

approximately the same as the value for the central line. The over-all linewidth for each resonance line is about $10d$.

Analysis of the Al^{27} NMR spectrum in Al_2O_3 using a two-spin Hamiltonian with dipole-dipole coupling predicts the correct shape and width of the resonance lines assuming a positive value for the magnetic moment μ and the quadrupole coupling constant eqQ . Since both μ and Q have been measured as positive,⁶ q is positive. This is in agreement with a calculation by Bersohn.⁷

An accurate determination of the magnitude of eqQ from the splitting of the NMR spectrum requires that the line separation be measured from the center of gravity of the line. This is not coincident with the position of zero slope for the satellite lines.

⁶ D. Strominger, J. M. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.* **30**, 585 (1958).

⁷ R. Bersohn, *J. Chem. Phys.* **29**, 326 (1958).

The relative position of the dipolar splitting on each of the resonance lines can be understood in terms of a simple physical model. One nearest neighbor nucleus with $I' = \frac{5}{2}$ would be expected to split each resonance into six equally spaced dipole transitions due to the six equally probable orientations of I_z' . However, those transitions for which the two nuclei can resonate via spin-spin interaction will be broadened and split further apart. Thus the splitting of the $\frac{5}{2} \rightarrow \frac{3}{2}$ resonance occurs when the neighboring spin is in the $\frac{5}{2}$ or $\frac{3}{2}$ states. Since μ is positive this must occur on the high-frequency side of the $\frac{5}{2} \rightarrow \frac{3}{2}$ resonance. Hence we can assign the $\frac{5}{2} \rightarrow \frac{3}{2}$ transition to the observed low-frequency resonance line and determine that eqQ is positive.⁸

⁸ After completion of this research we learned this effect was independently observed by Verber and interpreted in terms of the physical model which we outline here. See, C. M. Verber, H. P. Mahon, and W. H. Tanttla, following paper [*Phys. Rev.* **125**, 1149 (1962)], and C. Verber, thesis, University of Colorado, 1961 (unpublished).

Nuclear Resonance of Aluminum in Synthetic Ruby*

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The linewidth, line shape, and spin-lattice relaxation time T_1 have been measured as a function of temperature in single crystals of $(\text{Al}^{27})_2\text{O}_3$ having nominal Cr_2O_3 concentrations of 0%, 0.01, 0.1, 1.5, and 4% by weight. Of the two important contributions to the linewidth, the nuclear spin-spin interaction is 7 gauss and temperature-independent. The contribution from the paramagnetic ions increased from zero at 300°K to as much as 42 gauss, depending upon concentration, temperature, and static magnetic field. An anomalous structure in the aluminum resonance was evident in both the steady-state and pulsed nuclear induction data. The $\frac{1}{2}$ to $-\frac{1}{2}$ transition has a splitting of 2.84 gauss with a $3 \cos^2\theta - 1$ dependence on the angle between the c axis and H_0 . The splitting is independent of the observation frequency and chromium ion concentration. T_1 was observed to vary from 150 sec to 1.5 msec as a function of ion concentration and temperature, and to vary in a manner not correctly given by existing theory. Many of the samples were observed to have a nonunique T_1 .

I. INTRODUCTION

ONE of the most persistent problems in the field of nuclear magnetic resonance has been that of predicting the spin lattice relaxation times of nuclei in a crystalline lattice. Original theoretical work¹ yielded predictions which were off by many orders of magnitude. It was not until the realization that, for nuclei with $I < 1$, paramagnetic ions, if present, are the basis for the primary relaxation mechanism, that there was even qualitative agreement between experiment

and theory. The importance of paramagnetic impurities was noticed by Rollin and Hatton² who observed the dependence of the relaxation time of fluorine in CaF_2 upon the number of F centers present, and by Bloembergen³ who investigated a variety of materials and whose theoretical treatment forms the basis for most of the more recent work. In particular, the role of spin diffusion in determining the recovery rate of nuclear magnetization after saturation has been examined in detail by Blumberg.⁴ The shape of the free induction signal in solids has been discussed by Lowe and Norberg⁵ and related, through the Fourier

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[†] Some of this work was submitted by C. M. Verber to the Graduate School of the University of Colorado in partial fulfillment for the degree of Doctor of Philosophy.

I. Waller, *Z. Physik* **79**, 370 (1932).

² B. V. Rollin and J. Hatton, *Phys. Rev.* **74**, 346 (1948).

³ N. Bloembergen, *Physica* **15**, 386 (1949).

⁴ W. E. Blumberg, *Phys. Rev.* **119**, 84 (1960).

⁵ I. J. Lowe and R. E. Norberg, *Phys. Rev.* **107**, 46 (1957).

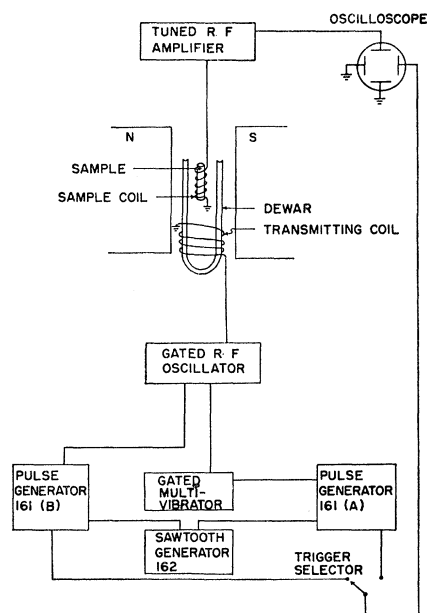


Fig. 1. Block diagram of pulsed induction system.

transform, to the shape of the continuous absorption line.

An essential feature of Bloembergen's theory is that the paramagnetic ions must remain in good thermal contact with the lattice at all times to be able to satisfactorily relax the nuclear spins. One method of determining if this condition is satisfied is to observe the behavior of the nuclear linewidths to see if they reflect the proper thermal behavior of the paramagnetic ions.

