[17] E. O. Kane, J. Phys. Soc. Japan Suppl. 21, 37 (1966); Phys. Rev. 159, 624 (1967).

[18] R. H. Ritchie, F. W. Garber, M. Y. Nakai, and R. D. Birkhoff, in *Advances in Radiation Biology*, edited by Leroy G. Augenstein, Ronald Mason, and Max Zelle (Academic, New York, 1969), Vol. III, pp. 1–28.

[19] R. H. Ritchie and V. E. Anderson, IEEE Trans. Nuclear Sci. NS-18, 141 (1971).

[20] For a recent review of this subject see *Studies in Penetration of Charged Particles in Matter*, NAS-NRC Publication No. 1133 (National Academy of Sciences, Washington, D. C., 1964).

[21] D. Penn, Phys. Rev. 128, 2093 (1962).

[22] W. Brandt and J. Reinheimer, Can. J. Phys. 46, 607 (1968).

[23] W. Brandt and J. Reinheimer, Phys. Letters 35, 109 (1971).

[24] L. Vriens and T. F. M. Bonsen, J. Phys. B 2, 1123 (1968).

[25] V. Fock, Z. Physik 98, 145 (1935).

[26] M. E. Rudd, D. Gregoire, and J. B. Crooks, Phys. Rev. A 3, 1635 (1971).

[27] U. Fano, Ann. Rev. Nucl. Sci. 13, 1 (1963).

[28] D. J. Bartelink, J. L. Moll, and N. I. Meyer, Phys. Rev. 130, 972 (1963).

[29] T. A. Carlson and M. O. Krause, Phys. Rev. 140, A1057 (1965).

[30] R. H. Ritchie, J. Appl. Phys. 37, 2276 (1966).

[31] The authors are indebted to R. N. Hamm for his work in numerically evaluating the Spencer–Attix equations in this connection.

PHYSICAL REVIEW B VOLUME 7, NUMBER 5 1 MARCH 1973

Paramagnetic Resonance and Relaxation of the Jahn–Teller Complex $[\mathrm{Ti(H_2O)_6}]^{3+}$

N. Rumin, C. Vincent, and D. Walsh

Eaton Electronics Laboratory, McGill University, Montreal, Quebec, Canada

(Received 1 August 1972; revised manuscript received 1 November 1972)

The measured g values of the ground-state doublet of Ti^{3+} in methylammonium aluminum alum at 4.2 °K and below are shown to be incompatible with static crystal field theory. The measured spin-lattice relaxation rates in the range 1.45–2.85 °K can be described by either a two-Orbach process or a T^9 Raman process. A dynamic Jahn–Teller model due to Ham, which includes the interaction between an E_g vibrational mode and the $^2T_2$ electronic state, gives theoretical results which agree with both the measured g values and the two-Orbach relaxation process. Consequently, the agreement with the Raman process would appear to be fortuitous The measured g values and the two-Orbach process are described by $g_\parallel = 1.37 \pm 0.01$, $g_\perp = 1.61 \pm 0.01$, and $1/\tau = 1.88\, e^{-14.52/T} + 390.81\, e^{-27.41/T}$ μsec^{-1}. The corresponding two excited doublets are at 10.5 ± 0.5 and 19.2 ± 2.0 cm^{-1}, respectively. Assuming a coupling to the E_g mode only, the deduced Jahn–Teller energy is 256 cm^{-1} and the effective mode frequency is 148 cm^{-1}. The ferroelectric transition from a structure with space group Pa3 to either space group $P2_1$ or $Pca2_1$ has a negligible effect on the EPR spectra, which in spite of the transition possess symmetry ($\bar{3}$).

