

# Calculation of Crystal-Field Energy-Level Splittings of the $Ti^{3+}$ Ion in $RbAl(SO_4)_2 \cdot 12H_2O$

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By considering a crystal-field model of  $D_{2h}$  point-group symmetry, the Stark energy-level separations of the  $Ti^{3+}$  ion in  $RbAl(SO_4)_2 \cdot 12H_2O$  have been calculated. Previously reported results of EPR experiments have revealed the existence of an orthorhombic crystal field, and through the application of group theory and quantum-mechanical perturbation theory, splitting values of 1050, 1320, and 20 300  $cm^{-1}$  have been obtained. In these calculations the contribution of the upper doublet  $E_g$  produced by the octahedral component of the field has been included and its importance is clearly established. The calculated value of the cubic splitting matches the result of optical spectroscopic measurements with  $Ti^{3+}$  in similar environments, reported by other workers. The magnitudes of the smaller orthorhombic splittings are compared with the predicted value of 1075  $cm^{-1}$  which was obtained from an earlier calculation by Van Vleck applied to a model with trigonal symmetry. The Jahn-Teller effect is discussed as a possible cause of the orthorhombic distortion.

## INTRODUCTION

FOR the trivalent titanium ion in rubidium alum, the crystal electric field is produced mainly by an octahedron of water dipoles which surround the paramagnetic ion. According to Lipson,<sup>1</sup> the octahedron has a slight distortion along the trigonal or  $\langle 111 \rangle$  axes of the lattice. However, since three different  $g$  factors, i.e., 1.895, 1.715, and 1.767 have been measured for  $Ti^{3+}$  in  $RbAl(SO_4)_2 \cdot 12H_2O$ ,<sup>2</sup> it is undoubtedly true that a further displacement of the ligands takes place when  $Ti^{3+}$  is substituted for  $Al^{3+}$ , resulting in a crystal field of less than axial symmetry. Of the work previously reported in the literature on the  $g$  factors of  $Ti^{3+}$ , the contributions which have direct bearing on the subject of this paper are those connected with the experiments on  $CsTi(SO_4)_2 \cdot 12H_2O$ ,<sup>3</sup> in which an axially symmetric crystal field was observed, with  $g_{11} = 1.25$  and  $g_{12} = 1.14$ . Attempts to relate these values of  $g$  to the crystal-field energy-level structure have been made by Bleaney,<sup>3,4</sup> Bose *et al.*,<sup>5</sup> and Réi.<sup>6</sup> In each case the calculations involved only the lower triplet  $T_{2g}$  of the  $O_h$  component of the crystal field (see Fig. 1).

In this paper, the results of the calculations differ considerably from those reported by the above authors, as would be expected, since the paramagnetic resonance spectra bear little resemblance in the two salts. However, it is very significant that the inclusion of the upper doublet  $E_g$ , although it complicates the work, is necessary in order to properly relate the experimental  $g$  factors to the crystal field structure. In the previous attempts to calculate the crystal-field splittings the

effect of  $E_g$  has been assumed to be negligible owing to the large cubic splitting ( $\sim 20\,300\,cm^{-1}$ )<sup>7</sup>. To illustrate the contribution of these upper levels, three methods of perturbation theory have been applied, each clearly establishing the need for considering the upper doublet. For the most part, the methods used are standard since the construction of molecular orbitals was not necessary in this case.

## GENERAL THEORY

The general Hamiltonian for a paramagnetic iron-group ion in a crystalline environment may be written as

$$\mathcal{H} = \mathcal{H}_C + U_c + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{H} \cdot (\mathbf{L} + g_e \mathbf{S}), \quad (1)$$

where  $\mathcal{H}_C$  = Coulomb energy,  $U_c$  = crystal electric field potential energy;  $g_e$  = spectroscopic splitting factor of a free electron  $\approx 2$ . For simplicity, the terms involving nuclear interaction have been omitted, since they do not affect the calculations to follow. For  $Ti^{3+}$ , the ground-state orbital term is  ${}^2D$ , which describes a fivefold orbital degeneracy. When the ion is subjected to the electric field produced by the surrounding octahedron of  $H_2O$  molecules, the coupling into the orbital angular momentum  $\mathbf{L}$  results in a removal of this degeneracy (Stark effect), the nature of which depends on the strength and symmetry of the crystal electric field. In Fig. 1, the splittings of the levels caused by