The purpose of this research has been to study the nuclear resonance of aluminum in ruby in the presence of paramagnetic chromium ions. Data for the nuclear spin-lattice relaxation time has been obtained and to justify its comparison with the predictions of Bloembergen's theory, the behavior of the nuclear linewidth has been examined. From the data obtained it has been possible to explain the behavior of the linewidths as being due to an essentially constant contribution due to the mutual interaction of aluminum nuclei, and a temperature and concentration dependent contribution due to the paramagnetic ions. The behavior of the linewidth follows Van Vleck's⁶ treatment fairly well.

The temperature-dependent part of the linewidths indicate an effective Cr^{3+} moment which can be calculated from the Boltzmann factor. Therefore, the paramagnetic ions are in good thermal contact with the lattice and one would expect the Bloembergen theory for the spin-lattice relaxation times to apply. However, the data disagree with the theory by orders of magnitude, especially at low temperatures. A

⁶ J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

modification of theory suggested in this work does not improve the situation. Since the measured relaxation times are in fair agreement with those determined by Spence and Cowan⁷ using a different method, it would seem that an improvement of this rudimentary theory is necessary to explain the data for the spin-lattice relaxation times of aluminum nuclei in ruby.

The aluminum nucleus has spin $\frac{5}{2}$ and a quadrupole moment. The corundum structure of ruby, which is of lower order than cubic, produces an electric field gradient at the site of the aluminum nucleus, resulting in a strong quadrupole perturbation on the Zeeman levels. Previous nuclear resonance in ruby includes that of Pound⁸ who measured the separation between the five resonance lines and determined the quadrupole coupling constant, and that of Veigele⁹ who measured the linewidth of various samples at room temperatures.

In the work being reported here, an anomaly was observed in the line shape of the less concentrated ruby samples which had not been previously reported. The anomaly was noticed in the shape of the absorption curves. This anomaly was in the form of an apparent splitting of the center line, and a distortion of the satellites. For the treatment of this splitting we refer to the paper by Silver, Kushida, and Lambe.¹⁰

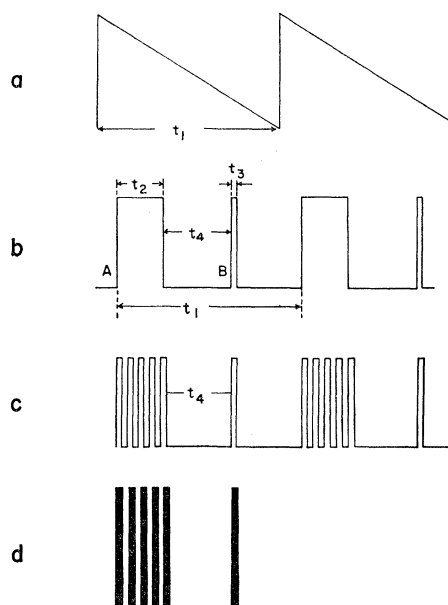


Fig. 2. Pulse sequence for T_1 measurements. The quantities t_1 , t_2 , t_3 , and t_4 are all variable. (a) Saw-tooth output of Tektronix 162. (b) Output of the two Tektronix 161 units. (c) Multivibrator triggered by pulse A; pulse B is unchanged. (d) rf output triggered by multivibrator and pulse B.

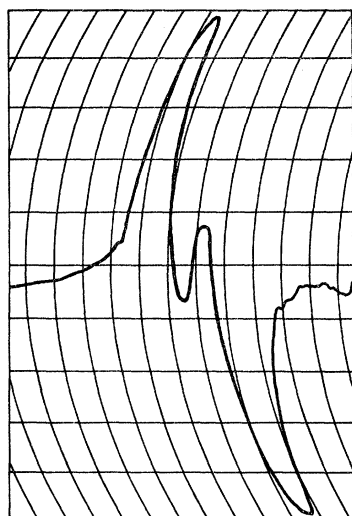
⁷ R. D. Spence and J. Cowan, *J. Chem. Phys.* **32**, 624 (1960).

⁸ R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

⁹ W. J. Veigele, thesis, University of Colorado, 1960 (unpublished).

¹⁰ A. H. Silver, T. Kushida, and J. Lambe, preceding paper [*Phys. Rev.* **125**, 1147 (1962)].

Fig. 3. Typical derivative of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ aluminum absorption line, clearly showing the line splitting. H_0 is constant and the frequency increases from left to right. Scale: 1 division = 2.7 kc/sec.



This article is in five sections. Section II gives the experimental procedures, Sec. III gives the data on the line splitting, Sec. IV gives the results of the line-width as a function of temperature and chromium ion concentration and Sec. V gives results of relaxation time measurements.

II. EXPERIMENTAL METHODS AND APPARATUS

The samples used were four synthetic ruby rods purchased from Linde Company Crystal Products Division. The crystals were in the form of right-circular cylinders, $\frac{1}{2}$ in. in diameter with the c axis of the hexagonal system lying within $\pm 5^\circ$ of the plane perpendicular to the cylindrical axis. The location of the a and b axes was unknown and of no vital interest in performing the experiment. The nominal Cr^{3+} concentrations of the four crystals were specified by the manufacturer as being 0.01%, 0.1%, 1.5%, and 4%, respectively. These concentrations refer to the relative proportion, by weight, of Cr_2O_3 in the initial mixture from which the crystals were grown.

The orientation of the c axis with respect to the magnetic field H_0 was determined to within $\pm 2^\circ$ by utilizing the fact that the quadrupole splitting of the five resonance lines is a function of angle, the splitting being greatest for θ , the angle between the c axis and the magnetic field, equal to 0° . Therefore, in order to orient the crystal, one simply had to plot H_0 for the resonance of a single satellite line, the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition for example, as a function of angle at a constant frequency.

