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Effect of Crystal-Growth Method on Electron Spin Relaxation in Ruby

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Measurements of spin-lattice relaxation times of single crystals of ruby have been carried out using the pulse saturation technique at a frequency of 9.27 kMc/sec and, generally, in the helium temperature range. Results for Verneuil-grown specimens agree with those already reported: concentration-dependent relaxation times, almost independent of crystal orientation. For specimens grown by the so-called vapor-phase modification, the relaxation time is longer and independent of concentration over a range 0.005 to 0.2 at.% Cr^{3+}. It exhibits strong angular dependence of the form predicted by Donoho, and calculation and experiment are in satisfactory quantitative agreement. It is concluded that vapor-phase rubies represent a "clean" magnetic system, and the suggestion is made that fast-relaxing impurity ions may account for the concentration-dependent parameter usually observed.

1. INTRODUCTION

THE presently accepted theories of spin-lattice relaxation (for example, the work of Kronig,[1] Van Vleck,[2] Orbach[3]) are based on the concept of a spin system which is coupled to the lattice through the modulation of the crystalline electrostatic field by lattice vibrations. At sufficiently low temperatures, the direct or one-phonon process is dominant and the predicted relaxation rate ($1/T_1$) is proportional to the absolute temperature T. At higher temperatures, the Raman or two-phonon process predominates and, in the ruby case (Cr^{3+} ions in the Al_2O_3 lattice) the relaxation rate is proportional to T^7. In those instances when the Orbach or resonant two-phonon process can occur, an exponential dependence of relaxation rate upon temperature is predicted. However, in each case, only an individual ion and its surrounding lattice is considered, and naturally no dependence of relaxation rate upon the concentration of the paramagnetic ions is predicted.

Experimental investigations of the relaxation rate of the trivalent chromium ion in ruby have been reported in the literature[4–7] and a marked dependence of T_1 upon concentration of the Cr^{3+} ion has been observed at low temperatures. For instance, at 4.2°K, Gill found T_1 to vary at least as rapidly as f^{-1}, in the range of concentration (f) between 0.01% and 0.7% Cr^{3+}. Feng and Bloembergen found the form of the temperature dependence to vary with concentration, changing from T^{-1} at low concentrations to approximately T^{-2} above about 0.2% Cr^{3+}.

During the examination of a number of rubies, we observed also that there was a marked spread of values of T_1, among samples of approximately the same chromium concentration. We have therefore carried out a detailed study of the relaxation process in a wide range of ruby samples, grown by three different methods. The results are presented and analyzed below; the dependence of measured relaxation parameters upon growth technique is shown. These results have been briefly reported elsewhere.[8]

2. EXPERIMENTAL DETAILS

Two spectrometers were used in the present work, both employing the pulse-saturation technique, and both operating at X band.

The first spectrometer was basically that described by Standley and Wright.[9] In this, both the monitoring signal and the microwave pulses were obtained from the high-power klystron by means of diode switches suitably mounted across the waveguide.

The second employed a Decca Radar Limited spectrometer as its monitor signal source and as its detector. In this spectrometer the signal klystron is phase-locked (at 9.27 kMc/sec) to a harmonic of a crystal-controlled oscillator, and this produces a very stable, low-noise source of microwaves. The detector is a superheterodyne receiver whose local-oscillator klystron is also locked, 30 Mc/sec away from the signal frequency. Facilities are available on the spectrometer for phase-sensitive detection at both 30 Mc/sec and at 33 cps, and pen-recorder display is provided. For our relaxation time measurements, however, the signal was detected after the 30 Mc/sec amplifier, and displayed on a Tektronix 535A oscilloscope.

The source of microwave pulses was an English Electric K350 klystron working in pulsed operation. The voltage applied to this valve was adjusted so that the working point was just below a klystron mode. Voltage pulses, sufficient to bring the tube into the oscillating condition, were then superimposed on this. A

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[1] R. de L. Kronig, Physica 4, 33 (1939).