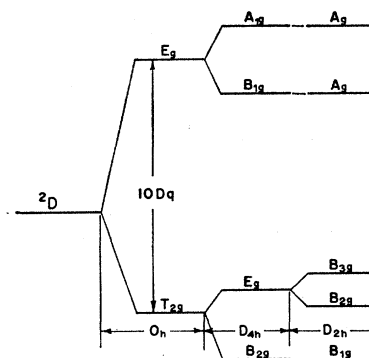


FIG. 1. Effects of crystal electric fields on the  ${}^2D$  orbital term.

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<sup>1</sup> H. Lipson, Proc. Roy. Soc. (London) **A151**, 347 (1935).

<sup>2</sup> G. F. Dionne, Can. J. Phys. **42**, 2419 (1964).

<sup>3</sup> B. Bleaney, G. S. Bogle, A. H. Cooke, R. J. Duffus, M. C. M. O'Brien, K. W. H. Stevens, Proc. Phys. Soc. (London) **A68**, 57 (1955).

<sup>4</sup> B. Bleaney, Proc. Roy. Soc. (London) **A63**, 407 (1950).

<sup>5</sup> A. Bose, A. S. Chakravarty, R. Chatterjee, Proc. Roy. Soc. (London) **A255**, 145 (1960).

<sup>6</sup> D. K. Réi, Fiz. Tverd. Tela **3**, 2525 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1838 (1962)].

<sup>7</sup> H. Hartmann and H. L. Schlafer, Z. Physik Chem. (Leipzig) **197**, 116 (1951).

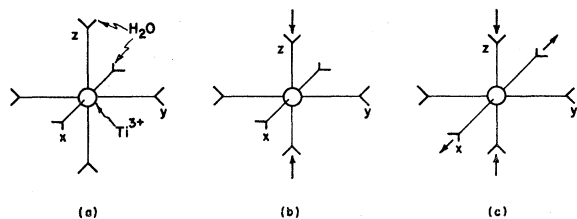


FIG. 2. Octahedra of  $\text{H}_2\text{O}$  dipoles: (a)  $O_h$  symmetry, (b)  $D_{4h}$  symmetry, and (c)  $D_{2h}$  symmetry.

crystal fields of  $O_h$ ,  $D_{4h}$ , and  $D_{2h}$  symmetry are shown, as determined by a straightforward application of group theory. This picture represents the orbital energy level scheme of the  $\text{Ti}^{3+}$  ion after the  $U_c$  perturbation is applied; the parameter  $10Dq$  depends on several factors which determine the field strength and is usually found by experiment.

To relate this theoretical discussion to the physical concept of a distorted octahedron of  $\text{H}_2\text{O}$  dipoles, one may consider the models sketched in Fig. 2. For convenience, the axes of the octahedra have been chosen to coincide with the  $x$ ,  $y$ , and  $z$  axes of the magnetic complex or  $g_{ij}$  tensor. In reality, this relationship may not be correct, but, since there is no available crystallographic information to clarify this question, these models may be considered as adequate to represent the origin of the crystal field of  $\text{Ti}^{3+}$  in  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

In addition to the orbital energy level structure, group theory also provides the basis vectors or eigenfunctions of the various levels. For the present problem, the holosymmetric point group  $D_{2h}$  of the orthorhombic system has been chosen to represent the crystal electric field symmetry and the orbitals may be expressed as follows<sup>8</sup>:

$$\begin{aligned} |4\rangle &= \frac{1}{2} |3z^2 - r^2\rangle, \\ |3\rangle &= \frac{1}{2}\sqrt{3} |x^2 - y^2\rangle, \\ |2\rangle &= \sqrt{3} |yz\rangle, \\ |1\rangle &= \sqrt{3} |xz\rangle, \\ |0\rangle &= \sqrt{3} |xy\rangle. \end{aligned} \quad (2)$$

These wave functions correspond to those in Fig. 3, where the complete energy level scheme is presented. The details of the representations and basis vectors were obtained from Wilson, Decius, and Cross.<sup>9</sup> To complete the problem, the splitting parameters  $\delta_1$ ,  $\delta_2$ , and  $\Delta$  can be related to the  $g$  factors by considering  $\lambda\mathbf{L}\cdot\mathbf{S}$  and  $\beta\mathbf{H}\cdot(\mathbf{L}+g_e\mathbf{S})$  as additional perturbations in the manner to be described in the following paragraphs.

