

that the amplitude of the signal and its phase shift with respect to the hf field are determined by $\text{Tr}(\mathbf{r}I_{\pm})$:

$$\langle I_{\pm} \rangle = e^{\mp i\varphi} \text{Tr}(\mathbf{r} \cdot I_{\pm}),$$

or, since

$$\begin{aligned} \text{Tr}(\mathbf{r}I_{\pm}) &= |\text{Tr}(\mathbf{r}I_{\pm})| e^{\pm i\alpha} : \\ I_x &= |\text{Tr}(\mathbf{r}I_{\pm})| \cos(\varphi - \alpha); \\ I_y &= -|\text{Tr}(\mathbf{r}I_{\pm})| \sin(\varphi - \alpha). \end{aligned}$$

The two modulation methods can therefore give different results only if \mathcal{H}_T is not the same in each case. Introducing again $H_0 = H_{00} - H_M \cos \omega_M t$ and $\dot{\varphi} = \omega_0$ for field modulation and $H_0 = H_{00}$ and $\dot{\varphi} = \omega_0 + \gamma H_M \cos \omega_M t$ for frequency modulation, we see that all contributions to \mathcal{H}_T remain the same, except $L_0 \dot{\varphi}$, which becomes

$L_0 \omega_0$ for the first, $L_0(\omega_0 + \gamma H_M \cos \omega_M t)$ for the second case. Since these terms concern only the lattice and since γH_M is assumed to be very small compared to ω_0 , with no chance of compensating $L_0 \omega_0$ considerably by parts of \mathcal{H}_0 , it seems justified to neglect $L_0 \gamma H_M \times \cos \omega_M t$. Although a more detailed and complicated calculation appears to be necessary to prove fully the equivalence of field and frequency modulation for this general case, we believe our discussion supports this equivalence strongly when $\gamma H_M \ll \omega_0$.

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Cross Relaxation in Ruby

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A pulsed microwave method has been used to study paramagnetic relaxation in synthetic ruby at Cr/Al concentrations from 0.02% to 0.3%, and over a wide range of fields and angles with respect to the crystal axis. The experimental frequency was 7.17 kMc/sec. At settings for which one interval between energy levels was twice as large as another, decay traces with two characteristic periods were observed. The more rapid decay was independent of temperature, and is attributed to a cross-relaxation process involving three spins. Similar behavior became apparent at all concentrations whenever two intervals approached the same value. At 0.3%, two period decay traces were observed for any arbitrary field and angle setting, indicating at this concentration, a general cross relaxation between the Zeeman levels in times of 0.3 millisecond and less.

INTRODUCTION

THE classical treatment of paramagnetic relaxation by Casimir and duPre^{1,2} assumes two systems, spins and lattice oscillators, physically interspersed but weakly coupled with each other. The coupling within each system is assumed to be strong, so that each is in a state of internal thermodynamic equilibrium characterized by a temperature, and relaxation is depicted as a kind of heat conduction whereby energy given initially to the spin system becomes transferred to the crystal lattice. A number of experiments have turned on the question of temperature equilibrium in the interacting systems, in particular on equilibrium within the spin system which, until the recent extension of acoustic techniques into the kilomegacycle range³ was the only one open to direct observation. De Vrijer and Gorter⁴ modified the spin equilibrium concept to account

for a "third" or "intermediate" relaxation effect which appeared in their experiments on the chromium alums. This effect was too slow to be due to simple spin-spin interaction and yet considerably faster than lattice relaxation. It was independent of temperature in the hydrogen to helium range, could be seen only in those salts where the spins were clearly separated into two classes due to the presence of two different magnetic complexes, and was explained in terms of transfers between subgroups within the spin system. Similar effects were later observed by Verstelle, Drewes, and Gorter⁵ in magnetically dilute materials.

These experiments were made by the nonresonant method. Magnetic resonance has made it possible to study the behavior of spin groups in more detail, and to observe different types of "intermediate" or "cross relaxation" between them. In the simplest case, where two spin groups have the same resonance frequency, energy transfer will take place in the spin-spin time, and for most purposes the spins will behave as a single group. If groups have a small frequency separation, as in the

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

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

³ H. Bommel and K. Dransfeld, *Phys. Rev. Letters* **1**, 234 (1958).