I. INTRODUCTION

The crystal structure of methylammonium aluminum alum suggests that the Ti^{3+} ion is subjected to a predominantly cubic field with a small trigonal component. In a cubic field field of octahedral symmetry the free-ion ^2D ground state is split into a $^2T_2$ and an excited ^2E, which is 2×10^4 cm^{-1} or so above the ground state and may be neglected for our purposes. The octahedron is slightly flattened (Sec. II); consequently, using standard crystal field theory the combined spin-orbit and trigonal field splits the ground state into three Kramers doublets, the g values of the ground state doublet being given by

$$g_\parallel = 2\left|\sin^2\theta - 2\cos^2\theta\right| ,$$
$$g_\perp = 2\left|\sqrt{2}\,\sin\theta\cos\theta + \sin^2\theta\right| , \tag{1}$$

where

$$\sin 2\theta = \frac{-\sqrt{2}\,\lambda}{[(V+\frac{1}{2}\lambda)^2 + 2\lambda^2]^{1/2}} ,$$

λ is the spin-orbit coupling, V is the trigonal splitting of the T_2 orbital state in the absence of spin-orbit coupling, and we have neglected covalency effects. The theory of Ti^{3+} in trigonal environments has received considerable attention,[1] and for all values of λ/V in Eq. (1), the inequality $g_\parallel \geq g_\perp$ holds. Our low-temperature paramagnetic-resonance spectra of Ti^{3+} in methylammonium minum alum, which is reported in Sec. III, gives for the ground doublet $g_\perp = 1.61 \pm 0.01$ and $g_\parallel = 1.37 \pm 0.01$, which is incompatible with static crystal field theory. The possibility that the trigonal field is reversed corresponding to a slightly elongated octahedron is untenable, since the resulting groundstate doublet is described by an effective spin $S_z' = \pm\frac{3}{2}$, which gives $g_\perp = 0$ contrary to experiment.

So far the discussion has neglected the Jahn–Teller coupling[2,3] between the lattice displacements and the T_2 orbital state. A T_2 orbital state can couple to both E_g and T_{2g} normal modes of vibration of the crystal, and it is customary to assume that the E_g mode is more strongly coupled than the T_{2g} mode,[2,4] although it is known for the excited state of the F^+ center in CaO that equal coupling to both E_g and T_{2g} modes is required to explain the experimental results.[5] Using the cluster approximation consisting of the transition-metal ion and its nearest neighbors and E_g coupling only, Ham[2] showed that the vibronic spectrum remained the same as that in the absence of the Jahn–Teller interaction except for the reduction by the Jahn–Teller energy E_{JT}, common to all states, where $E_{JT} = A^2/2\mu\omega^2$. A is the Jahn–Teller coupling coefficient, μ is the effective mass of the cluster, and ω is the E_g normal-mode frequency. For a cubic crystal, the vibronic ground state remains a triplet and all excited states are higher than the ground state by at least the vibrational energy $\hbar\omega$. The vibronic eigenfunctions are products of one of the T_2 electronic functions and simple harmonic-oscillator functions for a displaced two-dimensional oscillator belonging to the representation E_g. Matrix elements of various electronic operators between the vibronic states are then the product of an electronic matrix element and an oscillator-overlap integral. Within the vibronic ground state and to first order in perturbation theory all T_1 and T_2 operators (consequently, the spin-orbit coupling and a trigonal crystal field) are diminished from their value in the absence of the Jahn–Teller coupling by $\gamma = e^{-x/2}$, where $x = 3E_{JT}/\hbar\omega$. When second-order corrections due to the excited vibronic states are included, additional reduction factors, f_a and f_b, are introduced, which are defined by Ham.[2]

Consequently, with this model there is a partial quenching of both the spin-orbit interaction and the trigonal field giving rise to two low-lying excited Kramers doublets, whose presence may dominate, even below 4.2 °K, the spin-lattice relaxation rate by an Orbach process.[6] Indeed, the experimental rates reported in Sec. III are consistent with this interpretation. Furthermore, as shown in Sec. IV, if E_g coupling only is assumed, the resulting Jahn–Teller parameters, which are obtained by fitting the lowest vibronic splitting to the experimentally deduced excited states, yield $g_\perp = 1.72$ and $g_\parallel = 1.47$, which are in reasonable agreement with the measured g values.

