weak rf irradiation and cross relaxation. The results are the same as those of corresponding statistical mechanical calculations.⁶⁻⁸ Experiments on cross relaxation in LiF are reported which demonstrate the existence of some of the predicted effects. Some similar unexpected results of Goldburg¹¹ on cross relaxation in quadrupolar systems can be interpreted in the same way, as will be shown in a forthcoming paper by one of us (J.J.). All these experimental results very clearly show that cross relaxation is, in fact, as much influenced by the properties and state of the dipole-dipole subsystem as by those of the Zeeman subsystems.

In Secs. 5 and 6, a number of problems are discussed which have arisen while performing the experiments including preparation of a spin system with a low dipole-dipole temperature and properties of the free precession signals of such systems.

In Sec. 7, we discuss the case of spins with unequally spaced energy levels by means of density matrix techniques and show that the dipole-dipole temperature still is a fundamental concept in this case, whereas the concept of Zeeman temperatures loses much of its importance and should be replaced by that of the populations of the various isolated spin energy levels. The spin entropy can be computed easily, and used to discuss irreversible processes exactly as in the case of spins with equally spaced energy levels. The formalism which is proposed applies to any situation in which large numbers of equivalent "microscopic systems" are connected together by a weak, time-independent coupling.

In Sec. 8, we investigate the influence of the non-secular part of the dipole-dipole Hamiltonian on the thermodynamic properties of spin systems. A modified density matrix is proposed for the description of spin systems in quasiequilibrium, which is satisfactory in the whole range of magnetic fields (from zero to very large), and clarifies the quantitative discussion of processes such as adiabatic magnetization or demagnetization, as well as cross relaxation.

2. SPIN THERMODYNAMICS (SIMPLE CASES)

In this section, we discuss some thermodynamic properties of the spin system in a rigid lattice (solid) containing one or many spin species, subjected to a

large constant magnetic field \mathbf{H}_0 , in the case where the ordinary NMR spectrum of the system consists of a single, well isolated line for each spin species, spin-spin couplings alone being responsible for the width of these lines.

The spin Hamiltonian can be written as

$$\mathcal{H} = \sum_a \mathcal{H}_0^a + \mathcal{H}' + \mathcal{H}'', \quad (2.1)$$

where

$$\mathcal{H}_0^a = -\hbar \gamma^a \sum_n \mathbf{H}_0 \cdot \mathbf{I}^{an}$$

(we chose the z axis in the direction of \mathbf{H}_0). \mathcal{H}' is the part of the coupling between spins which commutes with $\sum_a \mathcal{H}_0^a$ (Van Vleck's¹² truncated spin-spin Hamiltonian: terms of the type $I_z I_z'$ between all spins and terms of the type $I_+ I_-'$ between like spins only), $\mathcal{H}_D = \mathcal{H}' + \mathcal{H}''$, where \mathcal{H}_D is the total spin-spin coupling. Superscripts are used to indicate spin species and to label the various spins of each kind, and subscripts to indicate "components" ($x, y, z, +, -$) of \mathbf{I} vectors and miscellaneous information.

It has been shown experimentally^{3,6} that, in the case of large H_0 and negligible rf magnetic fields, the energies corresponding to the various \mathcal{H}_0^a and to \mathcal{H}' are well insulated from one another. Following Anderson and Hartmann⁶ and Provotorov,^{7,8} we shall assume that the spin system can be described in terms of one spin temperature for each of the subsystems whose energy is an approximate constant of the motion and we shall thus write the density matrix ρ for the total spin system as¹³

$$\rho = \frac{1}{\mathcal{O}'} \exp \left[\left(\frac{-\mathcal{H}'}{kT_D} \right) + \sum_a \left(\frac{-\mathcal{H}_0^a}{kT^a} \right) \right], \quad (2.2)$$

$$\simeq \frac{1}{\mathcal{O}'} \left[1 - \left(\frac{\mathcal{H}'}{kT_D} \right) - \sum_a \left(\frac{\mathcal{H}_0^a}{kT^a} \right) \right],$$

where the T 's are the spin temperatures and \mathcal{O} and \mathcal{O}' are normalization constants. The term \mathcal{H}'' of (2.1) will produce weak couplings between the subsystems, resulting in slow changes in the various temperatures. Each of the subsystems being well isolated from the others and in internal equilibrium, the state of the complete system depends only upon a few spin temperatures; and properties such as energy, entropy, susceptibility, \dots , can be expressed as sums of independent contributions from each subsystem.

Treating energy in this way we obtain, using the linearized form of (2.2)

$$E = \text{Tr} \{ \rho \mathcal{H} \} = E_D + \sum_a E^a, \quad (2.3)$$

¹² J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹³ We only consider the case of "high temperatures" and use the first-order approximation in $1/T$ of ρ in the calculation of all quantities which are of the first order in $1/T$, such as energy, magnetization, susceptibilities \dots . Although this seems to be a wild approximation, even at extremely high temperature, one can easily show that the relative error involved is only of the order of $\hbar\omega/kT$ where ω is the dipole-dipole or Larmor frequency and T the dipole-dipole or Zeeman temperature.

¹¹ Walter I. Goldburg, Phys. Rev. **115**, 48 (1959).

where

$$E^a = \text{Tr}\{\rho \mathcal{H}_0^a\} = \hbar \gamma^a H_0 n^a = -\hbar \omega^a n^a \\ = -(1/kT^a)(H_0 \gamma^a \hbar)^2 \frac{1}{3} I^a (I^a + 1) N^a, \quad (2.4)$$

and

$$E_D = \text{Tr}\{\rho \mathcal{H}'\} = \hbar \langle \gamma \rangle \bar{H}_L n_D = -\hbar \omega_D n_D \\ = -(1/kT_D)(\bar{H}_L \langle \gamma \rangle \hbar)^2 \sum_a \left\{ \frac{1}{3} I^a (I^a + 1) N^a \right\}, \quad (2.5)$$

where

$$\bar{H}_L^2 = \text{Tr}\{\mathcal{H}'^2\} / \text{Tr}\left\{ \left(\sum_{a,n} \hbar \gamma^a I_z^{an} \right)^2 \right\}, \quad (2.6)$$

$$\langle \gamma \rangle^2 = \sum_a \left\{ \frac{1}{3} I^a (I^a + 1) (\gamma^a)^2 N^a \right\} / \\ \sum_a \left\{ \frac{1}{3} I^a (I^a + 1) N^a \right\}, \quad (2.7)$$

$$n^a = (1/kT^a) H_0 \gamma^a \hbar \frac{1}{3} I^a (I^a + 1) N^a, \quad (2.8)$$

$$n_D = (1/kT_D) \bar{H}_L \langle \gamma \rangle \hbar \sum_a \left\{ \frac{1}{3} I^a (I^a + 1) N^a \right\}. \quad (2.9)$$

N^a is the number of nuclei of type a , I^a their spin and $\omega^a/2\pi$ their Larmor frequency, E^a and E_D are the energies of the a and dipole-dipole subsystems. The local field \bar{H}_L introduced here is a function of the orientation of \mathbf{H}_0 with respect to the crystalline axis, and is somewhat smaller than the local field H_L introduced by Abragam and Proctor,³ which would be given by (2.6) after substituting the complete dipole-dipole Hamiltonian \mathcal{H}_D for its secular part \mathcal{H}' . The numbers n^a have a simple meaning: $(\gamma^a/|\gamma^a|)n^a$ photons at the Larmor frequency of a must be absorbed to bring the energy E^a to zero (saturation of the a magnetization). The auxiliary quantities ω_D , n_D , $\langle \gamma \rangle$ and \bar{H}_L ¹⁴ used in the discussion of the dipole-dipole system have been chosen in such a way that they play very much the same role as their counterparts ω^a , n^a , γ^a , and H_0 for the Zeeman systems.

If we now consider an idealized experiment, performed in a constant magnetic field, where we reversibly change the energy E of one of the subsystems by means of a thermal contact with a thermostat at a temperature T very close to that of the subsystem, we can write the change of its entropy S as

$$dS = (1/T)dE. \quad (2.10)$$

In the cases of interest here, we have relations of the type

$$E = -\alpha/T, \quad (2.11)$$

so that the entropy corresponding to a given energy is given by

$$S = (S)_{E=0} - \frac{1}{2} E^2 / \alpha. \quad (2.12)$$

We are only interested in changes in entropy, so that the terms $(S)_{E=0}$ will play no role in the calculations and we shall put them equal to zero for simplicity. (As a result of this, the "entropies" which are discussed below are always negative.) Combining Eqs. (2.4) to

(2.9) with (2.12) one obtains for the total spin entropy S

$$S = S_D + \sum_a S^a, \quad (2.13)$$

where

$$S^a = -(n^a)^2 \frac{1}{2} k / \frac{1}{3} I^a (I^a + 1) N^a = -(n^a)^2 \sigma^a$$

and

$$S_D = -(n_D)^2 \frac{1}{2} k / \frac{1}{3} \sum_a I^a (I^a + 1) N^a = -(n_D)^2 \sigma_D. \quad (2.14)$$

S^a and S_D are the entropies of the a and dipole-dipole subsystems and the σ 's, defined by (2.14), are introduced in order to simplify subsequent formulas.

