Relaxation Time Measurements in Ruby by a dc Magnetization Technique*

Shih-yu Feng† and N. Bloembergen

Gordon McKay Laboratory of Applied Science, Harvard University, Cambridge, Massachusetts

(Received 5 December 1962)

Relaxation-time measurements by observation of the recovery of the z component of the dc magnetization have been carried out in ruby. Harmonic cross-relaxation processes, involving two, four, and five spins, have been identified. The cross-relaxation time for the five-spin process is found to be proportional to $f^{-2.6}$, where $f = $ Cr:Al atom ratio. The spin-lattice relaxation time is proportional to f^{-1} for small f, but decreases faster at higher concentrations. The temperature dependence as T^{-1} or T^{-2} can be explained by a model of cross relaxation between single ions and exchange coupled pairs. The magnetic field dependence is small.

I. INTRODUCTION

THE observation of the time-dependent z component of the dc magnetization as a measure of the relaxation time(s) in spin systems was introduced about ten years ago.[1,2] A high-power microwave pulse saturates the magnetic resonance in the sample. The induced emf in a pickup coil, mounted outside the cavity, is proportional to the time derivative of the dc magnetization. The output of an integrating amplifier directly records the relaxation behavior of M_z^{dc}. The time dependence of this quantity is governed by the rate equations. The population of the ith spin level is given by[3]

$$dn_i/dt = \sum_j W_{ij}(n_j - n_i) + \sum_j (-w_{ij}n_i + w_{ji}n_j)$$

$$+ \sum_{jkl} w_{ij,kl} N^{-1}(n_j n_l - n_i n_k)$$

$$+ \sum_{nklmn} w_{ij,kl,mn} N^{-2}(n_j n_l n_n - n_i n_k n_m) + \cdots. \quad (1)$$

The last two terms represent cross-relaxation processes[4] in which two and three spins jump simultaneously. Higher order cross-relaxation terms should be added. The first term on the right-hand side of Eq. (1) represents the transitions induced by the externally applied microwave field. The second term represents the ordinary spin-lattice relaxation processes. The equations can be linearized in the populations n_i in the high-temperature approximation, $h\nu_{ij} \ll kT$. The sum of the populations in the four-spin levels of the Cr^{3+} ions in ruby is, of course, fixed by the number of Cr^{3+} ions, N. Transient solutions of Eqs. (1) will, therefore, consist of a linear combination of three exponential functions with three characteristic times. The dc magnetization

M_z is determined by the diagonal matrix elements and the populations in each level,

$$M_z^{dc}(t) = \sum_{i=1}^{4} \langle i | M_z | i \rangle n_i(t). \quad (2)$$

Experimental data often allow the distinction of two characteristic times. The faster time can be identified with temperature-independent cross-relaxation processes. The slower time sometimes has the order of magnitude of the w_{ij}^{-1}, the inverse of the spin-lattice transition probabilities. This is, however, not always the correct interpretation. In particular, it is not correct for ruby, where the slower time is found to depend on the Cr^{3+} concentration.

The following section will describe the experimental method and the results. The observed signals $M_z(t)$ can be matched with approximate solutions of the rate equations. The resulting values of the spin-lattice and cross-relaxation times have been determined as a function of the relative concentration f of Cr^{3+} ions, the temperature, and the external magnetic field. In the final section the results are compared with those of several other workers,[5–11] who observed the saturation or pulsed recovery of the microwave components of magnetization in ruby. Good agreement with these other data and with existing theoretical models is obtained.[12–15]

[1] R. W. Damon, Rev. Mod. Phys. **25**, 239 (1953).

[2] N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).

[3] N. Bloembergen, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 369.

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

[5] J. E. Geusic, Phys. Rev. **118**, 129 (1960).

[6] W. B. Mims and J. D. McGee, Phys. Rev. **119**, 1233 (1960).

[7] R. A. Armstrong and A. Szabo, Can. J. Phys. **38**, 1304 (1960).

[8] J. H. Pace, D. F. Sampson, and J. S. Thorp, Proc. Phys. Soc. (London) **76**, 697 (1960).

[9] J. C. Gill, Nature **190**, 619 (1961); Proc. Phys. Soc. (London) **79**, 58 (1962).

