

Spin-Lattice Relaxation of  $Ti^{3+}$  Ions in  $RbAl(SO_4)_2 \cdot 12H_2O$ 

GERALD F. DIONNE\*

*Eaton Electronics Research Laboratory, McGill University, Montreal, Canada*

(Received 2 March 1965; revised manuscript received 1 June 1965)

Spin-lattice relaxation measurements with small concentrations of  $Ti^{3+}$  ions in single crystals of  $RbAl(SO_4)_2 \cdot 12H_2O$  have been carried out between temperatures of 4.2 and 1.6°K. The experimental method involved the continuous-wave saturation technique in which comparison was made with a  $Cr^{3+}$  impurity of known relaxation time. Over the above temperature range, the values of  $T_1$  varied between 3.3 and 63 msec, indicating Raman behavior at 4.2°K. In general, the magnitudes of the relaxation times are much greater than had been expected, and this fact has been explained by applying the Van Vleck theory to the crystal-field model previously reported for this salt. Agreement between theory and experiment is remarkably good at 4.2°K, but breaks down at the lower temperatures, where the direct process begins to dominate. Cross relaxation with the  $Cr^{3+}$  impurity is discussed as a possible explanation for this discrepancy, and a qualitative comparison is made between the relaxation behavior of  $Ti^{3+}$  and  $Cr^{3+}$  ions in the light of current theories of spin-lattice interaction.

## INTRODUCTION

FOR many years, the spin-lattice relaxation of  $Ti^{3+}$  ions in the alum lattice has been a subject of discussion in the literature of the field. It has been believed that the relaxation time is extremely short. One reason is that early attempts to measure it were unsuccessful because of experimental limitations. This negative result led to the conclusion that the relaxation rate was too fast to be measured by techniques then available. A second reason for this assumption was based on the paramagnetic resonance measurements with  $CsTi(SO_4)_2 \cdot 12H_2O$ ,<sup>1</sup> which pictured the titanium ion as having a very low-lying orbital level (i.e.,  $<100 \text{ cm}^{-1}$ ) above the ground state in the crystal-field energy-level structure. According to the Van Vleck theory,<sup>2</sup> this would result in a short relaxation time and would be controlled by the Raman process to temperatures lower than 1.2°K.

In 1938, attempts to measure the spin-lattice relaxation time of  $CsTi(SO_4)_2 \cdot 12H_2O$  were made by Gorter *et al.*,<sup>3</sup> at 77°K and de Haas and du Pré<sup>4</sup> at 4.2 to 1.2°K. In both cases, a nonresonant technique was employed with little success since the values of the relaxation time could only be established as  $<10^{-7}$  sec in the former experiment and  $<10^{-8}$  sec in the latter. Since the samples studied were undiluted, large effects of spin-spin interaction were undoubtedly present and it is difficult to compare these results with those to be reported in this paper. For reasons outlined in earlier work,<sup>5</sup> the samples investigated were  $Rb\{TiAl\}(SO_4)_2 \cdot 12H_2O$  in which the  $Ti^{3+}$  ions were present in a concentration of about 0.02%. As a result, EPR studies were

possible and corresponding relaxation measurements could be carried out in a relatively straightforward manner. The significance of these measurements is thus twofold: They represent the first published values of the spin-lattice relaxation time of the  $Ti^{3+}$  ions in an alum lattice; and secondly, for the first time it is possible to apply the Van Vleck theory and calculations for titanium alum to specific experimental results.

## APPARATUS AND EXPERIMENTAL PROCEDURE

In the experiments described below the basic apparatus was an X-band microwave spectrometer as sketched in Fig. 1 and all measurements were made at liquid-helium temperatures. For the details of equipment and general experimental methods, the reader is referred to Kipling *et al.*,<sup>6</sup> for the details of sample preparation, the author's thesis may be consulted.<sup>7</sup>

The problem of measuring the spin-lattice relaxation time of  $Ti^{3+}$  in  $RbAl(SO_4)_2 \cdot 12H_2O$  was complicated by the fact that the paramagnetic resonance signals from an estimated  $10^{17}$  spins were too weak to permit application of the resonant-pulse saturation technique. On the other hand, the continuous-wave saturation method,<sup>8</sup> although applicable, cannot be considered as an accurate method because of the number of inherent assumptions. To resolve the dilemma, a compromise between the two approaches was adopted.

In the single-crystal samples investigated, a small trace of  $Cr^{3+}$  impurity was detected in a concentration estimated at 0.001%. Consequently, since the effects of spin-spin interaction vanish below about 1.0%<sup>9</sup> in  $Rb\{CrAl\}(SO_4)_2 \cdot 12H_2O$ , it may be concluded that the chromium lines were inhomogeneously broadened in these crystals and the spin-lattice relaxation time  $T_1$  would be at its maximum value for this concentration.

\* Present address: Advanced Materials Research and Development Laboratory, Pratt & Whitney Aircraft, North Haven, Connecticut.