⁴ F. W. de Vrijer and C. J. Gorter, *Physica* **18**, 549 (1952).

⁵ J. C. Verstelle, G. W. J. Drewes, and C. J. Gorter, *Physica* **24**, 632 (1958).

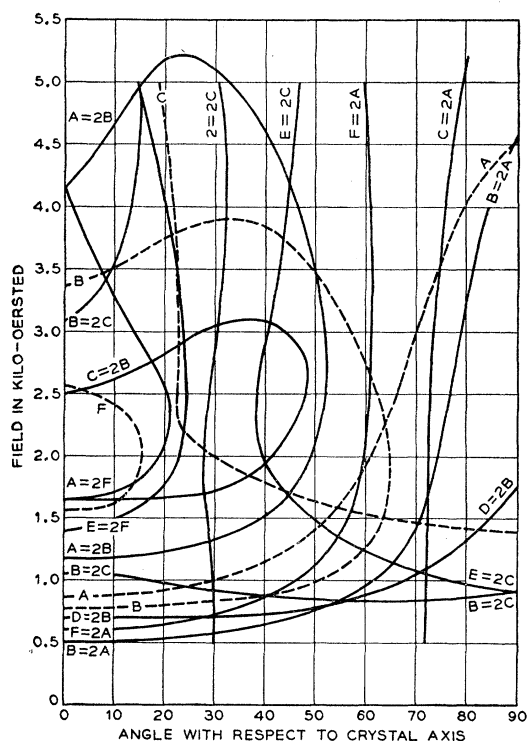


FIG. 1. Isofrequency plot and double frequency congruences for ruby. Broken lines show field and angles with respect to the crystal axis which give a resonance frequency of 7.17 kMc/sec. Heavy lines show settings at which one interval is twice another. At the intersection of a heavy line with a broken line, two intervals have resonance frequencies of 7.17 kMc/sec and 14.34 kMc/sec, or 3.59 kMc/sec and 7.17 kMc/sec.

components of a broad inhomogeneous line, transfer becomes slow enough to be described by intermediate relaxation times. These times lengthen as concentration is reduced or as the discrepancy in frequencies becomes larger, until eventually they become longer than the lattice times themselves. In this limit the spin groups are effectively separate from each other, and can be maintained at different temperatures, as in the operation of a three level maser. Spin groups belonging to different transitions in the level scheme commonly satisfy this criterion of isolation in dilute paramagnetic materials as is shown by the success of many maser tests.

In the experiments reported here a pulsed microwave apparatus has been used to examine relaxation in synthetic ruby. Cross-relaxation effects appear in the form

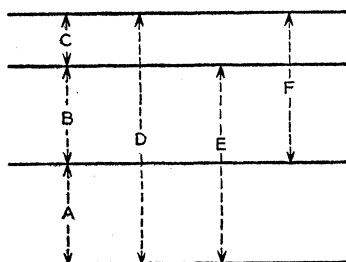


FIG. 2. Notation for the six transitions between the ruby levels.

of decay traces having two or more periods. We observed phenomena of this kind when two intervals approached the same value, when one interval became twice or half another, and when the concentration became high enough for spin isolation to break down quite generally.

EXPERIMENTAL

The pulsed microwave apparatus has been described in a previous paper.⁶ It provides a high-power pulse which disturbs the spin level populations, and a low-power c.w. signal to monitor the return to equilibrium. Results are recorded by photographing oscilloscope traces, each photograph showing two traces, one triggered after the re-establishment of equilibrium in order to provide a base line. Measurements were made on synthetic rubies having Cr/Al concentrations of 0.02%,