[2] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[3] R. Orbach, Proc. Roy. Soc. (London) **A264**, 485 (1961).

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

[7] A. A. Manenkov and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **42**, 75 (1962) [English transl.: Soviet Phys.—JETP **15**, 54 (1962)].

[8] K. J. Standley and R. A. Vaughan, Phys. Letters **10**, 33 (1964).

[9] K. J. Standley and J. K. Wright, Proc. Phys. Soc. (London) **83**, 361 (1964).

single diode switch mounted before the mixer was used to protect the mixer crystals. The voltage pulse used to switch the klystron, the suppression pulse, and also the triggering pulses for the oscilloscope, were all obtained by suitable modification to a Nagard Type 5002C pulse generator. It was possible to produce microwave pulses of about 2-W peak, variable in width between 3 μsec and 200 msec at recurrence frequencies between 0.1 cps and 50 kcps; relaxation times between 5 μsec and 2 sec have been measured using this apparatus.

To obtain the relaxation parameters, the oscilloscope display of the recovery curve was photographed and later replotted in semilogarithmic form.[10] When a single relaxation time was present, the resulting graph was a straight line whose slope gave T_1 directly. We believe that this method of analysis, though perhaps more laborious, is more reliable than the fitting of standard or generated exponentials if there is reason to suspect the presence either of nonexponential recovery curves[9] or of more than one relaxation-time constant.

The ruby samples, obtained from a variety of sources, had been made by three techniques:

(i) The Verneuil[11] process, in which solid oxides of aluminum and chromium are fed to an oxyhydrogen flame and the resulting molten mixture crystallizes in a boule on a seed-crystal below the flame tip.

(ii) The so-called "vapor-phase" modification of the Verneuil process, developed by Thermal Syndicate Limited. In this, aluminum and chromium are fed to the flame as halide vapors instead of as solid oxides.

(iii) The fluxed-melt technique, wherein the ruby crystals grow from a 'solution' of the oxides in lead oxide/lead fluoride flux. This process permits lower temperature growth of the rubies.

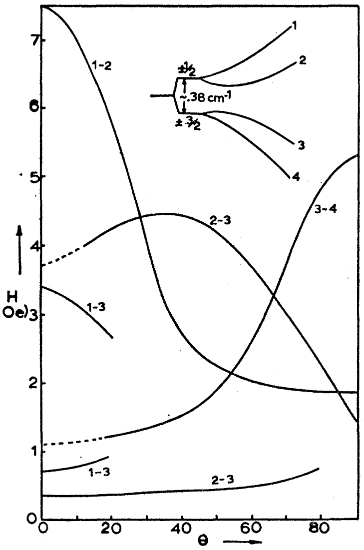

Fig. 1. Isofrequency resonance chart for ruby at 9.3 kMc/sec.

Below, we refer to these three techniques as V, VP, and FM respectively.

In all, we examined 14 samples in the concentration range up to 0.3 at. % Cr^{3+}, but only two FM rubies were available to us, grown by the Hirst Research Centre of the General Electric Company.

Six of the specimens used were analyzed spectrographically and their chromium content thus established within ±10%. Approximate concentrations in the other specimens were found from comparisons of the integrated intensities of the $|-\frac{1}{2}\rangle \leftrightarrow |+\frac{1}{2}\rangle$ absorption lines under fixed experimental conditions.

In order to compare the behavior of the different samples, it was important to reduce the possibility of effects due to cross relaxation and anomalous line broadening. Accordingly, the (1,3) transition at $\Theta=0$ and $H\approx 3{,}300$ G (Fig. 1) was studied, the two levels involved there relating to almost pure $|\pm\frac{1}{2}\rangle$ states. The relaxation parameters were found in the temperature range 1.6 to 4.2°K, and occasionally up to 90°K. Selected samples representing each manufacturing method were then examined in detail at 4.2°K, the relaxation parameters being determined as a function of angle for each transition, where this was experimentally possible.