3. EFFECTS OF A PROLONGED, WEAK, rf IRRADIATION

Provotorov⁷ and Anderson and Hartmann⁶ have already discussed the effects of prolonged irradiation with a weak rf field at a frequency close to the Larmor frequency of one of the spin species, in the absence of spin-lattice relaxation. As a first illustration of the use of the techniques outlined above, we shall rederive their result.

If the intensity of the rf field is low enough¹⁵ we can consider the rf field as a subsystem which is weakly coupled to the spin subsystems and whose only effect is to slowly change the spin temperatures. The "temperatures" characterizing the rf fields used in such experiments being extremely high, the changes in the entropy of the rf subsystem will be extremely small and we shall neglect them in the calculation.

The spin process involved can be described in the following way: One photon of energy $\hbar\omega$ is absorbed (ω is close to ω^1), one spin 1 flips ($\Delta n^1 = -1$), and the balance of energy goes into the dipole-dipole system:

$$-\hbar\omega + \hbar\omega^1 - \hbar\omega_D \Delta n_D = 0. \quad (3.1)$$

Starting from an initial situation described by $(n^1)_0$ and $(n_D)_0$, after absorption of ξ photons, the situation will be

$$n^1 = (n^1)_0 - \xi, \\ n_D = (n_D)_0 + \xi(\omega^1 - \omega) / \omega_D. \quad (3.2)$$

In the steady state of irradiation, the spin entropy

$$S = -(n^1)^2 \sigma^1 - (n_D)^2 \sigma_D - \dots \quad (3.3)$$

considered as a function of ξ , has its maximum value and the n 's are given by

$$(n^1)_s = \left\{ (n^1)_0 + \frac{\omega_D}{\omega^1 - \omega} (n_D)_0 \right\} \frac{(\omega^1 - \omega)^2 \sigma_D}{\sigma^1 \omega_D^2 + (\omega^1 - \omega)^2 \sigma_D}, \quad (3.4)$$

$$(n_D)_s = (n^1)_s \left\{ \sigma^1 \omega_D / \sigma_D (\omega^1 - \omega) \right\}. \quad (3.5)$$

The corresponding spin temperatures, which are usually very different from one another, are exactly those predicted by Anderson and Hartmann⁶ and Provotorov.⁷

¹⁴ For definiteness, \bar{H}_L and $\langle \gamma \rangle$ are chosen to be positive quantities.

¹⁵ The condition for this, when ω is close to one of the ω^a is discussed in Refs. 6 and 7. The case of irradiations at frequencies which induce multiple spin transitions will be discussed in a future paper.

Let us now consider the kinetics of this weak rf irradiation. As usual, the rate of absorption of photons, $d\xi/dt$, is proportional to the imaginary component $\chi''(\omega)$ of the rf nuclear susceptibility $\chi(\omega)$ which itself consists of two terms, $\chi_Z(\omega)$ and $\chi_D(\omega)$, originating from the terms in $\mathcal{H}C_0^1$ and in $\mathcal{H}C'$ in the density matrix ρ (2.2):

$$\frac{d\xi}{dt} = K\chi''(\omega) = K \left\{ n^1 \left(\frac{\chi_Z''}{n^1} \right) + n_D \left(\frac{\chi_D''}{n_D} \right) \right\}. \quad (3.6)$$

K is a constant proportional to the square of the rf field, $\chi_Z(\omega)$ is the susceptibility of a system characterized by $n^1 \neq 0$, $n_D = 0$ (i.e., the case of ordinary NMR absorption experiments in large magnetic fields) and $\chi_D(\omega)$ corresponds in the same way to the case $n^1 = 0$, $n_D \neq 0$. The quantities (χ''/n) appearing in (3.6) are independent of the state of the spin system because both χ'' and n are inversely proportional to the corresponding temperature. In the steady state of rf irradiation, $d\xi/dt = 0$ and the ratio n_D/n^1 is given by (3.5). This implies that, in all cases, one has

$$\begin{aligned} \chi_D''(\omega) &= \frac{n_D \sigma_D}{n^1 \sigma^1} \cdot \frac{(\omega - \omega^1)}{\omega_D} \chi_Z''(\omega) \\ &= \frac{T^1}{T_D} \cdot \frac{\bar{H}_L \langle \gamma \rangle}{H_0 \gamma^1} \cdot \frac{(\omega - \omega^1)}{\omega_D} \chi_Z''(\omega), \end{aligned} \quad (3.7)$$

which is just the relation already derived by Anderson and Hartmann⁶ between the rf susceptibilities $\chi''(\omega)$ of systems in which the order entirely lies in the dipole-dipole or in a Zeeman subsystem.

If we now introduce the values (3.2) of the n 's in (3.6), we obtain a differential equation for ξ , the solution of which approaches the steady-state value exponentially with a time constant t^* given by

$$\frac{1}{t^*} = K \frac{\chi_Z''(\omega)}{n^1} \left\{ 1 + \frac{\sigma_D}{\sigma^1} \left(\frac{\omega - \omega^1}{\omega_D} \right)^2 \right\}, \quad (3.8)$$

where the factor in the curly bracket represents the correction due to the finite "specific heat" of the dipole-dipole system.

The generalization of the above method to more complex situations, such as one photon—many spins processes for instance,¹⁶ is straightforward.

4. CROSS RELAXATION

Cross relaxation is a process in which two or more spins make simultaneous flips in such a way as to conserve Zeeman energy almost exactly, the energy balance being absorbed by the dipole-dipole subsystem. In the quantitative discussions of cross relaxation given

¹⁶ A. Abragam and W. G. Proctor, *Compt. Rend.* **246**, 2253 (1958); J. Philippot, R. Deltour, and J. Jeener, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963), p. 563.

TABLE I. Some properties of the nuclear spin system in a LiF crystal.

The superscripts are the mass numbers of the relevant nuclei (F^{19} , Li^7 , Li^6) and the p 's their natural abundances. $2N$ is the total number of nuclei in the crystal. The other symbols are defined in the main text. In the calculation of the local fields, the lattice constant of LiF has been taken as 4.01 Å and lattice vibrations have been ignored. The γ 's are given in $\text{sec}^{-1} \text{G}^{-1}$ and the σ 's in units of k/N .

$I^{19} = \frac{1}{2}$	$p^{19} = 1.0$	$\sigma^{19} = 2.0$	$\gamma^{19} = 2\pi \times 4005.5$
$I^7 = \frac{3}{2}$	$p^7 = 0.926$	$\sigma^7 = 0.432$	$\gamma^7 = 2\pi \times 1654.7$
$I^6 = 1$	$p^6 = 0.074$	$\sigma^6 = 10.1$	$\gamma^6 = 2\pi \times 626.5$
Dipole-dipole		$\sigma_D = 0.343$	$\langle \gamma \rangle = 2\pi \times 2220$
Cross-relaxation			$\gamma^{19} - 2\gamma^7 = \gamma_{\text{CR}} = 2\pi \times 696.1$
			$\gamma^{19} - 2\gamma^7 - \gamma^6 = 2\pi \times 69.6$
Local fields		$H_L = 7.77 \text{ G}$	
H_0 along [100]:	$\bar{H}_L = 5.76 \text{ G}$		$\omega_D = 2\pi \times 12800 \text{ sec}^{-1}$
H_0 along [110]:	$\bar{H}_L = 3.73 \text{ G}$		$\omega_D = 2\pi \times 8300 \text{ sec}^{-1}$
H_0 along [111]:	$\bar{H}_L = 2.74 \text{ G}$		$\omega_D = 2\pi \times 6100 \text{ sec}^{-1}$

by Bloembergen and his co-workers,^{10,17} little attention has been paid to the influence of the dipole-dipole temperature on the rate and steady state of the process. Provotorov⁸ has recently drawn attention to the fact that the dipole-dipole temperature should be taken into account in discussing cross relaxation. We shall now see how thermodynamics can be used to do this. For simplicity, we shall neglect spin-lattice relaxation and discuss the phenomena in the crystal LiF¹⁸ (see Table I) in which cross relaxation times have already been studied in detail by Pershan,¹⁷ and for which further experimental results are reported in this paper.

