

Paramagnetic Relaxation at Very Low Temperatures*

J. A. GIORDMAINE, L. E. ALSOP, F. R. NASH, AND C. H. TOWNES
Columbia University, New York, New York

(Received September 24, 1957)

A series of experiments using paramagnetic resonance at microwave frequencies and in the 1–4°K temperature range on $\text{Gd}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$, $\text{K}_2\text{Cr}(\text{CN})_6$, and $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ indicate the following characteristics for their relaxation: (1) It is the lattice-bath relaxation which limits the total rate of relaxation. (2) The spin-lattice relaxation time is several orders of magnitude smaller than the normally observed values of T_1 . (3) Breadth of the lattice modes is very much larger than the width of the resonances in diluted crystals, and in particular, for 1% paramagnetic concentration of the Cu salt, the breadth is several hundreds of megacycles/second. (4) Breadth of the lattice modes increases with increasing concentration of paramagnetic centers. (5) Two nearby resonances are rapidly brought to the same effective temperature by exchange of energy through the lattice modes. (6) The relaxation time T_1 is dependent on crystal size. Some consequences of these results are also discussed.

INTRODUCTION

EXPERIMENTAL measurements of paramagnetic relaxation at temperatures in the liquid helium range have for some time presented a number of puzzles—some in the rich variety of behavior which seems to occur, and some in apparent inconsistencies between the results of different experiments or between experimental results and any specific mechanism of relaxation which has been proposed. The phenomena involved are undoubtedly quite complex and variable, and will require much careful and detailed study for any very complete understanding. A number of preliminary experiments discussed here do, however, appear to help clarify the relative roles of relaxation of paramagnetic centers to the lattice vibrations, and of lattice vibrations to the surrounding constant-temperature bath. They also suggest a particular method of relaxation which appears to dominate in the paramagnetic salts studied, and which may be rather common.

DISCUSSION OF PRESENT SITUATION

It is usually assumed that, if the paramagnetic centers in a crystal have only two energy levels (spin $\frac{1}{2}$), the population difference ΔN between the two levels approaches its equilibrium value ΔN_0 according to the equation

$$\frac{d}{dt}(\Delta N - \Delta N_0) = \frac{-(\Delta N - \Delta N_0)}{T_1}, \quad (1)$$

where T_1 is the “longitudinal” relaxation time.^{1,2} ΔN_0 is determined by the Boltzmann distribution for the temperature of the bath or surroundings of the crystal. This implies that, at least for some sizable region in the crystal, all spins relax at the same rate, in an exponential fashion. It is furthermore expected that at the lowest temperatures, which would include those in

the liquid He range for most substances, the relaxation occurs through transfer of the energy from a single spin to a single vibrational mode of the crystal lattice which has essentially the same frequency. Systems having more than two levels ($S > \frac{1}{2}$) are somewhat more complex, but not essentially different. In its simplest form, the relaxation process described is assumed to be limited by the rate of transfer of energy from the spins to the lattice modes, which stay essentially at the equilibrium or bath temperature.² This situation allows the predictions^{3,4} that the relaxation time should be inversely proportional to the temperature, should decrease with increasing magnetic field H , and should be independent of the spin concentration and crystal size.

At least some of the relaxation measurements made with microwave techniques⁵ appear to agree with the above relaxation process. However, many other measurements of relaxation, particularly those using the magnetic susceptibility of paramagnetic crystals at audio-frequencies,^{6,7} give results which are quite inconsistent with this mechanism. The dependence of relaxation time on temperature, and on frequency (or H) is varied, but usually quite different from that predicted by the above mechanism. Benzie and Cook⁷ and Gorter *et al.*⁸ have found that the relaxation time in at least some cases depends on the size of the crystal, indicating that the time required for the excited lattice modes to deliver their energy to the boundaries of the crystal may be limiting rather than the time of relaxation of spins to the lattice. Such a dependence on sample size has not so far been reported from experiments at microwave frequencies.

In the rate of relaxation itself, there is striking disagreement between the results of measurements at

³ R. deL. Kronig, *Physica* **6**, 33 (1939).

⁴ J. H. Van Vleck, *Phys. Rev.* **57**, 426, 1052 (1940).

⁵ A. H. Eschenfelder and R. T. Weidner, *Phys. Rev.* **92**, 869 (1953).

⁶ Kramers, Bijl, and Gorter, *Physica* **16**, 65 (1950).

⁷ F. W. de Vrijer and C. J. Gorter, *Physica* **18**, 549 (1952).
 R. J. Benzie and A. H. Cooke, *Proc. Phys. Soc. (London)* **A63**, 201 (1950).

⁸ Van der Marel, Van den Broek, and Gorter, *Physica* **23**, 361 (1957).

* Work supported jointly by the Signal Corps, the Office of Naval Research, and the Air Force Office of Scientific Research.

¹ F. Bloch, *Phys. Rev.* **70**, 1 (1945).

² H. B. G. Casimir and F. K. DuPré, *Physica* **5**, 507 (1938).

microwave frequencies and those at audio-frequencies. In the microwave range, relaxation times T_1 have characteristically been measured by saturation of the sample. Bloch's equations¹ give for the absorption coefficient

$$A = A_0 / [1 + (\mu H_1 / \hbar)^2 T_1 T_2], \quad (2)$$

where A_0 is the absorption coefficient at very low power, H_1 is the rotating component of the applied magnetic field, μ is the dipole moment for the transition, and T_2 is the "transverse" relaxation time. When the resonance is homogeneously broadened, $T_2 = 1 / (2\pi\Delta\nu_s)$, where $\Delta\nu_s$ is the half-width at half-maximum absorption for the unsaturated resonance. Characteristically, values of T_1 measured by saturation techniques have been an order of magnitude or more shorter than those determined by dielectric relaxation techniques at audio-frequencies.⁹

DISCUSSION OF PROPOSED METHOD OF RELAXATION

A variety of experiments using microwave techniques has been carried out on $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{K}_3\text{Cr}(\text{CN})_6$ and $\text{Gd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ which appear to fix the most important relaxation process in these crystals. The experiments will be described below after a discussion of the proposed process, which may occur rather commonly in paramagnetic crystals at low temperatures.