Table I. Relaxation times for vapor-phase rubies.

		Relaxation time T_1		
Specimen No.	Concentration At. % Cr^{3+}	1.6°K msec	4.2°K msec	77°K μsec
1	0.005[a]	370	150	
2	0.017	540	230	27
3	0.018[a]	500	190	15–20
4	0.045	550	240	
5	0.047	350	140	33
6	0.050	540	200	
7[b]	0.087	550	215	29
8	0.20[a]	420	105	30

[a] Concentrations determined spectrographically.
[b] "Orange" ruby.

3. EXPERIMENTAL RESULTS

(a) The Effects of Change in Concentration

Some results of the measurements on the $|-\frac{1}{2}\rangle \leftrightarrow |+\frac{1}{2}\rangle$ transition are shown in Tables I, II, and III, together with the chromium content of each specimen. The concentrations of the VP rubies extend over a range of about 40:1. A variation in T_1 is seen to occur (Table I) outside the anticipated experimental error of ±10%, but it is clear that there is no variation which can be associated with change in concentration.

The concentration dependence observed by other workers was indeed observed by us in the relaxation behavior of V rubies (Table II), when relaxation times

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[10] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).
[11] M. A. Verneuil, Compt. Rend. **135**, 791 (1902).

approximately inversely proportional to concentration were obtained. These relaxation times were shorter than the corresponding values for the VP rubies. Samples 10, 11, and 12 were those used by Feng and Bloembergen[5]; it is both interesting and encouraging to note that the present results obtained by the pulse-saturation method are in substantial agreement with those measured by their dc-magnetization method.

Figure 2 shows the concentration independence of T_1 for VP specimens over the temperature range 1.6 to 4.2°K. Measurements carried out at 77°K (Table I) on several of the specimens suggest that this concentration independence extends also into the temperature region where the Raman process is dominant.

(b) Temperature Dependence

With the exception of sample 8 (in which general cross-relaxation effects were very noticeable) the measured relaxation times (Fig. 2) for all the VP rubies investigated follow closely the temperature dependence for the direct process, namely:

$$(1/T_1)=AT.$$

TABLE II. Relaxation times for Verneuil-grown rubies.

Specimen No.	Concentration At. % Cr^{3+}	T_1 (msec) 1.6°K	4.2°K
9	0.048	270	105
10	0.16[a]	105	35
11	0.21[a]	120	41
12	0.30[a]	70	20

[a] Concentrations determined spectrographically.

The recoveries obtained for samples 1 to 6, at the particular angle considered, followed an exponential form characterized by a single time constant. General cross-relaxation was, however, present in the two most concentrated samples 7 and 8, and up to three time constants could be detected in their recoveries. The longest of these was taken to be the spin-lattice relaxation time, and sufficient of the slow components was present in the recovery of sample 7 for an unambiguous determination of T_1 to be made. For sample 8, however, even using pulses up to 200 msec long, there was little long "tail" on the recovery and T_1 was estimated from the tangent to the curved semilogarithmic plot of the recovery. The presence of a faster component reduces the value of the longer time constant by an apparent amount, depending upon the relative magnitude of the two time constants and on their relative amplitudes. The estimated time constant for sample 8 may therefore be a little less than the true spin-lattice relaxation time, and its behavior does not necessarily reflect the temperature dependence of T_1. This would tend to make the results even more consistent with those obtained for the rest of the VP rubies.

TABLE III. Relaxation times for rubies of different growth methods.

Specimen No.	Growth method	Concentration At. % Cr^{3+}	T_1 (msec) 1.6°K	4.2°K
8	VP	0.20	420	105
11	V	0.21	120	41
13	FM	0.19	95	37

The measured relaxation times for the V and FM samples also follow closely a $1/T$ dependence (Tables II and III). General cross-relaxation was present in samples 11 and 13 to much the same extent as in sample 8 and several components could be resolved. When pulses up to 200 msec long were used, the last part of each semilogarithmic plot was straight. The time constants thus obtained were taken as T_1, since there was no indication at all of a further "tail" like that observed in the VP ruby, sample 8.