In the cross relaxation mechanism proposed by Bloembergen and Pershan,^{10,17} one F^{19} and two Li^7 spin-flips take place simultaneously. (A possible process involving Li^6 will be mentioned later.) Starting from the initial "populations" $(n^{19})_0$, $(n^7)_0$, and $(n_D)_0$, after ξ such processes, the "populations" are given by¹⁹

$$\begin{aligned} n^{19} &= (n^{19})_0 + \xi, \\ n^7 &= (n^7)_0 - 2\xi, \\ n_D &= (n_D)_0 - (H_0 \gamma_{\text{CR}} / \bar{H}_L \langle \gamma \rangle) \xi, \end{aligned} \quad (4.1)$$

where

$$\gamma_{\text{CR}} = \gamma^{19} - 2\gamma^7.$$

Introducing these values of the n 's (4.1) in the formulas (2.13), (2.14) for the total spin entropy S , we find the following expression for the steady-state value ξ_S of ξ , for which S is a maximum:

$$\xi_S = \frac{-\sigma^{19} (n^{19})_0 + 2\sigma^7 (n^7)_0 + (H_0 \gamma_{\text{CR}} / \bar{H}_L \langle \gamma \rangle) \sigma_D (n_D)_0}{\sigma^{19} + 4\sigma^7 + (H_0 \gamma_{\text{CR}} / \bar{H}_L \langle \gamma \rangle)^2 \sigma_D}. \quad (4.2)$$

¹⁷ P. S. Pershan, *Phys. Rev.* **117**, 109 (1960).

¹⁸ For simplicity, we neglect any quadrupolar splitting arising from imperfections in the cubic lattice of LiF.

¹⁹ The superscripts indicating the nuclear species are the mass numbers of the relevant nuclei: F^{19} , Li^7 , Li^6 .

Combining (4.1) and (4.2) will give us the steady-state values of the n 's. The results obtained here are equivalent to Pershan's in the approximation where one neglects dipole-dipole effects (i.e., $\sigma_D=0$) but examination of the numerical values of the quantities appearing in (4.2) in the case of a typical cross relaxation experiment shows that this approximation is a very rough one.

The effect of the dipole-dipole temperature on the kinetics of cross relaxation can be discussed by the method which has been used above to obtain Eq. (3.8). It gives rise to corrections to the classical relation^{10,17} between transition probabilities and observed relaxation times, a result already derived by Provotorov⁸ by another method.

In order to demonstrate the effects predicted by Eqs. (4.1) and (4.2), we have performed two experiments on a LiF crystal,²⁰ the results of which are shown in Figs. 1 and 2. Each experiment starts with the spin system close to thermal equilibrium with the lattice, in a large magnetic field, and is completed in a time short compared to the spin-lattice relaxation times. The spin system is prepared in a known state, in a magnetic field large enough to prevent cross relaxation (at least 150 G). The field is then lowered for a known time (0.2 sec) to the value H_{CR} and raised again to a large value where n^{19} and n_D are simultaneously measured by a pulse method (see Sec. 6). If H_{CR} is larger than 120 G, cross relaxation does not take place and one observes the prepared state unchanged; if H_{CR} is lower than 60 G, other processes "short circuit" the one F^{19} -two Li^7 mechanism and tend to equalize all spin temperatures. In the range of H_{CR} of interest here

²⁰ Notes about the experiments: The (0.7 cm³) LiF crystal, chosen by Harshaw Chemical Company for low paramagnetic contamination and absence of X-irradiation had a T_1 of 7 min for F^{19} and 15 min for Li^7 in a field of 7156 G. Before each experiment, the crystal was prepared in a standard state by a stay of 1 min in the earth field followed by 20 min in 7156 G. The timing of the experiments was approximately as follows: After saturation of F^{19} (experiment B only) the crystal, rf coil, and its BNC plug were moved with compressed air, in less than 2 sec, from the Varian magnet (7156 G) through a hexagonal "field pipe" (with the "transfer field" H_{TR} of approximately 230 G ON for experiment B only) to the system of coils producing the "sudden" and "cross relaxation" fields (in experiments A and C, these fields are turned ON automatically by the impact of the sample in the coils). In experiments A and B, the field is pulsed down to H_{CR} for 0.2 sec by turning the current in the "sudden" field coil OFF and ON (switching time: about 50 μ sec). Approximately 5 sec after the first transfer, the "transfer field" is turned ON and the sample is blown back to the 7156-G region where it is subjected to a somewhat-less-than-90° pulse at the NMR frequency of F^{19} (lasting 1.5 μ sec). Nine microseconds later, the amplifier has recovered and the F^{19} free-precession signal can be observed, processed by a pair of orthogonal phase sensitive detectors, the two components displayed on a double-beam oscilloscope (Tektronix 551) and photographed with a Polaroid film camera. The Zeeman and dipole-dipole signal amplitudes were read from the pictures by planimetry. The weak magnetic fields H_{CR} , H_{SM} and H_{TR} were measured with a flip-coil fluxmeter, by comparison with the 7156 G field (measured by NMR). No attempt was made to eliminate the approximately 0.6 G "earth's field." No correction has been applied to the experimental results to take into account spin lattice relaxation, finite duration of the "sudden" magnetization or other imperfections and perturbations.

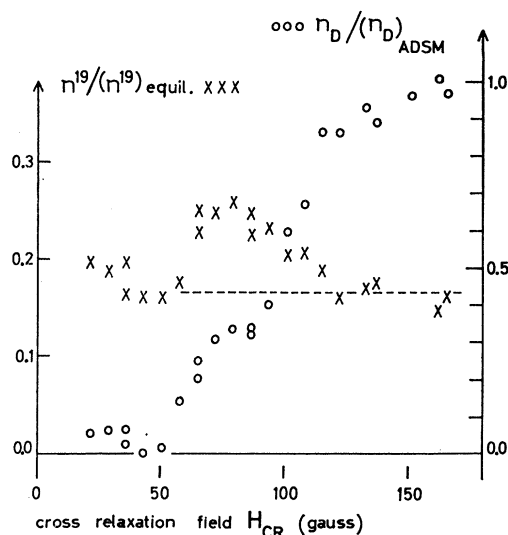


FIG. 1. Experiment A: Cross relaxation in LiF driven by a large initial dipole-dipole entropy (footnote 20) (H_{CR} and H_{SM} were both in a (0-1-1) plane, 15° away from the [100] direction). n_D and n^{19} are the degrees of dipole-dipole and Zeeman order (proportional to the corresponding energies) in the LiF crystal after a stay of 0.2 sec in the low magnetic field H_{CR} , ($n^{19})_{equil}$ corresponds to the thermal equilibrium situation in the large magnetic field H_0 (7156 G) and $(n_D)_{ADSM}$ is the degree of dipole-dipole order obtained by complete adiabatic demagnetization from (quasi-)equilibrium in H_0 (see footnote 20) followed by application of a magnetic field H_{SM} of approximately 150 G in less than 1.5 μ sec [no theoretical curve is shown here because we have not measured $(n^7)_0$ in this experiment].

(70 to 90 G), the cross relaxation time is short compared with 0.2 sec and one should observe the steady state given by (4.1) and (4.2).

In experiment A (Fig. 1), the system is prepared by complete adiabatic demagnetization followed by sudden magnetization (ADSM, see Sec. 5) in a state of large positive $(n_D)_0$ and negligible $(n^{19})_0$ and $(n^7)_0$. Cross relaxation is then "driven" by the dipole-dipole system and results in a decrease of n_D together with the build up of a positive n^{19} and a negative n^7 (the resulting nuclear magnetizations are large for each spin species but their sum is small).

Experiment B (Fig. 2) is analogous to Pershan's experiment¹⁷: the system is prepared, by a succession of 90° pulses at the F^{19} NMR frequency, in a state of large positive $(n^7)_0$ and negligible $(n^{19})_0$ and $(n_D)_0$. Cross relaxation is then "driven" by the Li^7 Zeeman system and results in a decrease of n^7 together with the build up of a positive n^{19} and a negative n_D . A comparison between Pershan's results¹⁷ (a cross relaxation time of 0.2 sec in a field of about 66 G in the [100] direction) and the results shown on Fig. 2 suggest that the rate process studied by Pershan probably was the "short-circuit" mechanism, and not the simultaneous one F^{19} -two Li^7 flip.

Abraham has pointed out to us that the process in which one F^{19} flips up and two Li^7 plus one Li^6 flip down, conserves Zeeman energy ten times more exactly than

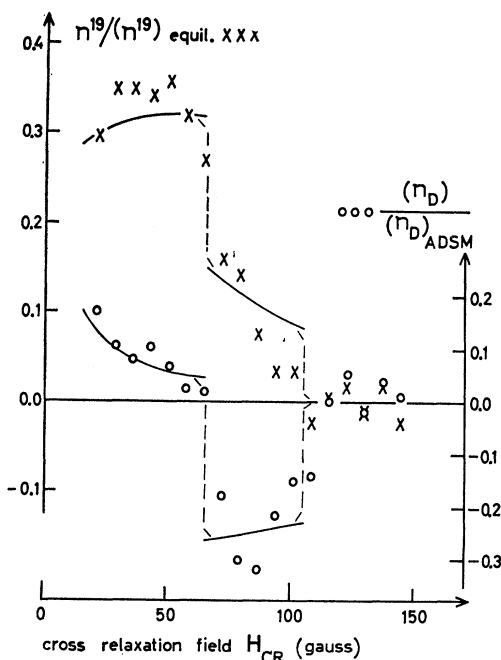


FIG. 2. Experiment B: Cross relaxation in LiF driven by a large initial Zeeman order of the Li⁷ system (footnote 20). (H_{CR} and H_{SM} were both in the [100] direction.) Symbols are explained in caption for Fig. 1. The curves shown are theoretical predictions [upper curves: $n^{19}/(n^{19})_{\text{equil}}$; lower curves: $n_D/(n_D)_{\text{ADSM}}$]. Between 105 and 65 G we have used formulas (4.1) and (4.2), corresponding to the one F¹⁹-two Li⁷ cross relaxation mechanism; between 65 and 20 G we have assumed equilization of all three spin temperatures. The initial condition used for the calculation was $(n^7)_0 = 0.73(n^7)_{\text{equil}}$, $(n^{19})_0 = (n_D)_0 = 0$.