<sup>8</sup> C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962), p. 64.

<sup>9</sup> E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 333.

## CALCULATIONS AND RESULTS

### A. Spin-Hamiltonian Method

By applying  $\lambda\mathbf{L}\cdot\mathbf{S} + \beta\mathbf{H}\cdot(\mathbf{L}+g_e\mathbf{S})$  as the perturbation, Pryce<sup>10</sup> developed the spin Hamiltonian in which the following relations were derived:

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}, \quad (3)$$

$$g_{ij} = g_e(\delta_{ij} - \lambda\Lambda_{ij}), \quad (4)$$

where  $g_e = 2$  in Pryce's definition,  $|n\rangle$  refers to the orbital wave functions (2) and the  $i$  and  $j$  subscripts to an  $x$ ,  $y$ , and  $z$  coordinate system. If the  $x$ ,  $y$ , and  $z$  axes represent the principal axes of the tensor, and the wave functions (2) are used in Eq. (3), the following expressions for the  $g$  factors are obtained:

$$\begin{aligned} g_x &= g_e(1 - \lambda/\delta_1), \\ g_y &= g_e(1 - \lambda/\delta_2), \\ g_z &= g_e(1 - 4\lambda/\Delta), \end{aligned} \quad (5)$$

where  $\delta_1 = E_1 - E_0$ ,  $\delta_2 = E_2 - E_0$ , and  $\Delta = E_3 - E_0$ . By choosing  $g_x = 1.895$ ,  $g_y = 1.715$ , and  $g_z = 1.767$ , with  $\lambda = 154 \text{ cm}^{-1}$  (free-ion value) and  $g_e = 2.0023$  for better accuracy, the splitting parameters may be calculated to be

$$\begin{aligned} \delta_1 &= 1070 \text{ cm}^{-1}, \\ \delta_2 &= 1310 \text{ cm}^{-1}, \\ \Delta &= 11\,500 \text{ cm}^{-1}. \end{aligned} \quad (6)$$

As indicated in Table I, the spin-Hamiltonian relations are valid only if  $\lambda \ll E_n - E_0$ ; this inequality is not well satisfied in this case.

### B. Nondegenerate Perturbation Method

In order to reduce the error inherent in the above calculations, more complete relations between the  $g$  factors and the splitting parameters may be obtained by applying nondegenerate perturbation theory, as

TABLE I. Crystal-field energy-level splittings.<sup>a</sup>

Perturbation method	Limit of validity	$\delta_1$ $\text{cm}^{-1}$	$\delta_2$ $\text{cm}^{-1}$	$\Delta$ $\text{cm}^{-1}$
Spin Hamiltonian	$\lambda \ll \delta_1$	1070	1310	11 500
Nondegenerate	$\lambda < \delta_1$	1050	1320	17 000
Degenerate	$\lambda \lesssim \delta_1$	1050	1320	20 300

<sup>a</sup> In the above table,  $\lambda = 154 \text{ cm}^{-1}$ .

<sup>10</sup> M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

outlined in Pake.<sup>11</sup> By this method, the perturbations  $\lambda\mathbf{L}\cdot\mathbf{S}$  and  $\beta\mathbf{H}\cdot(\mathbf{L}+g_e\mathbf{S})$  are treated separately, with nondegenerate theory used to correct the ground-state wave functions through the relation

$$\psi_{m'} = \psi_m - \sum_{k \neq m} \psi_k \frac{\langle k | \lambda\mathbf{L}\cdot\mathbf{S} | m \rangle}{E_k - E_m}, \quad (7)$$

where  $|m\rangle$  refers to  $|0\alpha\rangle$  and  $|0\beta\rangle$  and  $|k\rangle$  is any of the other wave functions (2) with the  $|\alpha\rangle$  and  $|\beta\rangle$  spin functions included.

