

Paramagnetic Relaxation in Nickel Fluosilicate

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 (Received February 17, 1959)

Physical models of the paramagnetic relaxation process are briefly reviewed, and a description is given of the pulsed microwave method of investigation. This method has been applied to the study at low temperatures of zinc/nickel fluosilicate at various magnetic dilutions, and an additional relaxation process has been observed which is associated with the sharing of energy among the spins.

The results depend only on the temperature and magnetic concentration, and are independent of all other experimental conditions provided that excessive power levels are avoided. The lack of size dependence indicates that the relaxation rate is not controlled by spatial diffusion of phonons. The temperature dependence which has been observed is too acute to fit the $1/T$ law of the simple "direct process" model, and suggests that the relaxation rate is controlled either by phonon combination probabilities or by a Raman type of interaction between phonons and spins.

I. INTRODUCTION

EXPERIMENTAL methods used in the study of paramagnetic relaxation may conveniently be classified under three headings. The "nonresonant" method, as described by Gorter,¹ and in several review articles^{2,3} has been used for many years and has contributed the greater part of the available data. Microwave resonance absorption provided a second method, and early experiments of this type are described by Eschenfelder and Weidner.⁴ In such experiments the degree of absorption is measured in a steady-state which results from a balance between power input from the microwave field and relaxation rate to the surroundings. More recently the resonance absorption technique has been extended to the study of transient conditions which are obtained when microwave power is applied in pulses. Experiments of this third type have been reported by Giordmaine *et al.*⁵ and by Davis *et al.*,⁶ and are the subject of the work described here.

Attempts to account theoretically for the results of "nonresonant" experiments culminated in the papers of Van Vleck.^{7,8} The first paper is devoted to a calculation of the relaxation times of titanium and chrome alum, the model being that acoustic waves in the thermal spectrum modulate the crystal field, that this distorts the orbital wave function and, through spin orbit coupling, the disturbance is then transmitted to the spin. Two types of interaction with the thermal spectrum are considered. In the "direct process," lattice modes having a frequency the same as the spin resonance frequency ex-

change quanta of energy with individual spins. The spins relax by emitting acoustic quanta, or "phonons," over a narrow band of frequencies into these modes. In the "Raman process" a spin interacts simultaneously with two lattice modes whose difference frequency is the spin-resonance frequency. This is a second order process and is less probable for any selected pair of frequencies, but the number of possible combinations is large and the probability increases rapidly with temperature. Direct processes should vary as T , and in the low-temperature range Raman processes should vary as $T^7(\text{Cr}^{3+})$ or $T^9(\text{Ti}^{3+})$. Theoretical estimates of the relative magnitudes of these two types of interaction indicate that direct processes will predominate in the liquid helium range, and will be superseded by Raman processes only at higher temperatures.

In the liquid helium range Van Vleck finds rough agreement with experiment for chrome alum, although not for titanium alum. However, even for chrome alum the dependence on temperature and on the magnitude of the mean dc field disagree with experiments. In discussing this, Van Vleck reviews certain assumptions in the theory. He points out that acoustic modulation of the crystal field is computed by assuming a normal thermal distribution of phonons in a simple lattice composed of similar atoms, whereas "conceivably the oscillations most active in modulating the cluster $\text{Cr}\cdot 6\text{H}_2\text{O}$ are not typical of the crystal as a whole and have a different distribution law."

A more fundamental difficulty is discussed in the second and third papers. He emphasizes that the low-frequency lattice oscillators have been "treated as a thermostat as far as interchange of energy with the spins is concerned," but that "it is impossible for the lattice oscillators to preserve a constant temperature in the face of frequent energy transfers with the spin." Van Vleck considers direct transfer of energy to the surroundings by the low-frequency oscillators themselves, and also combination of the low frequencies with other frequencies in the thermal spectrum, but concludes that there exists no adequate mechanism for

¹ C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1947).

² A. H. Cooke, *Reports on Progress in Physics* (The Physical Society, London, 1950), Vol. 13, p. 276.

³ C. J. Gorter, *Progress in Low-Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, Chap. IX.

⁴ A. H. Eschenfelder and R. T. Weidner, *Phys. Rev.* **92**, 869 (1953).

⁵ Giordmaine, Alsop, Nash, and Townes, *Phys. Rev.* **109**, 302 (1958).

⁶ Davis, Strandberg, and Kyhl, *Phys. Rev.* **111**, 1268 (1958).

⁷ J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

⁸ J. H. Van Vleck, *Phys. Rev.* **59**, 724, 730 (1941).

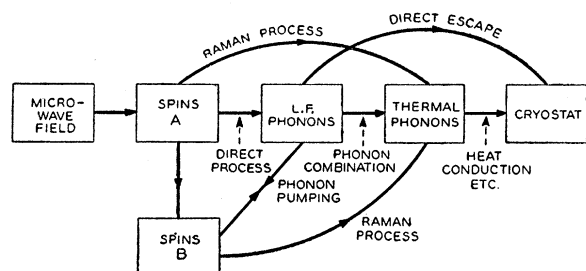


FIG. 1. Relaxation block schematic for a two level system. Spins have been divided into groups *A* and *B* to allow for cross pumping within the resonance line.

removing low-frequency phonons as fast as they are created by relaxation of the spins. Thus a significant piling up of energy in the low-frequency modes is to be expected.

This idea has been followed up in detail by Giordmaine *et al.*⁹ in a recent paper. They suggest that relaxation by direct processes rapidly brings about a state of equilibrium between spins and a band of lattice modes at the low-frequency end of the spectrum. The characteristic time for this (10 microseconds) is much shorter than the observed relaxation time, which is really controlled by the rate at which the low-frequency modes can transfer energy to the boundaries of the crystal. Because each of these modes is very often interrupted by interaction with a spin, they are broadened and constitute a band several hundred megacycles wide. A second group of spins, not directly disturbed but lying within this interval, will be brought into equilibrium with these lattice modes and thus, indirectly, with the first group of spins. Observations by microwave resonance of this "cross pumping" provide the chief experimental support for the model.

Other researchers have been concerned with the possibility that the whole crystal may rise in temperature above its surroundings⁹ or that a temperature gradient may be set up within the crystal itself.¹⁰

If these possibilities are taken into account, relaxation must be represented as a multistage process involving more than one characteristic time.¹¹ This will be true even for "nonresonant" experiments in which a similar kind of initial disturbance is given to all spins, although in microwave absorption experiments, where the disturbance is selectively applied to a fraction of the spins, an even more complex relaxation pattern may result. Figure 1 shows a schematic diagram for a two-level case such as we have investigated. The spins are divided into two groups, those resonating with the microwave field, and those too remote in frequency to be directly affected. This is to take account of the inhomogeneous broadening of the resonance line in nickel fluosilicate (i.e., the line

consists of groups of spins whose characteristic frequencies are too near to permit actual experimental resolution but too far apart to allow resonant spin coupling throughout the system). Transfer of energy between these spin groups has been observed in some of our experiments (Secs. V and VI).

The flexibility and directness of the pulsed microwave method offer great advantages when studying such a complex decay process. Power may be applied at an arbitrary level and for any required time to a chosen group of spins; the display then shows at once the relaxation history of these, or of any other spin group. Some of the ways in which these possibilities may be exploited are described in references 5 or 6, and in this paper.