It is proposed that, at least for the above salts, relaxation of the paramagnetic centers to the lattice is so rapid that it is not observed in most experiments, the relaxation time T_1 being determined by the rate at which energy can be conducted to the lattice boundaries by phonons or perhaps by spin diffusion. The spin relaxation to the lattice, which will be designated T_{1s} , appears to be as short as about 10^{-5} sec, while T_1 is many milliseconds or longer. Hence the spins and lattice modes come very quickly to the same temperature. Since normally the spin system has a very much greater heat capacity than do the lattice modes with which it interacts, this temperature is essentially the initial temperature of the spins. The observed relaxation time T_1 represents the time required for the lattice modes to repeatedly carry energy to the crystal boundary and thus dissipate the stored spin energy. Fröhlich and Heitler¹⁰ showed some time ago that

⁹ Gorter, van der Marel, and Bölger (see reference 12) have suggested an ingenious mechanism for explaining the discrepancy between values of T_1 obtained by microwave saturation and those from dielectric relaxation. At very low power levels, they suggest, relaxation is limited by the rate at which energy can be conducted to the surface by lattice modes, while at sufficiently high power levels one can show that relaxation from the spins to the lattice must necessarily become the "bottleneck," and hence is the rate which is measured under conditions of very large saturation. However, detailed examination of the amount of saturation involved in the microwave experiments and comparison with the large observed differences in measured values of T_1 seem to show that this explanation is not tenable.

¹⁰ H. Fröhlich and W. Heitler, Proc. Roy. Soc. (London) **A155**, 640 (1936).

energy is conducted to the crystal boundaries by successive transfer of excitation between adjacent paramagnetic sites at a negligible rate except perhaps in some very concentrated paramagnetic materials.

Consider now the number of lattice modes which interact with a given transition of the paramagnetic centers. It is important to note that these are not just those modes which have frequencies coinciding with the frequency distribution of paramagnetic resonances, as one might be tempted to assume for a single-phonon relaxation process. In fact, it seems quite clear that the lattice modes are considerably broadened by their interaction with the spins. For frequencies in the microwave range and temperatures near 1°K, each lattice mode has of the order of one phonon of energy. If there are effectively n modes which interact with the spins, and each of the N spins can exchange a phonon of energy with the lattice in a time T_{1s} , then each phonon is interrupted in a time

$$\Delta t = (n/N)T_{1s}. \quad (3)$$

The frequency range of the lattice modes which then interact strongly is of the order $2\Delta\nu_L = 1/\pi\Delta t$, and since N/n is very large, this range $2\Delta\nu_L$ may be enormously larger than the width of a given spin resonance.

If transverse and longitudinal polarizations of the lattice vibrations are assumed to have the same velocity v , then the number of modes per unit volume below a frequency ν is

$$N_{\text{tot}} = 4\pi\nu^3/v^3, \quad (4)$$

and the number per frequency interval is

$$\frac{d}{d\nu} N_{\text{tot}} = \frac{12\pi\nu^2}{v^3}. \quad (5)$$

Hence if $\Delta\nu_L \ll \nu$, expression (3) becomes

$$\Delta t = \frac{1}{2\pi\Delta\nu_L} \approx \frac{24\pi\nu^2}{v^3} \left(\frac{\Delta\nu_L}{N} \right) T_{1s}, \quad (6)$$

where N is the number of spins per unit volume which give a resonance at frequency ν . From (6), we have

$$\Delta\nu_L = \left(\frac{N}{T_{1s}} \frac{v^3}{48\pi^2\nu^2} \right)^{\frac{1}{2}}, \quad (7)$$

or

$$\Delta\nu_L = 4 \times 10^{-4} \left(\frac{N}{T_{1s}} \right)^{\frac{1}{2}}, \quad (8)$$

for the values $v = 2 \times 10^5$ cm/sec, and $\nu = 10^{10}$ /sec which are approximately correct for most of the microwave experiments. Thus with $N = 10^{19}$ /cm³ and $T_{1s} = 10^{-5}$, $\Delta\nu_L = 400$ Mc/sec. T_{1s} in the above expressions actually represents twice the spin-lattice relaxation time in the limit of 0°K and N the excess of spins in the lower state. If the temperature is high enough that each lattice

mode contains several quanta, then the spin lattice relaxation may be appreciably shorter than the value of T_{1s} appropriate to expression (7), and N should be replaced by $N/2 h\nu/kT$.

Van Vleck¹¹ pointed out in 1941 the broadening of the modes and quite clearly described a relaxation process of the general type suggested here. However, he rejected it primarily on the grounds that available experimental information indicated (a) a single relaxation time rather than a distribution, (b) no dependence of relaxation on crystal size as predicted by this process. Since that time, Benzie and Cooke⁷ and Gorter *et al.*⁸ have found clear evidence for both a distribution of relaxation times, and a dependence of relaxation time on size. Van Vleck argued further, for reasons which are less clear-cut, that broadening of lattice modes would probably not be large enough to allow relaxation times as short as those which are observed. Gorter, Van der Marel, and Bølger^{12,8} have also recently suggested that the lattice modes are importantly broadened by interaction with the spins, and that this is the source of certain deviations from predictions of the variation of relaxation time with frequency (or H).

Consider now further the particular numerical case which is taken above as an example. For a density of spins $N=10^{19}/\text{cm}^3$, the typical breadth of the paramagnetic resonance is a few or a few tens of Mc/sec, depending on the type of hyperfine structure present, and hence considerably smaller than $\Delta\nu_L$. This situation may occur with many normal conditions, and for some concentrated paramagnetic materials, $\Delta\nu_L$ may well be appreciably larger than the microwave frequency ν at which measurements are being made.

If a resonance at frequency ν is saturated, or partially saturated, by an input of microwave power, the temperature of all lattice modes in a range $\nu \pm \Delta\nu$ will then be raised, and these will bring the temperature of any other spin resonances in this range of frequency to essentially the same value as that of the resonance which is absorbing microwave power.