In a preliminary report[7] we showed that contrary to expectations the best fit to the spin-lattice relaxation rate for a Ti^{3+}-doped methylammonium aluminum alum crystal was described by a T^9 Raman process. As shown in Fig. 1, our results also support with considerable accuracy a T^9 Raman process. Nevertheless, in view of the close agreement between experiment and the E_g-coupled Jahn–Teller model, an agreement which has also been reported for a number of other T_2 orbital states with octahedral coordination,[4] it would appear that the agreement with a Raman process is fortuitous.

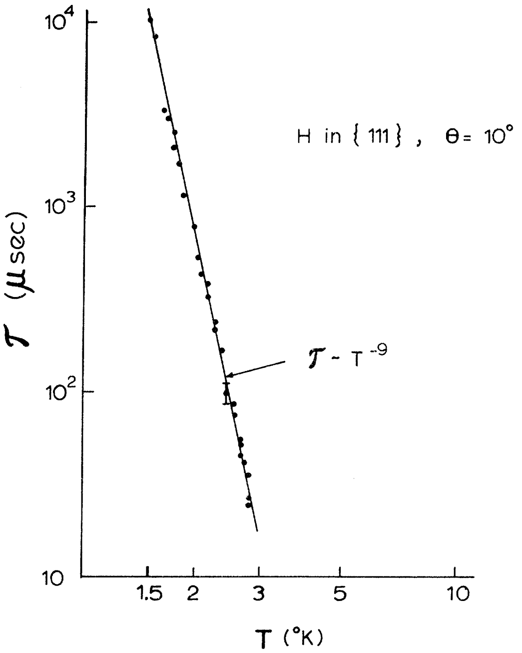

FIG. 1. Spin-lattice relaxation time vs T.

II. CRYSTAL STRUCTURE

The room-temperature structure of $CH_3NH_3Al(H_2O)_6(SO_4)_2 \cdot 6H_2O$ is cubic with space group Pa3 and four formula units per unit cell.[8] The four $[Al)H_2O)_6]^{3+}$ octahedra are slightly flattened with trigonal symmetry ($\bar{3}$), while the four $CH_3NH_3^+$ ions lie in general 24-fold position, so that the CN directions do not lie along the cube body diagonals, but each one is arranged with six orientations statistically at an angle to the diagonal.[9] Since according to Okaya *et al.*[9] the difference between α- and β-alum types is not adequately defined structurally, no attempt was made to classify methylammonium aluminum alum in either type. This conclusion has been contradicted recently by Cromer *et al.*[10] who consider both methylammonium aluminum alum and cesium aluminum alum to be members of the β alums. Low-temperature x-ray analyses have also been performed on methylammonium aluminum alum, which was shown on cooling, to undergo a ferroelectric transition in the region of 177 °K to space group

$P2_1$ by Okaya *et al.*[9] or to space group $Pca2_1$ at 170 °K by Fletcher and Steeple.[11] In either space group only the general position is available.

The electron paramagnetic resonance (EPR) at room temperature of chromic methylammonium aluminum alum in which Cr^{3+} have substituted for Al^{3+}, showed that the crystalline electric field possessed trigonal symmetry.[12] The EPR spectra at 90 °K and below were interpreted by a crystal field of orthorhomic symmetry[13] on the basis of observations that would in fact require a monoclinic field. More recently, the EPR of Cr^{3+}-doped methylammonium aluminum alum was observed between 90 and 300 °K.[14] A first-order ferroelectric transition was observed at 177 °K, where an abrupt change in the fine-structure splitting occurred which was described by a lowering of the trigonal symmetry to monoclinic. In addition, relaxation measurements of the proton magnetic resonance in the same crystal suggested that the ferroelectric transition resulted from a one-dimensional reorientation of the $CH_3NH_3^+$ ions.