II. CRYSTALLOGRAPHY AND PARAMAGNETIC RESONANCE SPECTRUM

$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ are both isomorphous with $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$, whose crystal structure has been determined by Pauling.¹² From this one deduces that the $(\text{H}_2\text{O})_6$ octahedra (with Zn or Ni at the center) and the F_6 octahedra (with Si at the center) are arranged in a CsCl-like structure, i.e., like a body-centered cube. Each $(\text{H}_2\text{O})_6$ octahedron has a small trigonal distortion—the space group is $R\bar{3}$, with one molecule in the rhombohedral unit cell.

There is no difficulty in diluting $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ with the diamagnetic $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$. It would, however, be dangerous to infer from this that the crystal is not strained when Ni atoms are substituted for some of the Zn atoms, since the ionic radius of Ni^{2+} is considerably less than that of Zn^{2+} . This is borne out by the fact that the unit cell of the Ni salt is about 3% smaller in volume than that of the Zn salt.

The observed paramagnetic resonance spectrum is in accord with the crystal structure described above; there is only one paramagnetic complex in the unit cell, and its resonance spectrum has axial symmetry about the crystal's trigonal axis. The resonance results are interpreted in terms of the spin Hamiltonian,

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + D(S_z^2 - \frac{2}{3}), \quad \text{with } S=1, \text{ and } g \approx 2.3.$$

Figure 2 shows the behavior of the energy levels when a magnetic field H is applied parallel to the axis. Most of our experiments were performed in zero field, where there is just a single resonance transition with frequency D/h . D is a measure of the small trigonal distortion in the $(\text{H}_2\text{O})_6$ octahedra, and its magnitude is thus quite sensitive to temperature¹³ and pressure,¹⁴ and also depends slightly ($\sim 10\%$) on dilution; at 4.2°K, with no applied stress, $D/hc = 0.13 \text{ cm}^{-1}$ for heavily diluted materials, and 0.12 cm^{-1} for the undiluted salt.

⁹ Gorter, Van der Marel, and Bolger, *Physica* **21**, 103 (1955); Van der Marel, Van den Broek, and Gorter, *Physica* **23**, 361 (1957).

¹⁰ J. Eisenstein, *Phys. Rev.* **84**, 548 (1951).

¹¹ L. C. Van der Marel, thesis, Leiden, 1958 (unpublished).

¹² L. Pauling, *Z. Krist.* **72**, 482 (1930).

¹³ R. P. Penrose and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A63**, 29 (1950).

¹⁴ W. M. Walsh and N. Bloembergen, *Phys. Rev.* **107**, 904 (1957); W. M. Walsh, *Bull. Am. Phys. Soc. Ser. II*, **3**, 178 (1958).

IIIa. THE PUMPING PARAMETER "v"

In these experiments we are concerned with measuring changes in the populations of two spin quantum states, that is, in the degree of microwave "pumping" of a spin system. It will be convenient to define a pumping parameter,

$$v = (N_B - N_A)/N, \quad (1)$$

where N_A and N_B are the populations of upper and lower states, and N is the total number of spins. For the sake of clarity, we consider first of all the simple case of two nondegenerate levels, and extend this later to apply to a scheme in which the lower level has a twofold degeneracy, corresponding to the case we have actually been studying.

In terms of the spin temperature T_s ,

$$v = \tanh(h\nu/2kT_s) \simeq h\nu/2kT_s \quad \text{when } h\nu/2kT_s \ll 1.$$

When microwave power is applied at the resonance frequency ν , the populations will tend to equalize and v will decrease; when power is removed, v will rise to a value v_0 which corresponds to the temperature of the surrounding cryostat. Such processes are commonly discussed in terms of the spin temperature, and it will be natural to speak of a buildup and a decay as the spin temperature rises and falls, although the parameter v is itself moving in the inverse sense.

The decay or rise of v is characterized by a probability W_L which is the reciprocal of the relaxation time T_1 . In fact there are two probabilities, one W_{AB} that a spin in level A makes a downward transition, and the other W_{BA} that a spin in level B moves up, but in a two-level system they can be combined as follows. In terms of W_{AB} and W_{BA} the populations obey the equations

$$\begin{aligned} dN_A/dt &= -W_{AB}N_A + W_{BA}N_B, \\ dN_B/dt &= -W_{BA}N_B + W_{AB}N_A. \end{aligned}$$

Substitution in terms of v

$$N_A = \frac{1}{2}N(1-v), \quad N_B = \frac{1}{2}N(1+v)$$

gives

$$dv/dt = W_{AB}(1-v) - W_{BA}(1+v). \quad (2)$$

In equilibrium with the cryostat, $dv/dt=0$ and $v=v_0$. Therefore

$$W_{AB}/W_{BA} = (1+v_0)/(1-v_0),$$

and we can express (2) in terms of v_0 and of a single probability $W_L = W_{AB} + W_{BA}$ in the form

$$dv/dt = W_L(v_0 - v). \quad (3)$$

If W_L is independent of v this may be integrated to give

$$(v_0 - v) = (v_0 - v_i)e^{-W_L t}, \quad (4)$$

where v_i is the initial value of v .

Next let us examine the interaction of the microwave field with the spins. The probability W_H that a particular

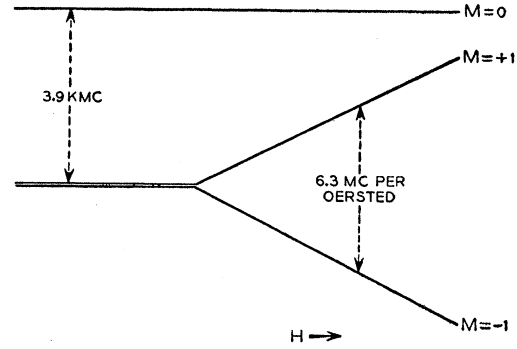


FIG. 2. Energy levels of (Zn, Ni) SiF₆ · 6H₂O.

spin undergoes a transition $M \leftrightarrow M-1$ is given by¹⁵

$$W_H = \pi g^2 \beta^2 [(S+M)(S-M+1)] H_1^2 / 4k^2 \Delta\nu, \quad (5)$$

where $H_1 \cos(2\pi\nu t)$ is the rf field acting on the spins, and $\Delta\nu$ is the line width. By an argument similar to that used in deriving (2), we find that in an rf field alone,

$$dv/dt = -2W_H v. \quad (6)$$

When the spins are simultaneously absorbing power from the rf field and relaxing to their surroundings, we must combine (3) and (6) to give

$$dv/dt = -2W_H v + W_L(v_0 - v). \quad (7)$$

If power is applied at a time $t=0$ to a spin system initially in equilibrium with the cryostat,

$$(v - v_\infty)/(v_0 - v_\infty) = e^{-(W_L + 2W_H)t}, \quad (8)$$

where v_∞ is the final value of v . This will lead to a steady-state in which

$$v_\infty/v_0 = (1 + 2W_H/W_L)^{-1}. \quad (9)$$

The decay after removal of power has already been given in (4).