The rate at which relaxation of the spin system occurs as a result of energy conducted from the interior to the boundaries of the crystal by phonons is difficult to calculate with surety because it depends in some detail on the frequency response of each mode. However, the large number of lattice modes available to transport energy, because $\Delta\nu_L$ may be much larger than the width of the paramagnetic resonance, does appear to remove the serious difficulty previously encountered (see, for example, reference 11) in understanding the rapidity of relaxation.

As a first approximation, suppose that all modes which interact strongly with the paramagnetic centers can conduct phonons to the crystal surface at a speed corresponding to the acoustic velocity $v=2 \times 10^5$ cm/sec. There are at least $n=24\pi^2\nu^2\Delta\nu_L/v^3 \approx \frac{1}{2} \times 10^{15}$ modes per

cm^3 in good thermal contact with the 10^{19} spins per cm^3 , so that for a crystal $\frac{1}{2}$ cm on a side, one might expect relaxation times T_1 of the order 1/40 sec. If it were assumed that only modes which fall approximately within the width of the paramagnetic resonance could carry away energy, than T_1 could not be shorter than about 1 sec, in disagreement with the common observation of relaxation times of the order of a few milliseconds. Furthermore, the broadened modes allow still smaller values of T_1 . Since the spins relax in a time $T_{1s} \sim 10^{-6}$ sec to lattice modes in the range $\nu \pm \Delta\nu_L$, they may relax to modes covering a much wider range of frequencies in the longer time which is comparable to the relaxation time T_1 . Suppose T_1 is 2×10^{-3} sec and the frequency response of each mode were Lorentzian. Then, in 10^{-3} sec, energy would be transferred from the spins to lattice modes in the range $\nu \pm 10\Delta\nu_L$, and the energy may be carried to the crystal boundary roughly ten times faster than that indicated above, indicating a relaxation time T_1 near 1/400 sec, as has been assumed. Any precise calculation must take into account the actual frequency spectrum of each mode, and also that phonons will tend to diffuse to the boundary as indicated below rather than to travel in straight lines.

Phonons in the frequency range $\nu \pm \Delta\nu_L$ will certainly interact strongly enough with the paramagnetic centers to be absorbed and re-emitted many times before reaching the surface, and hence their conduction of energy is not properly described above, but must be deduced from the diffusion equation

$$\frac{\partial m}{\partial t} - \frac{\partial}{\partial t}(\Delta N) = D_L \nabla^2 m, \quad (9)$$

where m is the density of phonon excitation (in excess of the equilibrium value). D_L , the diffusion constant, is given by $v^2\Delta t$, with t the mean lifetime of a wave packet of phonons. The density of phonon excitation is less than that of spin excitation ΔN by the factor n/N at very low temperatures, or $2n/N(kT/h\nu)^2$ when $kT \gg h\nu$ and T is the temperature of the spin or lattice system. Hence the spin excitation would decay, as a result of energy transfer by this group of modes, according to the equation

$$\partial \Delta N / \partial t = D_S \nabla^2 (\Delta N). \quad (10)$$

This equation applies accurately for small changes of ΔN , assuming that the spins and lattice modes are kept at the same temperature by rapid spin-lattice relaxation. Actually there is an additional term on the right-hand side of Eq. (10), $-2D_S/\Delta N (\nabla(\Delta N))^2$, which is assumed small in this treatment.

From (5) and the relation $\Delta\nu_L = (1/2\pi)\Delta t$ the diffusion coefficient is

$$D_S = \frac{n}{N} D_L = \frac{12\nu^2}{Nv}, \quad (11)$$

for $h\nu \gg kT$ and $D_S = 24\nu^2/Nv(kT/h\nu)^2$ for $h\nu \ll kT$.

¹¹ J. H. Van Vleck, Phys. Rev. **59**, 724 (1941).

¹² Gorter, Van der Marel, and Bølger, Physica **21**, 103 (1955).

The rate of decay of a distribution ΔN predicted by (10) depends on the nature of the distribution and boundaries. For example, a one-dimensional distribution $\cos(ax)$ along the x direction decays exponentially as $\exp(-D_s a^2 t)$. Any actual initial distribution may be expanded in Fourier series and each component would then have its own decay rate. Regions near the surface of a crystal would in general show faster decay rates than those in the interior. (See also Van Vleck, reference 11.)

If we assume the above type of diffusion, the longest decay rate for spins in a crystal of diameter L cm would be, for $h\nu \ll kT$, approximately

$$T_1 = \frac{L^2}{3\pi^2 D_s} = \frac{L^2 h^2 N v}{72\pi^2 (kT)^2}. \quad (12)$$

For $N = 10^{19}/\text{cm}^3$, $v = 2 \times 10^5$ cm/sec, $\nu = 10^{10}$ cps, and $L = \frac{1}{2}$ cm, this gives $T_1 \approx (2/T)$ sec.

Again, this predicted decay rate is long enough that the spins may give energies to modes with frequencies far outside the range $\nu \pm \Delta\nu_L$. These modes would give a much more rapid diffusion rate because they would have a much longer mean lifetime Δt , and may approach the case discussed earlier of direct flow of energy to the boundaries without scattering.