If the normalization constant is ignored (the error introduced is negligible), the corrected wave functions of the orbital ground-state  $B_{1g}$  of Fig. 3 are

$$\begin{aligned} |\psi_1\rangle &= |0\alpha\rangle - i(\lambda/2\delta_1)|1\beta\rangle - (\lambda/2\delta_2)|2\beta\rangle + i(\lambda/\Delta)|3\alpha\rangle, \\ |\psi_2\rangle &= |0\beta\rangle - i(\lambda/2\delta_1)|1\alpha\rangle + (\lambda/2\delta_2)|2\alpha\rangle - i(\lambda/\Delta)|3\beta\rangle. \end{aligned} \quad (8)$$

To calculate the Zeeman energy splitting of this ground-state Kramers doublet, it is only necessary to use degenerate theory in the usual manner by forming the  $2 \times 2$  matrix with elements of the type  $\langle \psi_i | \beta\mathbf{H} \cdot \mathbf{X}(\mathbf{L} + g_e\mathbf{S}) | \psi_j \rangle$ . Since this energy level separation  $\Delta E = g\beta H$ , expressions for  $g_x$ ,  $g_y$ , and  $g_z$  may be found by solving the matrix for  $H$  along the  $x$ ,  $y$ , and  $z$  axes separately.

For  $H = H_z$ , the matrix elements

$$\mathcal{H}_{ij} = \langle \psi_i | \beta H_z (\mathbf{L}_z + g_e S_z) | \psi_j \rangle$$

are as follows:

$$\begin{aligned} \mathcal{H}_{11} &= \left[ \frac{g_e}{2} - \frac{4\lambda}{\Delta} - \frac{\lambda^2}{2\delta_1\delta_2} - \frac{g_e\lambda^2}{8} \left( \frac{1}{\delta_1^2} + \frac{1}{\delta_2^2} \right) + \frac{g_e\lambda^2}{2\Delta^2} \right] \beta H_z, \\ \mathcal{H}_{22} &= -\mathcal{H}_{11}, \\ \mathcal{H}_{12} &= \mathcal{H}_{21} = 0. \end{aligned} \quad (9)$$

The secular equation becomes

$$\begin{vmatrix} \mathcal{H}_{11} - E & 0 \\ 0 & -\mathcal{H}_{11} - E \end{vmatrix} = 0 \quad \text{or} \quad E = \pm \mathcal{H}_{11}. \quad (10)$$

As a result,  $\Delta E = 2\mathcal{H}_{11} = g_z\beta H_z$  and

$$g_z = g_e - \frac{8\lambda}{\Delta} - \frac{\lambda^2}{\delta_1\delta_2} - \frac{g_e\lambda^2}{4} \left( \frac{1}{\delta_1^2} + \frac{1}{\delta_2^2} \right) + \frac{g_e\lambda^2}{\Delta^2}. \quad (11)$$

<sup>11</sup> G. E. Pake, *Paramagnetic Resonance* (W. A. Benjamin, Inc., New York, 1962), pp. 55-62.

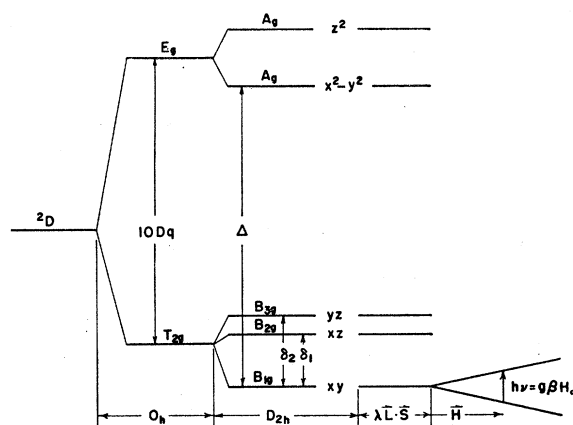


FIG. 3. Energy level structure of  $Ti^{3+}$  in  $RbAl(SO_4)_2 \cdot 12H_2O$ .