It may be remarked here that if one end of a leaky condenser of time constant $1/W_L$ is connected to a terminal at potential v_0 , and the other end is intermittently grounded through a resistance proportional to W_H , the voltage $v_0 - v$ across the condenser can be obtained from Eqs. (4), (8), and (9). Circuit analogs of this type can be of some help in visualizing more complicated situations, such as those described in Sec. V and VI.

Experimental observations and the parameter v are closely related to the magnetic "quality factor" Q_m . From the definition of Q_m it follows immediately that

$$1/Q_m = 4P_m/\nu H_1^2 V_c, \quad (10)$$

where P_m is the power absorbed by the magnetic material, and the effective volume V_c of the cavity is

¹⁵ See, for example, Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

defined by

$$\int_0 H^2 dV = H_1^2 V_c.$$

In unit time $W_H(N_B - N_A)$ quanta are absorbed from the microwave field; hence

$$\begin{aligned} P_m &= W_H(N_B - N_A)h\nu \\ &= W_H h\nu N v, \end{aligned} \quad (11)$$

and combining (5), (10), and (11), we see that

$$1/Q_m \propto v. \quad (12)$$

In the case of nickel fluosilicate in zero field this analysis must be modified to take account of the twofold degeneracy of the ground state (see Fig. 2). Writing $2N_B$ in place of N_B for the population of the ground state and $2W_{AB}$ for the downward transition probability, we have $N = N_A + 2N_B$, v defined as in Eq. (1), and $W_L = 2W_{AB} + W_{BA}$. Minor numerical differences occur during the derivation, but leave Eqs. (3) and (4) unchanged. In the microwave field the transition probabilities are W_H upward and $2W_H$ downward. This leads to the appearance of $3W_H$ in place of $2W_H$ in Eqs. (6), (7), (8), and (9). The absorbed power becomes

$$\begin{aligned} P_m &= 2W_H(N_B - N_A)h\nu \\ &= 2W_H h\nu N v; \end{aligned}$$

and the relation between v and T_s becomes

$$v \approx h\nu/3kT_s.$$

In our detection system, which is described in Sec. IIIb, the display is approximately linear in $1/Q_m$, and hence in v . Decay measurements thus give W_L directly, for if we match the observed display with a set of standard exponential curves, the fit gives a value for $[1/(v_0 - v)](dv/dt)$ which, by Eq. (3), is just W_L . On the other hand, Eq. (9) shows that measurements on the

steady-state would only give W_L in terms of W_H , and so the evaluation of W_L would demand a knowledge of the terms on the right-hand side of Eq. (5). This requires a measurement of power in the cavity, to obtain H_1^2 , and some assumption (often of dubious validity) must be made regarding $\Delta\nu$.

IIIb. APPARATUS AND EXPERIMENTAL PROCEDURE

The pulsed microwave apparatus is shown in block schematic form in Fig. 3. A 2K56 reflex klystron oscillator operating between 3.8 and 4.4 kMc/sec drives a PA7 Huggins traveling wave tube which is switched by a square wave form applied to its control grid. It delivers pulses of microwave power 1 watt in intensity with a duration adjustable between 1 microsecond and 1 millisecond and at a recurrence rate which can be varied between 2×10^4 per second and one in 20 seconds. The on-off power ratio at the output of the tube is > 70 db. A low-power cw signal is taken directly from the klystron and added to this signal through a directional coupler, and the combined power is fed to the cavity. The pulsed signal, which we term the "heater pulse," serves to pump or "heat" the spins, and the cw signal monitors their return to thermal equilibrium. The intensities of both signals can be separately varied by microwave attenuators, typical values at the cavity input coupling being 0.2 watt for the heater and 1 microwatt for the monitor. The monitor, essentially a spin thermometer, is set at a power level too low to produce any significant disturbance in the spins.

The cavity is rectangular in shape and operates in the TE_{011} mode. It is tuned by inserting a ceramic plunger (dielectric constant ~ 9), and power is fed in through a coaxial line ending in a loop. Coupling is controlled by rotation of the loop. The second weakly coupled loop shown in Fig. 3 is provided as a convenience for tuning the cavity, and is not connected with the main detection system. Power reflected at the main coupling is partly balanced by a microwave bridge, and the residual voltage is detected by means of a heterodyne oscillator and 60-Mc/sec i.f. system. The isolator shown in Fig. 3 is included to reduce the risk of local oscillator power feeding back into the cavity. Overloading of the later stages of the detection system during the heater pulse is prevented by modifying a stage of the i.f. amplifier so that it may be paralyzed by a wave form from the pulse generator.

The frequency of the reflex klystron oscillator is stabilized using the harmonics of a 20-Mc/sec quartz crystal frequency standard. An FM receiver is tuned between 60 and 70 Mc/sec to pick up the beat between the klystron's frequency and one of the 20-Mc/sec harmonics, and the voltage output from the discriminator of the receiver provides the correction signal. This correction signal is amplified and fed to the reflector of the klystron, the necessary voltage insulation being

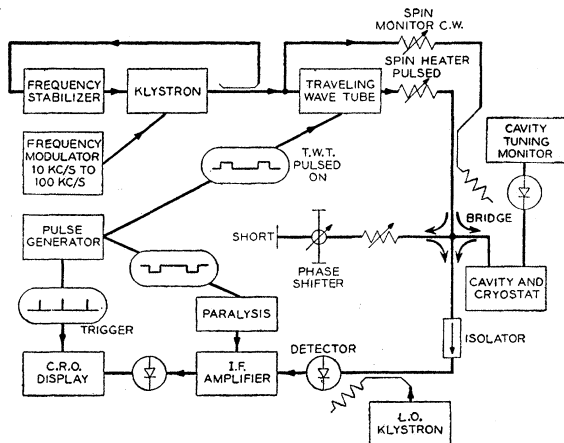


FIG. 3. Block schematic of apparatus used in single frequency relaxation experiments; in two frequency experiments a separate klystron drives the traveling wave tube.

obtained by using an amplifier with a 500-kc/sec carrier, and placing a high-voltage capacitor before the crystal diode demodulator.

Since we aim to measure spin population differences, it is essential that all observations should show χ'' changes only, in spite of small accompanying χ' changes which may occur during relaxation. The cavity should thus be on resonance whenever a measurement is made. To realize this condition we operate the klystron with a frequency sweep whose excursion is just sufficient to cover the resonance position 10 or 20 times in each relaxation half-life. The klystron stabilizing system has time constants longer than 1 millisecond; at the sweeping frequencies of 10 kc/sec to 100 kc/sec and at the amplitudes needed there is no appreciable disturbance of the stabilizer itself, which continues to hold the average microwave frequency at the required value.