It is interesting to note that expression (12) is independent of $\Delta\nu_L$ or hence of T_{1S} , and that it predicts the functional dependence of T_1 on the crystal size, temperature, and concentration of spins. As indicated above, conduction of energy by lattice modes considerably outside the range $\nu \pm \Delta\nu_L$, which do not suffer much scattering, may be quite important and may vitiate predictions from expression (12). T_1 should be proportional to L^2 if diffusion is the dominant method of energy conduction, or to L if the phonon paths are not interrupted in a distance comparable to L . If T_1 were essentially the same as T_{1S} , as is often assumed, then the relaxation time should be quite independent of crystal size. For cases where the lattice-bath relaxation is limiting, T_1 would probably never increase as rapidly as linearly with N , but if $\Delta\nu_L \ll \nu$, T_1 may be proportional to $N^{\frac{1}{2}}$ since the number of modes carrying energy to the crystal surface is proportional to $N^{\frac{1}{2}}$ and the amount of energy to be so dissipated is proportional to N . If $\Delta\nu_L \gg \nu$, then the number of modes in thermal contact with the spins is proportional to $(\Delta\nu_L)^3$ rather than to $\Delta\nu_L$, and T_1 would be expected to vary as $1/N^{\frac{1}{2}}$. Any spin diffusion, that is, transfer of energy between adjacent spins, would also tend to give shorter relaxation times with increasing N . The dependence of T_1 on N is further complicated by variations with N of the effectiveness of energy exchange between adjacent resonances, a process which will be discussed below in connection with experimental results on $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

As noted above, a relaxation process involving diffusion will exhibit a variety of relaxation times rather

than a single one. This may be the source of the distribution obtained^{7,8} from low-frequency measurements of relaxation times. It may also explain some, but probably not all, of the difference between values of T_1 measured by this technique and those measured by microwave saturation. As Benzie and Cooke have pointed out,⁷ the former method tends to emphasize the longer values of T_1 in any distribution, and the latter method emphasizes the shorter values.

EXPERIMENTAL OBSERVATIONS

Relaxation times were measured by two different types of techniques employing microwaves of frequency near 9000 Mc/sec. The first was the well-known saturation method mentioned briefly above. The second involved various ways of saturating the spins by pulsed or cw microwave energy, and measuring the rate at which equilibrium was restored by observing the absorption of a small microwave signal as a function of time after the saturating energy was removed. The small microwave signal was too weak to produce of itself an appreciable saturation. This method gives a very simple and direct measurement of T_1 and is also useful for examining whether the decay is strictly exponential.

One convenient method for such "decay time" observations was obtained by synchronously sweeping the frequency of two different klystron oscillators past the paramagnetic resonance. If, for example, the frequency is swept at a rate of 10 000 Mc/sec, and the two oscillators differ in frequency by 100 Mc/sec, then they pass through the resonance at times which differ by 10 milliseconds. The sweep is ordinarily repeated at a rate slow compared to the relaxation time T_1 . If the oscillator which just reaches the resonance is sufficiently powerful to saturate it, the second oscillator may be used as a probe of the extent to which equilibrium has been restored by relaxation. To make signals from the second oscillator more prominent, power from the first oscillator may be decreased after saturation has occurred by application of a square wave to its repeller. The time difference between saturation and probing may of course easily be varied by changing the frequency difference between the two oscillators or by changing the rate of sweep. This technique and a number of variants were used to obtain T_1 from decay rates.

In most of the cases examined, the "decay time" type of measurement yielded values of T_1 remarkably close (within a factor of three) to those obtained by saturation measurements, assuming expression (1) and that $T_2 = 1/(2\pi\Delta\nu_S)$, where $\Delta\nu_S$ is the half-width of the line at half-maximum. This was particularly surprising in the case of crystals with paramagnetic centers diluted more than one thousand-fold by nonparamagnetic atoms. In these cases the resonances were several or more oersteds wide, presumably because of hyperfine structure, and the average field produced at one paramagnetic center by the surrounding atoms was of the

TABLE I. Line breadths of the $-\frac{1}{2} \rightarrow \frac{1}{2}$ resonance in $\text{Gd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$.

Nominal concentration	Line breadth (total width in oersteds at half-maximum intensity)
10%	3.2 ± 0.3
1%	2.0 ± 0.4
0.1%	1.8 ± 0.4

order of one-hundred times smaller than this width. The present experiments were begun with the expectation that for such dilute salts the resonances would be far from "homogeneously" broadened, and that T_2 would have to be roughly one-hundred times longer than values deduced from the entire resonance width in order to satisfy Eq. (2).

Evidence that the lines were broadened by hyperfine structure, rather than by spin-spin interaction is given not only by a calculation of spin-spin interaction, but also from an examination of line width as a function of concentration. An example is given in Table I. It is evident that at least for concentrations below 1% nominal the line breadth is nearly independent of concentration and hence not due to spin-spin interaction.

Actual concentrations were measured roughly from the intensity of absorption, and found to be less than the nominal values by somewhat more than a factor of 10 for the cases listed in Table I. However, absorption intensities indicated that the relative abundances are correctly given by the nominal concentrations. The nominal concentrations are those of the liquid from which the crystals were grown. Evidently Gd does not deposit readily in the crystals containing a large majority of La so that a large difference in concentration between the crystal and the liquid occurred. No such large differences appeared in the other materials examined. Another peculiarity of the Gd crystals which was probably connected with the same difficulty was an extremely broad and weak background of paramagnetic absorption superimposed on the rather sharp resonance lines. This background varied from case to case, but was usually as wide as one-thousand oersteds, and appeared to contain in toto appreciably more spins than the sharp resonance lines. The background is thought to be due to paramagnetic ions which are either not randomly distributed or not in their normal positions in the crystal lattice.

Measured relaxation times T_1 for a given substance varied by factors of two or somewhat more with the particular transition and crystal involved, and with the temperature and concentration used. No very systematic study was made to isolate these several variables, except in the cases noted below, and therefore all details of the specific values found will not be listed here. However, typical values of T_1 obtained for a temperature of 1.3°K are listed in Table II, along with typical values of line widths. Line widths were also

found to vary from one transition to another by about a factor of two, and to vary slightly with concentration in the range of concentrations used. These variations have not been carefully studied and are not very significant for the present discussion.

It will be noted from Table II that values of T_1 obtained from saturation measurements and those from decay times agree fairly well. For the Gd salt, relaxation times obtained were rather variable, and it is not certain that the saturation value is significantly longer than that from decay times. For the Cu salt, T_1 given by saturation is clearly shorter than that from decay times. All cases are quite inconsistent with assuming that T_2 is given by spin-spin interaction.

The apparent "homogeneous" broadening which occurred in all these resonances was further confirmed by failure of all attempts to "burn a hole"¹³ in one of the resonances. This might have been expected to be particularly easy in the case of highly diluted $\text{Cu}(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ where the line breadth was rather large, and the relaxation time quite long.