By a similar procedure, it may be shown that

$$g_x = g_e - \frac{2\lambda}{\delta_1} + \frac{g_e\lambda^2}{4} \left( \frac{1}{\delta_1^2} - \frac{1}{\delta_2^2} \right) + \frac{2\lambda^2}{\delta_2\Delta} - \frac{g_e\lambda^2}{\Delta^2}, \quad (12)$$

$$g_y = g_e - \frac{2\lambda}{\delta_2} + \frac{g_e\lambda^2}{4} \left( \frac{1}{\delta_2^2} - \frac{1}{\delta_1^2} \right) + \frac{2\lambda^2}{\delta_1\Delta} - \frac{g_e\lambda^2}{\Delta^2}. \quad (13)$$

On substituting the values for  $g_x$ ,  $g_y$ ,  $g_z$ ,  $\lambda$ , and  $g_e$ , which were used for the spin-Hamiltonian equations, trial and error calculations yield the values of the splitting parameters given in Table I,

$$\begin{aligned} \delta_1 &= 1050 \text{ cm}^{-1}, \\ \delta_2 &= 1320 \text{ cm}^{-1}, \\ \Delta &= 17\,000 \text{ cm}^{-1}. \end{aligned} \quad (14)$$

It is interesting to note that Eqs. (11), (12), and (13) essentially reduce to the spin-Hamiltonian expressions (5) when the terms with  $\lambda^2$  are neglected. From the results of the calculations, it is evident that these higher order contributions significantly affect the value of  $\Delta$ . Since the validity of these latter calculations still depends on  $\lambda$  being less than  $\delta_1$ , a better value for  $\Delta$  may be obtained if this assumption is not made.

### C. Degenerate Perturbation Method

In the two previous cases, the crystal electric-field potential energy  $U_c$  has been treated as part of the unperturbed Hamiltonian, with the result that the spin-orbit coupling energy was assumed to be smaller than  $U_c$ . To avoid making this assumption, the problem may be solved by treating  $U_c$  and  $\lambda\mathbf{L}\cdot\mathbf{S}$  together in a degenerate perturbation approach. By this method, the wave functions of the ground-state Kramers doublet must be found from the diagonalization of the fol-

lowing  $10 \times 10$  matrix:

	$4\beta$	$3\alpha$	$2\beta$	$1\beta$	$0\alpha$	$0\beta$	$1\alpha$	$2\alpha$	$3\beta$	$4\alpha$
$4\beta$	$\Delta_4$	0	0	0	0	0	$\sqrt{3}\lambda/2$	$i\sqrt{3}\lambda/2$	0	0
$3\alpha$	0	$\Delta$	$i\lambda/2$	$\lambda/2$	$-i\lambda$	0	0	0	0	0
$2\beta$	0	$-i\lambda/2$	$\delta_2$	$-i\lambda/2$	$\lambda/2$	0	0	0	0	$-i\sqrt{3}\lambda/2$
$1\beta$	0	$\lambda/2$	$i\lambda/2$	$\delta_1$	$i\lambda/2$	0	0	0	0	$-\sqrt{3}\lambda/2$
$0\alpha$	0	$i\lambda$	$\lambda/2$	$-i\lambda/2$	0	0	0	0	0	0
$0\beta$	0	0	0	0	0	0	$-i\lambda/2$	$-\lambda/2$	$-i\lambda$	0
$1\alpha$	$\sqrt{3}\lambda/2$	0	0	0	0	$i\lambda/2$	$\delta_1$	$-i\lambda/2$	$-\lambda/2$	0
$2\alpha$	$-i\sqrt{3}\lambda/2$	0	0	0	0	$-\lambda/2$	$i\lambda/2$	$\delta_2$	$-i\lambda/2$	0
$3\beta$	0	0	0	0	0	$i\lambda$	$-\lambda/2$	$i\lambda/2$	$\Delta$	0
$4\alpha$	0	0	$i\sqrt{3}\lambda/2$	$-\sqrt{3}\lambda/2$	0	0	0	0	0	$\Delta_4$

(15)

A brief examination of this matrix reveals that two  $5 \times 5$  diagonal blocks are very weakly coupled to each other by small off-diagonal elements linking the  $|4\alpha\rangle$  and  $|4\beta\rangle$  states with the  $|1\alpha\rangle$ ,  $|1\beta\rangle$ ,  $|2\alpha\rangle$ , and  $|2\beta\rangle$  states. In order to make the solution manageable, it will be assumed that the effect of this upper level is negligible and the matrix will be reduced to