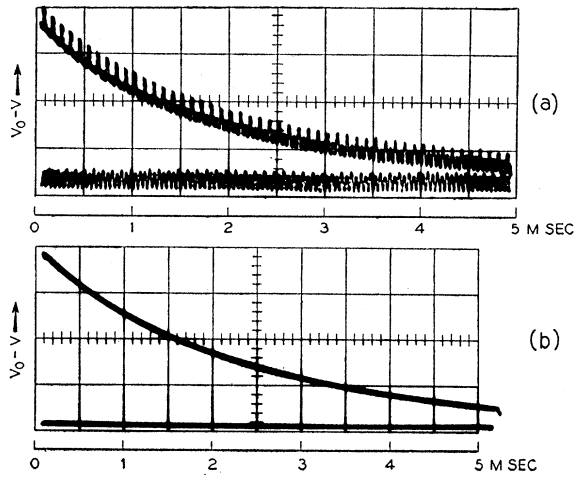


FIG. 4. Typical decay curves. In (a) the klystron is frequency modulated at 10 kc/sec to show the detuning effects of χ' changes. Minima correspond to on-tune settings and give χ'' values which are independent of χ' changes. When the χ' effect is small, it is possible to dispense with frequency modulation and superpose a number of traces as in (b).

The effects of this sweeping technique may be seen in Fig. 4(a). At the beginning of the relaxation period the cavity is tuned slightly off the average microwave frequency; the resonance position thus occurs near one extreme of the sweep. As relaxation proceeds, χ' changes, and the cavity resonance shifts until it is approximately in the middle. Measurements are made from the low points in the trace, which correspond to the on-tune position.

The rectified signal from the i.f. amplifier is smoothed by a RC network whose time constant may be chosen between 0.5 and 8 microseconds, and is then applied to a Tektronix 545 oscilloscope. At the end of the heater pulse, or at any selected time after this, a trigger from the pulse generator initiates the trace which displays spin relaxation. A second trigger, occurring before the next heater pulse at a time when no further relaxation

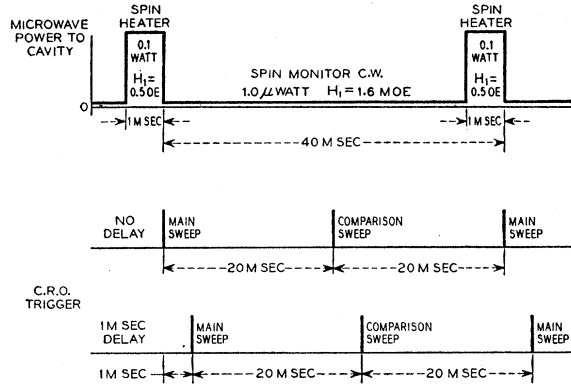


FIG. 5. Typical timing sequence. In each cycle of operation the CRO is triggered once to show the decay trace, and once to provide a base line. Triggers may be delayed to show decay after one or more half-lives.

effects are visible, starts the base line trace. If relaxation is genuinely complete, this base line will not move when the heater pulse is turned off altogether. In this way we are able to test whether the recurrence rate is slow enough to allow full relaxation to the bath temperature to occur before the next cycle of events begins. The timing sequence is shown in Fig. 5.

The size of the sample is chosen so that the paramagnetic losses do not change by more than 10% of the cavity losses during any observation. This we will now show gives a display which to the first order is linear in the pumping parameter v .

When a cavity is on resonance, the voltage reflection coefficient¹⁶ $E_r/E_i = (1-\alpha)/(1+\alpha)$, where $\alpha = Q_{\text{ext}}/Q_a$. Q_{ext} defines losses due to coupling alone; Q_a defines losses due to intrinsic cavity absorption and to absorption by the paramagnetic sample, so that

$$1/Q_a = 1/Q_c + 1/Q_m.$$

As relaxation progresses, Q_m tends towards Q_{m0} , and α and E_r tend towards the values α_0 and E_{r0} which they assume when relaxation is complete. In terms of the difference

$$\alpha - \alpha_0 = \frac{Q_{\text{ext}} \left[\frac{Q_{m0}}{Q_m} - 1 \right]}{Q_{m0}},$$

$$\frac{E_r - E_{r0}}{E_i} = \frac{1-\alpha}{1+\alpha} - \frac{1-\alpha_0}{1+\alpha_0} = -2 \frac{\alpha - \alpha_0}{(1+\alpha_0)^2} \left[1 + \frac{\alpha - \alpha_0}{1+\alpha_0} \right]^{-1}.$$

Expanding the latter as a series in $\alpha - \alpha_0$ and taking the first term, we have

$$\frac{E_r - E_{r0}}{E_i} \approx -2 \frac{\alpha - \alpha_0}{(1+\alpha_0)^2} = \frac{2Q_{L0}^2}{Q_{\text{ext}}Q_{m0}} \left(1 - \frac{Q_{m0}}{Q_m} \right),$$

¹⁶ This is derived from Eq. (3.4) of John C. Slater, *Microwave Electronics*, Bell Telephone Laboratories Series (D. Van Nostrand Company, New York, 1950).

where $1/Q_{L0} = 1/Q_{\text{ext}} + 1/Q_c + 1/Q_{m0}$. The terms of the series decrease in powers of $(\alpha - \alpha_0)/(1 + \alpha_0)$, that is, in powers of

$$\frac{Q_{L0}}{Q_{m0}} \left[\frac{Q_{m0}}{Q_m} - 1 \right].$$

If $Q_{L0}/Q_{m0} < 0.1$, the greatest error in taking only the first term will occur at the beginning of the relaxation cycle, and will not exceed 10% even if $1/Q_m \rightarrow 0$.

By Eq. (12), $1/Q_m \propto v$, and therefore

$$\frac{E_r - E_{r0}}{E_i} \sim \frac{2Q_{L0}^2}{Q_{\text{ext}}Q_{m0}} \frac{v_0 - v}{v_0}. \quad (13)$$

The difference in field vectors is not changed by adding a constant signal from the bridge arm in phase with E_r and E_{r0} , and it is detected by the superhet system as a difference between voltages proportional to E . Although tests showed that the output signal was linear in E over a wide range, we did not in practice allow the signal level to change by more than 50% during any relaxation cycle.

Oscilloscope traces were photographed and matched against a set of exponential curves produced on transparent film. In certain cases (Sec. V), where relaxation consisted of periods differing by an order of magnitude, we subtracted the longer period before measuring the shorter one. In the more typical case (Fig. 4) the traces appeared to be approximately exponential. Comparison with the transparencies did often show pronounced deviations, but in many such cases an analysis into two or more components would have been a largely arbitrary procedure, and we preferred simply to measure the fractional decay rate as a function of the time after the end of the heater pulse. This is easily done by making a tangential fit between the transparency and the photograph, and observing the time after the end of the heater pulse where this fit occurs.

The accuracy of measurement depends on the noise level, the magnitude of the right-hand term in Eq. (13), and on the degree of nonexponentiality in the trace. Although in exceptionally favorable cases [e.g., Fig. 4(b)] this may be as good as $\pm 5\%$, the limits are generally $\pm 10\%$. Certain results specifically mentioned later on may have larger errors.

IV. INDEPENDENCE OF EXPERIMENTAL CONDITIONS

We have worked with crystals having magnetic dilutions of 0, 4, 7, 11, 55, 200, 500 zinc atoms per nickel atom (alluded to here in as $D0$, $D4$, \dots), and we have made a number of tests to find out which factors control relaxation behavior. Only temperature, concentration, and heater pulse duration appeared to be significant, and the remaining changes, discussed below, had small effects, or, to within the accuracy of our measurements, no effect at all.

(i) Repeated Heating and Cooling of a Crystal

In a sequence of experiments, at a particular dilution, we have used the same crystal several times, allowing it to warm up to room temperature between each run. Although this led to the formation of small cracks within the crystal and a deterioration of the surface, it did not affect the relaxation properties.