In terms of the relaxation process discussed above, the apparent "homogeneous" broadening is an immediate consequence of the lattice modes being broader in frequency than the paramagnetic resonances, and in their being at essentially the same temperature. In this case, the usual derivation of Eq. (2) does not apply, since the saturating microwaves act at a given time on only a small group of paramagnetic centers which differ in frequency from the existing radiation by not much more than $1/(2\pi T_{2S})$, where T_{2S} is the value of T_2 produced by spin-spin interaction. In the dilute salts considered, $1/(2\pi T_{2S})$ is of the order of one-hundredth of the total resonance width. However, one can show that when the microwave field is not too large, the energy given by the field to this small group of spins, if one assumes a long T_{2S} , is the same as what would be given to the entire group of spins, assumed to be homogeneously broadened and hence with a much smaller value of T_{2S} . From this fact and the assumption that the energy thus taken from the microwave field is shared with all spins involved in the resonance line, Eq. (2) can be justified with $T_2 = 1/(2\pi\Delta\nu_S)$ and T_1 the same as the decay time. Thus the proposed mode of relaxation predicts observed features of the apparent homogeneous broadening.

In the case of the Cu salt, an accurate measurement of T_1 by saturation techniques was difficult with the particular experimental arrangement used because of the very small power level at which the Cu resonances saturated. However, the value obtained by assuming T_2 is given by the line width was appreciably smaller than the values from decay-time measurements, and in contrast to the much closer agreement found for the other two salts. This behavior is not unexpected from the proposed mode of relaxation. If saturation of one

¹³ Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

of the Cu resonances immediately saturates an additional seven neighboring resonances, then the effective line width may be considered to be approximately eight times that of a single resonance, and the value of T_2 used in expression (2) should be one-eighth that deduced from the line width. This would increase T_1 by a factor of eight to 16 sec, which is more nearly comparable with the values obtained from decay-time measurements. Thus, if measurements are made with sufficient refinement, the differences between values of T_1 obtained by saturation and by decay-time techniques should allow a determination of approximately how many spins are saturated by excitation of a single line.

This suggests another possible reason why saturation measurements have usually yielded shorter relaxation times than does examination of paramagnetic relaxation at low frequencies. The latter is a nonresonant technique which is assumed to act on all spins at the same time. The former has in the past been assumed to saturate only one particular resonance. If there are nearby resonances of roughly equal intensity, then these resonances may also be saturated through action of the phonons, and the measured value of T_1 will be too small by a factor n .

The case of Gd, where the saturation relaxation time is slightly longer than the value from decay-time measurements, is not very clear. Experimental results were much more erratic for Gd than for the other two salts, presumably because of the broad background of absorption. The long relaxation time obtained from saturation might be interpreted as a slight tendency of the line to saturate inhomogeneously. More probably, the line is broadened "homogeneously," but the values of T_1 obtained from each type of measurement are strongly affected by the broad background of absorption. Thus if the decay-time measurement were made by an initial saturation of too short a duration, spins involved in the broad background would not have had time to be fully saturated, and their later absorption of energy would have produced an apparent T_1 which is too short. On the other hand, the value of T_1 obtained from saturation measurements is also shortened as the result of a process similar to that indicated for the Cu case with both the broad paramagnetic absorption and additional resonances contributing to the energy loss. It is very difficult to know which of these effects which modify T_1 would dominate for the particular experimental conditions.

Considerable effort was made to "reverse" spins by adiabatic fast passage in order to obtain a two-level solids state maser.¹⁴ To achieve and detect such a reversal, the two synchronously swept klystrons were again used. It was expected that spin reversal would occur when the first or saturating klystron was swept through the resonance in a time as short as about T_{2s}

TABLE II. Typical values of line width and relaxation times T_1 at a temperature of 1.3°K.

Substance and transition (In each case the para- magnetic ion was diluted by 1% or more.)	Diluting ion	ΔH (Total width in oersteds at half- maximum intensity)	T_1 from decay time (sec)	T_1 from satura- tion (sec)
Gd ₂ (Mg) ₃ (NO ₃) ₁₂ ·24H ₂ O $M = -1/2 \rightarrow -1/2$	La	2.0	7×10^{-3}	15×10^{-3}
K ₃ Cr(CN) ₆ $M = -1/2 \rightarrow -1/2$	Co	12	3×10^{-2}	4×10^{-2}
Cu(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O $M = 1/2 \rightarrow -1/2$ $M_I = 3/2 \rightarrow -3/2$	Zn	20	20	2

and produced a field strength H_1 sufficiently large that $\hbar/\mu H_1$ was smaller than this time. For a very rapid sweep through one of the Gd lines it was found, as expected, that the resonance appeared to saturate as power output of the first klystron was increased to near the field strength calculated to be necessary. That is, absorption of energy from the first klystron reached a limit. However, under these conditions the second probing klystron detected essentially no difference in the absorption from that observed in the normal equilibrium condition, even at times as short as one millisecond after adiabatic fast passage or saturation by the first klystron. This is in contrast with the decay time of many milliseconds which had been measured under more static conditions. If the sweep was slowed until the first klystron passed through the resonance in a time longer than about 10^{-5} sec, saturation was easily and normally detected by the second klystron, and it decayed in the normal times of about 10^{-2} sec. The microwave field strength used was about 0.1 oersted, so that an individual hyperfine component of the Gd resonance, which had a total width of 2 oersteds, was excited during a time of about 10^{-6} sec for this sweep rate.

The observed very fast relaxation appears to be the spin-lattice relaxation time T_{1s} , which is near 10^{-5} or 10^{-6} sec as assumed in the initial discussion of the relaxation mechanism. A saturation or reversal of a group of spins in a time shorter than 10^{-6} sec can occur without an effect during that time on the other spins of nearby frequency. However, for any excitation occurring during a time longer than 10^{-5} sec, the spins have an opportunity to relax to the lattice modes, which then saturate other spins. A similar experiment on Cu(NH₄)₂(SO₄)₂·6H₂O was done by fixing the klystron frequency at the cavity resonance and sweeping the magnetic field. Again, excitation due to a rapid sweep through a single resonance decayed very rapidly while that due to a slower sweep decayed at the normal rate, with $T_1 \approx 10$ sec. In this case, the value of T_{1s} obtained from the sweep rate at which an appreciable residual saturation began to appear was 2×10^{-4} sec. The larger value of T_{1s} for the copper salt is reasonable in view of the longer relaxation time T_1 . A very rapid sweep

¹⁴ Combrisson, Honig, and Townes, Compt. rend. 242, 2451 (1956).

through all eight resonances, in contrast with that through a single one, gave a large residual saturation which decayed at the normal rate.