Continuous Induction System

The experimental arrangement for measuring line-widths consisted of a modified Pound-Knight marginal oscillator, the output of which was amplified by a phase-sensitive detector and recorded on an Esterline

Angus graphic ammeter. The magnetic field was held constant and the frequency was swept by a motor-driven capacitor in the tank circuit of the oscillator. By using a speed reducer, any sweep speed from 2 to 50 (kc/sec)/min could be obtained.

It was found necessary to use a low-level oscillator¹¹ for obtaining some of the data for the dilute crystals at low temperatures to avoid saturating the nuclear resonance.

Pulsed Induction System

The timing circuit, which makes use of a number of commercially available Tektronix units, is similar to the arrangement of Gutowsky.¹² The sequence is initiated by the Tektronix 162 [Figs. 1 and 2(a)] which puts out a negative-going-positive sawtooth with a period t_1 .

The two number 161 units are triggered by the negative-going sawtooth and put out a square pulse of any length up to 100 msec [t_2 and t_3 in Fig. 2(b)]. By triggering both number 161 units with the same sawtooth, one then has a sequence of two pulses in which the interval between pulses t_4 , the individual pulse lengths t_2 and t_3 , and the repetition rate of the entire sequence t_1 , is known and easily controllable.

In order to saturate the entire spin system, a number of intense pulses were applied in a time greater than T_2 so that the entire spin system was saturated as far as could be determined by observation of the free induction signal [Figs. 2(c) and 2(d)].

The rf oscillator followed the basic circuit of Hahn¹³ except that a dual input to the rf switch was provided so that the oscillator could be triggered by either the Tektronix 161 (B) or the multivibrator, with a minimum of pickup between the two units.

The sample coil consisted of twelve turns of 0.035 in. pure silver wire, insulated by dipping the wire into a dilute solution of Glyptal in acetone. It was necessary to use silver rather than copper to avoid confusion due to the nuclear resonance of copper which occurs

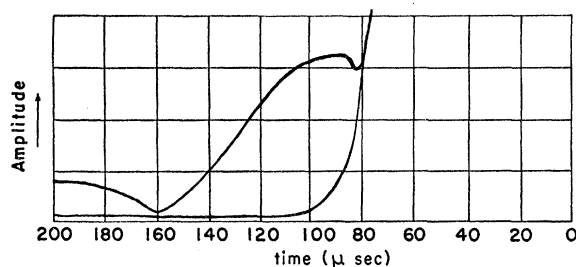


Fig. 4. $\frac{1}{2} \rightarrow -\frac{1}{2}$ free-induction signal in 0.01% ruby at 4°K and $\theta = 0^\circ$. The beat structure is consistent with the line splitting shown in Fig. 3.

¹¹ F. N. H. Robinson, J. Sci. Instr. **86**, 481 (1959).

¹² J. C. Buchta, H. S. Gutowsky, and D. E. Woessner, Rev. Sci. Instr. **29**, 55-60 (1958).

¹³ E. L. Hahn, Phys. Rev. **80**, 580 (1950).

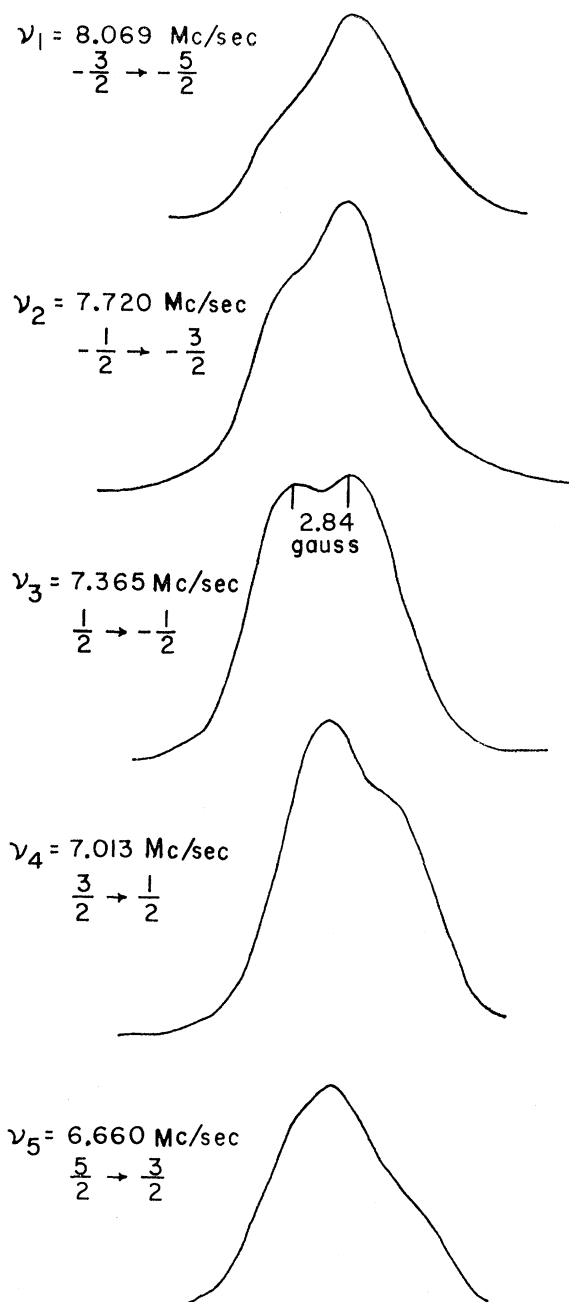


FIG. 5. The five nuclear absorption lines of Al in ruby at 4.2°K, $\theta=0^\circ$ and Cr^{3+} concentration of 0.01%. The vertical scale is arbitrary and not necessarily the same for the five lines.

at very nearly the same frequency as the aluminum resonance.

The receiver, a tuned rf amplifier, had an over-all voltage gain of 1000 and a bandwidth of 500 kc/sec. A tuned input with a Q of about 100 was used for the experiment. The use of a tuned input enhances the signal to noise ratio by a factor $Q^{1/2}$, so that with the tuned input the over-all gain was 10^4 and a nuclear signal of $0.2 \mu\text{v}$ could be seen.