In the Raman region, the relaxation times for the VP specimens tend to follow more of a T^{-5} than the expected T^{-7} dependence, in agreement with the results of other workers.[4,6] It is not obvious that this is really significant, since the Raman process may not be completely dominant in this range of temperatures; moreover the experimental error in determining T_1 has increased at 90°K.

(c) The Angular Dependence of the Relaxation Parameter

The variation of relaxation time with crystal orientation for different transitions has been experimentally investigated, and compared with the results of a theoretical investigation by Donoho[12] in which he predicted the form of the angular dependence. In Donoho's work, values of the components of the G tensor[13] obtained experimentally by Hemphill and Donoho[14] from static

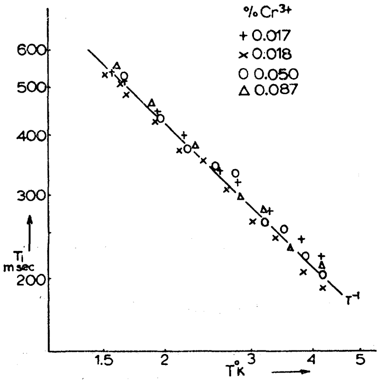

FIG. 2. Temperature dependence of T_1 for four VP rubies.

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[12] P. L. Donoho, Phys. Rev. 133, A1080 (1964).

[13] Defined as a coefficient which, multiplying the strain, gives the change in crystal field energy under lattice strain.

[14] R. B. Hemphill and P. L. Donoho (to be published).

strain measurements, were used to compute the phonon-induced transition probabilities for the direct process between the various energy levels. These were then used to solve the rate equations, governing the dynamic behavior of the spin system, which are of the form:

$$dn_i/dt=\sum_{j=1}^{4}W_{ji}n_j-W_{ij}n_i,\quad i=1,2,3,4,$$

where n_i is the population of level $|i\rangle$ and W_{ij} is the transition probability between levels $|i\rangle$ and $|j\rangle$.

Such a set of equations will in general yield three independent relaxation times for the four-level system, and a solution is obtained of the form

$$n/n_0=1+A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}+A_3e^{-t/\tau_3},$$

where n is the instantaneous value of the population difference of the two levels between which resonance is being observed, and n_0 is its thermal equilibrium value. τ_1, τ_2, and τ_3 are three time constants (not in general simply related to the $T_1^{(ij)}$ defined for the pairs of levels $|i\rangle$ and $|j\rangle$), and A_1, A_2, and A_3 are the relative amplitudes of the contributions from these.

Values of A_1, A_2, and A_3, and τ_1, τ_2, and τ_3 were computed numerically by Donoho, and are presented in his paper as a function of angle for the various transitions at $\nu=9.3$ kMc/sec. The strong angular dependence of the relaxation times is a consequence of the variation in admixture between states as Θ changes.

In most cases, one relaxation time, usually the longest, dominates the behavior; when two relaxation times are important, they are usually nearly equal. A_3, the amplitude of τ_3, is nearly always negligible compared with A_1 and A_2, and the present results are therefore analyzed in terms of two component relaxation times only, τ_1 and τ_2.

It was pertinent to ask if data which could legitimately be compared with Donoho's could readily be extracted from experimental recovery curves. Accordingly, curves were numerically constructed using Donoho's values of A_1, A_2, τ_1, and τ_2, and these were then plotted in semilogarithmic form. The time constants were taken from these in the usual way. Only when $A_1 \gg A_2$ was the value of the longest time constant obtained equal to τ_1. When A_1 and A_2 were similar in magnitude, two time constants, intermediate in value between τ_1 and τ_2, were resolved if τ_1 and τ_2 were very different but only one intermediate time constant was obtained if $\tau_1 \simeq \tau_2$.