<sup>1</sup> B. Bleaney, G. S. Bogle, A. H. Cooke, R. J. Duffus, M. C. M. O'Brien, and K. W. H. Stevens, Proc. Phys. Soc. (London) **A68**, 57 (1955).

<sup>2</sup> J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

<sup>3</sup> C. J. Gorter, P. Teunissen, and L. J. Dykstra, Physica **5**, 1013 (1938).

<sup>4</sup> W. J. de Haas and F. K. du Pré, Physica **5**, 969 (1938).

<sup>5</sup> G. F. Dionne, Can. J. Phys. **42**, 2419 (1964).

<sup>6</sup> A. L. Kipling, P. W. Smith, J. Vanier, and G. A. Wootton, Can. J. Phys. **39**, 1859 (1961).

<sup>7</sup> G. F. Dionne, Ph.D. thesis, McGill University, Montreal, 1964 (unpublished).

<sup>8</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

<sup>9</sup> J. Vanier, Can. J. Phys. **42**, 494 (1964).

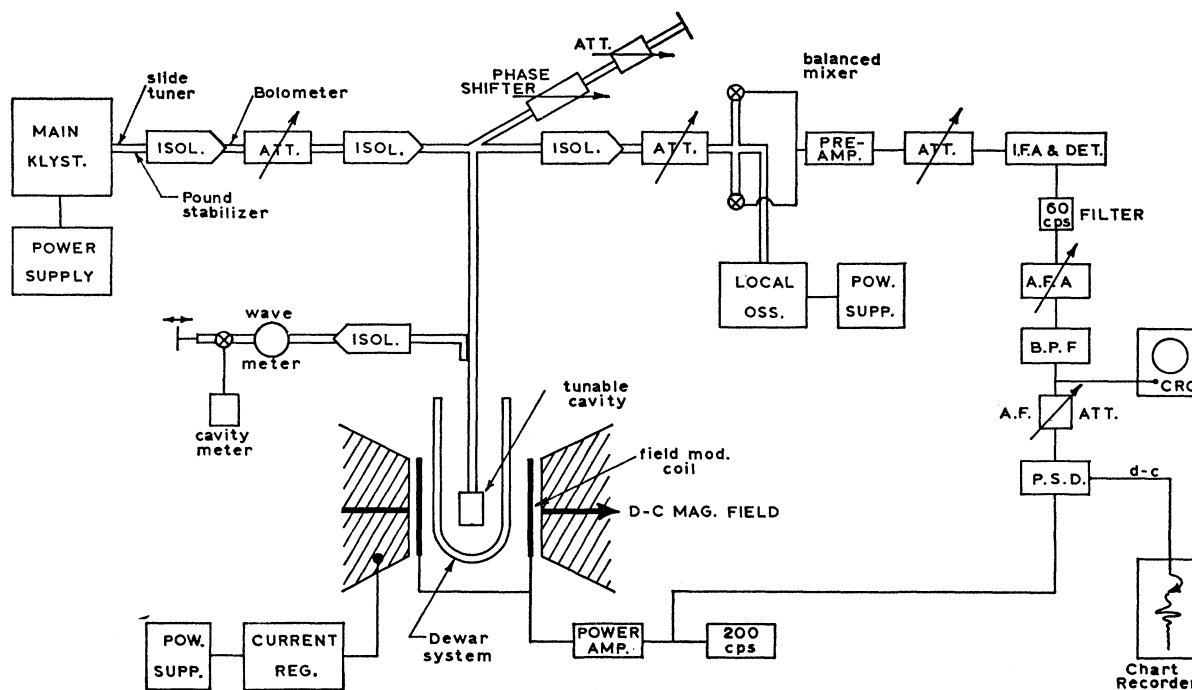


Fig. 1. Block diagram of modified X-band paramagnetic resonance spectrometer used for measuring spin-lattice relaxation times.

This latter conclusion was clearly established by Vanier<sup>10</sup> in conjunction with his above work on line broadening. Therefore, it may be assumed that the  $T_1$  values for  $Cr^{3+}$  in these samples are the same as those measured separately using the pulse-saturation method with any single crystal of  $Rb\{CrAl\}(SO_4)_2 \cdot 12H_2O$  as long as the concentration of  $Cr^{3+}$  is less than 1.0%. Thus, to measure  $T_1$  for an ion of unknown relaxation time, a comparison method can be used by relating its saturation behavior to that of a  $Cr^{3+}$  ion in the same lattice. The following theory indicates the method more specifically:

Since the basic ideas of paramagnetic resonance and relaxation have been expounded in a number of excellent publications,<sup>11-13</sup> it is convenient to simply quote the more pertinent results of the theory. In EPR experiments, the signal observed at resonance is caused by a power absorption  $A$  which may be expressed by

$$A = \frac{1}{2} \chi_0 \omega_0^2 H_1^2 Z \rho(\nu), \quad (1a)$$

where

$$Z = (1 + 2VT_1)^{-1} \quad (\text{saturation factor}), \quad (1b)$$

$\chi_0$  = dc magnetic susceptibility,

$\omega_0$  = resonance angular frequency  $2\pi\nu_0$ ,

$H_1$  = amplitude of microwave radiation,

$\rho(\nu)$  = EPR line-shape function,

<sup>10</sup> J. Vanier, Ph.D. thesis, McGill University, Montreal, 1963 (unpublished).