Bloembergen and Pershan's process (see Table I). One thus expects the probabilities (or relaxation times) of the two processes to be of comparable magnitudes in magnetic fields which differ by a factor of 10, approximately, and the process suggested by Abragam should still be observable in fields of several hundred gauss. Due to the low natural abundance of Li⁶ (7.4%), this new process should not cause very large changes in the "populations" of Li⁷ and F¹⁹ in our experiments, and we shall not discuss its effects in this paper.

5. SUDDEN APPLICATION OF A LARGE MAGNETIC FIELD TO A SPIN SYSTEM

In some of the experiments described in this paper, we have prepared a spin system (the nuclear spins in a crystal of LiF) in a state of low dipole-dipole temperature and high Zeeman temperatures, starting with spins in thermal equilibrium in a large magnetic field, by adiabatic demagnetization to zero field followed by sudden application of a magnetic field H_0 large enough to isolate the dipole-dipole system from the Zeeman systems.²¹ A sufficient criterion for the necessary rate of increase of the field is that none of the spins should

precess more than a small (negligible) angle in the time τ between zero field and quasi-isolation (at a field qH_L ; $q \sim$ a few units) between dipole-dipole and Zeeman systems

$$\tau \ll 1/\gamma_{\text{max}} q H_L. \quad (5.1)$$

In the case of LiF, using γ^{19} for γ_{max} and the value of 30 G for qH_L ($q \sim 4$), value at which Pershan¹⁷ has observed cross relaxation times as long as ten milliseconds we obtain $1/\gamma_{\text{max}} q H_L = 13 \mu$ sec which is much longer than τ in our experimental conditions where a field H_0 of about 150 G is turned on in less than 1.5 μ sec.²²

Abragam and Proctor³ have shown that adiabatic demagnetization of a spin system, initially in thermal equilibrium at temperature T in a large field H , results in a system at a lower spin temperature T_S , described by the following density matrix

$$\rho_0 = (1/\mathcal{P}) \{1 - (\mathcal{C}' + \mathcal{C}'')/kT_S\}, \quad (5.2)$$

where $T_S = T(H_L/H)$. After the sudden magnetization to a field H_0 , at time $t=0$, the density matrix will begin with the initial value ρ_0 , but the Hamiltonian will have changed from $\mathcal{C}' + \mathcal{C}''$ to \mathcal{C} [formula (2.1)], so that the equation of motion for $\rho(t)$ after magnetization is:

$$i\hbar \partial \rho(t) / \partial t = [\mathcal{C}, \rho(t)], \quad \text{with } \rho(0) = \rho_0. \quad (5.3)$$

In order to simplify the discussion of the solutions of this equation we shall use an interaction representation in which each new operator \tilde{A} will be the following function of the corresponding operator A :

$$\tilde{A} = U^{-1} A U, \quad (5.4)$$

where

$$U = \exp\{-it(\mathcal{C}' + \sum_a \mathcal{C}_0^a)/\hbar\}.$$

In this representation, Eq. (5.3) goes over into

$$i\hbar \partial \tilde{\rho}(t) / \partial t = [\tilde{\mathcal{C}}''(t), \tilde{\rho}(t)], \quad \text{with } \tilde{\rho}(0) = \rho_0, \quad (5.5)$$

a formal solution of which is given by

$$\tilde{\rho}(t) = M \rho_0 M^{-1}, \quad (5.6)$$

where

$$M = \exp\left\{-\left(i/\hbar\right) \int_0^t \tilde{\mathcal{C}}''(t') dt'\right\}.$$

$\tilde{\mathcal{C}}''(t)$ is a sum of terms which depend on t through factors $\exp(i\omega t)$, the values of ω being distributed with a width of the order of ω_D (the "dipole-dipole frequency") around the sums and differences of the Larmor frequencies of pairs of nuclei (the value zero of the difference is excluded). As a result, the time integral of $\tilde{\mathcal{C}}''/\hbar$ will be a small oscillating quantity, of order of magnitude H_L/H_0 , and a series expansion of M in

²² This is achieved without the use of high-power equipment by first passing a current of about 2 A for a few milliseconds through an auxiliary inductance and a well-insulated high-current penthode (Philips E130L), and then forcing part of this current to flow through the coil around the sample by suddenly biasing the penthode beyond cutoff.

²¹ Related experiments are reported by R. L. Strombotne and E. L. Hahn, Bull. Am. Phys. Soc. 6, 508 (1961).

powers of H_L/H_0 will lead to a convenient classification of the various possible phenomena

$$M = 1 + (H_L/H_0)M_1 + \dots \quad (5.7)$$

In the present paper, we only consider the case of H_0 much larger than H_L , and limit our discussion to times t not much longer than $T_2 \sim 1/\omega_D$ (i.e., processes which become very slow for large H_0 will be neglected), so that only terms of order 1 and (H_L/H_0) will be of importance in the discussion of the density matrix after sudden magnetization. Combining Eqs. (5.2), (5.4), (5.5), (5.6), and (5.7), we can write these terms as

$$\begin{aligned} \rho(t) = (1/\mathcal{P})[& 1 - (1/kT_s)\{\mathcal{F}' & (a) \\ & + \mathcal{F}''(-t) & (b) \\ & + (H_L/H_0)U[M_1, \mathcal{F}']U^{-1} & (c) \\ & + (H_L/H_0)U[M_1, \mathcal{F}'']U^{-1} & (d) \\ & + \dots \}]. \end{aligned} \quad (5.8)$$

As a very first approximation, we can neglect terms (c) and (d) of (5.8) because they contain the small factor (H_L/H_0) and term (b) because it oscillates around zero, and we are left with term (a) which describes a situation with a dipole-dipole temperature equal to T_s , the initial spin temperature in zero field, and no nuclear magnetization (infinite Zeeman temperatures).

Let us now consider the behavior of energy in this problem. The total magnetic moment being zero in zero field, the sudden magnetization will not change the spin energy, which can be computed very easily in zero field as

$$E = \text{Tr}\{\rho_0 \mathcal{F}\} = - (1/kT_s)(1/\mathcal{P})[\text{Tr}\{\mathcal{F}'^2\} + \text{Tr}\{\mathcal{F}''^2\}]. \quad (5.9)$$

In computing the energy after sudden magnetization, using (5.8) for ρ , one must not forget that the Hamiltonian now contains a term \mathcal{F}_0 which is the product of H_0 with the nuclear magnetization, so that term (d) of (5.8), which describes a net nuclear magnetization will give rise to a contribution of order 1 (and not H_L/H_0) to the energy. For simplicity, we pursue the discussion in the case of a single magnetic ingredient (of Larmor frequency ω_0 in the field H_0) and write \mathcal{F}'' as a sum of four operators

$$\mathcal{F}'' = \mathcal{F}''_{-2} + \mathcal{F}''_{-1} + \mathcal{F}''_{+1} + \mathcal{F}''_{+2}, \quad (5.10)$$

where the terms in $I_-I'_-$, $I_-I'_z$, $I_+I'_z$, and $I_+I'_+$ are respectively included in \mathcal{F}''_{-2} , \mathcal{F}''_{-1} , \mathcal{F}''_{+1} , and \mathcal{F}''_{+2} . The case of many spin ingredients can be treated in a similar way, and the results are straightforward generalizations of those given here. In the limit of times t short compared with T_2 , the small spread in frequency of the various terms of \mathcal{F}'' can be neglected, and the contributions of order 1 of the various terms of (5.8) to energy can be evaluated easily [the symbols (a),

(b), (d) in (5.11) correspond to those in (5.8)]:

$$\begin{aligned} E = \text{Tr}\{\rho(t)\mathcal{F}\} = & - (1/kT_s)(1/\mathcal{P})[\text{Tr}\{\mathcal{F}'^2\} & (a) \\ & + (\text{Tr}\{\mathcal{F}''_{+1} + \mathcal{F}''_{-1}\}^2) \cdot \cos\omega_0 t \\ & + \text{Tr}\{\mathcal{F}''_{+2} + \mathcal{F}''_{-2}\}^2 \cdot \cos 2\omega_0 t & (b) \\ & + (\text{Tr}\{\mathcal{F}''_{+1} + \mathcal{F}''_{-1}\}^2)(1 - \cos\omega_0 t) \\ & + \text{Tr}\{\mathcal{F}''_{+2} + \mathcal{F}''_{-2}\}^2(1 - \cos 2\omega_0 t) & (d) \\ & + \dots]. \end{aligned} \quad (5.11)$$

Expression (5.11), which obviously agrees with (5.9), shows that the total energy is independent of time, as it should be, and that part of this energy oscillates at frequencies ω_0 and $2\omega_0$ back and forth between the dipole-dipole energy associated with the nondiagonal terms $\mathcal{F}''_{+1} + \mathcal{F}''_{-1}$ and $\mathcal{F}''_{+2} + \mathcal{F}''_{-2}$ of ρ and the Zeeman energy associated with the longitudinal nuclear magnetization originating from $[M_1, \mathcal{F}']$. As time goes on, the various terms of \mathcal{F}'' and M_1 will progressively come out of phase with each other, and one expects that the amplitude of the oscillations of the longitudinal nuclear magnetization will decay to zero in times of the order of T_2 , in very much the same way as an ordinary free precession signal. After times longer than T_2 , the energy will consist of two comparable terms corresponding to a dipole-dipole temperature T_s and to a very high Zeeman temperature of the order of $(H_0/H_L)^2 T_s$.