On the other hand, as will be shown in Sec. III, at liquid-helium temperatures the crystal field of Ti^{3+}-doped methylammonium aluminum alum retains trigonal symmetry ($\bar{3}$) and presumably it is a reflection of the fact that the ferroelectric transition has a negligible effect on the $[Ti(H_2O)_6]^{3+}$ octahedron, which in the E_g-coupling approximation is undergoing large tetragonal Jahn–Teller distortions, although the crystal field still possesses trigonal symmetry due to tunnelling between the three equivalent distorted configurations of the octahedron. A trigonal cyrstal field at low temperature was also observed for cesium titanium alum[15] and claimed to have been observed for Ti^{3+}-doped cesium aluminum alum.[16] Since both crystals have space group $Pa3$ at room temperature and a ferroelectric transition is not expected at low temperatures, the crystal field should retain trigonal symmetry, the origin of which is mainly due to the trigonally distorted octahedron of water molecules[10] and not the more distant SO_4 group.[17] The Ti^{3+} g values are also unusual for both crystals, a full understanding of the EPR spectra of which will probably require the addition of the Jahn–Teller effects. However, since the environment is different from that in methylammonium alum we do not expect their g values to be the same as those reported in Sec. III.

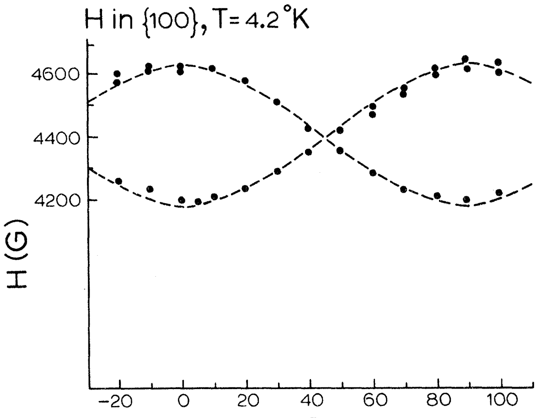

FIG. 3. Angular variation of EPR with H in {100} plane. $\nu = 9.43$ GHz.

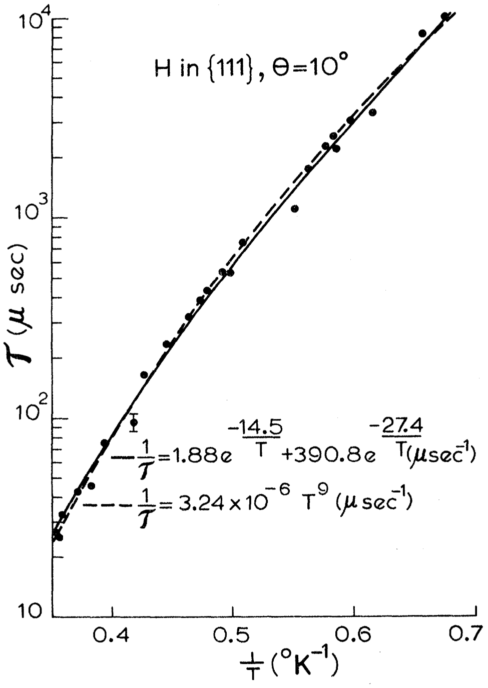

FIG. 2. Arrhenius plot of spin-lattice relaxation results shown in Fig. 1.

III. EXPERIMENT

Both the EPR and spin-lattice relaxation measurements were performed with a conventional X-band superheterodyne spectrometer,[18] using pulse saturation techniques for the relaxation measurements and a low-power monitor signal to detect the recovery to equilibrium. All relaxation measurements were performed with helium exchange gas (approximately 20 Torr.) in the microwave cavity to eliminate vibration from the boiling liquid helium. Temperatures in the cavity were measured with a calibrated carbon resistance thermometer. The recovery signal was fed to a specially designed 24-channel signal averager and consequently the experimental points in Figs. 1 and 2 represent the average of approximately 100 recoveries, all of which are simple exponentials. The concentration of Ti is nominally 0.1 at. %.

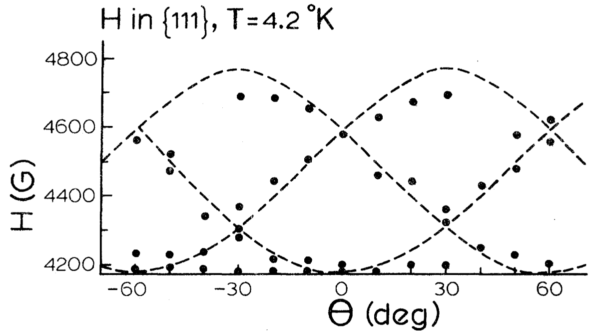

FIG. 4. Angular variation of EPR with H in {111} plane. $\nu = 9.43$ GHz.