[10] G. S. Bogle and F. F. Gardner, Australian J. Phys. **14**, 381 (1961).

[11] P. L. Donoho and R. B. Hempill, in Proceedings of the Eighth Conference on Low-Temperature Physics, London, 1962 (unpublished).

[12] N. Bloembergen and P. S. Pershan, in *Advances in Quantum Electronics*, edited by J. S. Singer (Columbia University Press, New York, 1961), p. 373; J. H. Van Vleck, *ibid.* p. 388.

[13] J. C. Gill and R. J. Elliott, in *Advances in Quantum Electronics*, edited by J. S. Singer (Columbia University Press, New York, 1961), p. 399.

[14] M. Hirono, J. Phys. Soc. Japan **16**, 766 (1961).

[15] A. Kiel, Phys. Rev. **120**, 137 (1960).

II. EXPERIMENTAL METHOD AND RESULTS

Figure 1 is the block diagram of the experimental system. The klystrons were V-58 and $2K33$ in the X band and the K band, respectively. All amplifiers employed have a flat response to very low frequencies, because the relaxation times are of the order of 100 msec. Figure 2 shows the relative positions of the cavity, the ruby crystal, and the pickup coil. A second coil, away from the sample and connected in opposite sense with respect to the first one, compensates for any undesired pickup from time-varying stray magnetic fields. The integrator not only converts dM_z/dt to M_z, but also improves the signal-to-noise ratio by narrowing the effective bandwidth. The experimental error in the data is estimated to be 5% in case of concentrated samples and about ten times higher in case of very dilute samples.[16]

Figure 3 shows a typical relaxation signal before and after integration, in the absence of cross relaxation. Only one characteristic time can be distinguished. During saturation of the spin transition at ν_{ij}, this time may be identified approximately with τ, where $\tau^{-1} = 2W_{ij} + w_{ij} + w_{ji}$. The relaxation at the end of the microwave pulse may be identified with $T_1 = \frac{1}{2}w_{ij}^{-1}$. Rigorously there should be three characteristic times which are combinations of all w_{kl}'s in the limit of extreme dilution. The observed signal is, however, satisfactorily described by a single exponential, characteristic of the relaxation behavior of a two-level system. The interpretation will be given in Sec. III.

At certain particular values of crystal orientation and the magnetic dc field H_0, however, cross-relaxation
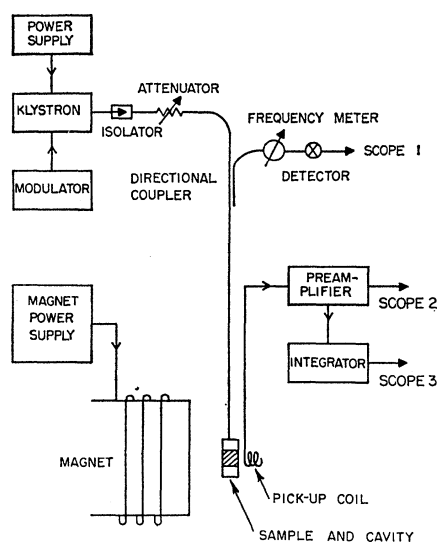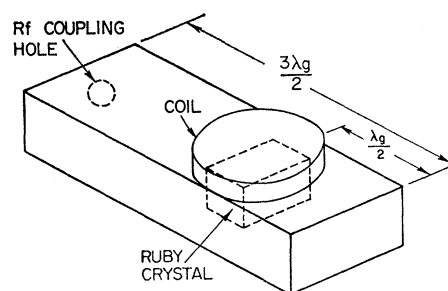

FIG. 2. Cavity, ruby crystal, and the pickup coil.

signals were observed as shown in Fig. 4. This case, where the field $H_0 = 2990$ G, makes an angle of $21°$ with the trigonal axis, is identified as a five-spin cross-relaxation process. The four-spin states can still be labeled approximately by the magnetic quantum-quantum numbers m_s, which are good quantum numbers if H_0 is parallel to the trigonal axis. Although the energy of the spin system is conserved in the simultaneous transitions of five spins indicated in Fig. 4(b), the dc magnetization changes by about nine Bohr magnetons, $-5(-3/2) + 3(-1/2) + 2(3/2) = +9$.