(ii) Environment

The crystals were grown in the form of plates and mounted by the edges in a light frame of polyfoam. They had no contact with any dense object, and more than $\frac{2}{3}$ of their surface was exposed to the cryostatic environment. Experiments were made first with gaseous helium at different pressures in contact with the crystal, and then with liquid helium in contact. Such comparisons could be made during a single experimental run by admitting liquid helium through a valve mounted in the top of the cavity. No changes were seen except in those cases where the power level was high enough to cause crystal heating [see (iv) below].

(iii) Monitor Power Level

Monitor power entering the cavity was normally about 1 microwatt. We have never observed any difference when increasing this by 6 db.

(iv) Average Heater Power Level

We have seen changes associated with a high average heater power level. They first appear as a small shift in the base line, but at higher power the decay trace becomes shallower (corresponding to less change in χ'') and its decay time shorter. When the power level is reduced (e.g., by reducing the recurrence rate) it sometimes takes seconds for the display to return to normal. Small base line shifts corresponding to spin temperature rises of 5% have been seen at average powers as low as 400 microwatts, (this with a $D7$ crystal at 2.2°K and helium gas at 20-mm pressure in contact), but considerably higher powers were needed before changes in the relaxation time became measurable. We believe this effect is due to an over-all heating of the crystal. It has seldom amounted to a serious experimental problem, and we have nearly always been able to work with the heater power at a safe level. For the two most concentrated crystals, $D0$ and $D4$, the heating which arose from the relaxation of a single pulse became significant, and showed up as a long tail at the end of the decay trace. This is not surprising since, in such concentrated crystals, a large part of the heat capacity resides in the spins themselves, and the lattice does not provide an adequate heat reservoir. The thermostatic role devolves on materials in contact with the surface; some observations made with gas contact suggest that a surface layer of helium atoms may be playing an important part.

(v) *Crystal Size and Form*

Relaxation times were measured for *D7*, *D55*, and *D200* crystals in the form of flat plates 4 mm thick. The plates were then thinned down by more than 2:1, and the measurements repeated. Measurements between 1.8 and 4.2°K showed that the results were the same before and after this change in the shortest dimension. Eventually the *D200* crystal was crushed so that the largest particles passed through a 1-mm sieve. This gave times which were 30% faster over the temperature range 1.8°K to 4.2°K. The change barely lay outside experimental error, and may have been connected with the fact that the crushed grains were irregularly oriented. The longest time constant associated with the cooling of a flat plate of thickness l is given by $\tau = (l^2/\pi^2)(c_p/K)$. Independence of l in the above tests indicates that this time τ must be considerably shorter than the shortest observed relaxation time, and that no appreciable temperature gradient can exist within the crystal.

(vi) *Initial Spin Temperature When Relaxation Begins*

We reduced the power in the heater pulse, (whilst ensuring that it was long enough to produce steady-state conditions) so that we could observe relaxation from lower initial spin temperatures. This was done with *D7*, *D11*, and *D55* crystals at various temperatures, halving and in some cases quartering the initial value of $v_0 - v$. Lower initial spin temperatures consistently gave slightly longer relaxation times, although the changes were almost within the experimental error and in no case exceeded 20%. The decay curves obtained with the *D11* crystal and one of our *D55* crystals deviated considerably from exponential form, and we compared several starting from different initial states to see if the relaxation rate depended on the instantaneous spin temperature, irrespective of how it was reached. It appeared, however, that the relaxation rate depended more on the time elapsed since the end of the heater than on any other factor. *D200* and *D500* crystals showed changes in the characteristics of a fast decay component when the intensity of the heater pulse was varied. This is discussed in Sec. V.

(vii) *Duration of the Heater Pulse*

In crystals of medium concentration, and over a wide range of durations in the very dilute ones, this made no difference. For the most concentrated crystals no effect was noticed which could not be ascribed to heating as discussed in (iv) above. For *D200* and *D500* crystals new forms of relaxation appeared when the heater pulse was short, as discussed in Sec. V.

(viii) *Changes in the Experimental Frequency*

Because of the large width of the resonance line it was possible to select frequencies over a range of

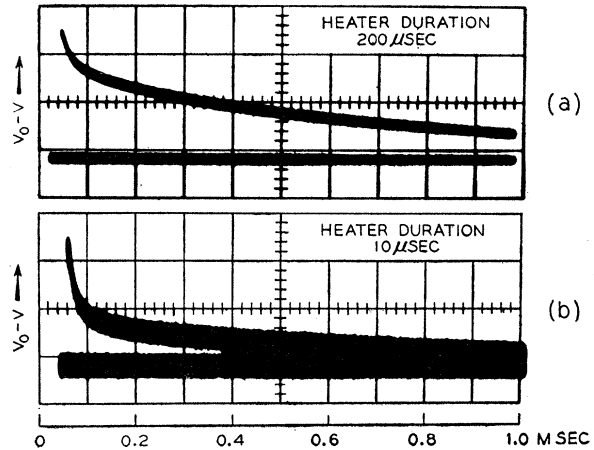


FIG. 6. Relaxation with two decay periods in a *D200* crystal. The short period is associated with the sharing of energy throughout the line, the long period with lattice relaxation. (a) If the heater pulse is long, a considerable amount of sharing occurs before observation begins. (b) If the heater pulse is short, most of the sharing takes place after the pulse has ended.

several hundred megacycles, some corresponding to positions near the center of the line and others corresponding to positions in the wings up to 400 Mc/sec away. In no case did this yield any difference in relaxation rate outside experimental error, and nothing was seen which, when compared with results on concentration dependence, would suggest a lower effective concentration of spins in the wings of the line. On the contrary, the results strongly indicated that the whole "inhomogeneous" line relaxed as a unit. This is consistent with the observations on energy sharing discussed in Secs. V and VI.

V. FORM OF DECAY CURVE; SHARING TIME

The decay traces did not follow the exact exponential law of Eq. (4). Some appeared exponential at first sight but revealed discrepancies when examined more closely, while others obviously contained components differing by orders of magnitude. Very slow periods associated with heating could be eliminated for all but *D0* and *D4* crystals (Sec. IV. iv). *D11* and one *D55* specimen showed a continuous fall in decay rate over a 3:1 range during relaxation. *D7* and a different *D55* specimen changed by less than 30%, and would have been accounted perfect exponentials in the absence of a definite experimental base line. In *D200* and *D500* crystals a new fast relaxation phenomenon was observed.