	$0\alpha$	$1\beta$	$2\beta$	$3\alpha$	$0\beta$	$1\alpha$	$2\alpha$	$3\beta$
$0\alpha$	0	$-i\lambda/2$	$\lambda/2$	$i\lambda$	0	0	0	0
$1\beta$	$i\lambda/2$	$\delta_1$	$i\lambda/2$	$\lambda/2$	0	0	0	0
$2\beta$	$\lambda/2$	$-i\lambda/2$	$\delta_2$	$-i\lambda/2$	0	0	0	0
$3\alpha$	$-i\lambda$	$\lambda/2$	$i\lambda/2$	$\Delta$	0	0	0	0
$0\beta$	0	0	0	0	0	$-i\lambda/2$	$-\lambda/2$	$-i\lambda$
$1\alpha$	0	0	0	0	$i\lambda/2$	$\delta_1$	$-i\lambda/2$	$-\lambda/2$
$2\alpha$	0	0	0	0	$-\lambda/2$	$i\lambda/2$	$\delta_2$	$-i\lambda/2$
$3\beta$	0	0	0	0	$i\lambda$	$-\lambda/2$	$i\lambda/2$	$\Delta$

(16)

It can be shown that the secular equations of both  $4 \times 4$  submatrices are identical (as expected, since the result should be four Kramers doublets) and take the form

$$E^4 + AE^3 + BE^2 + CE + D = 0, \quad (17)$$

where

$$A = -(\delta_1 + \delta_2 + \Delta),$$

$$B = \delta_1\delta_2 + \delta_1\Delta + \delta_2\Delta - \frac{3}{2}\lambda^2,$$

$$C = \frac{1}{4}\lambda^2(5\delta_1 + 5\delta_2 + 2\Delta) - \delta_1\delta_2\Delta + \frac{5}{8}\lambda^3,$$

$$D = \frac{1}{8}\lambda^3(2\Delta - 4\delta_1 - 3\delta_2) - \frac{1}{4}\lambda^2(\delta_1\Delta + \delta_2\Delta + 4\delta_1\delta_2) + \frac{3}{4}\lambda^4.$$

For the ground-state Kramers doublet, the eigenfunctions for the two matrices become

$$\begin{aligned} |\psi_1\rangle &= a|0\alpha\rangle + b|1\beta\rangle + c|2\beta\rangle + d|3\alpha\rangle, \\ |\psi_2\rangle &= a|0\beta\rangle + b|1\alpha\rangle - c|2\alpha\rangle - d|3\beta\rangle, \end{aligned} \quad (18)$$

where  $a^+a + b^+b + c^+c + d^+d = 1$  for normalization. The relations between these coefficients follow directly from the matrices of (16), the signs being slightly different

in the two wave functions, and may be expressed as

$$\begin{aligned} a &= i \frac{\frac{1}{2}\lambda^3 - \lambda(\delta_1 - E)(\delta_2 - E) - \frac{1}{4}\lambda^2(\delta_1 + \delta_2 - 2E)}{\frac{1}{4}\lambda^2(3E - \delta_1 - \delta_2 + \lambda) - E(\delta_1 - E)(\delta_2 - E)} \times d, \\ b &= \frac{\frac{1}{4}\lambda^2(\lambda - E) - \frac{1}{2}\lambda(\lambda - E)(\delta_2 - E)}{\frac{1}{4}\lambda^2(3E - \delta_1 - \delta_2 + \lambda) - E(\delta_1 - E)(\delta_2 - E)} \times d, \\ c &= i \frac{\frac{1}{2}\lambda(\lambda - E)(\delta_1 - E - \frac{1}{2}\lambda)}{\frac{1}{4}\lambda^2(3E - \delta_1 - \delta_2 + \lambda) - E(\delta_1 - E)(\delta_2 - E)} \times d. \end{aligned} \quad (19)$$