<sup>11</sup> E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1958).

<sup>12</sup> G. A. Woonton, *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1961), Vol. 15, p. 163.

<sup>13</sup> G. E. Pake, *Paramagnetic Resonance* (W. A. Benjamin, Inc., New York, 1962).

$V$  = radiation-induced transition probability,  
 $T_1$  = spin-lattice relaxation time.

From quantum-mechanical arguments, it may be shown that for  $Ti^{3+}$

$$V = g^2 \beta^2 H_1^2 \left| \left\langle \frac{1}{2} | S_x | -\frac{1}{2} \right\rangle \right|^2 \rho(\nu), \quad (2)$$

where  $g$  = spectroscopic splitting factor,  $\beta$  = Bohr magneton. For low microwave powers,  $2VT_1 \ll 1$  and  $Z \sim 1$ ; when  $H_1^2$  becomes very large, saturation occurs and  $Z \rightarrow 0$ . As a result, since  $A$  is proportional to  $Z$ ,

$$A_s/A_u = Z(H_{1s}/H_{1u})^2 = Z \times 10^{r/10} \quad (3)$$

where the subscripts  $s$  and  $u$  refer to the saturated and unsaturated conditions, respectively, and  $r$  is the power ratio in dB.

In this experiment, it was possible to obtain a direct measurement of  $Z$  by taking the ratio of the amplitudes of the saturated to unsaturated signals; the increase in power (dB) before the bridge was compensated for by an equivalent increase in attenuation after the bridge, shown in Fig. 1. With this procedure, the ratio of the signals depends only on  $Z$ , since the total attenuation of the system is kept constant. In this manner, the saturation factor  $Z$  could be measured as a function of microwave power incident on the sample and the relaxation time of the  $Ti^{3+}$  ions could be obtained by comparing the saturation curve with that of the  $Cr^{3+}$  ions at  $Z = 0.5$  (an arbitrary value). Thus, from Eq. (1b),

$$T_{1t} = T_{1c} (V_c/V_t), \quad (4)$$

where  $t$  and  $c$  refer to  $Ti^{3+}$  and  $Cr^{3+}$ , respectively. Re-

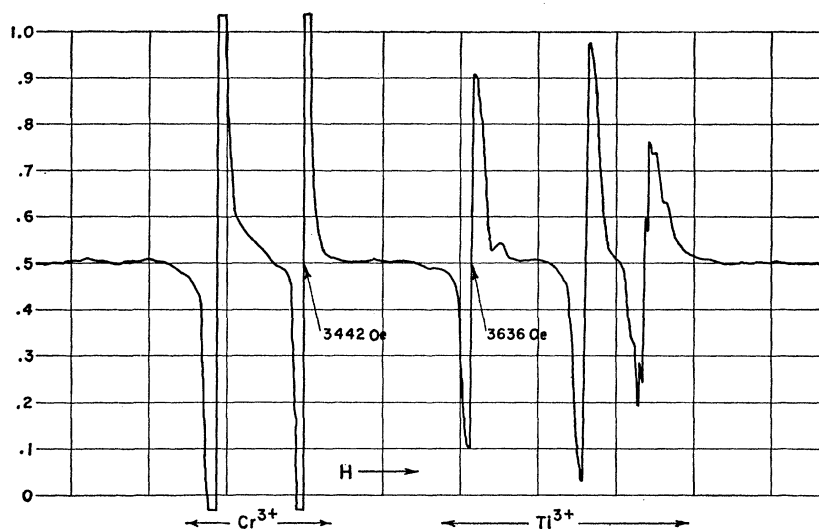


FIG. 2. Chart recording of EPR spectrum with dc magnetic field in the [100] direction of the alum lattice.

writing (4) and expressing  $V_t$  and  $V_c$  more explicitly, the relation becomes

$$T_{1t} = T_{1c} [g_c^2 \rho_c(\nu)_{\max} M_c^2 / g_t^2 \rho_t(\nu)_{\max} M_t^2] \times 10^{\Delta r/10}, \quad (5)$$

where  $g_t$  and  $g_c$  refer to the respective  $g$  factors in the direction of the microwave magnetic fields, and  $M_t$  and  $M_c$  to the respective matrix element factors in Eq. (2). For Lorentzian and Gaussian line shapes, it may be shown that the absorption linewidth  $d\nu$  is inversely proportional to  $\rho(\nu)_{\max}$  if  $\rho(\nu)$  is defined by  $\int_0^\infty \rho(\nu) d\nu = 1$ .<sup>11</sup> Consequently, the ratio of line widths can replace the ratio of line-shape functions if it is assumed that the proportionality constants are the same for both  $\text{Ti}^{3+}$  and  $\text{Cr}^{3+}$ . Hence, the only assumption required is that the two paramagnetic ions have the same line-shape function, a situation which should be expected since they share the same sites in the same crystal at extremely low concentrations.