III. ANOMALOUS LINE SHAPES

While investigating the variation of the aluminum nuclear spin linewidth as a function of temperature and concentration, a splitting of 2.84 gauss was observed in the line shapes of the less concentrated crystals (Fig. 3). Figure 4 shows the beat structure resulting from the splitting in the free induction signal following a 90° pulse.

The depression appeared in the center of the absorption line for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition and on the edges for the satellite transitions. The numerical integrations of the data (Fig. 5) show this distinctly. The effect was independent of temperature, aside from the fact that the increased signal-to-noise ratio made observation easier at lower temperatures. There was no dependence upon the Cr^{3+} ion concentration except that the effect was washed out by the paramagnetic line broadening in the more highly concentrated crystals. The effect was also independent of the applied magnetic field at which the resonances were observed. The magnitude of the distortion of the center transition had a $3 \cos^2\theta - 1$ dependence, θ being the angle between the c axis and the magnetic field H_0 .

The first attempt at explaining this effect was a very careful analysis of the crystal structure of Al_2O_3 in order to determine if there might exist two sets of sites at which the crystalline magnetic field differed by the appropriate amount. However, this as well as a number of other explanations failed to agree qualitatively with the experimental evidence. For example, any effect based upon two sets of aluminum sites with differing electric field gradients must be discarded because the distortion is not more evident in the satellite lines than in the center resonance. Also, the magnetic field independence precludes the inclusion of any effects due to atomic diamagnetism.

The explanation of the anomaly which we believe to be correct is based upon the structure of the ruby crystal which enables one to see experimentally the direct effects of lifetime broadening. This effect has been explained in a manner more satisfactory than our method and we refer to the explanation given by Silver *et al.*¹⁰

IV. LINEWIDTH AS A FUNCTION OF Cr^{3+} ION CONCENTRATION

The width of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ resonance as measured between the maximum and minimum slope of the composite line, was determined for the 4%, 1.5%, 0.1%, and 0.01% samples at a variety of temperatures and magnetic fields. The data were taken for $\theta=0^\circ$ and are listed in Table I. The approximate values of ΔH have been calculated from Van Vleck's expression⁶ for $\langle \Delta \nu^2 \rangle$ and are also given in Table I. The values listed differ by less than 2% from the exact expression for the $\frac{1}{2}$ to $-\frac{1}{2}$ transition given by Kambe and Ollum¹⁴

¹⁴ K. Kambe and J. Ollum, J. Phys. Soc. Japan **11**, 50 (1956).

TABLE I. Comparison of calculated and measured linewidths (linewidths are in gauss and H_0 is in kilogauss).

Temperature (°K)	0.01%			0.1%			1.5%			4%		
	ΔH (meas)	ΔH (calc)	H_0	ΔH (meas)	ΔH (calc)	H_0	ΔH (meas)	ΔH (calc)	H_0	ΔH (meas)	ΔH (calc)	H_0
1.7	9.2	7.5	9.5	8.8	9.7	8.9	25.4	27.3	8.45	43.3	43.0	8.5
4	7.8	7.3	9.5	9.1	9.2	8.9	10.3	9.7	4.64	14.1	14.1	4.87
							11.2	11.3	5.9	17.6	16.0	5.7
							12.2	13.3	7.23	19.6	18.3	6.78
							13.8	15.2	8.62	20.4	20.2	7.64
							18.5	17.3	10.0	22.2	23.4	8.64
										27.6	24.8	9.73
78	7.2	7.0	8.65	7.3	7.0	8.8	7.9	7.1	6.6	7.2	7.1	6.6
300	7.1	7.0	8.65	6.8 ^a	7.0	6.6	6.4 ^a	7.0	6.6	6.7 ^a	7.0	6.6

^a From reference 9.

for a system with quadrupole perturbation. The information obtained indicates that the variation of the linewidth is governed by the behavior of the paramagnetic ions.

From the data at 300° and 78°K for all of the samples and for the 0.01% sample at all temperatures it is evident that there is a large and reasonably constant contribution to the linewidth due to the mutual interaction of the aluminum spins (ΔH_{Al-Al}) which is of the order of 7 gauss. In order to obtain the contribution to the linewidth due to the chromium ion impurity, the aluminum nuclear spin-spin interaction will be taken to be constant for all samples at all temperatures and will be subtracted from the measured linewidth, getting

$$\Delta H_{Cr} = (\Delta H_{meas}^2 - \Delta H_{Al-Al}^2)^{1/2}$$

for each data point. (For simplicity, Gaussian line shapes have been assumed.)

We now assume that the paramagnetic ions can be treated, for the most part, as a system of rapidly flipping spins. Here rapid flipping implies that the paramagnetic T_2 must be less than $1/\Delta\nu_s$ for the nuclear resonance line, where $\Delta\nu_s$ is the width which the nuclear resonance line would have if the paramagnet spin were static. If true, each nuclear spin samples the field produced at its site by the paramagnet in all of its various spin orientations. When examined, the nuclei then have a width which is a function of the time-average moment of the Cr^{3+} ion. Thus the Cr^{3+} ion can be considered to have an effective magnetic moment which is the Boltzmann average of the moments due to its four spin states. The Hamiltonian for the Cr^{3+} spin system is

$$3c = g\beta\mathbf{S} \cdot \mathbf{H} + D[S_z^2 - 5/4], \quad (1)$$

where the magnetic moment of the chromium ion is $\mu = g\beta\mathbf{S}$ and D is the zero-field splitting¹⁵ due to the crystalline fields. Solution of the secular equation¹⁶ for this system gives four roots which may be used to

obtain the average effective chromium moment which is seen by those nuclei with sufficiently long T_2 .

$$\mu_{eff} = \frac{\sum_{m=-3/2}^{3/2} \mu_m e^{-E_m/kT}}{\sum_{m=-3/2}^{3/2} e^{-E_m/kT}} = \frac{3g\beta}{2} \left\{ \frac{e^{-2chD/kT}(e^{-3x/2} - e^{3x/2}) + \frac{1}{3}(e^{-x/2} - e^{x/2})}{e^{-2chD/kT}(e^{-3x/2} + e^{3x/2}) + (e^{-x/2} + e^{x/2})} \right\} \quad (2)$$

for D given in cm^{-1} , where c is the speed of light, h is Planck's constant, $x = g\beta H/kT$, k is the Boltzmann constant, and T is the temperature.