This remark should not obscure the fact that, at times t of a few T_2 after the sudden magnetization, the density matrix is very far from being describable in terms of two spin temperatures, as can be seen easily by direct calculation. The way in which spin temperatures again become a good description of a spin system after a pulse experiment is still a very intriguing but unsolved problem.

The various methods which have been proposed for preparing a spin system in a state of low dipole-dipole temperature (this paper and Ref. 6) can be considered as methods for transferring negative entropy from the Zeeman subsystems to the dipole-dipole subsystem. Adiabatic demagnetization followed by sudden magnetization (ADSM) will not cause this transfer with the highest possible efficiency, because sudden magnetization is followed by an irreversible process which creates some entropy. One can easily show that the ratio of (negative) dipole-dipole entropy S_D created to (negative) zero field spin entropy destroyed in ADSM is equal to $(\bar{H}_L/H_L)^2$, and thus depends upon the orientation of H_0 relative to the crystal axes. Anderson and Hartmann's "adiabatic demagnetization in the rotating frame" (ADRF) being a reversible process will give a maximum efficiency. However, in systems containing many different spin species, the preparation of the lowest possible dipole-dipole temperature would require successive ADRF of each spin species.

Starting with a LiF crystal in thermal equilibrium in a large magnetic field, the techniques discussed above

will give the following (theoretical) value for the ratio of n_D (to which the magnitude of the observed dipole-dipole signal is proportional) to the maximum possible value $(n_D)_{\max}$:

Technique	$n_D/(n_D)_{\max}$
ADSM—in general	\bar{H}_L/H_L
— \mathbf{H}_0 along $[100]$	0.74
— \mathbf{H}_0 along $[110]$	0.48
— \mathbf{H}_0 along $[111]$	0.35
ADRF—of F^{19} only	0.75
—of Li^7 only	0.66
—of Li^7 and F^{19}	1.00

(5.12)

In order to check the above prediction that n_D obtained by ADSM is proportional to \bar{H}_L , we have performed experiment C in which the crystal of LiF, already used in experiments A and B of Sec. 4, was subjected to ADSM with the suddenly applied field \mathbf{H}_{SM} in various directions perpendicular to $[0-1-1]$ and n_D was then rapidly measured in a large magnetic field of constant orientation with respect to the crystal axes. The results of experiment C are shown on Fig. 3 as a function of the orientation of \mathbf{H}_{SM} together with the corresponding calculated values of \bar{H}_L .

6. NOTES ABOUT PULSE EXPERIMENTS

We consider a rigid lattice containing one or many spin species, subjected to a large constant magnetic field \mathbf{H}_0 in the z direction. The Hamiltonian of the spin system is given by (2.1), where

$$\mathcal{H}' = \sum_{a,a',n,n' \leq n} A^{an,a'n'} I_z^a I_z^{a'n'} + \sum_{a,n,n' < n} B^{an,an'} (I_+^a I_-^{an'} + I_-^a I_+^{an'}). \quad (6.1)$$

Further discussions will be simplified if we use the interaction representation ($\hat{\cdot}$) defined by

$$\hat{A} = R^{-1} A R, \quad \text{where } R = \exp \left\{ -\frac{i t}{\hbar} \sum_a \mathcal{H}_0^a \right\}. \quad (6.2)$$

As far as the spin variables of spins of one species are concerned, this is equivalent to the use of a new frame of coordinates rotating around \mathbf{H}_0 (i.e., the z direction)

$$\begin{aligned} \hat{\rho}_\theta(0) = \rho(0) - (-\gamma^b \hbar H_0 / \mathcal{O} k T^b) \{ & -(1 - \cos\theta) \mathcal{L}_z^b + \sin\theta \mathcal{L}_x^b \} \\ & - (1/\mathcal{O} k T_D) \{ -\sin^2\theta \sum_{n,n' < n} [(A^{bn,bn'} - 2B^{bn,bn'}) (I_z^{bn} I_z^{bn'} - I_x^{bn} I_x^{bn'})] \\ & - (1 - \cos\theta) \sum_{n,n',a \neq b} [A^{bn,an'} I_z^{bn} I_z^{an'}] \\ & + \sin\theta \cos\theta \sum_{n,n' < n} [(A^{bn,bn'} - 2B^{bn,bn'}) (I_z^{bn} I_z^{bn'} + I_x^{bn} I_x^{bn'})] \\ & + \sin\theta \sum_{n,n',a \neq b} [A^{bn,an'} I_x^{bn} I_z^{an'}] \}. \quad (6.5) \end{aligned}$$

Free Precession Signals

Neglecting small oscillating terms caused by \mathcal{H}'' , one can write the x component $M_x(t)$ of the magnetization of spins b after the θ^b pulse as

$$M_x(t) = \bar{M}_x(t) \cos\omega^b t + \bar{M}_y \sin\omega^b t, \quad (6.6)$$

²³ The pulse has to last for a large number of rf cycles, but is short compared to T_2 .

²⁴ The techniques of calculation used in this section are those discussed by I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957). We have repeatedly used the property that the trace of an operator which never conserves the Zeeman energy is equal to zero.

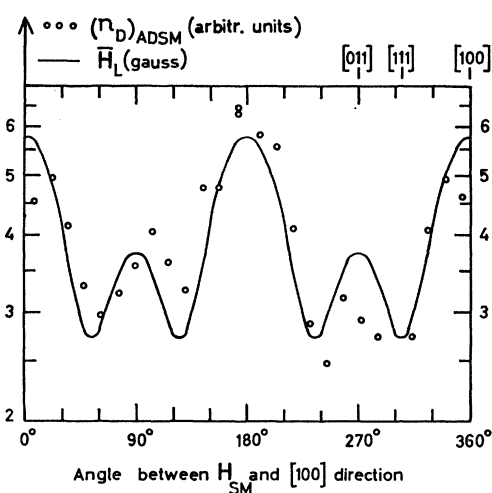


FIG. 3. Experiment C: Influence of the orientation of the suddenly applied magnetic field \mathbf{H}_{SM} (in a $(0-1-1)$ plane) on the degree of dipole-dipole order $(n_D)_{ADSM}$ resulting from complete adiabatic demagnetization followed by sudden magnetization (ADSM) in a LiF crystal (footnote 20). The measured values of $(n_D)_{ADSM}$ are proportional to the amplitude of the dipole-dipole component of the F^{19} free precession signal. The F^{19} Zeeman signal observed after ADSM was very small and varied with orientation between 0.1 and 0.2 times its value before ADSM. The \bar{H}_L curve was computed from formula (2.6).

at the Larmor frequency of these spins (the two frames coincide at $t=0$).

The application of a short intense²³ pulse (a "θ pulse") of transverse rf magnetic field H_1 rotating around H_0 at the Larmor frequency $\omega^b/2\pi$ of b spins, such that

$$(H_1)_x = (\text{pulse around } t=0) \sin\omega^b t \quad (6.3)$$

(rf field in the y direction in the rotating frame), has an appreciable effect only on b spins and transforms the original density matrix $\rho(t)$ into $\rho_\theta(t)$ which, when extrapolated back to $t=0$ with $H_1=0$, is given by²⁴

$$\hat{\rho}_\theta(0) = \exp\{-i\theta \mathcal{L}_y^b\} \hat{\rho}(0) \exp\{i\theta \mathcal{L}_y^b\}, \quad (6.4)$$

where \mathcal{L}_y^b is the y component of $\mathcal{L}^b = \sum_n \mathbf{I}^{bn}$. In the case of a system which can be described in terms of spin temperatures before the pulse, $\rho(0)$ is given by (2.2), and expression (6.4) can be written

where the x and y components of $\mathbf{M}(t)$ in the rotating frame are given by

$$\bar{M}_x(t) = \text{Tr}\{\gamma^b \hbar \mathcal{L}_x^b Q \hat{\rho}_\theta(0) Q^{-1}\}, \quad (6.7)$$

$$\bar{M}_y(t) = \text{Tr}\{\gamma^b \hbar \mathcal{L}_y^b Q \hat{\rho}_\theta(0) Q^{-1}\}, \quad (6.8)$$

where

$$Q = \exp\{-it\mathcal{H}'/\hbar\}. \quad (6.9)$$

Introducing expression (6.5) for $\rho_\theta(0)$ into (6.7) and (6.8), one obtains

$$\bar{M}_x(t) = (\gamma^b \hbar / \mathcal{O} k T^b) [\sin\theta] \text{Tr}\{\mathcal{L}_x^b Q (\gamma^b \hbar H_0) \mathcal{L}_x^b Q^{-1}\}, \quad (6.10)$$

$$\begin{aligned} \bar{M}_y(t) = & (\gamma^b \hbar / \mathcal{O} k T_D) \{ [\sin\theta] \text{Tr}\{\mathcal{L}_y^b Q \sum_{n,n',a \neq b} (A^{bn,an'} I_x^{bn} I_x^{an'}) Q^{-1}\} \\ & + [\frac{1}{2} \sin 2\theta] \text{Tr}\{\mathcal{L}_y^b Q \sum_{n,n' < n} \{ (A^{bn,bn'} - 2B^{bn,bn'}) (I_x^{bn} I_x^{bn'} + I_x^{bn} I_x^{bn'}) \} Q^{-1}\} \}. \end{aligned} \quad (6.11)$$