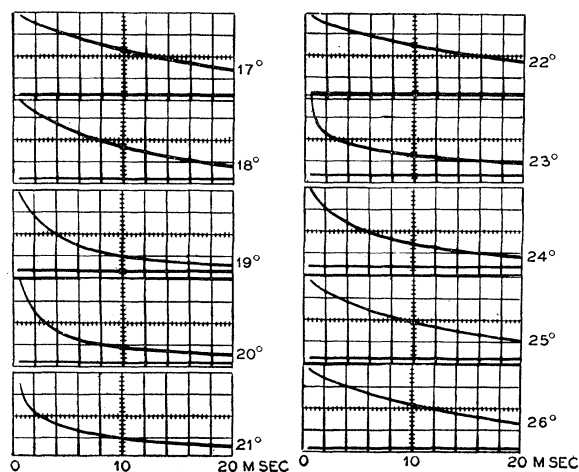


FIG. 3. Relaxation in interval *B*. At 22° $B=C$; on either side of this setting, cross relaxation leads to a decay trace with two periods. (Concentration=0.1%, pump pulse duration=0.15 millisecond.)

0.05%, 0.1%, 0.15%, and 0.3%, at a signal frequency of 7.17 kMc/sec. The transition diagram for this frequency is shown by the broken lines in Fig. 1, letters being used to designate transitions as in Fig. 2. In order to study relaxation behavior as intervals were varied relative to each other, the angle between the crystal axis and the external magnetic field was changed in one degree steps, adjustments being made in the field so as to maintain the interval under study at a constant resonant frequency of 7.17 kMc/sec.

Figure 3 shows relaxation in interval *B* in the neighborhood of the setting for which $B=C$ (22° and 3.8 kilo-oersted). On either side of this position the separation between *B* and *C* increases at the rate of 300 Mc/sec per degree. Decay traces near 22° show two periods, a fast one corresponding to the drain of energy from *B* to *C* and a slow one corresponding to the joint relaxation

⁶ K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

of both intervals. The smaller the discrepancy between the frequencies of B and C the faster the rate of transfer by cross relaxation, until at 22° transfer takes place while the pump pulse is applied and is already complete when observation begins. Even when the intervals are separated by several hundred megacycles, transfer is rapid compared with lattice relaxation. A 600 Mc/sec difference between B and C gave a transfer time of 3 milliseconds at 0.1% concentration. This time was unaffected by changing the temperature from 4.2°K to 20°K but was very sensitive to concentration. At 0.15% and with the same B to C separation the transfer time shortened to 1 millisecond, whereas at 0.02% no cross relaxation could be detected at such large frequency separations. (Experiments on the relaxation of potas-

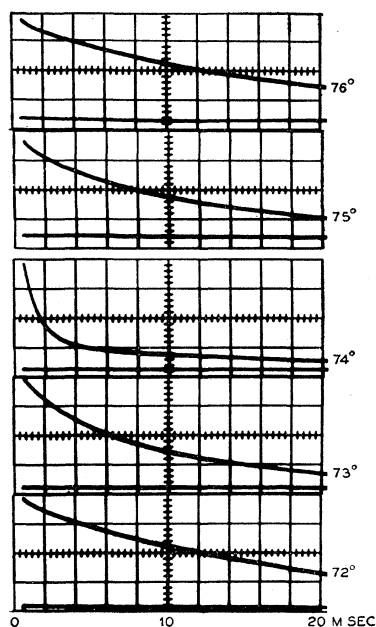


FIG. 4. Relaxation in interval A at 74° where $C=2A$; cross relaxation occurs with a time constant of 1 millisecond. (Concentration = 0.1%, pump pulse duration = 0.1 millisecond.)

sium chromicyanide in the neighborhood of an equal frequency setting have been reported by Wagner, Castle, and Chester.⁷)

THREE SPIN RELAXATION

A similar transfer phenomenon could be seen when a second interval became twice or half the size of the interval under observation. Figure 4 shows the relaxation behavior of interval A for angles in the vicinity of 74° . At 74° and 3.55 kilo-oersted C is twice A , the difference between C and $2A$ being 570 Mc/sec per degree on either side of the exact setting. The transfer time was much longer than in the case when two intervals were set equal, and the effect could not be seen

⁷ P. E. Wagner, J. G. Castle, and P. F. Chester, Bull. Am. Phys. Soc. 4, 21 (1959).

TABLE I. Three spin transfer times (in milliseconds).