According to Van Vleck, the mean-square deviation of the frequency of the resonance line of spins characterized by S and g in the presence of spins characterized by S' and g' is

$$\langle \Delta\nu^2 \rangle_{av} = \frac{3}{4} S(S+1) h^{-2} g^4 \beta^4 \sum_k \left(\frac{3\gamma_{jk}^2 - 1}{r_j^3 k} \right)^2 + \frac{1}{3} S'(S'+1) h^{-2} \sum_{k'} \left[\tilde{A}_{jk'} + \frac{(1 - 3\gamma_{jk'}^2)}{r_j^3 k'} g' \beta' \right]^2. \quad (3)$$

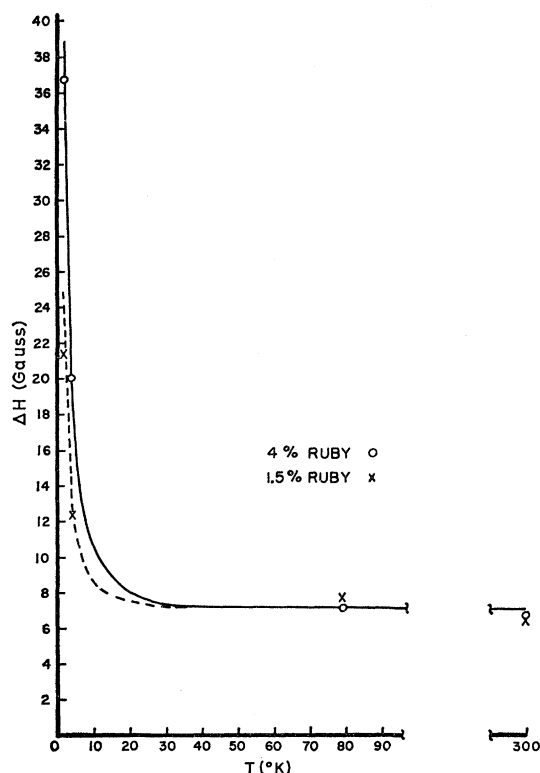
The exchange term $\tilde{A}_{jk'}$ is zero in the present case. The first term of (3) is simply $\langle \Delta\nu^2_{Al-Al} \rangle_{av}$.

To evaluate the second term we will multiply $g'\beta'$ by μ_{eff}/μ , thereby using the effective strength of the Cr^{3+} dipole moment. In the sum in this term, the k' refers to the metal-ion sites which are occupied by a chromium ion. For a crystal of molar concentration C , as we move the reference point j through the crystal, on the average only CN out of each N sites specified by a given k' will be occupied. We can, therefore, account for the concentration by multiplying the geometrical factor by C .

Changing from frequency to magnetic field and using the appropriate numerical factors, (3) becomes, for $r_{jk'}$ expressed in angstroms,

$$\langle \Delta H^2 \rangle_{av} = 7^2 + 2.7 \times 10^9 (\mu_{eff}/\mu)^2 C \times \sum_{k'} [(1 - 3 \cos^2 \theta)/r_{jk'}^3]^2 (\text{gauss})^2, \quad (4)$$

¹⁵ J. E. Geusic, Phys. Rev. **102**, 1252 (1956).¹⁶ Arthur A. Vuylsteke, *Elements of Maser Theory* (D. Van Nostrand Company, Princeton, New Jersey, 1960), p. 290.

FIG. 6. ΔH vs T with $H_0 = 7000$ gauss.

If we use the calculated geometric factor of 0.0176 \AA^{-6} we get, for ΔH at 4°K and four percent Cr^{3+} concentration, a value of 358 gauss. This is obviously much too large. To obtain agreement with experimental observation we need to use $4.8 \times 10^{-5} \text{ \AA}^{-6}$ for the geometric factor. To obtain this number it is necessary to omit the influence of all nuclei within 6.3 \AA of a Cr^{3+} ion from the calculation, that is, the influence of nuclei in the 50 nearest aluminum sites.

The results of this calculation for ΔH are presented in Figs. 6 and 7. In the first figure, ΔH is plotted versus T for $H_0 = 7000$ gauss and in the second figure, ΔH is plotted versus H_0 for $T = 4^\circ$. As can be seen, the experimental values of the linewidth agree quite well with the theoretical curves.

The calculated values for all the experimental points are presented in Table I along with the measured linewidths. The assumption of a single geometric correction is seen to yield good over-all agreement.

Discarding the nuclei nearest the impurities can be justified because they are inhomogeneously broadened to such an extent that the spectrometer cannot see them and they do not contribute to the observed linewidth. For example, at 4° the effective chromium moment is $5.9 \times 10^{-21} \text{ gauss-cm}^3$. This causes a field of 220 gauss at a site 3 \AA away from the ion. This is far in the wings of the resonance line, and although there are relatively few nuclei which lie in this field, they

TABLE II. Results of T_1 measurements (all times in seconds).