Equation (6.11) is exactly the expression derived by Anderson and Hartmann⁶ for the envelope of the free precession signal of a system in which T_D is finite and the T^a 's infinite.

It is obvious from (6.10) and (6.11) that the rf phases of the Zeeman and dipole-dipole free precession signals are mutually orthogonal, and that these two signals can, thus, be separated very easily by the use of coherent pulse instrumentation with two orthogonal phase-sensitive detectors.

Effects of Successive, Widely Separated Pulses

[*Note added in proof.* We have now investigated the effect of a pair of pulses separated by a time of the order of T_2 , as a function of the difference φ between the rf phases of the two pulses. The calculations indicate that when φ differs from 0 or π , the pulse pair will cause a partial transfer of degree of order from the Zeeman

subsystem to the dipole-dipole subsystem, and vice versa. Experiments have been undertaken to make a quantitative check of the theoretical prediction.]

Immediately after a θ^b pulse, the spin system cannot be described in terms of spin temperatures, but it will relax, with a characteristic time probably of the order of magnitude of T_2 , to a state which is described by a new set of spin temperatures $T_{D\theta}$, T^a_θ .

In the approximation in which $M=1$ [formula (5.6)], the dipole-dipole and Zeeman energies are constants of the motion in the absence of rf magnetic field, and their value after the pulse can be computed using expression (6.5) for the density matrix after the pulse. Knowing the energies, one can compute the spin temperatures and predict the effects of further pulses, provided that the time separation between pulses is larger than a few T_2 . Elementary computations give the following result (E and E_θ are the energies before and after one θ^b pulse)

$$E^a_\theta = E^a \quad (a \neq b), \quad (6.12)$$

$$E^b_\theta = E^b \cos\theta, \quad (6.13)$$

$$\begin{aligned} E_{D\theta} = & E_D - \sin^2\theta \left[\frac{1}{3} I^b (I^b + 1) \right]^2 \sum_{n,n' < n} (A^{bn,bn'} - 2B^{bn,bn'})^2 \\ & - (1 - \cos\theta) \frac{1}{3} I^b (I^b + 1) \sum_{n,n',a \neq b} \left[\frac{1}{3} I^a (I^a + 1) (A^{bn,an'})^2 \right]. \end{aligned} \quad (6.14)$$

Equation (6.14) shows that a comparison of the effects on the dipole-dipole system of $\pi/2$ and π pulses on spins b will give information about the relative strength of the couplings between spins b and spins b , and between spins b and other spins. In the case of a single-spin species, and in the absence of exchange interactions (pure dipole-dipole coupling), (6.14) becomes

$$E_{D\theta} = E_D (1 - \frac{3}{2} \sin^2\theta); \quad (6.15)$$

π pulses have no effect on E_D and $\frac{1}{2}\pi$ pulses multiply it by $-\frac{1}{2}$. If exchange interactions are present, the $\frac{3}{2}$ coefficient in (6.15) will be modified and measurements of the effect of $\frac{1}{2}\pi$ pulses on E_D will give information about the relative strength of the dipole-dipole and exchange couplings.

θ Pulses and Linear Response

In first approximation, the response of a spin system to a small perturbing magnetic field is a linear function of the perturbation. We shall now see to which extent this idea can be used to correlate the rf susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ (i.e., the response to a small linearly polarized transverse magnetic field) with the free precession signal following a θ^b pulse. A small rotating rf field \mathbf{H}_1 described by $H_{1x} + iH_{1y} = \exp(i\omega t)$ will thus cause a response \mathbf{M} where $M_x + iM_y = 2\chi(\omega) \times \exp(i\omega t)$. A θ^b pulse with \mathbf{H}_1 in the y direction of the rotating frame of coordinates can be described as

$$H_{1x} + iH_{1y} = i \int f(\omega) \exp(i\omega t) d\omega, \quad (6.16)$$

where $f(\omega)$ is a real function of ω , symmetric around the Larmor angular velocity ω^b of the b spins, roughly constant in the range of ω where $\chi(\omega)$ is appreciably different from 0 in the neighborhood of ω^b , and falling to zero outside this range. An elementary calculation shows that $\theta^b = 2\pi\gamma^b f(\omega^b)$. In the linear approximation, the response to a θ^b pulse (6.16) is given by

$$M_x + iM_y = i \int 2\chi(\omega) f(\omega) \exp(i\omega t) d\omega. \quad (6.17)$$

Using the Kramers-Kronig relations²⁵ to eliminate $\chi'(\omega)$, we can rewrite this response as

$$\theta^b (2/\pi\gamma^b) \exp(i\omega^b t) \int \chi''(\omega) \exp[i(\omega - \omega^b)t] d\omega. \quad (6.18)$$

The absorption part of the susceptibility $\chi''(\omega)$ is the sum of two terms $\chi''_Z(\omega)$ and $\chi''_D(\omega)$, where $\chi''_Z(\omega)$ is the imaginary part of the usual rf susceptibility of a system with $|n^b| \gg n_D$ and $\chi''_D(\omega)$ is given by (3.7). Evaluating the integral in (6.18) in this way, one finds a free precession magnetization which is given by (6.6) after replacing the functions of θ in the square brackets in (6.10) and (6.11) by θ (i.e., the first term of their series expansion for small angles).

This shows that the linear response theory can be used to express the free precession signal as the Fourier transform of the susceptibility, in the sense of Eqs. (6.16) and (6.17), in the case of small θ . In the case of large θ , a single correction factor $(\sin\theta)/\theta$ multiplies the linear approximation of the Zeeman signal, whereas two different such factors, $(\sin\theta)/\theta$ and $(\sin 2\theta)/2\theta$, have to be introduced for the two parts of the dipole-dipole signal which originate from interactions between neighbors of different or like species. As a result of this, the *shape* of the Zeeman signal does not change with θ , and that of the dipole-dipole signal changes with θ for systems with many spin species and not for systems of one spin species, as already noted by Anderson and Hartmann.⁶

7. SPINS WITH UNEQUALLY SPACED ENERGY LEVELS: DENSITY MATRIX, ENTROPY

The possibility of describing the state of a spin system which is not in complete internal equilibrium in terms of a small number of temperatures or populations depends upon the existence of some kind of gap in the spectrum of relaxation times of the system: subsystems must exist, inside which strong coupling results in a fast evolution towards a state of internal quasiequilibrium describable in terms of populations or a spin temperature. The weak couplings between these subsystems and with the lattice then result in slow changes of the populations or temperatures.

We shall now discuss the density matrix and the entropy for a simple example of such a system. Consider a system of spins localized on a rigid lattice (solid), the ordinary rf absorption spectrum of which consists of well separated lines. This spectrum can be interpreted as the superposition of the spectra of a small number of different kinds of microscopic systems, spins or group of a few tightly coupled spins,²⁶ the linewidth originating partly in the ("spin-spin") couplings between microscopic systems and partly in fluctuations from point to point in the environment of the microscopic systems ("inhomogeneous broadening"). The total spin Hamiltonian can be written as

$$\mathcal{H} = \sum_a \mathcal{H}_0^a + \mathcal{H}' + \mathcal{H}'', \quad (7.1)$$

where

$$\mathcal{H}_0^a = \sum_n \mathcal{H}_0^{an}, \quad (7.2)$$

where \mathcal{H}_0^{an} is that part of the Hamiltonian of the isolated n th microscopic system of type a , which gives rise to the average spectrum of energy levels of type a . Fluctuations from point to point of the individual microscopic system Hamiltonian and couplings between microscopic systems are included in $\mathcal{H}_S = \mathcal{H}' + \mathcal{H}''$. \mathcal{H}' contains the terms of \mathcal{H}_S which commute with $\sum_a \mathcal{H}_0^a$ and \mathcal{H}'' those which do not.