The application of microwave power initially tends to equalize the population of the state $m_s = -1/2$ and $-3/2$. This causes a decrease in the total magnetic quantum number. As the population in the states $m_s = -3/2$ increases, a cross-relaxation process proportional to $n_{-3/2}{}^5 - n_{-1/2}{}^3 n_{3/2}{}^2$ becomes effective. The total magnetic quantum number increases rapidly and the change in dc magnetization reverses sign. This "cross-over" effect is very striking, as a comparison of Fig. 4 with Fig. 3 shows. Finally, after the microwave power is cut off, the signal $M_z(t)$ recovers exponentially to its initial value.

A theoretical description of the signal may be obtained by approximating the rate equations (1) in the following way: The presence of level 2 with $m = +1/2$ is ignored. It does not take part in the cross-relaxation process and its influence on the spin-lattice relaxation is neglected. The populations of levels 1, 3, and 4, with approximate quantum numbers $m_s = -1/2$, $-3/2$, and
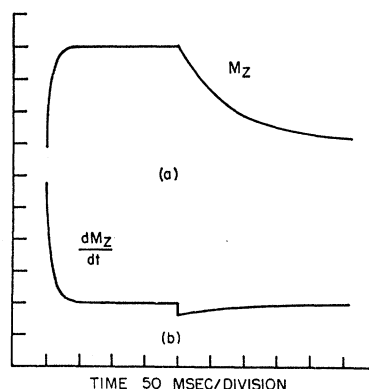

FIG. 1. Block diagram of equipment to measure the relaxation of the longitudinal component of magnetization.

FIG. 3. Sketch of signal at 3025 G, 8400 Mc/sec, 4.2°K, $H_{dc} \| c$ axis, concentration 0.08%, (a) after integration, (b) before integration.

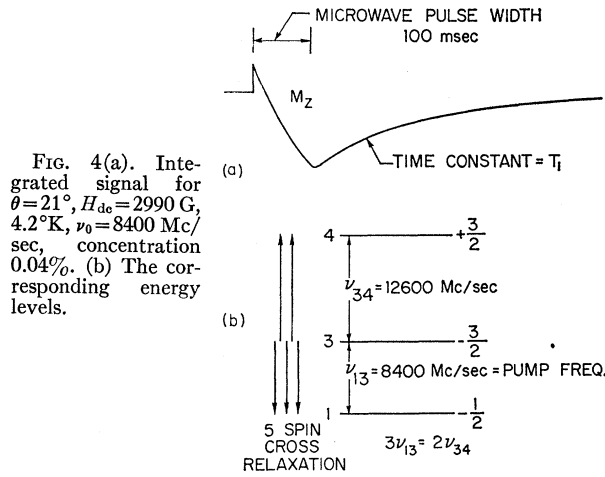TIME 50 MSEC/DIVISION

[16] Further details about the experimental equipment may be found in S. Feng, Ph.D. thesis, Harvard University, 1962 (unpublished).

FIG. 4(a). Integrated signal for $\theta=21°$, $H_{dc}=2990$ G, 4.2°K, $\nu_0=8400$ Mc/sec, concentration 0.04%. (b) The corresponding energy levels.

$+3/2$, respectively, satisfy the relation $n_1+n_3+n_4=\frac{3}{4}N$. The rate equations (1) then reduce to a set of two independent equations. During the strong saturating microwave pulse these may be written in the form,

$$\dot{n}_1-\dot{n}_3=-\frac{n_1-n_3}{\tau}-\frac{8}{38}\frac{3(n_1-n_3)-2(n_3-n_4)}{T_{21}}, \quad (3)$$

$$\dot{n}_3-\dot{n}_4=\frac{n_1-n_3}{2\tau}-\frac{7}{38}\frac{2(n_3-n_4)-3(n_1-n_3)}{T_{21}}, \quad (4)$$

where $\tau=\frac{1}{2}W_{13}^{-1}$ is the characteristic time under the radiation and T_{21} is the cross-relaxation time. The spin-lattice relaxation term is neglected since its rate is slow compared with the other two processes during the pulse. When the microwave pulse is cut off, the rate equations may be written as