Interval relation	Observation interval	Cr/Al Concentration in %				
		0.3	0.15	0.1	0.05	0.02
$B=2A$	A	0.08	0.4	1.2	4	50
$C=2A$	A	0.06	0.35	1	4	50
$A=2B$	B	0.08	0.4	1.3	4.5	70
$E=2C$	C	...	0.2	0.7	2.8	50
$C=2B$	C	...	0.14	0.4	1.5	40
$A=2C$	C	0.05	0.18	0.6	2.4	55
$B=2C$	B	0.07	0.5	1	3.5	...
$D=2B$	C	0.2	0.6	13

when there were such large discrepancies in the frequency relation. The traces in Fig. 4 were obtained with a 0.1% ruby at 4.2°K , and show a transfer time of 1 millisecond. No change was observed to within an experimental accuracy of 20% when the temperature was raised to 20°K , but the rate of transfer increased rapidly with concentration, varying as $c^{2.4}$ over the range from 0.02% to 0.3%.

Fields and angles for which there is a two to one relation between intervals are shown by the heavy lines in Fig. 1. Where these crossed the 7.17 kMc/sec isofrequency plot a two period relaxation trace could be observed. At 8 such settings transfer times were measured as a function of concentration, and the results are shown in Table I. Concentration dependence followed the same power law in all cases. Transfer rates were almost entirely independent of temperature from 20°K to 2.2°K . Small changes were observed between 4.2°K and 2.2°K , some times becoming slower and others faster, but these changes lay barely outside experimental error. They may possibly be attributable to the redistribution of the total populations belonging to the cross relaxing intervals at lower temperatures.

Simultaneous observations in two intervals have been made by Geusic⁸ who finds at 90° and 1.7 kilo-oersted ($D=2B$), a pump signal applied to B saturates D and gives inversion in A . He also reports higher order cross-relaxation effects corresponding to $D=3B$, $D=4B$, and $D=4B$ at certain settings.

GENERAL CROSS RELAXATION

At a concentration of 0.3%, two period decay traces were observed at all field and angle settings. Figure 5 shows the relaxation of interval A at 80° , 4.05 kilo-oersted, and 4.2°K . It consists of a 0.14 millisecond fast period and a 30 millisecond slow period, whose relative proportions depend on the duration of the pump pulse in the manner shown. At different settings on the isofrequency diagram (Fig. 1) fast decay times were found ranging from 0.3 millisecond (in F near 0°), to 0.04 millisecond (in C at low fields). There were also abrupt changes at settings which correspond to a 2:1 ratio between intervals. For example in the immediate vicinity of 74° and 3.55 kilo-oersted, where $C=2A$, the

⁸ J. Geusic, Phys. Rev. 118, 129 (1960).

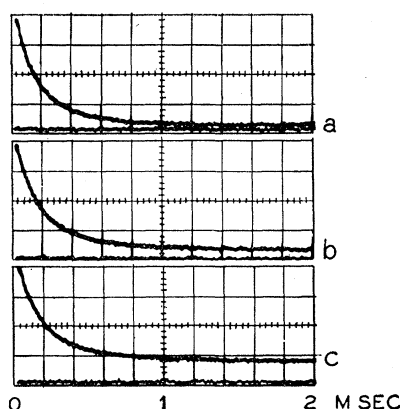


FIG. 5. General cross-relaxation phenomena in 0.3% ruby for interval *A* at 80° to the crystal axis. The cross-relaxation time is 0.14 millisecond, and the slow, lattice time 30 milliseconds. Pump pulse durations are: (a) 0.05 millisecond, (b) 0.3 millisecond, (c) 1 millisecond. With longer pump times some transfer takes place during the pulse, and a higher over-all level of excitation remains after the spin system has come into thermal equilibrium. Temperature is 4.2°K . At 2.1°K the slow period changed to 70 milliseconds, but the fast period was unaltered.

fast component in the relaxation of *A* speeded up from 0.13 to 0.04 millisecond. It has been assumed here that this shortening of the time is due to a simple superposition of the decay rates due to this general fast decay and to three spin cross relaxations. The values given in Table I under 0.3% have been obtained by subtracting the decay rate measured to one side from that measured on the exact two-to-one setting. The general fast decay rates were unchanged when the temperature was reduced to 2.2°K , thus behaving in a way which is typical of cross relaxation processes, and suggesting that the fast decay is due to the transfer of energy between the pumped interval and other intervals in the level scheme. In these terms it is also possible to account for the form of the traces in Fig. 5. In traces (b) and (c) where the pumping time was longer, more transfer was able to take place before the termination of the pump pulse, and a higher over-all spin temperature remained after cross relaxation. A test was made to see if the fast decay period might instead be due to phonon diffusion or merely to heating effects, by replacing the specimen by another of half the thickness but the same volume. No change in behavior could be observed.