Figure 6 shows relaxation traces obtained with a *D200* crystal. Figure 6(a) was taken with a heater pulse 1000 μ sec long, and Fig. 6(b) with a heater pulse 50 μ sec long. The decay rates in Fig. 6(a) range between 1 and 2 msec^{-1} ; in Fig. 6(b) similar decay rates are found in the long tail, but they are preceded by components an order of magnitude faster. The faster ones, which are found after subtracting the slow component, have a

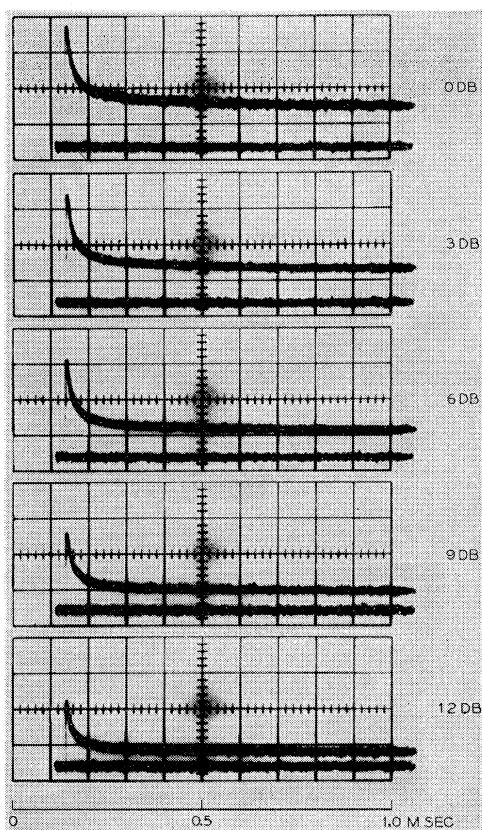


FIG. 7. Two component relaxation at various heater power levels, and with a heater pulse duration of 20 microsec. At high powers more of the line is directly pumped, and a higher over-all spin temperature remains after sharing out.

range of values between 100 and 10 msec^{-1} with an average of about 20 msec^{-1} . Figure 7 shows the way in which the fast relaxation phenomenon depends on the heater power level. Power was decreased in steps of 3 db in going from top to bottom of the picture; the heater pulse duration was 100 μsec . Apart from a change in the distribution of fast components, the most notable feature in Fig. 7 is the increase in relative importance of the slow component at high power levels. The initial spin temperature only increased by a factor of 1.8:1 over the whole 12 db range.

We examined this fast relaxation phenomenon by changing the experimental conditions in the following ways.

(i) The environment was changed from gas to liquid; also the crystal was thinned down from 4 mm to 1.5 mm, and finally crushed so that the largest grains passed through a 1-mm sieve. None of these measures had any effect.

(ii) The dilution factor was changed from 200 to 500:1. This had only a slight effect on the slow component (see Sec. VII) but slowed down the average fast component to 5 msec^{-1} . We have seen slight indication

of the fast fall phenomenon with *D55* but have not been able to observe it at all with more concentrated crystals.

(iii) The temperature was reduced from 4.2 to 2.0°K. This changed the slow component by a factor of 10:1. The mean fast component was slowed down by a factor of approximately 2:1.

(iv) The operating frequency was changed from 3.9 kMc/sec, in the center of the inhomogeneous line, to a value of 4.1 kMc/sec nearer the wings. This had no appreciable effect on the slow component (Sec. IV. viii), but there was a perceptible lengthening of the fast component.

(v) A small dc magnetic field of ~ 60 oe was applied along the crystal axis. This caused a small reduction in χ'' , as might be expected to result from increased broadening of the line, but it did not have any measurable effect on the slow decay component. The fast component was slowed down by $\sim 3:1$ in both the *D200* and the *D500* crystal. A small magnetic field thus produced effects similar to those resulting from an increase in dilution.

It should be remembered that the observed spectrum of fast components depends to some extent on heater pulse conditions, and that the above average values are only approximate. A slowing down in all components will tend to emphasize those which were shortest, and may thus distort the average in such a way as to lead to an underestimate of the actual change.

We have named this fast decay time the "sharing time" because we believe that it shows the sharing of energy between those spins being directly pumped and others in more remote parts of the "inhomogeneous" line. If the heater pulse is short and ends while sharing is still incomplete, then the sharing process will continue after the heater pulse is cut off. A long heater pulse allows time for the establishment of a dynamic equilibrium between microwave pumping, energy sharing, and lattice relaxation, such that the whole line is more or less evenly pumped and only a slight redistribution occurs when the heater is cut off. This slight redistribution does, however, show up, and is more pronounced in the *D500* than in the *D200* crystal. The dependence on heater power level suggests that spins in the near neighborhood of the microwave frequency, although contributing little to the observed χ'' , are being more effectively pumped at the higher power levels, and are therefore able to give more in the ultimate sharing out. The small 60 oe field might be expected to raise the degeneracy of the lower energy level, and to sort out spins in the crystal into two groups. The way in which this field hinders communication of energy throughout the line strongly suggests the presence of resonant spin transfers at some stage in the sharing out mechanism.

VI. TWO FREQUENCY EXPERIMENTS

In order to obtain a clearer indication of the sharing process, we performed experiments in which the heater

frequency and the monitor frequency were separated by an interval of 200 Mc/sec. The heater frequency was set at ~ 3.9 kMc/sec in the middle of the resonance line, and the monitor frequency was set at ~ 4.1 kMc/sec. A *D*200 crystal was mounted in the tunable two mode cavity shown in Fig. 8. Figure 9(a) shows the results obtained at 4.2°K with a 50- μ sec heater pulse; 9(b) and 9(c) show the results obtained with a small 60-oe field and a 100- μ sec heater pulse at 4.2°K and 2.0°K, respectively. All three traces show evidence of the competition which occurs after the heater pulse is cut off between the buildup due to energy sharing and the normal spin lattice decay. In cases 9(b) and 9(c) an actual rise in the spin temperature is clearly visible, since here the sharing out process has been slowed down by the external field. In experiments with a 60-Mc/sec interval between heater and monitor frequencies we have not been able to observe this buildup effect. This may be because the energy transfer time is too short across the narrower frequency interval, or because the gain from one group of spins is outweighed by the loss to others in remoter parts of the line.

The heater power and duration necessary for these observations may be guessed from the results of the

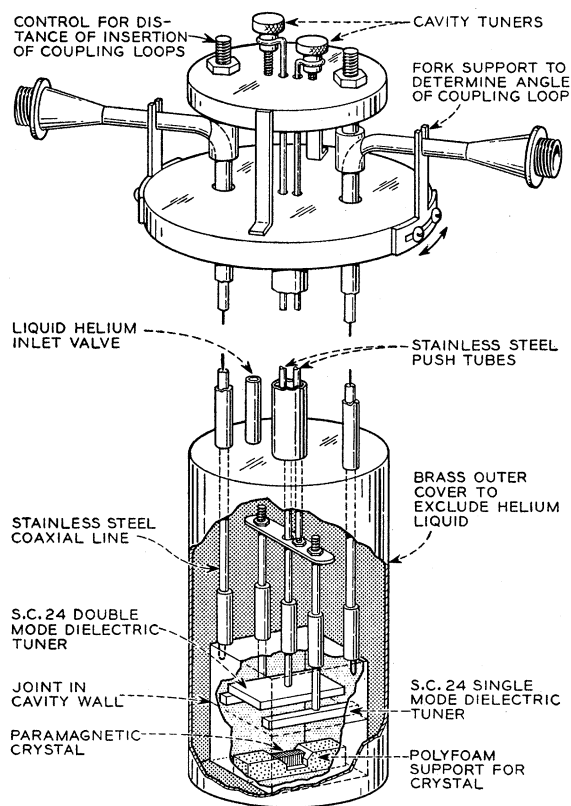


FIG. 8. Two mode cavity showing tuning and coupling arrangements. In single frequency experiments a simplified version of this was used. For experiments above 4.2°K a second cylindrical cover was added, and the intermediate space was evacuated to provide thermal insulation.