$$\dot{n}_1-\dot{n}_3=\frac{n_1-n_3-(n_1{}^0-n_3{}^0)}{T_1}$$

$$-\frac{8}{38}\frac{3(n_1-n_3)-2(n_3-n_4)}{T_{21}}, \quad (5)$$

$$\dot{n}_3-\dot{n}_4=-\frac{n_3-n_4-(n_3{}^0-n_4{}^0)}{T_1}$$

$$-\frac{7}{38}\frac{2(n_3-n_4)-3(n_1-n_3)}{T_{21}}. \quad (6)$$

The set of Eqs. (3) and (4), or (5) and (6), can be solved exactly, and the time dependence of M_z,

$$M_z(t)=\left[-\tfrac{1}{2}n_1(t)-\tfrac{3}{2}n_3(t)+\tfrac{3}{2}n_4(t)\right]\beta$$

is thus determined. If the numerical values $T_{21}=2\times10^{-2}$ sec, and $T_1=0.2$ sec are chosen, and a calculated value $\tau=0.5\times10^{-3}$ sec, one finds

$$M_z(t)=-0.49\exp(-2000t)+3.3\exp(-7.94t) \quad (7)$$

during the microwave pulse, and

$$M_z(t)=-2.86\exp(-5t)+0.03\exp(-50t) \quad (8)$$

after the microwave pulse. The solutions reproduce the shape of the observed signal in Fig. 4 satisfactorily.

Other cross-relaxation signals were observed for four-spin and two-spin processes, shown in Figs. 5 and 6. They can be analyzed in a similar manner.

For the most dilute crystal ($f=0.04\%$) the cross-relaxation signal was observed only in the vicinity of the harmonic point. But for higher concentrations, such a signal was observed over a very wide range of crystal orientations. Figure 7 shows the orientation dependence of the cross-relaxation time T_{21}, which is independent of temperature for the five-spin process mentioned above. The concentration dependence is as $f^{-2.6}$ at the harmonic point.[5–7] For the most concentrated crystal (0.55%) many cross-relaxation processes are always present and no dependence on the orientation was found.

Size dependence was not found at 0.55% concentration. The two samples were cut from the same host crystal. They were 195 and 2055 mg in weight each. This rules out phonon-heating phenomena. A true spin-lattice interaction is measured.
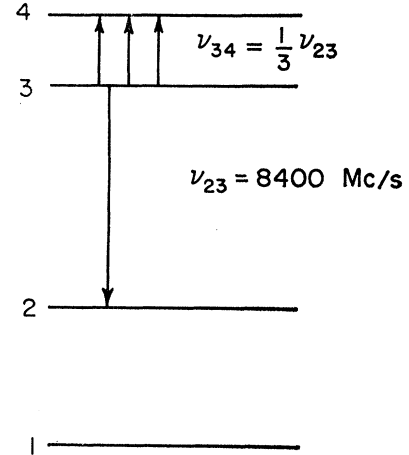

FIG. 5. Energy levels and the 4-spin cross-relaxation process at $H_{dc}=1020$ G, $\theta=73°$, $\nu_0=8400$ Mc/sec.

The spin-lattice relaxation time T_1 is roughly inversely proportional to the concentration f, as shown in Fig. 8.

Some variation of T_1 for the different transitions between spin levels is observed. Table I shows that the relaxation time is nearly independent of the frequency at which T_1 is measured.
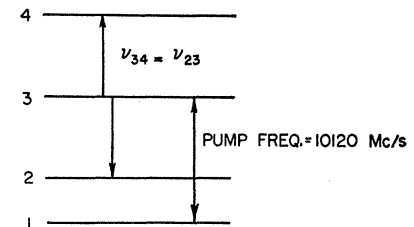

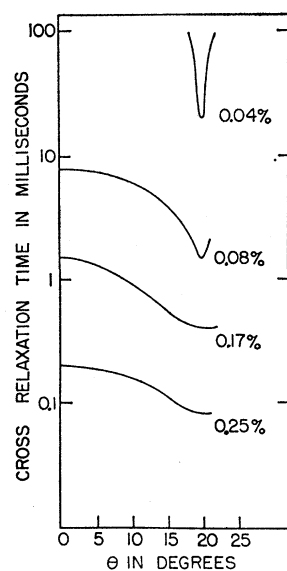FIG. 6. Energy levels and the 2-spin cross-relaxation process at $H_{dc}=760$ G, $\theta=28°$, $\nu_0=10120$ Mc/sec.