Temperature (°K)	Sapphire	0.01%	0.1%	1.5%
1.7	...	12-60	15.5	...
4	...	6-23	0.1-0.8	0.01
78	150	5.8	0.07	0.03-0.06
300	10.4	0.5-1.2	0.02-0.06	0.0015-0.0078

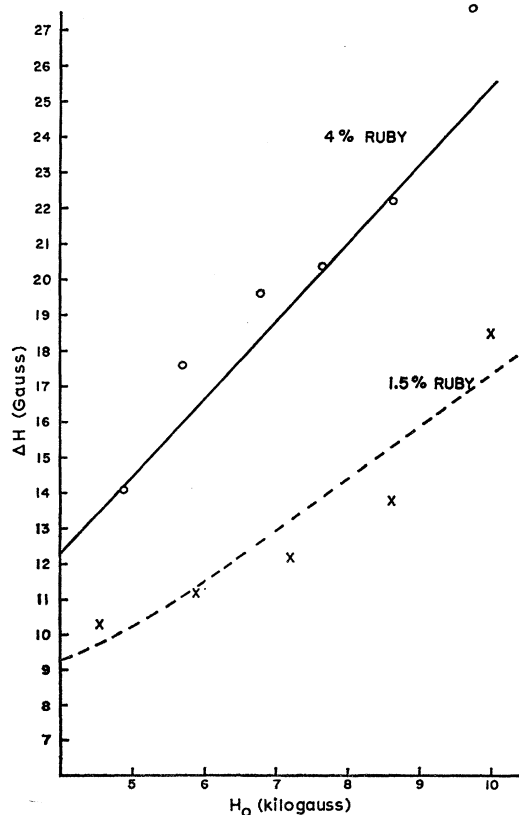
give a large contribution to the calculated second moment. They do not, however, contribute to the observed line and must therefore be eliminated from the calculation.

If some of the nuclei close to the Cr^{3+} ions do not satisfy the criterion for time averaging, they see very large fields and certainly can be deducted from the theoretical calculation.

V. RELAXATION TIME MEASUREMENTS

Pulsed nuclear induction techniques were used to measure the spin lattice relaxation times for the ruby samples as well as for a pure sapphire rod.

The results of the T_1 measurements are presented in Table II. T_1 measurements were of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition at 9 Mc/sec. As explained previously, a straight line on the semilogarithmic plot of Eq. (2)

FIG. 7. ΔH vs H_0 at $T = 4^\circ\text{K}$.

determines a unique T_1 . However, the majority of the semilogarithmic plots for the ruby did not yield a unique T_1 . In this representation the data were approximated by two or more straight lines in some cases [e.g., Fig. 8(a)] or by a continuous curve for others [e.g., Fig. 8(b)], rather than a single straight line as indicated in the corresponding treatment of the sapphire data [Fig. 8(c)]. For this reason Table II indicates a range of relaxation times for most of the samples.

The process of spin-lattice relaxation entails a transfer of energy from the nuclear spin system to the crystal lattice. Among the mechanisms by which this transfer can take place are interactions with paramagnetic impurities^{2,3} and interactions between the nuclear quadrupole moment and the crystalline electric field gradient¹⁷ by means of indirect phonon interactions.

It is immediately evident from the data that the Cr^{3+} ions provide the primary relaxation mechanism for the aluminum nuclei. A theory for the relaxation of nuclear spins in a diamagnetic crystal containing paramagnetic impurities has been developed by Bloembergen.³ In particular, Bloembergen studied

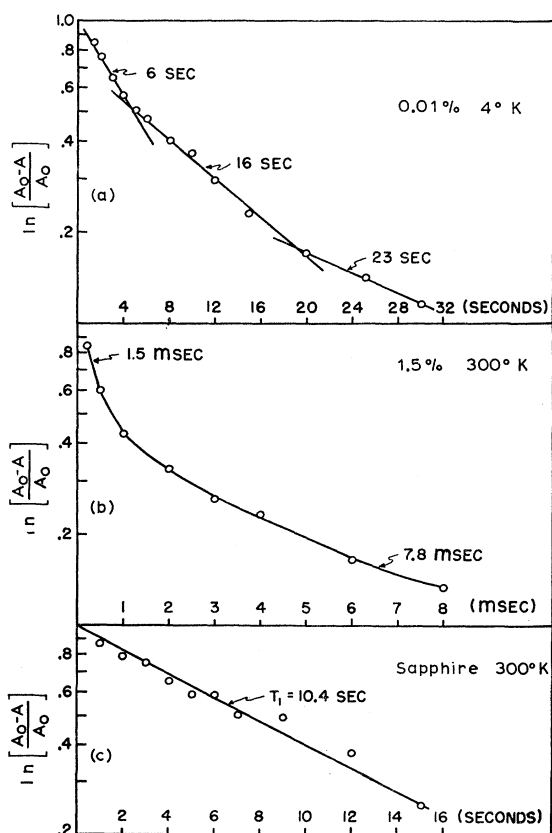


FIG. 8. Plot of the logarithm of the fractional attenuation, $(A_0 - A)/A_0$, of the free-induction signal vs the time t .

¹⁷ J. Van Kranendonk, Physica 20, 781 (1954).