At 0.3% the slow, or lattice relaxation part of the trace was a good exponential, and, since it was at least two orders slower than general cross relaxation, the two times were easy to separate. In more dilute specimens, and away from cross relaxation points corresponding to an equality of intervals or a double frequency relation, it was often difficult to resolve the two effects well enough to determine either time as a function of concentration. The mixing of the two relaxation processes may be illustrated by reference to a series of measurements made on the *C* transition at 90° and 1.4 kilo-oersted. At 0.3% and 4.2°K the fast component

was 0.04 millisecond, and the slow component 30 milliseconds. At 0.15% the fast period had lengthened to 1.1 milliseconds, and a slow period of 100 milliseconds could still be seen. The 0.1% specimen gave a time of 5 milliseconds which was at first mistaken for the true lattice time. Further experiments showed, however, that this time was almost independent of temperature, varying only from 6 milliseconds to 4 milliseconds in the entire range from 2.2°K to 20°K , and that the decay trace was a poor exponential at the end of which a long tail could just be distinguished. 0.05% gave decay times which were considerably longer, but the traces were of indeterminate form, whilst at 0.02% the decay trace was a fair exponential with a time constant of approximately 500 milliseconds at 4.2°K . The prominence of cross-relaxation phenomena for this particular setting is probably due to the nearness of intervals *B* and *E*, *B*, the nearer of the two, being 2.3 kMc/sec above *C* at 90° and 1.4 kilo-oersted. (Similar cross-relaxation times could be obtained in the vicinity of the *B=C* setting at 22° and 3.8 kilo-oersted by adjusting the frequency difference to 1 kMc/sec.)

DISCUSSION

The combination of spins to form states which couple to the rf field at some multiple of the Larmor frequency has been considered by Van Vleck in a discussion of line broadening.⁹ If now the rf field is replaced by the local field of another spin which is able to make a transition corresponding to the appropriate multiple frequency, we have the possibility of an interchange of energy between spin groups whose frequencies are harmonically related. More generally, energy will be conserved in a group of three spins if the transition frequencies ν_1, ν_2, ν_3 are such that

$$\nu_1 + \nu_2 = \nu_3. \quad (1)$$

Two of the spins form a combined level system containing an interval $h(\nu_1 + \nu_2)$ in which the states are mixed by dipolar interactions, and this may resonate with the interval $h\nu_3$ belonging to the third spin. An analogous problem arises in the nuclear relaxation of lithium fluoride, and has been discussed by Pershan.¹⁰

Cross relaxation adds a term to the equations for the rate of change of level populations, and will, if rapid compared with lattice relaxation, tend to establish a characteristic relation between spin temperatures in the cross relaxing intervals. Suppose that the three intervals $h\nu_1, h\nu_2, h\nu_3$, lie between pairs of levels X_1 and Y_1 , X_2 and Y_2 , X_3 and Y_3 whose populations are $x_1, y_1, x_2, y_2, x_3, y_3$, respectively. If w is the probability for a three spin transfer, the additional term in the equations for dx_1/dt , dy_1/dt , etc., is $w(x_1x_2y_3 - y_1y_2x_3)$. This will tend to bring about a steady state with $x_1x_2y_3 = y_1y_2x_3$, which, in terms of spin temperatures T_1, T_2, T_3 belonging to each of the

⁹ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹⁰ P. S. Pershan Phys. Rev. **117**, 109 (1960).