FIG. 7. Change of the cross-relaxation time with orientation at various concentrations.

TABLE I. Spin-lattice relaxation times for various lines at 4.2°K.

Line	Relaxation times (msec)	Frequency
1–3	200	X band
1–3	100	X band
2–3	80	X band
3–4	100	X band and K band
1–4	120	K band
2–4	120	K band

Basic theoretical considerations show that, in the limit of very small concentration with random distribution of the magnetic ions, an n-spin cross-relaxation process should have a concentration dependence f^{-n+1}. This prediction is confirmed by more elaborate calculations of Hirono.[14] Armstrong and Szabo[7] and Kiel[15] arrived at similar conclusions.

It should be noted that the concentration range over which the pure five-spin process could be followed is very small. It is apparent from Fig. 7 that many competing mechanisms should be considered for concentrations $\geq 0.1\%$. The deviation from the theoretical f^{-4} dependence is not to be regarded as serious. Perhaps the experimental data indicate a slight preference for clustering of the Cr^{3+} ions instead of a completely random distribution.

The longer characteristic time, identified with a spin-lattice relaxation time T_1, is found to be dependent both on temperature and on concentration. At low temperature the concentration dependence is approximately as f^{-1}, as shown in Fig. 8. At low concentration T_1 is proportional to T^{-1}, while at high concentration it goes as T^{-2}. This behavior is shown in Fig. 9. These results are in excellent agreement with the much more extensive

The temperature dependence of the relaxation time is more interesting, as shown in Fig. 9. At low concentrations, T_1 is inversely proportional to the temperature T, and at high concentrations, T_1 is inversely proportional to T^2. At some intermediate concentration T_1 goes as T^{-1} at lower temperatures and as T^{-2} at higher temperatures. Both K- and X-band measurements show essentially the same temperature dependence.

III. DISCUSSION AND COMPARISON WITH THEORY

The experimental results described above corroborate earlier findings of cross-relaxation effects in ruby near harmonic points.[5–7,10] Mims and McGee found that a three-spin process had a concentration dependence T_{21} proportional to $f^{-2.4}$, whereas we find for the five-spin process a $f^{-2.6}$ dependence.
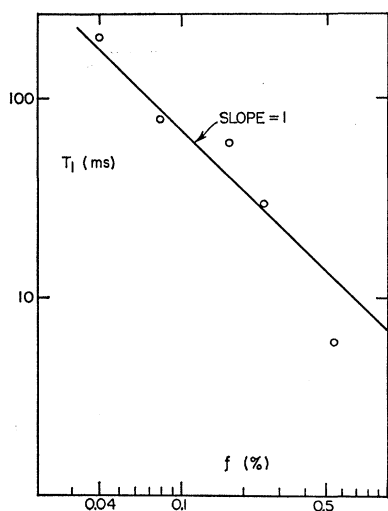

FIG. 8. Change of spin-lattice relaxation time T_1 with concentration f.
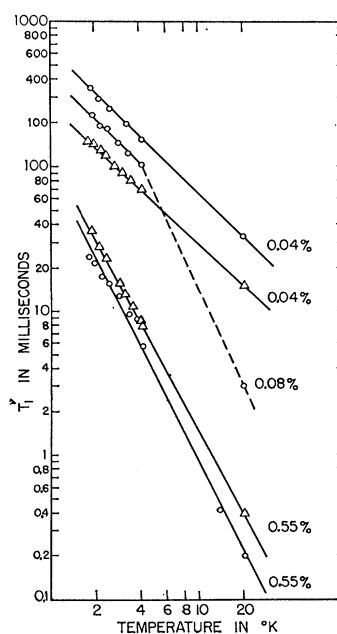

FIG. 9. Dependence of T_1 on temperature at different concentrations ○: 8400 Mc/sec, △: 23 000 Mc/sec.

measurements of Gill.[9] He, as well as Statz[17] and co-workers, also found that the relaxation time of resolved resonance lines originating in excited multiplet states of ion pairs is several orders of magnitude shorter than the values for single ion lines.