In order to measure  $d\nu_t$  and  $d\nu_c$ , it was first necessary to measure  $dH_t$  and  $dH_c$  in Oe. To express these line widths in terms of frequency, the variation in  $g$  factors must be taken into account as follows:

$$d\nu_t/d\nu_c = g'_t dH_t / g'_c dH_c = H_c dH_t / H_t dH_c, \quad (6)$$

where  $g'_t$  and  $g'_c$  are the  $g$  factors in the directions of the dc magnetic fields,  $\mathbf{H}_t$  and  $\mathbf{H}_c$ , respectively. With these modifications, Eq. (6) becomes

$$T_{1t} = T_{1c} (g_c^2 H_c dH_t M_c^2 / g_t^2 H_t dH_c M_t^2) \times 10^{\Delta r/10}. \quad (7)$$

Thus, to determine the magnitude of the relaxation time of  $\text{Ti}^{3+}$ , it is only necessary to substitute the values of the various quantities in (7) and measure  $\Delta r$  experimentally.

### EXPERIMENTAL RESULTS

In Fig. 2, a chart recording of the EPR spectrum along a {100} axis is given to indicate the resonance lines

involved in these measurements. The particular direction was chosen because the  $\text{Ti}^{3+}$  spectrum is simplest, as may be seen from the spectrum in a {110} plane, shown in Fig. 3. In this comparison method, the two resonance lines used were the  $\text{Ti}^{3+}$  line at 3636 Oe and the main  $\text{Cr}^{3+}$  line ( $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition) at 3442 Oe. With these values for  $H_t$  and  $H_c$ , together with the values of the other variables given in Table I, Eq. (7) is reduced to

$$T_{1t} = 10.6 \times 10^{\Delta r/10} \quad (8)$$

where

$$\Delta r = r(\text{Ti}^{3+}) - r(\text{Cr}^{3+}).$$

In Table I, the  $g$  values were established by the experimental situation,  $g_t$  being an average value of the  $\text{Ti}^{3+}$   $g$  factor in the plane of  $\mathbf{H}_t$ , which in this case, was a {100} plane.<sup>5</sup> The values of  $M^2$  were calculated from  $|\langle \frac{1}{2} | S_x | -\frac{1}{2} \rangle|^2$  and  $dH$  was taken as the peak-to-peak separation of the resonance line derivative (i.e.,  $d\chi''/dH$ ). In order to obtain values for the power levels in decibels below 1 W, the intersections with the horizontal line  $Z=0.5$  were chosen as indicated in Fig. 4. As stated previously, the  $T_1$  value for  $\text{Cr}^{3+}$  in Rb alum, used as a standard in these measurements, was obtained from a separate experiment. A sample containing 0.1% concentration of  $\text{Cr}^{3+}$  was studied using the resonant-pulse saturation method; in the [100] direction the relaxation time was found to be 1.5 msec, the value

TABLE I. Experimental data and results.

Units	Ion			
	$\text{Cr}^{3+}$ 4.2	$\text{Ti}^{3+}$ 4.2	$\text{Ti}^{3+}$ 2.2	$\text{Ti}^{3+}$ 1.6
Temperature	°K			
$g$	...	1.975	1.765	1.765
$H$	Oe	3442	3636	3636
$dH$	Oe	8.7	13.1	13.1
$M^2$	...	0.98	0.25	0.25
$r$	dB	48.5	43.4	54.1
$T_1$ (meas)	msec	1.5	3.3	39
$T_1$ (calc)	msec	...	4.5	440
				1200