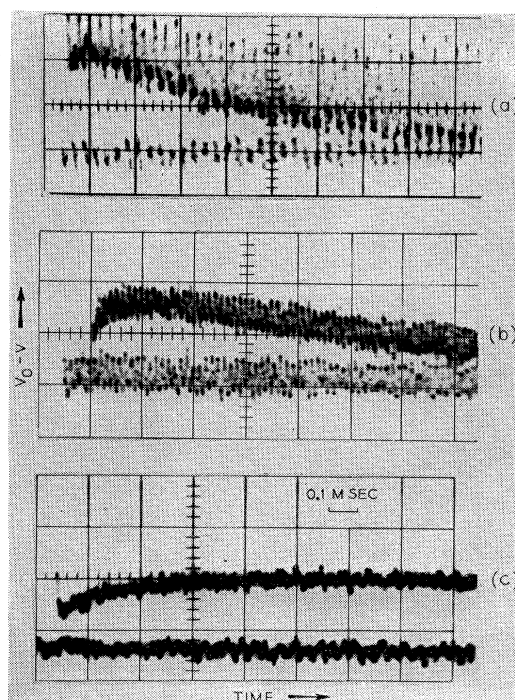


FIG. 9. Build up at frequencies 200 Mc/sec away due to the sharing out of energy. Heater pulse ends where the upper trace begins. (a) *D*200 crystal at 4.2°K with 50 microsec heater pulse. (b) *D*200 crystal at 4.2°K with 100-microsec heater pulse and a 60-oe external field to hinder communication between spins. (c) *D*200 crystal at 2.0°K with 500-microsec heater pulse and a 60-oe external field.

experiments on the fast initial decay described in Sec. V. At settings favorable for a demonstration of the sharing phenomenon, the resulting pumping level throughout the line is comparatively low, and therefore a comparatively poor signal-to-noise ratio is to be expected in the two frequency experiments. The large amplitude frequency sweep visible in Fig. 9 was needed to ensure that the observed effects represented genuine changes of spin populations at the monitor frequency, and that they did not merely stem from χ' changes due to pumping at the heater frequency nearby.

VII. TEMPERATURE AND CONCENTRATION DEPENDENCE

We have measured relaxation rates at temperatures between 1.8°K and 4.2°K. Dependences ranged from $T^{1.6}$ to T^3 between 2°K and 3°K, and from $T^{2.2}$ to T^4 between 3°K and 4°K, with a general tendency for more concentrated crystals to follow lower power laws. Relaxation rates of the *D*200 crystal were measured up to 9°K. The cavity and its contents were connected to an electrical heating coil, and isolated from the cryostat by an evacuated space; temperatures were measured by a calibrated carbon resistance thermometer.¹⁷ In this

¹⁷ O. V. Lounasmaa, *Phil. Mag.* **30**, 652 (1958).

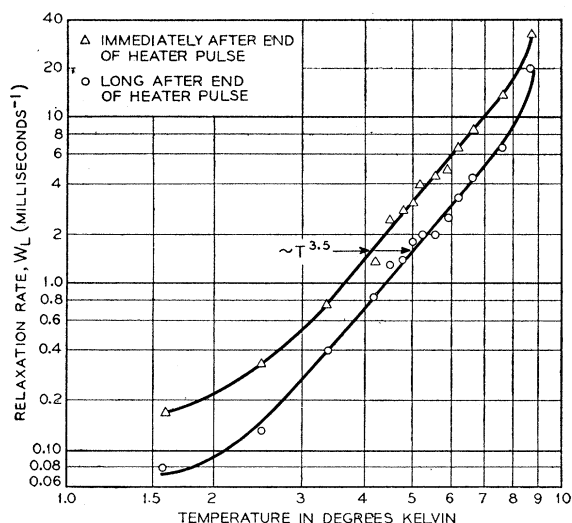


FIG. 10. Relaxation rate and temperature for a *D200* crystal. Relaxation rates vary according to how soon after the heater pulse they are measured, but the choice of a measurement point does not greatly affect the resulting temperature dependence.

case, relaxation varied as $T^{3.5}$ over most of the range, as shown in Fig. 10.

Figure 11 shows relaxation rates at 4.2°K and 2.2°K as a function of dilution factor. In plotting these curves, we have used Zn/Ni ratios determined by chemical analysis of the crystals. The result at *D4* is joined by a broken line, since it is possible that this was affected by crystal heating (Sec. IV. *iv*). Measurements were made at the half decay point except for *D500*, which was measured at three quarters decay to eliminate the last traces of energy sharing effects; (the difference in W_L between half and three quarters decay is usually small).

VIII. DISCUSSION OF RESULTS

Although the resonance line is inhomogeneously broadened, and may conceal a small splitting of the ground level, the experiments on energy sharing, and the identity of results at different frequencies in the line, show that we are observing relaxation rates characteristic of a two level system. These rates do not depend on particular experimental conditions, and in our work are not being modified by heating, either of the inside of the crystal with respect to the outside or of the whole crystal with respect to the cryostat.

Of the experiments aimed at revealing any effects due to energy transport to the crystal boundaries, all have produced negative results. Changes in gas pressure, changes from gas to liquid environment, and gradual deterioration of the crystal surface have not altered relaxation times, nor has the formation of small cracks within the crystal, nor deliberate reductions in size. We conclude that energy transport to the boundary is not a limiting factor. In view of the difficulty of carrying the whole energy of relaxation in a band of low-

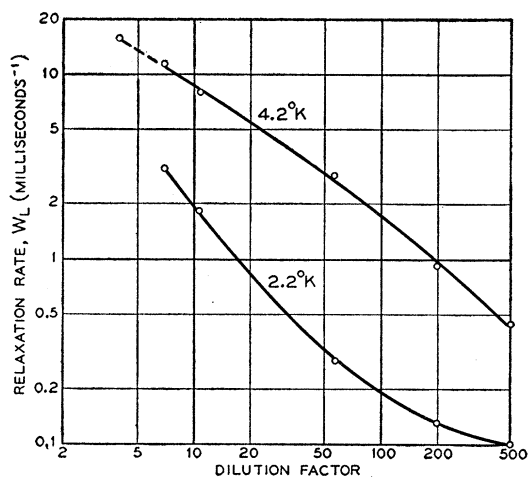


FIG. 11. Relaxation rate at the half decay point and magnetic dilution factor. The measurement for *D4* at 4.2°K may have been disturbed by crystal heating and is shown joined with a broken line.

frequency modes, it seems likely that frequency conversion of low-frequency phonons occurs with a relatively high probability throughout the crystal, or that spin relaxation itself takes place through a Raman type of process.