Equation (18) may now be treated in the same manner as (8) to determine the Zeeman energy splitting and the three  $g$  factors. In this case,  $g_e$  will be treated as 2 in the perturbation  $\beta\mathbf{H} \cdot (\mathbf{L} + g_e\mathbf{S})$  in order to simplify calculations. For the dc magnetic field along the  $z$  axis,  $H = H_z$  and the matrix elements  $\mathcal{H}_{ij} = \langle \psi_i | \beta H_z (L_z + 2S_z) | \psi_j \rangle$  are equal to

$$\begin{aligned} \mathcal{H}_{11} &= [(a^+a - b^+b - c^+c + d^+d) + 2i(a^+d - d^+a) - i(b^+c - c^+b)]\beta H_z, \\ \mathcal{H}_{22} &= -\mathcal{H}_{11}, \\ \mathcal{H}_{12} &= \mathcal{H}_{21} = 0. \end{aligned} \quad (20)$$

Thus,  $\Delta E = 25C_{11} = g_z \beta H_z$  and

$$g_z = 2(a^+a - b^+b - c^+c + d^+d) + 4i(a^+d - d^+a) - 2i(b^+c - c^+b). \quad (21)$$

In the  $x$  and  $y$  directions, the expressions for the  $g$  factors are

$$g_x = 2(a^+a + b^+b - c^+c - d^+d) - 2i(a^+b - b^+a) + 2i(c^+d - d^+c), \quad (22)$$

$$g_y = 2(a^+a - b^+b + c^+c - d^+d) + 2(a^+c + c^+a) - 2(b^+d + d^+b). \quad (23)$$

The determination of the orbital energy level separations  $\delta_1$ ,  $\delta_2$ , and  $\Delta$  must be carried out by trial and error, beginning with the secular Eq. (17) and continuing until suitable values for the  $g$  factors are obtained. To illustrate this approach and to verify the values given in Table I,

$\delta_1 = 1050 \text{ cm}^{-1}$ ,  $\delta_2 = 1320 \text{ cm}^{-1}$ ,  $\Delta = 20\,300 \text{ cm}^{-1}$ , and  $\lambda = 154 \text{ cm}^{-1}$  will be substituted into (17), with the result that

$$E^4 + AE^3 + CE + D = 0,$$

where

$$A = -2.267 \times 10^4 \text{ cm}^{-1},$$

$$B = 4.949 \times 10^7 \text{ cm}^{-2},$$

$$C = -2.782 \times 10^{10} \text{ cm}^{-3},$$

$$D = -3.032 \times 10^{11} \text{ cm}^{-4}.$$

The solution of lowest energy is  $E = -10.72 \text{ cm}^{-1}$ . If this value is used in Eq. (19) and  $d$  is chosen as real and positive, after normalization

$$d = 0.007868,$$

$$a = -i0.9961,$$

$$b = -0.06899,$$

$$c = i0.05412.$$

Finally, from (21), (22), and (23) the  $g$  factors are found to be

$$g_z = 1.892, \quad g_x = 1.715, \quad g_y = 1.767.$$

If the value for  $g_e$  of 2.0023 had been used, all of these values would be greater by about 0.002 and would fall within the estimated experimental error of  $\pm 0.002$ .<sup>2</sup>

#### DISCUSSION AND CONCLUSIONS

Before any comments are made concerning the results of these calculations, in which effects of covalent bonding have been ignored, it is important to note that the value of  $\lambda = 154 \text{ cm}^{-1}$  is for the  $Ti^{3+}$  free ion. In a crystalline environment this value could be reduced by covalent bonding. As a result, the values of the energy level separations calculated in this paper may be correspondingly higher than they are in reality. How-

ever, it should also be mentioned that Van Vleck<sup>12</sup> has shown that  $\sigma$  bonding should not exist in this case and Bleaney *et al.*<sup>3</sup> have pointed out that there is little evidence of  $\pi$  bonding in hydrated iron-group compounds.

According to Hartmann and Schlafer,<sup>7</sup> the value of  $10Dq$  (or  $\Delta$  in this case) is approximately  $20\,300 \text{ cm}^{-1}$  for the  $Ti^{3+}$  ion in the field of an octahedron of  $H_2O$  dipoles. This measurement was the result of optical spectroscopic experiments with several compounds, including  $CsTi(SO_4)_2 \cdot 12H_2O$  and  $TiCl_3 \cdot 6H_2O$ . Within the validity of the crystal electric field model and the assumptions made in the calculations, this agreement is remarkably good. Further indication of this consistency lies in the fact that the  $Rb\{AlTi\}(SO_4)_2 \cdot 12H_2O$  crystals have the characteristic violet color of the  $Ti(H_2O)_6^{3+}$  ion.