Figure 3 shows the angular dependence of the EPR signal at 4.2 °K with H in a {100} plane. The strain-broadened lines are approximately 20 G wide. Occasionally, a double resonance was observed (both in {100} and {111} planes), the cause of which is not known, but appears to be due to the development of noticeable cracks as a result of the temperature cycling. The lifetime of a crystal rarely exceeds a dozen measurements for the same reason. The angular dependence of the spectra at 1.5 is identical to that at 4.2 °K. Figure 4 shows the angular dependence at 4.2 °K for the same crystal with H in a {111} plane, the 1.5 °K spectra of which is identical. The dashed curves in Figs. 3 and 4 represent a best fit to the experimental points, and correspond to four inequivalent Ti^{3+} ions per unit cell, each ion being situated in a trigonal environment corresponding to a distortion along one of the four possible [111] directions of the neighboring octahedron of water molecules. The corresponding g values are $g_{\parallel} = 1.37 \pm 0.01$ and $g_{\perp} = 1.61 \pm 0.01$.

Figure 1 shows the spin-lattice relaxation time vs temperature for another sample (with similar Ti concentration) whose spectra in a {111} plane is identical to that in Fig. 4. All points are for $H = 4480$ G in a {111} plane with $\theta = 10°$ (with θ defined in Fig. 4). The continuous line represents a T^9 Raman process. Figure 2 shows an Arrhenius plot of the same relaxation results as that in Fig. 1. As discussed in Sec. IV, in spite of the close agreement with a Raman process, there is reason to anticipate an Orbach process in the relaxation rate. In fact, there are two possible Orbach processes and consequently the deviation from the lower-temperature linear plot, which would reflect a single Orbach process, was computer fitted to include a second Orbach process. These two Orbach relaxation rates, which are represented by the continuous curve, are described by the expression

$$1/\tau = 1.88 e^{-14.52/T} + 390.81 e^{-27.41/T}\ \mu\text{sec}^{-1}\ .$$

The dashed curve represents the T^9 Raman process, which was included for comparison purposes.

IV. EIGENVALUES AND *g* FACTORS IN THE PRESENCE OF A DYNAMIC JAHN-TELLER DISTORTION

The cluster approximation consisting of E_g coupling only to the $^2T_2$ orbital state has explained successfully the low-temperature properties of Ti^{3+} in Al_2O_3.[4,19] The theory is directly applicable to Ti^{3+} in methylammonium aluminum alum except the trigonal splitting parameter V is considerably less than that in Al_2O_3 and has the opposite sign. V can be estimated by comparing the distortion in Al_2O_3 with that obtained from the x-ray analysis of Fletcher and Steeple.[11] We estimate the distortion in Al_2O_3 to be a factor of four or five times larger than that in methylammonium aluminum alum, and since $V = 700\ \text{cm}^{-1}$ for Ti^{3+} in Al_2O_3,[4] we have chosen $V = -\lambda$. The three lowest Kramers doublets then take the form

$$\begin{aligned} &|\pm X_{\pm}\rangle\ , && E = 0 \\ \sin\theta\,&|\pm X_0\rangle \pm \cos\theta\,|\mp X_{\pm}\rangle\ , && E = \delta_1 \\ \mp\cos\theta\,&|\pm X_0\rangle + \sin\theta\,|\mp X_{\pm}\rangle\ , && E = \delta_2 \end{aligned} \qquad (2)$$

where ± has been added to the vibronic states $|X_0\rangle$, $|X_+\rangle$, and $|X_-\rangle$ to indicate the value of S_z for the spin $S = \frac{1}{2}$. The vibronic states are defined in Eq. (9) of Bates and Bentley.[19] θ in Eq. (2) will be defined later. The doublet $|\pm X_{\pm}\rangle$ corresponds to an effective spin $S_z' = \pm\frac{3}{2}$ with $g_{\perp} = 0$ and is the ground-state doublet for Ti^{3+} in Al_2O_3. We expect δ_2 to be negative and to be the lowest energy. With $V = -\lambda$, δ_1 and δ_2 are given by[4]