The experimentally determined angular dependence for the VP rubies followed closely that predicted by Donoho, but with about half the expected magnitude. Representative data obtained with sample 4 (at 4.2°K) are compared with Donoho's in Figs. 3 and 4, wherein the Donoho computed values of τ_1 and τ_2 have been reduced by a factor of 2.

The (2–3) High-field Transition (Fig. 3)

These data are included here because of the strong angular dependence, both predicted and experimentally observed. A_2 and A_3 are negligible compared with A_1, for this transition and only one time constant is expected, namely τ_1, which one therefore identifies with T_1. This was indeed experimentally the case. The experimental point at 40° may be explained in terms of harmonic cross relaxation ($\nu_{23}=2\nu_{34}$ at about 42°),

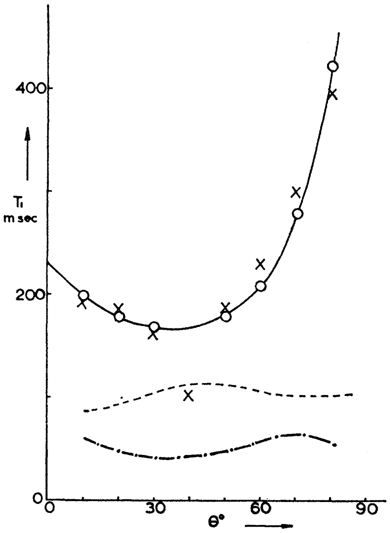

FIG. 3. Comparison of experimental and calculated data for the (2–3) transition. —— is the Donoho curve and ○ the calculated values (see text). × are experimental points for VP specimen No. 4 and ---- and —·—·— the experimental curves for V specimens Nos. 9 and 11. Each specimen is representative of its class.

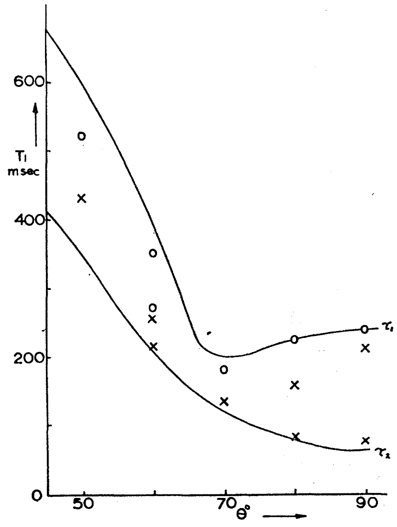

FIG. 4. Comparison of experimental and calculated data for the (3–4) transition above $\Theta=50°$. Symbols as for Fig. 3.

which results in a decrease in the observed lattice relaxation time over several degrees on either side of the exact harmonic angle. A harmonic point at about 83° ($\nu_{23}=\nu_{34}$) may account for the experimentally obtained value of T_1 at 80° being apparently slightly low.

All recoveries for this transition (except at harmonic angles) were closely exponential and showed no dependence on pulse width when this was varied between 15 μsec and 200 msec. The angular dependence of T_1 at 1.6°K also followed a similar form, with the value of T_1 increased according to $(1/T_1)=AT$. Similar data were obtained with other VP crystals.

(3–4) Transition (Fig. 4)

The intensity of this absorption line permitted measurements of relaxation time to be made over only a limited range of angles. Donoho, in his paper, shows that both τ_1 and τ_2 have comparable amplitudes over the range 50°–70°, whereas by 90°, only τ_1 is important. Both τ_1 and τ_2 are shown in Fig. 4 (solid lines) together with the values of the time constants one would expect to measure, obtained from a numerical analysis of Donoho's results. At 60°, this analysis predicts that two time constants will be observed, with values intermediate between τ_1 and τ_2, since $A_1<A_2$. At 50°, however, $A_1>A_2$, and only one time constant will be observed and the recovery is expected to be exponential. It should be noted that the value of this single time constant is considerably less than τ_1. This effect was referred to in explaining the observed temperature dependence of the relaxation time in sample 8.