In the case of $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, the spin excitation produced during a fast sweep through a single resonance is undoubtedly divided after a time appreciably greater than T_{1S} among the eight resonances. For Gd, the cavity response was somewhat narrower than the paramagnetic resonance. Hence the excitation energy is probably transferred partially to other spins in the same resonance, partially to spins in the very broad background absorption noted above, and partially to some of the six nearby resonances of somewhat different frequency. With the energy thus far divided, the resonance would show a response within about 10% of the normal value any time much longer than T_{1S} after the initial adiabatic fast passage, and this small residual effect would not have been noticed in the experiments mentioned. A rapid sweep through all eight Cu lines should, of course, be expected to produce a large residual saturation because all spins are excited by the sweep.

In addition to a very rapid spin-lattice relaxation, two alternative explanations suggest themselves for the short lifetime of the excitation produced by a fast passage. One possibility would be a loss of energy by radiative damping and the other the exchange of energy between two nearby spins which are not necessarily in the same local field, resulting in a "diffusion" spreading of excitation energy to all parts of a given resonance line. A rough calculation of the diffusion process shows that it is much too slow. Consider, for example, the case where a central part of a resonance is saturated over a width ΔH_0 , the entire line width is ΔH , and the field produced at a given spin by its paramagnetic neighbors is approximately $\Delta H_1 = \mu N$, where N is the spin density and μ the Bohr magneton. The time required for the energy to spread by diffusion a distance ΔH_0 in both directions is approximately

$$\frac{(\Delta H_0)^2 (\Delta H)^3}{16\pi^2 (\Delta H_1)^6 \gamma^2}$$

where γ is 2.8×10^6 (cycles/sec)/oersted. For a typical paramagnetic substance diluted to 0.1% and with $\Delta H_0 = 1$ oe, $\Delta H = 15$ oe, this expression gives a time constant of about 8 sec, which is of course much longer than the observed 10^{-5} sec during which the excitation energy was dissipated. This calculation is also pertinent to our failure to "burn a hole" in any of the resonances observed, which might be also attributed to diffusion if the rate of diffusion were sufficiently fast.

The rotating component of magnetization for a system of spins subject to its own radiation field and to spin-spin interaction decays with the damping time¹⁵ τ , which is analogous to a relaxation time. Radiative

damping is apparently also too slow to account for the very short lifetime of the excitation produced during fast passage.

For the special case of negligible spin-spin interaction ($T_2 = \infty$), the radiation damping time is

$$\tau = \tau_\infty = 1/(2\pi\gamma Q f M_0),$$

where f is the filling factor of the microwave cavity in which the material is located, Q its quality factor, and M_0 the magnetization at the beginning of radiation. In the experimental situation described, $f \sim 8 \times 10^{-3}$, $N = 2.8 \times 10^{17}/\text{cc}$, $Q \sim 5 \times 10^3$, and $M_0 \sim S\mu^2 H/kT$, where μ is the Bohr magneton and $T = 1.3^\circ\text{K}$. This yields $\tau \sim 1 \times 10^{-7}$ sec, which is considerably larger than the value 2×10^{-8} obtained for T_2 from the line width. Now when $T_2 \ll \tau_\infty$, it can be shown that the total fractional change in M_z due to radiation damping is

$$\frac{\Delta M_z}{M_0} = \frac{T_2}{2\tau_\infty} (1 - \cos^2\theta),$$

where θ is the initial angle between M_0 and the z axis. This gives $\Delta M_z/M_0 \sim \frac{1}{10}$, indicating that radiation damping cannot play a major role in decay of the excitation in this case. Furthermore, no appreciable radiation of energy from the paramagnetic material was observed experimentally.

That each resonance appears to be homogeneously broadened has already been indicated and discussed. What seems to be an even more striking manifestation of the same phenomena occurs in $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, where saturation of a single resonance almost immediately produces saturation in other resonances which are nearby in frequency. There are two equivalent sites for Cu^{++} ions in this crystal which, except for special orientations of the crystal with respect to the magnetic field, give two distinct resonance frequencies. Each of these is split by hyperfine structure into four more or less equally spaced and equally intense components. In some cases additional hyperfine components appear, due to breakdown of selection rules. Hyperfine components of the two Cu isotopes are largely overlapping, and do not produce important doubling. For crystals of 10% concentration, saturation of any one of these eight components results in a roughly equivalent amount of saturation in all the other eight lines—which of course includes those due to the second set of Cu^{++} ions. This phenomenon is particularly easy to observe in $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ because the relaxation time T_1 is as long as 20 sec, so that immediately after saturation of one resonance and elimination of the saturating radiation, the magnetic field may be varied for examination of saturation and relaxation of the other resonances. The time required for energy to be transferred to resonances other than the one being excited was too short to be detected, or hence appreciably less than one second. It is possible that similar effects occur in the

¹⁵ S. Bloom, J. Appl. Phys. 28, 800 (1957).

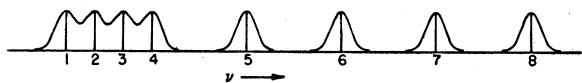


FIG. 1. Relative positions and widths of resonances for $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ for a particular crystal orientation.

other salts examined, but the experimental arrangement did not allow examination of more than one resonance within their shorter time of relaxation.