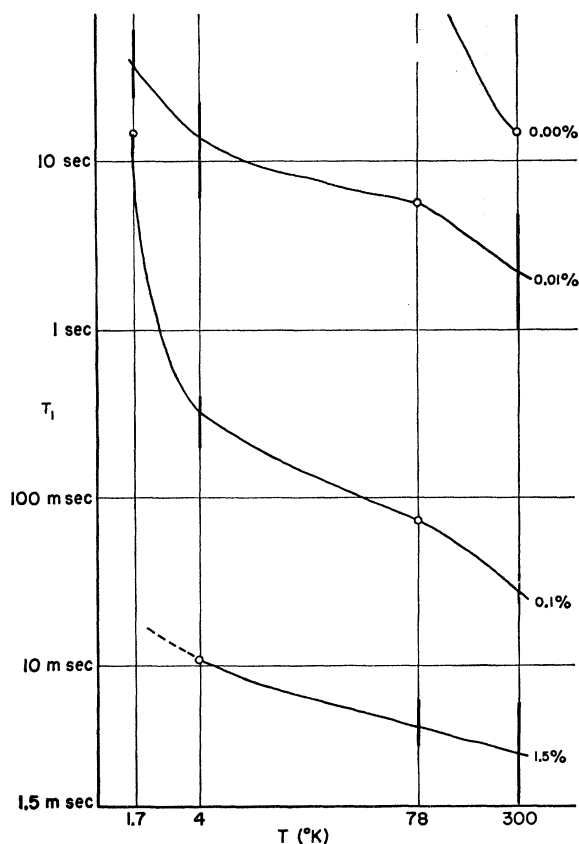


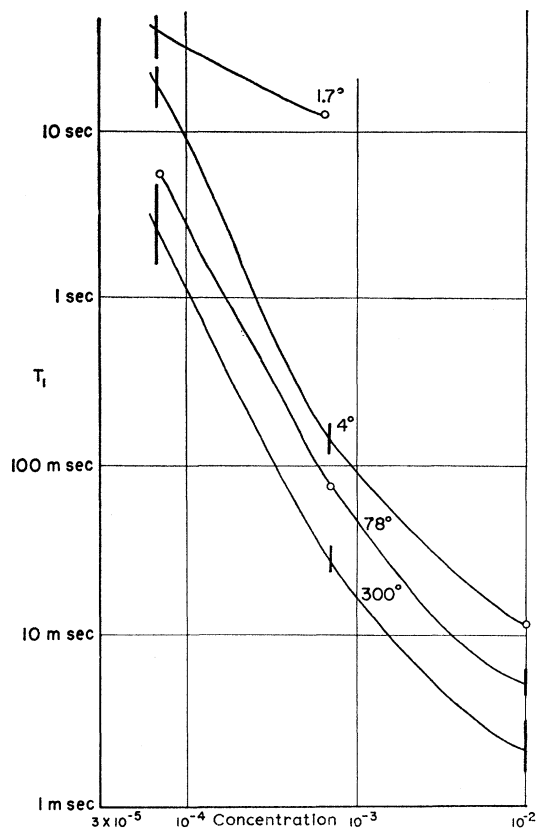
FIG. 9. Plot of T_1 vs temperature at various concentrations of Cr^{3+} .

potassium-aluminum alum in which a known percentage of the aluminum ions were replaced by chromium ions. The T_1 data presented in Figs. 9 and 10 exhibit a very strong qualitative agreement with Bloembergen's results as presented in Figs. 9 and 11 of his paper.

Lattice vibrations present in the crystal cause a fluctuating electric field which, in turn, distort the orbital motion of the electrons of the paramagnetic ions. Then, via the spin-orbit interaction, transitions are induced between the four spin states of the Cr^{3+} ion. The strength of this interaction determines the paramagnetic spin-lattice relaxation time, and causes a fluctuating magnetic field at the sites of the nuclei surrounding the ion. The Fourier spectrum of this fluctuating field contains components at the Larmor frequency of the aluminum nuclei, and this field can therefore induce $\Delta m = 1$ nuclear spin transitions. From these considerations Bloembergen developed Eq. (5) in which the nuclear T_1 is expressed as a function of a parameter τ , to which he originally ascribed the characteristic time for paramagnetic spin-lattice relaxation.

$$T_1 = \left[\frac{3}{2} \gamma_{\text{Al}}^2 \gamma_{\text{Cr}}^2 \hbar^2 S(S+1) \right]^{-1} \pi (1 + \tau^2 \nu_0^2) r^6 / \tau. \quad (5)$$

Here γ is the appropriate magnetogyric ratio, S is the electron spin of the paramagnetic ion, r is the distance

FIG. 10. Plot of T_1 vs concentration at various temperatures.

between the ion and the nucleus in question, and the angular dependence has been neglected. The resonance frequency ν_0 was 9 Mc/sec for the entire experiment. For ruby we have, to a very good approximation of Eq. (5), when $\tau^2\nu_0^2 \gg 1$,

$$T_1 = 3 \times 10^{45} (\tau r^6). \quad (6)$$

Let us now use the available data on the ionic spin-lattice relaxation time in ruby for τ in Eq. (6) to predict the nuclear T_1 . Since the only data available to us for τ are those for the 0.1% ruby,¹⁸ comparison will be made with the experimental values obtained for this crystal.

Some general remarks on Eq. (6) are in order before we proceed with the specific case of the 0.1% ruby. Equation (6) determines the contribution to the spin-lattice relaxation time of nuclei in the time-varying field of the flipping electron paramagnetic moment.

If the paramagnetic ion concentration is high and τ is short, then all the nuclei are relaxed by the direct interaction described by Eq. (6). On the other hand, if the paramagnetic ion concentration is low and τ short, then most of the nuclei relax by spin diffusion to the paramagnetic impurity centers. In the latter

TABLE III. Cr^{3+} spin lattice relaxation time in 0.1% ruby.

Temperature (°K)	Measured (sec)	Estimated (sec)
1.4	59.0×10^{-3}	
1.7		55×10^{-3}
4.2	22.5×10^{-3}	
20.3	6.0×10^{-3}	
77	4.4×10^{-3}	
300		10^{-6}

case, Bloembergen defines a sphere of radius $r=b$ around the paramagnetic ion inside of which the field that a nucleus sees from the paramagnetic ion is greater than the nuclear dipole-dipole interaction. Inside of this sphere there is little, if any, nuclear spin diffusion, whereas outside the sphere there is nuclear spin diffusion. The field from the paramagnetic impurity that a particular nuclear moment sees depends on whether or not it time averages the z component of the field from the flipping paramagnetic moment. If $\Delta\nu_s > 1/\tau$, where $\Delta\nu_s$ is the shift in resonance frequency of the nuclear moment caused by the static paramagnetic ion, then the nuclear moment sees the field from the static paramagnetic ion; if $\Delta\nu_s < 1/\tau$, the nucleus sees the time average field from the paramagnetic ion. Using the value of $\Delta\nu_s$ equal to the nuclear dipole-dipole interaction 7.7 kc/sec ($=7$ gauss), we can calculate the value of b to use for in Eq. (6). We present the results in Table IV in which we indicate whether the time-average chromium moment has been used to calculate b or whether the static moment has been used.