For simplicity, we shall consider the case where each line of the complete spectrum originates from a transition between a single pair of levels in one kind of microscopic system. In this case (neglecting possible cross relaxations), spin diffusion will not affect the occupation number (population) of the energy levels of the isolated microscopic system. In order to emphasize the important roles of these populations, we introduce the operators \mathcal{N}_m^a the eigenvalues of which are the number N_m^a of microscopic systems of type a in their m th eigenstate (m^a) of energy \mathcal{E}_m^a . In a representation in which the microscopic systems are individually quantized, \mathcal{N}_m^a is defined by

$$\mathcal{N}_m^a | \text{state } A \rangle = N_m^a (\text{in state } A) \cdot | \text{state } A \rangle. \quad (7.3)$$

The Hamiltonian \mathcal{H}_0^a can then be written as

$$\mathcal{H}_0^a = \sum_m \mathcal{E}_m^a \mathcal{N}_m^a, \quad (7.4)$$

where the sum extends over the g^a eigenstates of each microscopic system of type a . The density matrix describing a system for which we only know the probabilities p_m^a of finding an arbitrary microscopic system of type a in the state (m^a) is

$$\rho = \exp\left\{ \sum_{a,m} (q_m^a \mathcal{N}_m^a) \right\}, \quad (7.5)$$

where $q_m^a = \log p_m^a$ and, of course, $\sum_m p_m^a = 1$.

Using the same arguments as Anderson and Hartmann,⁶ or Provotorov,⁷ as many others have done already, we can now write a density matrix for the

²⁵ See for instance the discussion given in Ref. 1 (Abragam), pp. 93-96.

²⁶ For instance, the two different types of proton pairs (water molecules) in gypsum.

complete spin system in quasiequilibrium as

$$\rho = (1/\mathcal{O}') \exp\{(-\mathcal{H}'/kT_S) + \sum_{a,m} (q_m^a \mathcal{H}_m^a)\}. \quad (7.6)$$

In the discussion of processes involving only two energy levels \mathcal{E}_i^a and \mathcal{E}_j^a , it is sometimes convenient to introduce a temperature T_{ij} defined by

$$\frac{1}{kT_{ij}} = \frac{\ln(N_i^a/N_j^a)}{\mathcal{E}_i^a - \mathcal{E}_j^a} = \frac{q_i^a - q_j^a}{\mathcal{E}_i^a - \mathcal{E}_j^a}, \quad (7.7)$$

but it is obvious that these temperatures, which generalize the notion of Zeeman temperature, are by no means independent of one another and are much less convenient characteristics of the state of the system than are the probabilities p_i^a or the average occupation numbers $N_i^a = N^a p_i^a$ (where N^a is the total number of microscopic systems of type a). In contrast to this, the notion of spin-spin temperature T_S retains all its importance because it describes the state of the very complex spin-spin subsystem.

In what follows, we shall restrict ourselves to the case of high temperatures and it is then convenient to replace the occupation numbers N_i^a by the deviations n_i^a from their value N^a/g^a at infinite temperature

$$n_i^a = N_i^a - N^a/g^a = N^a(p_i^a - 1/g^a), \quad (7.8)$$

with obviously: $\sum_i n_i^a = 0$.

The energy of the spin system, $E = \text{Tr}\{\mathcal{H}\rho\}$ can be computed easily²⁷ by using the first-order approximation of ρ in $1/T_S$ and the n_m^a :

$$E = E_S + \sum_{a,m} E_m^a, \quad (7.9)$$

where

$$E_S = -(1/kT_S)(1/\mathcal{O}) \text{Tr}\{\mathcal{H}^2\} \quad (7.10)$$

and

$$E_m^a = N_m^a \cdot \mathcal{E}_m^a, \quad (7.11)$$

or

$$E_m^a = n_m^a \cdot \mathcal{E}_m^a.$$

(\mathcal{O} is the total number of eigenstates of the complete spin system.)

A computation of the entropy using the standard formula $\text{entropy} = -k \text{Tr}\{\rho \ln \rho\}$ requires the use of an expansion of ρ to the second order in $1/T_S$ and the n_m^a . [Using a first-order expansion gives factors of 1 instead of the factors $\frac{1}{2}$ appearing in formulas (7.14) and (7.15).] The result, which can be checked by computing the difference S between entropy and entropy at infinite temperature by the simple thermodynamic technique used in Sec. 2, is

$$\text{entropy} = k \ln \mathcal{O} + S, \quad (7.12)$$

where

$$S = S_S + \sum_{a,m} S_m^a, \quad (7.13)$$

where

$$S_S = -\frac{1}{2}(1/kT_S^2)(1/\mathcal{O}) \text{Tr}\{\mathcal{H}^2\}, \quad (7.14)$$

²⁷ The following operators can be shown to have a trace equal to zero (or have been so chosen): \mathcal{H}_0^a , \mathcal{H}' , \mathcal{H}'' , $\mathcal{H}_0^a \mathcal{H}'$, $\mathcal{H}_0^a \mathcal{H}''$, $\mathcal{H}' \mathcal{H}''$.

and

$$S_m^a = -\frac{1}{2}(k g^a / N^a) (n_m^a)^2. \quad (7.15)$$

8. INFLUENCE OF THE NONSECULAR PART OF THE SPIN-SPIN COUPLING ON THE THERMODYNAMIC PROPERTIES OF A SPIN SYSTEM

A spin system in complete thermodynamic equilibrium, i.e., a system in which all temperatures are equal to T , is described by the density matrix

$$\rho_{\text{equil}} = (1/\mathcal{O}) \exp\{-(\mathcal{H}_0 + \mathcal{H}' + \mathcal{H}'')/kT\}. \quad (8.1)$$

If we use the formalism which has been proposed by Anderson and Hartmann⁶ and Provotorov,⁷ we shall describe the same situation by the density matrix [see formulas (2.2) and (7.6)]

$$\rho = (1/\mathcal{O}') \exp\{-(\mathcal{H}_0 + \mathcal{H}')/kT\}. \quad (8.2)$$

In the limit of a large magnetic field H_0 (i.e., widely separated energy level differences of the isolated microscopic systems), the relative differences in the energies, entropies \dots , calculated from the exact (8.1) and approximate (8.2) density matrices are very small, of the order of $(H_L/H_0)^2$, and can usually be neglected (H_L is the "local" magnetic field, due to the influence of the neighbors of each spin). On the other hand, the discrepancy which exists between the exact density matrix (8.1) for the one-temperature situation (which usually exists in low H_0) and the density matrix used to describe situations with many different spin temperatures (8.2) leads to ambiguities in the quantitative discussion of processes such as adiabatic magnetization or demagnetization, or cross relaxation, because one has to "jump" from one type of density matrix to the other. The following discussion gives a partial solution of these problems.

Let us first consider the case of a single-spin species (N spins with equally spaced isolated spin energy levels). Following Philippot,⁹ we note that the two operators \mathcal{H}_0 and \mathcal{H}' [see formula (2.1)] which commute with each other can be simultaneously diagonalized, and we introduce as base vectors the eigenstates $|L, n\rangle$ of $(\mathcal{H}_0 + \mathcal{H}')$, satisfying the relations

$$\begin{aligned} \mathcal{H}_0 |L, n\rangle &= L \hbar \omega_0 |L, n\rangle, \\ \mathcal{H}' |L, n\rangle &= E'_{Ln} |L, n\rangle. \end{aligned} \quad (8.3)$$

L is an integer (or a half-integer for an odd number of odd spins) and n describes all the other quantum numbers. Neglecting the "nonsecular" part \mathcal{H}'' of the spin-spin Hamiltonian, the corresponding eigenvalues of the energy are

$$L \hbar \omega_0 + E'_{Ln}, \quad (8.4)$$

the usual two-spin temperature density matrix (2.2) is an exact stationary state of the problem, and the probability of finding the system in the state $|L, n\rangle$ is given by

$$(1/\mathcal{O}') \exp\{-L \hbar \omega_0 / kT_Z - E'_{Ln} / kT_D\}. \quad (8.5)$$

The influence of \mathcal{H}'' on the eigenstates and eigenvalues of the energy just discussed will be small if H_0 is larger than H_L , and we can then evaluate it by ordinary time-independent perturbation theory: In second order in (H_L/H_0) , the energy of the eigenstate corresponding to $|L, n\rangle$ can be written as

$$L\hbar\omega_0 + E'_{Ln} + E''_{Ln}, \quad (8.6)$$

where [see (5.10)]

$$E''_{Ln} = (1/\hbar\omega_0) \{ \langle L, n | [\mathcal{H}''_{+1}, \mathcal{H}''_{-1}] | L, n \rangle + \frac{1}{2} \langle L, n | [\mathcal{H}''_{+2}, \mathcal{H}''_{-2}] | L, n \rangle \}. \quad (8.7)$$

A complete discussion of the perturbations due to \mathcal{H}'' , even in second order only, is very difficult because the eigenstates $|L, n\rangle$ are unknown. Nevertheless, some average properties can be evaluated as traces (as in Van Vleck's method of moments).¹² For instance, the average value of E''_{Ln} for all states of given L is given by

$$(E''_{Ln})_{\text{av. over } n} = L\hbar\omega'', \quad (8.8)$$

where

$$\omega'' = \frac{1}{2}\omega_0 \text{Tr}\{\mathcal{H}''^2\} / \text{Tr}\{\mathcal{H}^2\}.$$

One can also show that E''_{Ln} is not directly correlated to the first approximation dipole-dipole energy E'_{Ln} in the sense that

$$\sum_{L, n} \{ E'_{Ln} E''_{Ln} \} = 0, \quad (8.9)$$

by writing this sum as a trace and noting that a reversal of all spins will leave E'_{Ln} unaffected, but change the sign of E''_{Ln} .