More detailed examination of this "cross saturation" between resonances for various concentrations yielded other interesting observations. For concentrations of 1% and less, an asymmetry was evident in the behavior of the two different Cu^{++} sites. Most observations were made with crystal orientations such that one set of Cu^{++} ions gave a series of four lines separated by about 100 oe, and the second set of ions produced four more closely spaced lines on the low-frequency side of the first series with relative spacing as indicated in Fig. 1. For a concentration of 1%, saturation of the resonance labeled as 5 in this figure would saturate almost completely all lines. Saturation of 1, 2, 3, or 4 would saturate completely all lines in the same group, but the amount of saturation of 5 and other resonances was small. This is the asymmetry referred to above. Similar asymmetry was observed between each of the last four lines and the first group of four, with excitation of 5, 6, 7, or 8, being more effective in saturating 1, 2, 3, and 4 than these latter were in saturating 5, 6, 7, or 8. The effectiveness of one resonance line in saturating another was also found to vary noticeably and systematically with their separation in frequency for concentrations of 1% and less. For 1% concentration the separation between lines which strongly saturated each other was limited to about 400 oe or 1100 Mc/sec, and for 0.1% concentration the maximum separation over which strong cross saturation occurred was smaller by a factor of 2 or 3. One set of pertinent experimental observations on cross saturation is given in Table III.

The presence of cross saturation can be easily understood in terms of the suggested relaxation mechanism, and seems to afford evidence that the lattice modes are excited in a wide band, and to the same temperature as the spins. The frequency spread of the interaction (~ 2200 Mc/sec for the 1% concentration) is a measure of $\Delta\nu_L$, but is probably of the order of ten times as large as $\Delta\nu_L$ since cross saturation can probably occur in times as long as one second rather far into the wings of the frequency distribution of the excitation. The rate of decrease with decreasing N of the frequency spread for cross saturation is in reasonable agreement with the expectation that $\Delta\nu_L$ is proportional to $N^{1/2}$. Furthermore, the observed magnitude of $\Delta\nu_L$ is consistent with a value of T_{1S} near 2×10^{-4} sec, which is the experimental value obtained above.

The observed asymmetry can occur whenever there

TABLE III. Experimental observations on cross saturation in $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ diluted to 1% Cu^{++} ions by Zn^{++} . (Lines may be identified by number from Fig. 1.)

Line saturated by micro-waves	Lines which were saturated	Lines which were partially saturated	Lines which were not noticeably saturated
1	1, 2, 3, 4		5, 6, 7, 8
2	1, 2, 3, 4	5	6, 7, 8
3	1, 2, 3, 4	5, 6	7, 8
4	1, 2, 3, 4	5, 6, 7	8
5	1, 2, 3, 4, 5, 6, 7, 8		
6	1, 2, 3, 4, 5, 6, 7, 8		
7	5, 6, 7, 8	1, 2, 3, 4	
8	5, 6, 7, 8		1, 2, 3, 4

is a fixed rate of transfer of energy between two lines, but one releases energy to the bath more readily than the other. Thus if lines 1, 2, 3, and 4 interact somewhat less strongly with the lattice modes than do lines 5, 6, 7, and 8, they will interact with somewhat fewer modes and relax more slowly. This means that a fixed rate of transfer between, say, lines 4 and 5 as a result of phonon action may saturate line 4 when energy is flowing in the opposite direction. An attempt was made to measure separately the relaxation time for line 4 and line 6 in the most dilute (0.1%) crystal where interaction was minimized. The result showed the relaxation time of 4 to be 1.5 times as long as that for 6, which is roughly what was expected. However, the measurement was not sufficiently accurate to be completely conclusive. It may be noted that lines 4 and 6 are produced by Cu^{++} ions which are situated equivalently in the lattice. However, their surroundings are not oriented in the same way with respect to the applied magnetic field, and hence their spin-lattice interactions need not be identical.

It is instructive to compare relaxation and $\Delta\nu_L$ for the three crystals mentioned here with these characteristics of paramagnetic impurities in Si. The latter seems to be an example where the spin-lattice relaxation T_{1S} is the limiting time in the relaxation process. For 10^{16} impurities per cm^3 in Si, let $T_{1S} \approx T_1 = 10$ sec, which is approximately the observed value of the relaxation time. Then $\Delta\nu_L \approx 3 \times 10^4$ cycles/sec from (8). Actually $\Delta\nu_L$ should be even smaller than the value given by (8), since this expression assumes that every spin interacts with every lattice mode, or that $\Delta\nu_L$ is larger than the resonance line width. In any case, dissipation at the crystal surface may produce a lattice mode width of the order of 10^5 cycles/sec, so that such a value is reasonable for the present example. In the range of 8 Mc/sec which is the width of the paramagnetic resonance, there are about 3×10^{12} modes, which can carry 6×10^{17} phonons per second to the boundaries of a crystal nearly one centimeter in diameter. Hence the lattice-bath relaxation is very rapid compared with T_{1S} for the spin-lattice relaxation. This situation is consistent also with experimental

observations for these resonances of holes "burned" with widths somewhat less than one Mc/sec.¹⁶

Several alternate explanations of cross saturation were considered. One supposed a very rapid relaxation between hyperfine components for each set of Cu^{++} ions, and an approximate coincidence of one of the forbidden hyperfine transitions of one set of ions with a transition of the other set. However, calculation showed that any near coincidence of this type is impossible. Furthermore, such rapid nuclear relaxation appears quite unlikely except possibly through quadrupole coupling, which would have produced noticeably stronger interaction between alternate lines than between adjacent ones.

A second possible explanation of cross saturation involved exchange of energy between two different lines as a result of a slight overlap of the wings. That is, it might be assumed that one resonance extended far enough toward a second resonance so that spins precessing at the frequency of the second resonance could excite transitions in and hence saturate the first resonance. To investigate the validity of such an assumption, an attempt was made to saturate one of the lines by intense microwave radiation which differed in frequency by various amounts from that of the resonance. Such experiments were carried out on a crystal with 0.1% concentration. It was found that a microwave field of 0.16 oe at a frequency 140 Mc/sec from the resonance frequency produced a rather small saturation. This is to be compared with the field of about 0.01 oe produced by all spins having the frequency of an adjacent line which is about 280 Mc/sec away from the resonance frequency. This appears to rule out cross saturation due to a direct interaction between the spins in adjacent lines, since it cannot be supposed that spins in the adjacent line produce a complete saturation by direct spin-spin interaction while the considerably larger microwave field which is also closer to the resonance frequency fails to do so.