Although the energy sharing observations are in general agreement with those reported by Giordmaine *et al.*,⁵ their original model could not be applied in this case without some modifications to allow for lack of dependence on size and on the surface contact medium. The effect of small magnetic fields in slowing down energy sharing would be particularly difficult to fit into their picture, and suggests rather that spin-spin interactions are involved; that these cannot be neglected has already been pointed out by Bloembergen *et al.*¹⁸ and Anderson.¹⁹

Even where energy sharing effects seemed absent, there were cases in which the decay deviated considerably from the exponential form. In looking for a possible significance in this, we tried to fit decay curves of *D200* and *D11* crystals with a simple model, in which a phonon band loses energy by Newton's law of cooling, and is at all times in temperature equilibrium with the spins. This did not lead to encouraging results, and we did not proceed with more sophisticated variations on the theme since two general properties of the decay curves were unfavorable to this kind of interpretation. The form was only slightly changed by going to a lower initial spin temperature, and the degree of exponentiality varied from one crystal to another, even being different for two *D55* specimens. As the decay rate varies with concentration, it seemed likely that these deviations indicated no more than the existence of local irregularities in the spin density. (The energy

¹⁸ Bloembergen, Shapiro, Pershan, and Artman, *Phys. Rev.* **114**, 445 (1959).

¹⁹ P. W. Anderson, *Phys. Rev.* **114**, 1002 (1959).

sharing results do not necessarily prove that there is enough spatial spin diffusion to average out such irregularities.)

Temperature dependences lie between $T^{1.6}$ and T^4 . If relaxation were limited by the rate at which low-frequency phonons could combine with others in the thermal spectrum, this would be a plausible result, although the lowest power laws might require some additional explanation. (Herring²⁰ has calculated low-frequency phonon combination probabilities and obtained power laws of this type.) Leaving aside the question of "bottlenecks," our results do not agree with direct process theory, and yet the highest temperature dependence is not as great as that predicted by Van Vleck for the Raman process. This could mean that the experiments were made in a range where direct processes are being superseded by Raman processes, although the steady $T^{3.5}$ law found for the *D200* crystal between 3°K and 8°K makes such an explanation unlikely in that case. Interpretation might prove easier if there were a larger body of theoretical literature relating to the Raman process: since Van Vleck's calculation there have been many studies of phonon properties which might prove relevant, such as those of the mode spectrum of crystals, and of the restrictions imposed by the need to conserve both energy and momentum.

In common with many other experimenters we find an increase in the relaxation rate at higher concentrations. This does not follow from the model of direct or Raman processes alone, although "bottlenecks" in the relaxation could introduce a concentration dependence. However, models based on a bottleneck in low-frequency phonons tend to predict a slower rate for higher concentrations. Heating of the crystal could on some assumptions lead to an acceleration, but we believe we have excluded this possibility in our experiments. The

deviations from exponentiality suggest another line of thought. These point to the possibility of there being different relaxation rates in different regions of the crystal. It is only one step further to postulate the existence of a fraction of fast relaxing centers, such as might be found in paramagnetic clusters or situated near flaws in the crystal. Some degree of communication exists between spins, and this might at high enough concentrations be sufficient to transfer energy to a fast relaxing sink.

IX. CONCLUDING REMARKS

Our results do not agree with the predictions of any current theory. A possible way of explaining them is to assume that the relaxation rate is controlled by a Raman type of process. Alternatively, if one wishes to explain them on the basis of a "direct" process, one needs to postulate that any excess of low-frequency phonons is rapidly eliminated by phonon combination. We have found no evidence for a pile up of low-frequency phonons in a part of the thermal spectrum, although we cannot entirely exclude the possibility. At first sight, the sharing phenomenon might be thought to support a "pile up" model, but in fact the dependence on small magnetic fields rather suggests that mechanisms involving spin-spin interaction are responsible. In concluding, it should be emphasized that the results reported here for one particular substance represent no more than a partial contribution towards solving the problem, and cannot be generalized into laws of paramagnetic relaxation.

X. ACKNOWLEDGMENTS

We wish to thank Mr. J. D. McGee for assistance with these experiments and Mr. H. R. Hartford for growing the crystals. We should also like to express our indebtedness to Dr. K. Dransfeld and Dr. J. P. Gordon for numerous discussions during the course of this work.

²⁰ C. Herring, Phys. Rev. **95**, 954 (1954).

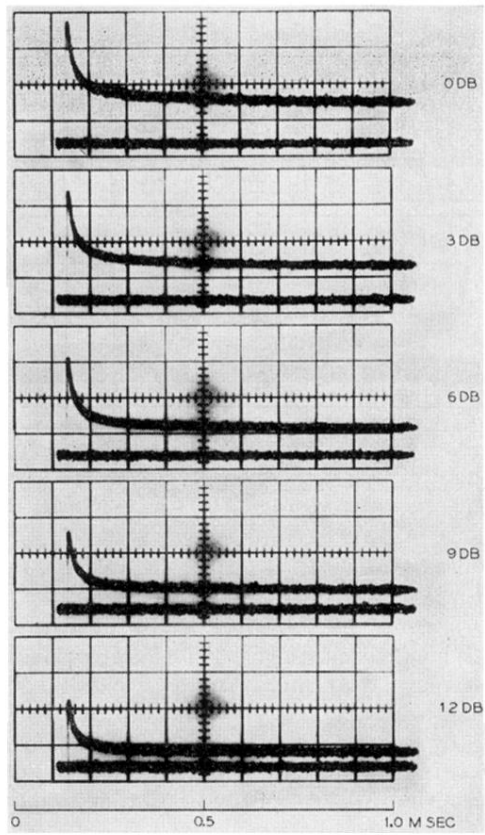


FIG. 7. Two component relaxation at various heater power levels, and with a heater pulse duration of 20 microsec. At high powers more of the line is directly pumped, and a higher over-all spin temperature remains after sharing out.

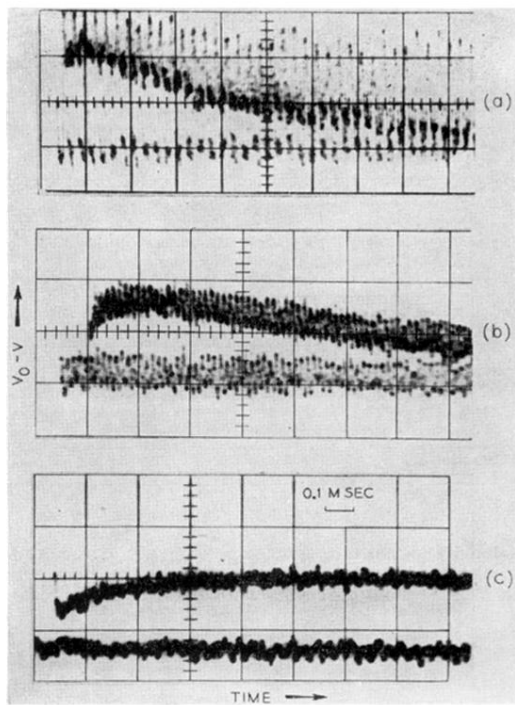


FIG. 9. Build up at frequencies 200 Mc/sec away due to the sharing out of energy. Heater pulse ends where the upper trace begins. (a) *D*200 crystal at 4.2°K with 50 microsec heater pulse. (b) *D*200 crystal at 4.2°K with 100-microsec heater pulse and a 60-oe external field to hinder communication between spins. (c) *D*200 crystal at 2.0°K with 500-microsec heater pulse and a 60-oe external field.