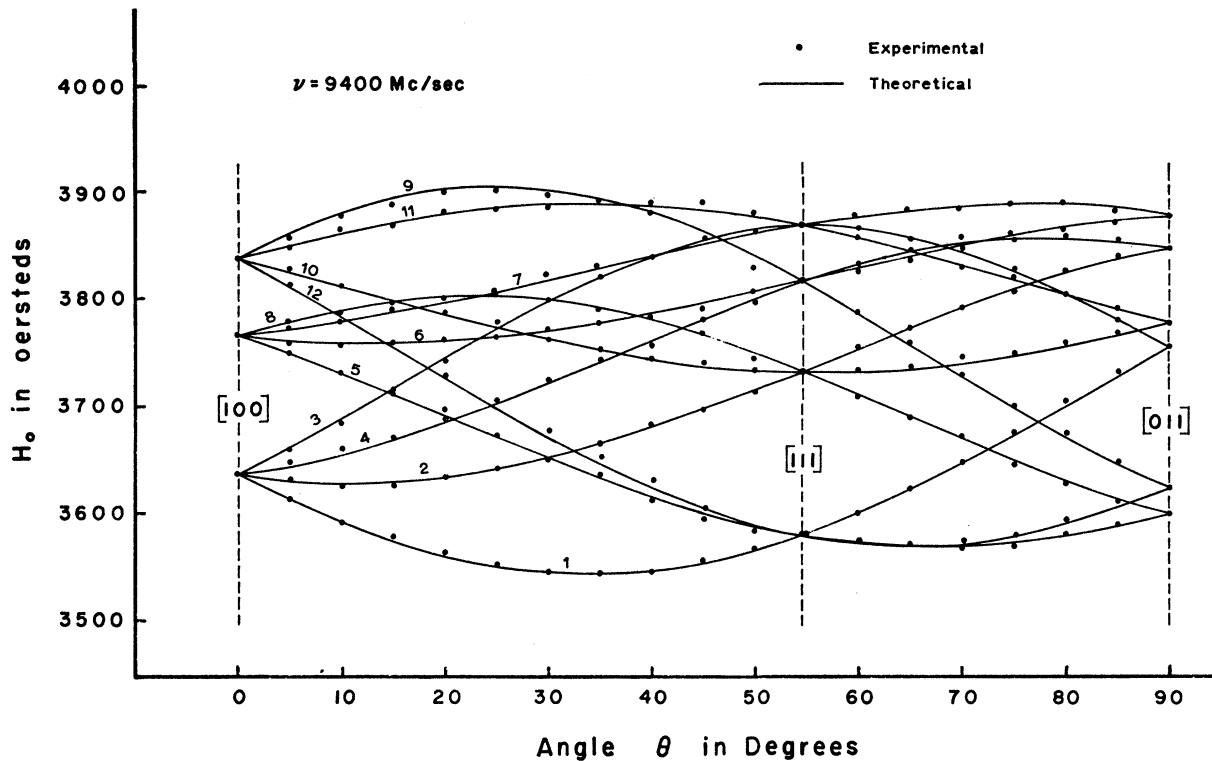


FIG. 3. Angular dependence of the EPR spectrum with the magnetic field rotated in a  $\{110\}$  plane.

entered in Table I. Since there would remain the objection that this measurement was not carried out with the titanium-doped sample, an attempt was made to compare the  $Cr^{3+}$  saturation curves of both samples under the same conditions. These two curves are shown in Fig. 4 and agree within experimental error.

Since saturation curves were carried out with the sample at  $4.2^\circ K$ ,  $2.2^\circ K$  (near the He  $\lambda$  point), and  $1.6^\circ K$ , it was possible to ascertain by means of Eq. (8) that the spin-lattice relaxation time of  $Ti^{3+}$  in Rb alum

varied from 3.3 to 63 msec over this temperature range. A clearer picture of this temperature dependence may be found in Fig. 5 where it is shown how the behavior is roughly approximated by a  $T^{-3}$  function. More realistically, the variation may be represented as a transition from Raman to direct regions as indicated by the  $T^{-9}$  or  $T^{-7}$  and  $T^{-1}$  functions, respectively. Undoubtedly, this latter model is correct to some extent, since only a combination of both processes could give rise to an effective  $T^{-3}$  dependence. However,

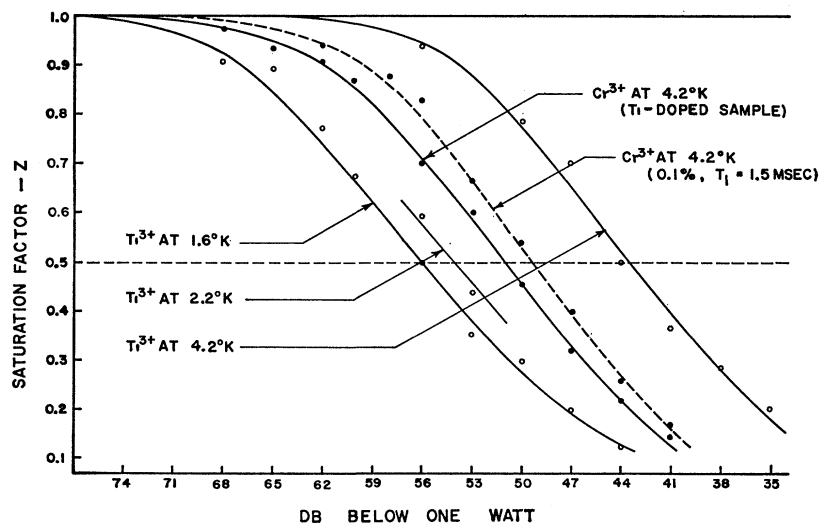


FIG. 4. Experimental saturation curves used in the measurement of  $T_1$ .