The interpretation of the combined temperature and concentration dependence of the relaxation time of single ions has been discussed by several authors.[9,12,13] There is rapid cross relaxation between the single-ion spin levels and those of excited spin multiplets of ion pairs. The latter relax fast via a Finn-Orbach-Wolf[18] mechanism to the singlet ground state of the ion pair. There is a distribution of splittings between the multiplet and singlet in the ion pair depending on the distance between the two Cr^{3+} ions. A reasonable distribution of multiplet splittings in the ion pair states can account for all observed features. In very dilute materials the direct spin-lattice relaxation process becomes dominant. This process is proportional to T^{-1} and independent of concentration.

The magnetic field dependence of T_1 appears to be very small. No difference has been detected on the same resonance observed at X and K band shown in Table I. Pace, Sampson, and Thorp[8] have found that values of T_1 at 34600 Mc/sec are somewhat shorter, perhaps by a factor two, than those measured at X band in rubies of the same concentration.

In the more concentrated rubies the absence of a magnetic field or frequency dependence can be understood, if the explanation given above for relaxation in these specimens is adopted. Neither the cross-relaxation time to the ion pair states, nor the relaxation from the excited ion pair states to the ground state are field dependent. Since Fig. 8 shows that T_1 is concentration dependent down to the lowest concentrations used, this may explain the absence of the field dependence in these experiments. Gill found that T_1 depends on concentration even at $f=0.01\%$.

At very low concentrations the direct spin-lattice relaxation process may dominate.[11,19] In this case the transition probabilities between states which are not Kramers' conjugates are expected to have w_{ij} proportional to ν_{ij}^2. Transitions between Kramers pairs, e.g., $m_s \rightarrow \frac{1}{2} \rightarrow -\frac{1}{2}$, should have probabilities w proportional to ν_{ij}^4. These should, however, be very small, since these processes can only occur in higher approximation.[20]

Orbach[21] suggested that the zero-field splitting may explain the approximately constant value of T_1 for transitions between the spin quartet levels, if the magnetic field is varied between 0 and 5000 G. The three characteristic times have been determined for the rate equations (1), in which only terms with w_{ij} connecting $|m_s| = 3/2 \rightarrow 1/2$ levels have been kept. If these w_{ij} are assumed to be proportional to ν_{ij}^2, the result is indeed that the average relaxation rate is essentially independent of H_0 below 4000 G and increases approximately linear with H_0 to 15 000 G. This is also compatible with the observations of Pace et al. in high fields, and those of Gill and us in fields below 4000 G.

IV. CONCLUSIONS

The observation of the relaxation behavior of the dc component of magnetization can be carried out successfully in rather dilute paramagnetic spin systems at liquid-helium temperature. The method has the advantage of simplicity. The microwave system can be rudimentary. The only requirement is sufficient intensity to saturate a resonance line. It should be feasible to accomplish this in an untuned transmission line. The relaxation behavior at many different field strengths and different spin transitions can thus be studied rather rapidly.

The experimental results corroborate earlier findings about the temperature concentration and magnetic field dependence of the spin-lattice relaxation time in ruby. Higher order harmonic cross-relaxation processes are also readily detected. The "crossover" of the M_z magnetization shown in Fig. 4 is a special feature of the present technique, which aids in the identification of cross-relaxation processes.

The general characteristics of the experimental observations are well explained by existing theories. The implications for the operation of ruby masers which prompted many of the experimental relaxation studies have been discussed elsewhere.[3,10,12]

[17] H. Statz, L. Rimai, M. J. Weber, and G. A. DeMars, Suppl. J. Appl. Phys. 32, 218S (1961).
[18] C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) 77, 261 (1961).
[19] Y. Nisida, J. Phys. Soc. Japan 17, 1519 (1962).

[20] R. Orbach, Proc. Phys. Soc. (London) 77, 821 (1961).
[21] R. Orbach (private communication). The authors are indebted to Professor Orbach for several helpful discussions.