Using these results, we can write the energy (8.6) as

$$L\hbar(\omega_0 + \omega'') + E'_{Ln} + (E''_{Ln} - L\hbar\omega'') \quad (8.10)$$

and describe the influence of \mathcal{H}'' as a systematic shift in the NMR frequency superimposed on small "random" perturbations of the dipole-dipole energy. If we now apply the standard arguments^{6,7} to write down a two-spin temperature density matrix, the probability of the state which originates from $|L, n\rangle$ in the absence of \mathcal{H}'' will be given by

$$(1/\mathcal{Q}'') \exp\left\{ -L\hbar(\omega_0 + \omega'')/kT_Z - (E'_{Ln} + E''_{Ln} - L\hbar\omega'')/kT_D \right\}. \quad (8.11)$$

In the high-temperature approximation and neglecting terms of order higher than $(H_L/H_0)^2$, the average energy computed with this probability distribution is the same as that computed with the density matrix

$$\rho = \frac{1}{\mathcal{Q}''} \exp\left\{ -\frac{(\mathcal{H}_0 + \mathcal{H}'')}{kT_Z} - \frac{\mathcal{H}'}{kT_D} \right\}, \quad (8.12)$$

which differs from the classical form by the addition of the term $-\mathcal{H}''/kT_Z$ in the exponential. This density matrix avoids the ambiguities mentioned in the first part of this section: in the high-field region, it gives the thermodynamic properties more accurately than

does the previously proposed density matrix (2.2) and in the low-field region, where good heat contact between the Zeeman and dipole-dipole subsystems equalizes T_Z and T_D , it goes over to the exact formula (8.1). Another result in favor of formula (8.12) is that if one starts with a density matrix of the form (8.12) *without* the term in \mathcal{H}'' and solves the equation of motion for $\rho(t)$ as outlined in Sec. 5, the solution executes rapid oscillations around the density matrix (8.12) *with* the term $-\mathcal{H}''/kT_Z$ included.

The calculation outlined above in the case of a single-spin species can be extended in a straightforward way to the case of many spin species and unequally spaced energy levels, with the following result, which, as above, is obtained in the limit of very high temperatures, includes all energy terms up to the order of (linewidth/line separation),² and goes over smoothly to the right expression whenever lines overlap and come in thermal equilibrium with each other, or when a transition frequency approaches zero.

We first decompose the "nonsecular" part of the coupling, \mathcal{H}'' , in a sum of terms according to the type of transition which they generate. For an \mathcal{H}'' which only couples pairs of microscopic systems, the general term in this decomposition, $\mathcal{H}''(A \rightarrow B, F \rightarrow G)$, will contain all the operators which simultaneously cause a transition of one microscopic system from state A to state B and of another one from F to G , or the complete inverse (A and B , or F and G can be the same state). To each term $\mathcal{H}''(A \rightarrow B, F \rightarrow G)$ there will correspond in the exponential of the density matrix (7.6) an additional contribution given by

$$\frac{q_A - q_B + q_F - q_G}{\mathcal{E}_A - \mathcal{E}_B + \mathcal{E}_F - \mathcal{E}_G} \cdot \mathcal{H}''(A \rightarrow B, F \rightarrow G). \quad (8.13)$$

When the energy difference (i.e., line separation) $\mathcal{E}_A - \mathcal{E}_B + \mathcal{E}_F - \mathcal{E}_G$ becomes comparable to the linewidth, $\mathcal{H}''(A \rightarrow B, F \rightarrow G)$ will give rise to cross relaxation and one can easily verify that the steady state of cross relaxation is characterized by

$$-\frac{1}{kT_S} = \frac{q_A - q_B + q_F - q_G}{\mathcal{E}_A - \mathcal{E}_B + \mathcal{E}_F - \mathcal{E}_G}. \quad (8.14)$$

If one now collects all the terms in the exponential of (7.6) corrected by (8.13), which are proportional to $-1/kT_S$, one finds in this case the original term \mathcal{H}' plus two new terms:

$$\mathcal{H}' + \mathcal{H}''(A \rightarrow B, F \rightarrow G) + \frac{1}{2}(\mathcal{N}_A - \mathcal{N}_B + \mathcal{N}_F - \mathcal{N}_G)(\mathcal{E}_A - \mathcal{E}_B + \mathcal{E}_F - \mathcal{E}_G), \quad (8.15)$$

which shows clearly how $\mathcal{H}''(A \rightarrow B, F \rightarrow G)$ effectively becomes a part of \mathcal{H}' when the line separation goes to zero. Using (7.6) corrected by the additional terms (8.13), one can, for instance, give an unambiguous discussion of experiments in which the energy levels

are moved with respect to one another by changing some parameter (usually magnetic field, electric field, or orientation) of the spin Hamiltonian.

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Observation of Cr^{4+} in $\alpha\text{-Al}_2\text{O}_3$ †

R. H. HOSKINS AND B. H. SOFFER

Korad Corporation, A Subsidiary of Union Carbide Corporation, Santa Monica, California

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The paramagnetic resonance spectrum of single crystals of $\alpha\text{-Al}_2\text{O}_3$ containing chromium grown under conditions favoring the stabilization of Cr^{4+} has been observed. Data were taken at X band at liquid-helium temperatures. A single absorption line was observed which is attributed to a $\Delta M = \pm 2$ transition. The crystal-field splitting parameter is inferred from the temperature dependence of the strength of the resonance to be $D \cong +7 \text{ cm}^{-1}$. The spectroscopic splitting factor is $g_{11} = 1.90_{-0.01}^{+0.02}$. A distribution of lower symmetry fields gives rise to an asymmetric line; the range of E values deduced from this asymmetry is $0 \lesssim E \lesssim 0.05 \text{ cm}^{-1}$, where $2E$ is the zero-field doublet splitting. Optical absorption data and radiation effects are presented.

I. INTRODUCTION

THE paramagnetic resonance spectra of iron group ions in the $\alpha\text{-Al}_2\text{O}_3$ host lattice have been the subject of study for some years. The only ion of the $3d^2$ configuration which has received attention is V^{3+} . Optical-absorption measurements on V^{3+} in $\alpha\text{-Al}_2\text{O}_3$ have been made by Pryce and Runciman¹ and spin-resonance studies are reported by Zverev and Prokhorov² and by Lambe and Kikuchi.³ No work has been reported on the isoelectronic species Cr^{4+} in any host lattice. We have performed spin-resonance and optical-absorption measurements on single crystals of $\alpha\text{-Al}_2\text{O}_3$ containing chromium which have been grown under conditions favoring the stabilization of Cr^{4+} , rather than the usual valence state Cr^{3+} (ruby). The crystals, which are bright orange in color and show only a very faint red fluorescence under ultraviolet or green excitation due to a background of Cr^{3+} , bear no visual resemblance to ordinary ruby.

The spin-resonance properties of Cr^{3+} ($S = \frac{3}{2}$) in the axial electric field of $\alpha\text{-Al}_2\text{O}_3$ have been studied extensively.⁴⁻⁶ The crystal-field splitting of 0.38 cm^{-1}

gives rise to a rich and predictable spectrum from Cr^{3+} when resonance measurements are carried out at X-band microwave frequencies. The $S = 1$ spin state of Cr^{4+} is readily discernible from such background Cr^{3+} absorptions by its distinctive behavior in regard to number of lines, angular dependence, temperature dependence, and saturation behavior. A paramagnetic resonance-absorption line has been found which is attributable to a system of $S = 1$ which we propose is Cr^{4+} .

Optical-absorption measurements have revealed the intense spectra of defect centers rather than the absorptions of the Cr^{4+} ion. The purpose of this paper is to point out the stable existence of the species Cr^{4+} in $\alpha\text{-Al}_2\text{O}_3$ and to describe the spin-resonance properties of this ion.

II. EXPERIMENTAL

The crystals were grown by the Verneuil method. Substitution of tetravalent chromium for trivalent aluminum requires a method of charge compensation. In this case, anionic compensation was used; N^{3-} was substituted for O^{2-} . This substitution can be effected by the incorporation of nitrides in the powder feed.⁷ In order to maximize conversion of Cr^{3+} to Cr^{4+} , the samples were oxidized under one atmosphere of oxygen at 1400°C for approximately 16 h. Because of complications which can be introduced into the spin-resonance spectrum by other transition metal ions, especially iron, great care was taken to prevent impurity contamination. Values of chromium concentration

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