$$\begin{aligned} \delta_1 &= \tfrac{1}{4}\gamma\lambda\left[1 - \tfrac{25}{6}(f_a/\gamma)\lambda/\hbar\omega\right] - \tfrac{1}{2}A\ , \\ \delta_2 &= \tfrac{1}{4}\gamma\lambda\left[1 - \tfrac{25}{6}(f_a/\gamma)\lambda/\hbar\omega\right] + \tfrac{1}{2}A\ , \end{aligned} \qquad (3)$$

where

$$A^2 = \tfrac{1}{4}\gamma^2\lambda^2 17\{1 + [(f_a/\gamma)\lambda/\hbar\omega]^2 \tfrac{1}{36} - \tfrac{1}{3}(f_a/\gamma)\lambda/\hbar\omega\}. \qquad (4)$$

The reduction factors f_a, f_b, and γ are tabulated by Ham[2] and Macfarlane *et al.*[4] for various values of $x = 3E_{JT}/\hbar\omega$. Since, for a definite value of x, f_a, f_b, and γ are fixed, the right-hand side of Eq. (3) or Eq. (4) contains only two unknowns. From Fig. 2 the first and second excited states are at 10.5 and 19.2 cm^{-1}, respectively, above the ground state. For reasonably acceptable values of of $\hbar\omega$ the best agreement with these results is given by $\delta_1 = 8.7\ \text{cm}^{-1}$ and $\delta_2 = -10.5\ \text{cm}^{-1}$. The various splittings are shown qualitatively in Fig. 5. For the range of x we shall encounter $f_a/\gamma = \frac{1}{2}$. Thus, from Eq. (3) we find $\hbar\omega/\lambda = 1.1$. When this is inserted in Eq. (4) we obtain $\gamma = 10.1/\lambda$. With $\lambda = 135\ \text{cm}^{-1}$ we finally get the following reduction factors:

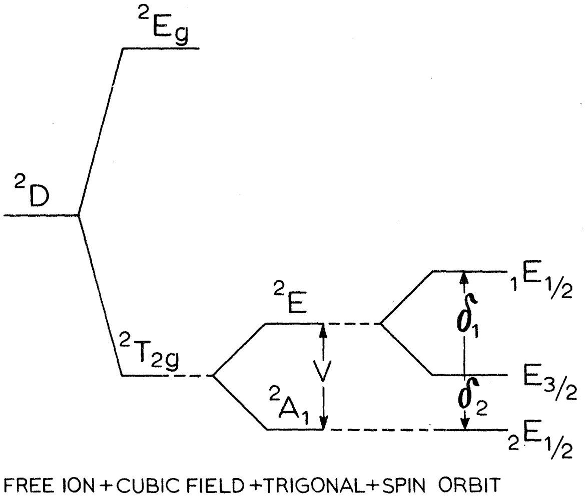

FIG. 5. Energy levels of Ti^{3+} in methylammonium aluminum alum.

$$\gamma = 0.75; \quad f_a = 0.035; \quad f_b = 0.25$$

corresponding to $x = 3E_{JT}/\hbar\omega = 5.2$ and $\hbar\omega = 148$ cm^{-1}. Analytical expressions for $g_\parallel$ have been given by Macfarlane[20,21] for the two Kramers doublets at energy δ_1 and δ_2 in Eq. (2). Our ground-state doublet is given by

$$\mp\cos\theta\,|\pm X_0\rangle + \sin\theta\,|\mp X_\pm\rangle \,, \qquad (5)$$

where for our parameters, $\tan 2\theta = \frac{2}{3}\sqrt{2}$. (It also happens to be independent of $\lambda/\hbar\omega$.) The corresponding $g_\parallel$ is given by

$$g_\parallel = 2\,|a\cos^2\theta + b\sin^2\theta + c\sin 2\theta| \ .$$

With our parameters plus a covalency factor $k = 0.9$, we find $a = 0.976$, $b = 0.963$, $c = -0.048$, from which we obtain $g_\parallel = 1.47$.