three intervals, is equivalent to the distribution given by

$$\nu_1/T_1 + \nu_2/T_2 = \nu_3/T_3. \quad (2)$$

If $\nu_1 = \nu_2$ and $T_1 = T_2$, Eqs (1) and (2) reduce to

$$2\nu_1 = \nu_3; \quad 2\nu_1/T_1 = \nu_3/T_3, \quad (3)$$

and the equilibrium is thus characterized by a single spin temperature in the cross relaxing intervals. Although cross relaxation was observed at settings corresponding to the general three spin relation (1), the particular case (3) would actually suffice to explain all the results given here. For example, when $A+C=B$ we also have $D=2B$, or if $A+E=C$ then at the same time $F=2A$. In a four level scheme the general three spin interaction with all intervals different cannot be distinguished experimentally, since whenever a set of intervals satisfy (1) there is also a two-to-one relation, or a simple equality of intervals elsewhere in the scheme. Where there is such an alternative way of taking intervals, it can easily be shown by relations (2) or (3) that either assumption leads to the same distribution of spin temperatures. At least five levels would be needed to distinguish the general case without ambiguity. At first sight it might appear that this requirement is excessive and that three spin transfer should be observed in any material with a three level scheme, since Eq. (1) automatically holds for the larger interval and its two component smaller intervals. Indeed there is no reason why a group of three spins in appropriate levels in such a material should not take part in mutual flips, but this would not affect the population distribution, since the movement across the large interval would be compensated by an opposite movement across each of the two smaller intervals.

The transfer of excitation between intervals which have no simple sum or difference relation connecting them requires the simultaneous interaction of many spins, or the presence of an additional energy reservoir to conserve energy. The problem has been extensively discussed by Bloembergen *et al.*,¹¹ who suggested that excitation may be spread over a wide frequency band by three or four spin energy conserving transfers acting in conjunction with multiple spin interactions such as gives rise to an experimental linewidth. If for instance a wide inhomogeneous line is pumped near its center, four spin interactions will transfer excitation simultaneously to the upper and lower wings, thus bridging a large gap, and "linewidth" interactions will diffuse

energy locally. In our experiments with ruby, energy transfer phenomena have been observed at settings which are separated from two, three, or four spin cross-relaxation settings by a gap many times the normal observational linewidth. It may be noted, however, that the chromium spins in ruby differ from many other paramagnetic centers in having a high exchange interaction, which, between nearest neighbor chromium pairs amounts to 250 cm^{-1} .¹² Although the forces acting between more distant spins are not known there seems a likelihood that a large exchange energy reservoir may be involved in cross-relaxation phenomena in this material.

Since cross relaxation is sensitive to changes of concentration it is attractive to postulate this as the source of the concentration dependences which present a difficulty in the theory of paramagnetic relaxation. However, it seems unlikely that this explanation can be made to serve in more than a few isolated instances. Cross relaxation is characterized by temperature independence, whereas many measurements made by the nonresonant method show increasingly large variation with temperature at the higher concentrations.¹³ From our measurements on ruby we may cite two results obtained at opposite ends of the concentration range, where it was easiest to discount cross-relaxation effects. At 0.3% the lattice time remaining after the comparatively rapid transfer processes was 30 milliseconds at 4.2°K and 90° to the crystal axis. At 0.02% the corresponding time was 500 milliseconds, which can be taken as a lower limit even if one allows for the possibility of some residual cross relaxation at this dilution. The two times are not strictly comparable since the 0.02% value relates to one transition only, whereas the 0.3% value is a mean for all transitions. Nevertheless, a change of this magnitude strongly suggests that concentration dependence is here a property of lattice relaxation itself as well as of the various cross relaxation processes with which it may become confused.

ACKNOWLEDGMENT

We should like to thank E. O. Schulz du Bois for lending us the originals of energy level diagrams published in the Bell System Technical Journal¹⁴ which were used in the preparation of Fig. 1.

¹² L. Rimai, H. Statz, M. J. Weber, G. A. deMars, and G. F. Koster, Phys. Rev. Letters **4**, 125 (1960).

¹³ L. C. Van der Marel, J. van den Broek, and C. J. Gorter, Physica **23**, 361 (1957).

¹⁴ E. O. Schulz du Bois, Bell System Tech. J. **38**, 271 (1959).

¹¹ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).