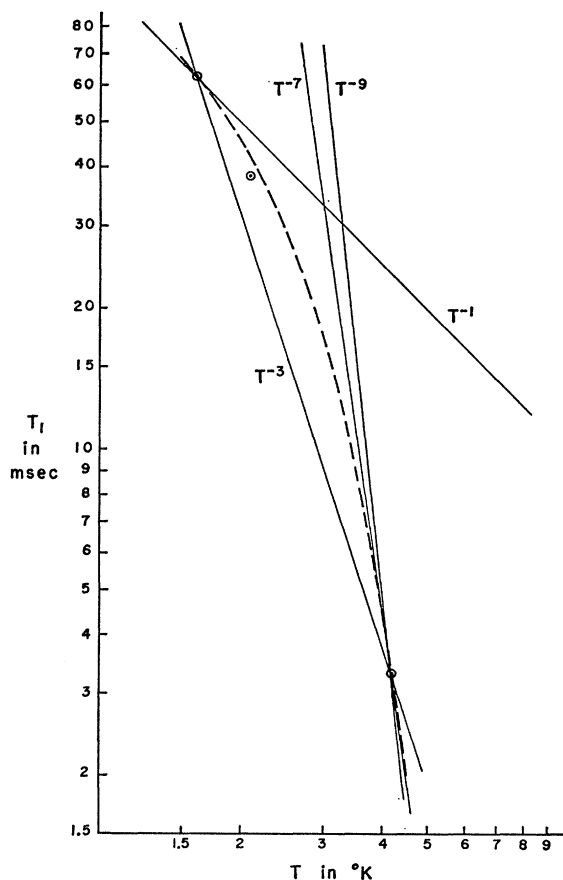


FIG. 5. Temperature dependence of the spin-lattice relaxation time of  $Ti^{3+}$  in  $RbAl(SO_4)_2 \cdot 12H_2O$  in the liquid helium range.

with more experimental data the dashed-line curve would probably prove to be a more reasonable function.

With regard to the accuracy of the measurements, it has been decided that the above results can be quoted to within a factor of 2. There are many sources of error which are inherent in continuous-wave saturation measurements and a complete discussion may be found in the author's thesis.<sup>7</sup> In this case, the error arises mainly from the measurement of  $\Delta r$  which is accurate to about  $\pm 2$  dB. The results for  $T_1$ , which are quoted to two figures in Table I, must only be considered as most probable values.

### THE VAN VLECK THEORY

In 1940, Van Vleck<sup>2</sup> published a classic paper on the theory of spin-lattice relaxation in which he carried out detailed calculations for the relaxation times of  $Ti^{3+}$  and  $Cr^{3+}$  in an alum lattice for both direct and Raman processes. Unfortunately, the system of ligands considered was a trigonally distorted octahedron of  $H_2O$  molecules, a situation which differs slightly from that of the present case, which involves orthorhombic symmetry. However, the structure of the lower triplet

of the Stark-splitting scheme for the tetragonal model is identical to that of the trigonal case with the splitting characterized by Van Vleck's semiempirical parameter  $\Delta$ . From a physical standpoint, it is this energy-level separation which determines the effect of the crystal field on the relaxation time and it would be expected that, once the proper matrix elements and transition probabilities were calculated from time-dependent perturbation theory, the final expressions for  $\tau$  with a tetragonal field would not stray far from Van Vleck's results.

If the argument is carried a step further, it may be reasoned that the results may also apply to orthorhombic symmetry since the basis vectors are the same as those of the tetragonal case. As indicated in Fig. 6,  $\Delta$  must be considered as an effective or average splitting  $\Delta'$  somewhere between  $\delta_1$  and  $\delta_2$ . A straightforward analysis<sup>7</sup> of Van Vleck's derivation of the spin-lattice transition probability for the direct process indicates that the effective splitting as it appears in Eq. (33) may be obtained from the relation

$$\Delta'^{-4} = \frac{1}{4}(\delta_1^{-2} + \delta_2^{-2})^2. \quad (9)$$

With  $\delta_1 = 1050 \text{ cm}^{-1}$  and  $\delta_2 = 1320 \text{ cm}^{-1}$ ,<sup>14</sup>

$$\Delta' = 1100 \text{ cm}^{-1}. \quad (10)$$

For the Raman process, the theory is too complicated to allow a simple estimate of  $\Delta'$  and the above value is also used in this case.

With the values of the pertinent variables given by Van Vleck's Eq. (33), the expression for the direct process with  $K=0$  (the magnetically dilute case) becomes

$$T_1 = 3.32 \times 10^{14} H_0^{-4} T^{-1} \quad (11a)$$

$$= 1.91 T^{-1} \text{ for } H_0 = 3636 \text{ Oe.} \quad (11b)$$

For the Raman process,

$$T_1 = 1.82 \times 10^8 T^{-9}. \quad (12)$$

On substituting  $H_0 = 3636 \text{ Oe}$  into (11a), the equation then represents the correct experimental condition of

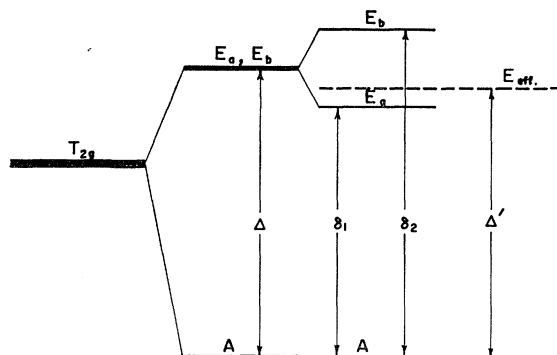


FIG. 6. Modification of energy-level model for  $T_{2g}$  level in  $D_{2h}$  crystal field used in applying Van Vleck theory.