We note that most of the contributions to $g_\perp$ will come from the left-hand component of Eq. (5). Thus

$$g_\perp = 2.002\cos^2\theta = 1.72 \ .$$

V. DISCUSSION

We have shown that static crystal field theory cannot explain the ground-state g values of Ti^{3+} in methylammonium aluminum alum. It would also be impossible to account for the two excited Kramers doublets at 10.5 and 19.2 cm^{-1}, which are deduced from the relaxation data of Fig. 2, without invoking both unrealistic crystal field parameters and covalency factors.[1,22] On the other hand a model in which only E_g normal modes of vibration of the crystal are considered to interact with the $^2T_2$ state, gives good agreement with both the energy levels of the two excited Kramers doublets and the ground-state g values. Actually, the reduction factors were obtained by fitting the theoretical splittings to those deduced from the Orbach relaxation rates. These reduction factors were then used to calculate the ground-state g values. Table I shows a comparison between the observed and calculated splitting and g factors.

The theoretical values have been obtained by choosing the trigonal splitting to be equal to the spin-orbit coupling. Although better agreement for the g values can probably be achieved by varying the trigonal parameter as well as the spin-orbit coupling, this is hardly justified at this stage, since our primary aim has been to decide whether the model itself is a reasonable one or not. In addition, the relative position of the two excited Kramers doublets is very important, and a more accurate value for the second-excited doublet will require relaxation measurements using nanosecond techniques. Magnetic-susceptibility measurements which are underway in this laboratory, may also supply the required information, since the g values of the two excited doublets are quite different.

In view of the close agreement of the relaxation rate with a T^9 Raman process, the validity for choosing the two-Orbach relaxation process arises. The main justification for this is the close agreement between the theoretical values of Sec. IV and the experimental results as shown in Table I. This also puts our interpretation in line with that for the T_2 orbital state of other transition-metal ions in insulating crystals of octahedral coordination.[4,23] Finally, recent preliminary relaxation measurements in a {111} plane indicate a considerable variation of the relaxation rate with the magnetic field direction. This anisotropy is not expected for a Raman process.

VI. CONCLUSION

From paramagnetic resonance studies, at X-band in the liquid-helium temperature range, of

TABLE I. Observed and calculated splitting and g factors for the $^2T_2$ ground term of $Al(CH_3NH_3)(SO_4)_2 \cdot 12H_2O : Ti^{3+}$.

	Observed	Calculated[a]
First excited doublet	10.5 ± 0.5 cm^{-1}	10.5 cm^{-1} [b]
Second excited doublet	19.2 ± 2.0 cm^{-1}	19.2 cm^{-1} [b]
$g_\parallel$	1.37 ± 0.01	1.47
$g_\perp$	1.61 ± 0.01	1.72
$\hbar\omega$	...	148 cm^{-1}
E_{JT}	...	256 cm^{-1}

[a] Parameters are $V = -\lambda$, $\lambda = 135$ cm^{-1}, $k = 0.9$, $\gamma = 0.075$, $f_a = 0.035$, and $f_b = 0.25$.

[b] For a definite value of $x = 3E_{JT}/\hbar\omega$, γ, f_a, and f_b are fixed. The value of x is obtained by fitting the theoretical splittings to the experimental values.

the ground-state doublet of Ti^{3+} in methylamonium aluminum alum we deduced that there are four inequivalent ions per unit cell, each ion being situated in a trigonal environment corresponding to a distortion along one of the four possible [111] directions of the surrounding octahedron of water molecules. The corresponding g values are shown to be incompatible with static crystal field theory.[24] Spin lattice relaxation measurements have also been performed in the range 1.45–2.85 °K. Although the relaxation rate is shown to follow a T^9 Raman process with considerable accuracy over this temperature range, evidence is presented which demonstrates that the two-Orbach process, which describes the relaxation data with comparable accuracy, is probably the correct interpretation and the agreement with the Raman process is fortuitous. A model developed by Macfarlane *et al.*[4] and Bates and Bentley,[19] which considers the interaction between an E_g vibrational mode and the $^2T_2$ electronic state, gives theoretical results which agree favorably with both the measured g values of the ground state and the first two excited doublets. Finally, the ferroelectric transition from a structure with space group $Pa3$ to either space group $P2_1$ or $Pca2_1$ has a negligible effect on the EPR spectra, which in spite of the transition possess trigonal symmetry $(\bar{3})$.[25]