The form of the angular variation of the experimentally determined relaxation times is seen to agree closely with that predicted, bearing in mind that Donoho's values have been reduced by an *arbitrary* factor of two. A faster component, identified with τ_2, was obtained from the initial part of the recovery over the range 60 to 90°.

Similar satisfactory agreement was found for the other two transitions, when allowance was made for the occurrence of harmonic cross relaxation.

A very different state of affairs was found to exist with the V rubies, however. Very little variation in relaxation time with crystal orientation was observed in any of these specimens, in agreement with the findings of Gill.[4] This is strikingly shown in the case of the (2–3) transition (Fig. 3) for samples 9 and 11. Similar results were found for the other transitions.

No reliable results were obtained with the FM samples. These were physically small and anomalously great line widths at many angles other than $\Theta=0$, severely reduced the intensity of the absorption peak. (The line-width data will be discussed elsewhere). Such data as were obtained were similar to those found with V and not VP samples.

4. DISCUSSION

The experimental data obtained with the VP rubies are in substantial agreement with the theoretical predictions of Donoho. Moreover, at least up to concentrations of 0.2 atomic % Cr^{3+}, there is no dependence of the relaxation time upon concentration. Thus, for this system, theory and experiment are in accord. This is not the case with V rubies—experimental values are often an order of magnitude less than those predicted, there is negligible variation with angle, and there is a marked variation with concentration. Thus, in V rubies at helium temperatures, one is not observing the direct relaxation to the lattice of the Cr^{3+} ion. One is led to postulate the presence of a fast-relaxing impurity, to which the excited Cr^{3+} ion easily and rapidly communicates its energy, and which then relaxes to the lattice. It is the relaxation of the Cr^{3+} system which is monitored, without there being a simple test of whether it is a true spin-lattice relaxation which is observed. Even for V rubies there is evidence from the acoustic-absorption measurements of Dobrov and Browne[15] that the true spin-lattice relaxation time is long, and independent of concentration, whereas the relaxation parameter measured by spin-echo techniques, for the same specimens, is fast and concentration-dependent.

It has been suggested[16] that the observed concentration dependence of relaxation times in ruby occurs when relaxation takes place via exchange coupled pairs. The spectrum produced by such pairs is quite complex, and the relaxation mechanism envisaged is a modified Orbach two-phonon process taking place via excited levels in the pair spectrum. Gill, however, has calculated the effect of relaxation via pairs, and has concluded that below a concentration of about 0.2% Cr^{3+}, the coupling is too weak, and the pair lines too few to account for the observed relaxation behavior. (This effect may, however, influence the relaxation behavior of more concentrated specimens). Specimens 8, 11, and 13 are all of similar concentration and experimentally it is observed that the pair spectra are also very similar in both form and intensity: the observed marked difference in relaxation behavior of particularly specimens 8 and 11 (Table III) is thus unlikely to stem from this cause.

General cross-relaxation[17] is also unlikely to be the explanation, since this was observed to be present to much the same extent in both specimens 8 and 11. Mims and McGee pointed out that this effect, being a spin-spin interaction, should be independent of temperature; all the relaxation times measured were dependent upon temperature. Concentration dependence is also observed in dilute V rubies where general cross relaxation is negligible.

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[15] W. I. Dobrov and M. E. Browne, *Paramagnetic Resonance* (Academic Press Inc., New York, 1963) p. 447.

[16] J. H. Van Vleck, *Quantum Electronics* (Columbia University Press, New York, 1960) p. 392.