The relative independence on the temperature of the measured values of T_1 at 78° and 300°K indicate that the relaxation process may be limited by the rate at which the energy of the nuclei can spin diffuse to the ions, and therefore the T_1 calculated at $r=b$ may not be a good approximation to the measured T_1 . On the other hand, the values of T_1 calculated at $r=b$ at 4° and 1.7°K should be a better approximation to the measured T_1 . In the latter two cases, the relaxation process is likely not spin-diffusion limited. Two modifications of the Bloembergen theory in an attempt to

TABLE IV. Comparison of theory with the measured T_1 values for 0.01% ruby.

Temperature (°K)	Time average? ^a	T_1 calculated at $r=b$ (sec)	T_1 measured (sec)	Spin diffusion limited?
1.7	No	2.94×10^8	15.3	No
4	No	1.2×10^8	0.4	No
78	Yes	2.9×10^{-4}	0.07	Yes
300	Yes	4×10^{-7}	0.04	Yes

^a Following Bloembergen, the electronic T_1 has been used to decide if the nucleus sees a time average electron moment, (i.e., if $\Delta\nu_s < 1/T_1$ electron). The criteria for time averaging should be if $\Delta\nu_s < 1/T_2$ (electron), as is evident from the behavior of the nuclear linewidth at low temperatures. Although the predicted T_1 's are then closer to experiment by an order of magnitude, they still are larger by two orders of magnitude.

¹⁸ J. H. Pace, D. F. Sampson, and J. S. Thorp, Phys. Rev. Letters 4, 18 (1960).

improve the large discrepancy between prediction and experiment are to no avail.

First, an improvement of the theory was attempted by evaluating the diffusion barrier at $r=d$, where d is the distance of a nucleus from a paramagnetic impurity where

$$a[(\partial/\partial r)(H_{\text{para}})]_d = 7 \text{ gauss}, \quad (7)$$

where a is the lattice constant, H_{para} the field from a paramagnetic ion, and the partial derivative is evaluated at the distance d . This did not improve the results substantially.

A second attempt to improve the theory has to do with the rate at which the electrons undergo transitions between spin levels. It has been suggested that, at very low temperatures, the time variation in the local field at the nuclei may have a significant contribution from the mutual spin exchange of the electrons.

The rate of the ionic spin-flip process and the magnitude of the local field variation at the nuclei are, however, uncertain in the 0.1% ruby crystal. For a crystal in which the ions are widely spaced, the paramagnetic spin-spin interaction is very weak and thus the spin flip rate will be slow. When spin exchange does occur in the dilute ruby, the change in the local field at the nuclei may be almost as effective as that produced by spin transitions in the ionic spin-lattice relaxation process. For higher concentrations, the ion flip rate is more rapid, but the magnetic field change at large distances (i.e., from two ions in adjacent sites which undergo a spin exchange) will be considerably less than that due to a single ion undergoing a transition (electron spin lattice relaxation).

Kikuchi¹⁹ has measured the width of the paramagnetic resonance to be 24 gauss in a 0.1% ruby. Although it is difficult to estimate the contribution to the width due to mutual spin flips, it does not seem unreasonable that this process should contribute at least 10% of the measured width. (For a 1% ruby, the width measured has increased to between 45 and 70 gauss.)¹⁵ We thus would have a characteristic time for spin exchange of the paramagnets of less than 5×10^{-8} sec in the 0.1% sample.

If we use 5×10^{-8} sec for τ in Eq. (5) and the value for r of the nuclear spin diffusion barrier at 1.7°K,

¹⁹ C. Kikuchi, J. Lambe, G. Makhov, and R. W. Terhune, J. Appl. Phys. 30, 1061 (1959).

we would then predict T_1 to be less than 10 msec which is much less than the 15.5 sec measured at 1.7°K. Thus, although the ion spin flips occur at a rapid rate, their strength in the nuclear relaxation process is much less than that for spin transitions due to electron lattice relaxation.

The ion spin exchange rate is of course temperature independent. The only temperature dependence possible in this nuclear relaxation mechanism is therefore through the change in the nuclear spin diffusion barrier.

Let us try a combination of the spin-lattice and spin-flip mechanisms to predict the measured nuclear T_1 's. We will assume a strength for the electron spin exchange that will yield the 15.5 sec observed at 1.7°K, and which will of course be constant at all temperatures. Since the T_1 predicted by the ion lattice relation process alone is 275 sec, we are correct in neglecting it at this temperature. We have now to explain the 0.4-sec T_1 observed at 4°K by the decrease in the nuclear spin barrier and the increased rate due to the electron spin-lattice process. The spin diffusion barrier decreases from 11.5 Å at 1.7°K to 9.2 Å at 4°K so that the spin exchange process is more effective by a factor of $(11.5/9.2)^6$ or 3.8. T_1 remains almost unchanged by the electron spin lattice relaxation mechanism (which by itself gives about 100 sec for the nuclear T_1) and thus the predicted T_1 at 4°K is 4 sec, an order of magnitude less than observed.

Thus, not only does the existing theory fail to account for nuclear spin diffusion at high temperatures where its predictions differ from experiment by a factor of 10^5 , but it defies our rudimentary attempts to patch it up at liquid He temperatures.

The data for the 0% chromium and the other concentrations are included for completeness. From Fig. 8 it is apparent that a unique T_1 for the 0% chromium (sapphire) exists and the relaxation process at 300°K for this specimen is by the nuclear quadrupole interaction with the lattice vibrations. The lack of a unique T_1 for most of the samples does not serve to differentiate between a spin diffusion limited relaxation and a direct interaction. One can safely say that in the higher concentration crystals the nuclear spin-lattice relaxation is by the direct interaction without spin diffusion, since the linewidth is so large that essentially all nuclei lie inside the spheres of radius b .