As an additional check on the proposal that lattice-bath relaxation is the limiting process for the crystals examined, the relaxation time was measured for different sizes of crystals of the same material. The relaxation time for a crystal of $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 10% concentration and measuring near 4 mm on a side was found to be approximately 10 sec. This crystal, and some others grown at the same time, were then broken up into small pieces no larger than about 1 mm on a side, held together in a small open plastic sack, and inserted in the microwave cavity for a measurement of the relaxation. As in all experiments reported here, the cavity contained liquid helium, which surrounded the individual crystals. The resonance observed was a broad smear of width equal to the total spread of the previous eight lines, since the orientation of each individual crystal was random. The relaxation time T_1 for the

collection of small crystals was 0.7 sec, showing a very distinct dependence of relaxation on crystal size. The crystal sizes and shapes were not sufficiently well known to test whether the relaxation time varies as L or L^2 for this salt in accordance with the two extreme cases discussed above. However, some other experiments where relaxation was measured before and after a single crystal was sawed into several pieces indicate that the relaxation time varies with size more slowly than L^2 .

No specific test was made of the dependence of relaxation time on N . An examination of the various measurements accumulated during the course of the above experiments suggests that, for the three salts studied, the relaxation time does increase with increasing N as expected. However, no definite conclusions can be drawn because when N was varied, the shape and size of the sample also varied. In most of the experiments, the total number of spins used was kept constant in order to give the absorption signal a certain fixed strength. Since the number of spins is proportional to NL^3 , and for diffusion the relaxation time should be proportional to NL^2 , it is not surprising that no very large differences in relaxation time were noted except in the experiment with many small crystals, which was specifically designed to test a dependence on L . For some salts there is information in the literature showing variations of T_1 with concentration, and indicating that in rather concentrated salts T_1 usually decreases with increasing concentration.¹⁷ Hence presumably $\Delta\nu_L > \nu$ for these cases. The expected dependence of T_1 on N is complicated and variable enough, that a satisfying test of these expectations will require more complete examination of parameters for the particular crystal involved.

The dependence of relaxation time on crystal size and shape should be remembered in any comparison of relaxation times for various concentrations and for various techniques. It is possible that still another of the reasons why microwave saturation measurements have appeared in the past to give shorter relaxation times than have dielectric relaxation measurements is a consistent use of smaller samples in the former case.

IMPLICATIONS OF RELAXATION PROCESS FOR MASERS

Although the salts examined have a rather long relaxation time T_1 , they are not very favorable for use in a two-level maser¹⁴ if the spin-lattice relaxation is as short as indicated, since any negative temperature which is produced would decay at a rate given by the spin-lattice relaxation T_{1S} and not T_1 . This would not prevent oscillation of a 3-level maser under close to the same conditions expected for a homogeneously broadened line and with $T_{1S} = T_1$. However, it could considerably narrow the band width of the 3-level system as a maser. Even though an entire resonance line

¹⁶ G. Fehr (private communication).

¹⁷ See, for example, R. J. Benzie, Proc. Phys. Soc. (London) **A64**, 507 (1951).

may appear to be homogeneously broadened, the driving microwave field would produce negative temperatures over a band width given by the spin-spin interaction or by the field strength, and any part of the line which extended beyond this band width would be saturated and at a large positive temperature rather than at a negative temperature. Thus the band width for amplification may be limited to approximately the width of spin-spin interaction or of the driving field.

SUMMARY

The results discussed above appear to show that, for relaxation of the paramagnetic resonances in $\text{Gd}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$, $\text{K}_3\text{Cr}(\text{CN})_6$, and $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ at liquid helium temperatures:

1. It is the lattice-bath relaxation which limits the total rate of relaxation.

2. The spin-lattice relaxation time is several orders of magnitude smaller than the observed values of T_1 , and is of the order of 10^{-5} sec for the Gd and 10^{-4} for the Cu case.

3. Breadth of the lattice modes is very much larger than the width of the resonances in the diluted crystals, and in particular for 1% paramagnetic concentration of the Cu salt, the breadth is several hundreds of megacycles/second.

4. Breadth of the lattice modes increases with increasing concentration of paramagnetic centers.

5. Two nearby resonances are rapidly brought to the same effective temperature by exchange of energy through the lattice modes.

6. The relaxation time T_1 is dependent on crystal size.

It is also suggested that

1. The lattice-bath relaxation is rather commonly the limiting process for relaxation of paramagnetic salts, and for such cases:

2. The broadening of lattice modes by spin-lattice interaction is sufficient to remove the previous difficulty in understanding the rapidity of observed relaxation at liquid He temperatures.

3. The relaxation time will increase with increasing density of paramagnetic centers for many substances which have rather long relaxation times, and decrease with increasing density for those which relax more rapidly.

4. There is a distribution of relaxation times because diffusion or other forms of transport of phonons to the crystal surface is involved.

5. Much of the apparent discrepancy between relaxation times obtained by saturation methods and those from paramagnetic relaxation at low frequencies can be explained by the distribution of relaxation times, the dependence of relaxation on crystal size, and saturation of more than a single resonance line at one time by phonon action.

The present preliminary observations suggest a number of additional experiments and refinements which should be interesting and valuable for a more detailed and quantitative examination of the relaxation process. It seems probable that more detailed investigation of a variety of substances will reveal a variety of situations where different relaxation processes dominate. However, the type of situation which seems to occur in the cases examined here is probably normal for many similar salts.

ACKNOWLEDGMENTS

The authors are grateful to Mr. A. L. McWhorter and Mr. J. W. Meyer for supplying the samples of $\text{K}_3\text{Cr}(\text{CN})_6$ used. They have also profited from interesting discussions on the subject of paramagnetic relaxation with Professor C. J. Gorter, Professor B. Bleaney, and Professor J. H. Van Vleck.