ACKNOWLEDGMENTS

This work was supported in part by a grant from the National Research Council of Canada. The authors thank R. Knispel, Physics Department, University of Waterloo, for bringing their attention to Ref. 14, and J. D. H. Donnay, Département de Géologie, Université de Montréal, for a critical reading of Sec. II.

---

[1] H. M. Gladney and J. D. Swalen, J. Chem. Phys. 42, 1999 (1965).

[2] F. S. Ham, Phys. Rev. 138, A1727 (1965).

[3] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenriech (Academic, New York, 1968), Vol. 20, p. 91.

[4] R. M. Macfarlane, J. Y. Wong, and M. D. Sturge, Phys. Rev. 166, 250 (1968).

[5] A. E. Hughes, J. Phys. C 3, 627 (1970).

[6] K. W. H. Stevens, Rep. Prog. Phys. 30, 189 (1967).

[7] K. P. Lee, N. Rumin, and D. Walsh, J. Phys. C 1, 946 (1971).

[8] H. Lipson, Phil. Mag. 19, 887 (1935).

[9] Y. Okaya, M. S. Ahmed, R. Pepinsky, and V. Vand, Zeit. Für Kristall 109, 367 (1957).

[10] D. T. Cromer, M. I. Kay, and A. C. Larson, Acta Cryst. 21, 383 (1966).

[11] R. O. W. Fletcher and H. Steeple, Acta Cryst. 17, 290 (1964).

[12] D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) A204, 188 (1950).

[13] J. M. Baker, Proc. Phys. Soc. (London) B69, 6333 (1956).

[14] D. W. O'Reilly and Tung Tsang, Phys. Rev. 157, 417 (1967).

[15] B. Bleaney, G. A. Bogle, A. H. Cooke, R. J. Duffus, M. C. M. O'Brien, and K. W. H. Stevens, Proc. Roy. Soc. (London) A68, 57 (1955).

[16] G. A. Woonton and J. A. MacKinnon, Can. J. Phys. 46, 59 (1968).

[17] G. F. Dionne and J. A. MacKinnon, Phys. Rev. 172, 325 (1968).

[18] G. Feher, Bell Syst. Tech. J. 36, 449 (1957).

[19] C. A. Bates and J. P. Bentley, J. Phys. C. 2, 1947 (1969).

[20] R. M. Macfarlane, Phys. Rev. 184, 603 (1969).

[21] In Eq. (3) of Ref. 20 the factor 2.002 should read 1.001 R. M. Macfarlane (private communication).

[22] J. H. Van Vleck, Discuss. Faraday Soc. 26, 96 (1958).

[23] In fact, the perturbation approach of Refs. 4 and 19, which may be questionable for ions in Al_2O_3, is certainly valid here since the trigonal field, which is comparable with the spin-orbit coupling is considerably less than $3E_{JT}$.

[24] This unusual property Ti^{3+} is not unique for methylammonium alum. $g_\perp$ has also been found to be greater than $g_\parallel$ for KTi $(C_2O_4)_2 \cdot 2H_2O$ [G. S. Bogle and J. Owen (unpublished)]. See, K. D. Bowers and J. Owen, Rep. Prog. Phys. 18, 304 (1955). A similar behavior is predicted for $TiCl_36H_2O$, although there is some doubt about the interpretation of the results [see H. M. Gladney and J. D. Swalen, Jr. Chem. Phys. 42, 2007 (1965)].

[25] Some of the discrepancies the spectra of Fig. 4 have been assumed to be due primarily to crystal misalignment.