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

Crystal defects and physical imperfections were found to be present to much the same extent in both types of ruby, and are probably the result of the intrinsic limitations of any high-temperature growth process. Although accurate analysis of all specimens was not carried out, sufficient data were available to suggest that greater amounts of chemical impurities were likely to be present in V samples (the total content was, of course, still small, $<0.002\%$ by weight in the best V samples). It is thus possible that impurity ions may constitute the fast-relaxing centers.

It is known that ferric iron (Fe^{3+}) is often present as an impurity in ruby crystals. There is a high probability that an iron esr line will be found within a few line widths of any Cr^{3+} transition, and that cross relaxation to these lines may speed up the recovery of the Cr^{3+} transition. However, the relaxation time of the Fe^{3+} ion was measured on the impurity lines present in specimen 9, and found to be of the same order as that for the Cr^{3+} ion in this sample, namely about 20 msec at 4.2°K and 45 msec at 1.6°K. These times may already have been reduced by some other center present and, in themselves, are insufficiently short to explain, convincingly, the observed effects. Also, the amount of Fe^{3+} ion present even in V rubies varies greatly between specimens of the same concentration, and was present to much the same extent in all the samples analyzed spectrographically, including both V and VP rubies.

Chromium in a valence state other than trivalent may act as an impurity ion. Hoskins and Soffer[18] reported the spectrum of Cr^{4+} in the Al_2O_3 lattice at X band—a single line with $g\approx 1.9$, certainly not broad enough to overlap all the Cr^{3+} transitions. The observed transition, $\Delta m=2$, originates in an excited doublet some 7 cm^{-1} above the ground state. Thus, although Hoskins and Soffer reported a fairly short relaxation time for this line, it is reasonable to expect that the efficiency of the Cr^{4+} ion as the fast cross relaxer would be very temperature-dependent. This is not the affect observed in V rubies. In fact, specimen 7 was orange in color and the Cr^{4+} spectrum was detected, yet the Cr^{3+} relaxation times were similar to those in pink VP rubies with Cr^{4+} undetectable.

Two other possible impurities are Fe^{2+} and Cr^{2+} ions. It is known that iron enters the lattice as Fe^{2+} in the growth of sapphire by the Verneuil technique if one attempts to increase the Fe^{3+} content above a certain level. It therefore seems possible that if iron is present in ruby, some may be in the form of Fe^{2+}. Also, if the appropriate charge compensation occurs, chromium may go in as Cr^{2+}. Al'tshuler *et al.*[19] have shown, from calculations of the resonant absorption coefficients of phonons by transition metal ions, that these two ions may be very strongly coupled to the lattice. This would lead to broadened absorption lines and allow cross relaxation to take place over a very wide range of field strengths. The intensity of the absorption lines from these ions would also be reduced, and they would consequently be very difficult to detect. The two ions would both have to be associated with some form of charge compensating mechanism, and this could possibly be an additional feature of the fast relaxing mechanism. If they are to be identified with the fast relaxing centers, these two ions must be absent from VP rubies. The reason for this may be in the selective volatility of the constituent materials in this process.

5. CONCLUSION

The results presented above indicate that VP rubies represent a "clean" magnetic system, for which the measured relaxation parameter is in substantial agreement with the presently accepted theories of spin-lattice relaxation. It is thought that this is the first report of such agreement between predicted and measured relaxation times, over a wide range of concentrations, for iron group ions in a ceramic type crystal.

Results obtained with V rubies exhibit characteristics very similar to those reported by other workers. One explanation for this anomalous behavior is the presence of fast-relaxing impurity ions, possibly Fe^{2+} or Cr^{2+}. The identity of the fast relaxer has not yet been established.

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[18] R. H. Hoskins and B. H. Soffer, Phys. Rev. **133**, A490 (1964).

[19] S. A. Al'tshuler, B. I. Kochelaev, and A. M. Leushin, Usp. Fiz. Nauk. **75**, 459 (1961) [English transl.: Soviet Phys.—Usp. **4**, 880 (1961)].