<sup>14</sup> G. F. Dionne, Phys. Rev. **137**, A743 (1965).

dc magnetic field. Both (11b) and (12) may be plotted as in Fig. 7, where the experimental values are shown with their estimated range of accuracy.

At 4.2°K, the comparison between theory and experiment is remarkable, if one accepts the validity of the calculations. Not only does the theory indicate that Raman processes should dominate at this temperature, a conclusion which has already been drawn from the experimental results, but the actual values of  $T_1$  agree well within the estimated error. However, at lower temperatures the parallel breaks down. According to the Van Vleck theory, the process should now be direct, which may be true, but the discrepancy between the measured and calculated values at 1.6°K is about a factor of 20. Unfortunately, the picture is clouded by possible effects of cross relaxation with  $Cr^{3+}$  impurity ions which were used in the comparison method of measurement described earlier.

On this subject, it must be stated that for the concentration of  $Cr^{3+}$  involved ( $\sim 0.001\%$ ), no effects of cross relaxation should be expected at 4.2°K, where the titanium and chromium relaxation times are almost the same. On the other hand, since  $Cr^{3+}$  is in a direct process at liquid helium temperatures, its  $T_1$  value at 1.6°K is considerably shorter than either the measured  $Ti^{3+}$  value or the Van Vleck prediction. What is being suggested here is that conceivably the titanium  $T_1$  may fit the Van Vleck direct process function, but cross relaxation with the faster relaxing chromium has caused it to appear shorter than it is in reality. Until spin-lattice relaxation measurements are made with samples free from the  $Cr^{3+}$  impurity, the extent to which cross relaxation has affected the measurement will not be known and both the precision of the theory and exact nature of the relaxation processes must remain in the realm of speculation. However, for the paramagnetic ion concentrations and the nature of their EPR spectra involved in these measurements, large effects of cross relaxation may be considered as unlikely, even at this lowest temperature.

In concluding this section, it should be mentioned that Van Vleck ignored the effect of the upper doublet  $E_g$  from the cubic component of the crystal field<sup>14</sup> ( $\sim 20\,000\text{ cm}^{-1}$  above the ground state). Although the contribution of this level is small, there should be an additional term in the spin-lattice Hamiltonian which would tend to reduce any calculated values of  $T_1$ . In the present problem, such a correction would provide a better agreement between theory and experiment since the calculated relaxation times are greater than the measured ones.

## DISCUSSION AND CONCLUSIONS

As mentioned earlier, the only other relaxation experiments reported on  $Ti^{3+}$  in an alum lattice were by Gorter *et al.*<sup>3</sup> at 77°K and by de Haas and du Pré<sup>4</sup> in the liquid helium range of 4.2°K and lower. In both

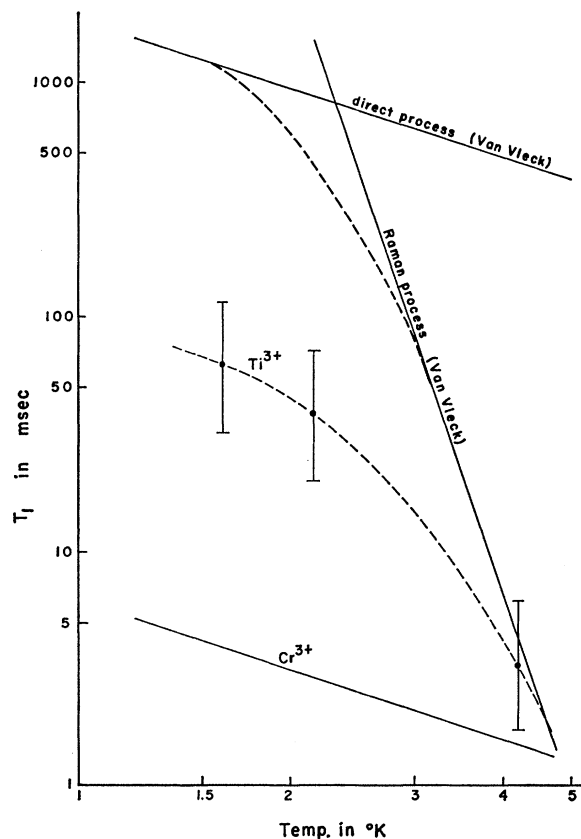


FIG. 7. Comparison between measured  $T_1$  values and calculations based on the theory of Van Vleck.

cases dispersion was not observed and for the latter measurements, which are of importance here, the value of  $\tau$  was established as  $< 10^{-3}$  sec at 1.2°K in marked contrast to the value of  $T_1$  of  $63 \times 10^{-3}$  sec at 1.6°K. When one considers that the highest value of  $H_0$  used by the above authors was only 2000 Oe in comparison to the 3636 Oe employed in this recent work, the difference is even more pronounced, to the extent to which the direct process is involved [see Eq. (11a)].

To account for this discrepancy, some pertinent facts should be pointed out. To begin with, the previous measurements were carried out with undiluted CsTi alum, with the result that  $\tau$  cannot be equated to  $T_1$  since dipole-dipole interaction undoubtedly influenced the result. In other words, de Haas and du Pré did not obtain a real measurement of  $T_1$ , which is  $\tau$  for the limiting dilute case (i.e.,  $K=0$ ). Since spin-spin interaction tends to reduce  $\tau$ , particularly for the direct process [see Van Vleck, Eq. (32)], this effect could conceivably account for the difference in results. Secondly, as Van Vleck has indicated, there is reason to question the reliability of these previous measurements because the samples studied may have been affected by dehydration. Finally, the EPR results of Bleaney *et al.*<sup>1</sup> suggest that the smallest orbital splitting of  $Ti^{3+}$  in

CsTi alum is not more than about  $100 \text{ cm}^{-1}$ . Although Van Vleck points out that such an orbital splitting is difficult to explain, he does admit that it could account for the apparent fast relaxation, provided that the Raman process is dominant. Since no dispersion was observed, there was no way of determining the temperature dependence of  $\tau$  and hence, no insight into the type of relaxation process was derived from the experiments. As a result, it is not possible to compare the results of the two series of experiments on a quantitative basis. The host lattice,  $\text{Ti}^{3+}$  ion concentration, method of measurement, and conditions of measurement differed in the two cases; in fact, the only variable which was common to both was the paramagnetic ion.

With regard to the magnitude of the relaxation time, it may be concluded that  $T_1$  for  $\text{Ti}^{3+}$  in Rb alum is not only greater than had been anticipated, but also greater than that for  $\text{Cr}^{3+}$  ions<sup>10</sup> under similar conditions. The corresponding temperature dependence indicates a dominant Raman process for titanium, while chromium is controlled by the direct process. Both of these results are caused by the nature of the crystal-field energy-level structure.

In the case of  $\text{Ti}^{3+}$ , the crystal-field splitting  $\Delta$  is larger than had originally been anticipated and the relaxation time is consequently longer than expected, although it is still governed by the Raman process at  $4.2^\circ\text{K}$ . On the other hand,  $\text{Cr}^{3+}$  has a splitting value of more than an order-of-magnitude greater ( $>10^4 \text{ cm}^{-1}$ ) than that of  $\text{Ti}^{3+}$  and has direct process temperature dependence at  $4.2^\circ\text{K}$ . However, from the effect of  $\Delta$  alone in the Raman and direct processes, one would expect  $\text{Cr}^{3+}$  to have a weaker spin-lattice interaction than  $\text{Ti}^{3+}$ . In addition, the effect of this energy-level separation is insufficient to explain the fact that the chromium transition temperature is significantly higher than that of titanium. At this point, the interpretation becomes more involved as other factors, including ionic radii and spin-orbit coupling constants, must be considered in comparing the two ions, but the main difference arises from the value of the spin  $S$ .

It has been shown explicitly by Mattuck and Strand-

berg<sup>15</sup> that a term exists in the spin-lattice interaction Hamiltonian which contains the spin anticommutator  $S_x S_y + S_y S_x$ . Further study has revealed that this term only has effect on the spin-phonon transition probability when  $S > \frac{1}{2}$ . As a result, the relaxation time of  $\text{Cr}^{3+}$  with  $S = \frac{3}{2}$  is influenced by this additional interaction term which causes it to give up its energy to the lattice at a more rapid rate than the magnitude of its orbital splitting alone would dictate. Since the relaxation of  $\text{Ti}^{3+}$  is not affected by the anticommutator term, this could account for the relative magnitudes of  $T_1$  for the two ions. Furthermore, the results of the above authors also indicate that the contribution of this term is more significant in the direct process [Eq. (71)] than in the Raman process [Eq. (74)], a fact which could account for the higher transition temperature of  $\text{Cr}^{3+}$ .

In conclusion, it may be stated that the results of these experiments reveal that the  $\text{Ti}^{3+}$  in  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  has a spin-lattice relaxation behavior which follows the predictions of Van Vleck both in the approximate magnitude of  $T_1$  and its temperature dependence which is mainly Raman in nature at  $4.2^\circ\text{K}$ . Although the comparison with theory breaks down at lower temperatures as discussed above, it is still evident that the spins of the  $\text{Ti}^{3+}$  ions interact less strongly with the lattice than do those of the frequently studied  $\text{Cr}^{3+}$  ions. On a qualitative basis, this may be considered as a partial experimental verification of the current theories of spin-lattice relaxation.

#### ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor G. A. Woonton and Dr. J. Vanier for their interest in this work and for many illuminating discussions on both theoretical and experimental aspects of the research. The author is also grateful to the National Research Council for providing a studentship during his years of graduate study at McGill University. The project was supported by the Defense Research Board through Grant DRB 9512-20.

<sup>15</sup>R. D. Mattuck and M. W. P. Standberg, *Phys. Rev.* **119**, 1204 (1960).