With regard to the smaller splittings, the values of  $\delta_1 = 1050 \text{ cm}^{-1}$  and  $\delta_2 = 1320 \text{ cm}^{-1}$  represent a great departure from the trigonal splitting estimated at less than  $100 \text{ cm}^{-1}$  for  $CsTi(SO_4)_2 \cdot 12H_2O$ ,<sup>3-6</sup> based on the EPR results at liquid-helium temperatures. On the contrary, these values make reasonable agreement with the calculation of  $800 \text{ cm}^{-1}$ <sup>5</sup> based on the magnetic susceptibility measurements between  $100$  and  $300^\circ K$  of Dutta-Roy *et al.*<sup>13</sup> with the same  $CsTi$  alum. It has been suggested by Bose *et al.*<sup>5</sup> that a change in the degree of crystal electric-field distortion may take place between  $100$  and  $4.2^\circ K$  to account for this large discrepancy in trigonal splitting values.

For the  $Ti^{3+}$  ion in rubidium alum it is evident that a further distortion of the  $H_2O$  octahedron has destroyed the trigonal symmetry which normally exists at the trivalent sites. However, it is reasonable to expect that the magnitude of this distortion is small in relation to the trigonal one and can be thought of as a perturbation on it. This is verified partly by the fact that the values of  $\delta_1$  and  $\delta_2$  are close, indicating that the doublet  $E_g$  in the trigonal field is only slightly split (see Fig. 1, where the  $D_{4h}$  field can represent a trigonal or  $D_{3d}$  field since the Stark level scheme is the same for these lower three orbital levels). As a result, the foregoing results for the cesium salt should be considered as pertinent, if only on a qualitative basis.

One final aspect of this lower symmetry crystal-field splitting involves the calculations of Van Vleck.<sup>14,15</sup> In these papers, Van Vleck discusses three contributing factors in the trigonal distortion of the  $Ti^{3+}$  crystal field in an alum lattice: (i) the direct effect of distant atoms, which represents the lattice in general, (ii) the indirect effect of distant atoms, which represents the mechanical distortion of the  $H_2O$  octahedron by the

<sup>12</sup> J. H. Van Vleck, *J. Chem. Phys.* **3**, 807 (1935).

<sup>13</sup> S. K. Dutta-Roy, A. S. Charkravarty, and A. Bose, *Indian J. Phys.* **33**, 483 (1959).

<sup>14</sup> J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939).

<sup>15</sup> J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939).

lattice in general, and (iii) the Jahn-Teller effect. The results of his calculations based on a dipole model for the trigonal field give a total splitting from all three sources of  $1075\text{ cm}^{-1}$  of which  $550\text{ cm}^{-1}$  is due to a Jahn-Teller effect.<sup>16</sup> This work of Val Vleck is interesting not only because his prediction of the energy level splitting closely approximates the values calculated in this paper, but also because of the implication of the Jahn-Teller effect. In one of his papers,<sup>15</sup> he points out that a linear combination of tetragonal and trigonal types of distortion could produce a lower energy than either acting alone. The suggestion being made here is that such a Jahn-Teller distortion, which would be less than axially symmetric, could account for the observed

<sup>16</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 435 (1940).

crystal field symmetry of  $\text{Ti}^{3+}$  ions in  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . However, since there is no direct evidence of this effect and ample reason to expect an additional ligand displacement because  $\text{Ti}^{3+}$  is a larger ion ( $0.76\text{ \AA}$ ) substituted for a smaller  $\text{Al}^{3+}$  ion ( $0.51\text{ \AA}$ ), a Jahn-Teller effect in this material must remain in the realm of speculation.

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## Low-Temperature Heat Capacities of Indium and Tin\*

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The heat capacity of indium has been measured between 0.08 and  $4.2^\circ\text{K}$  in the normal state ( $H = 1000\text{ Oe}$ ) and between  $0.1^\circ\text{K}$  and the critical temperature in the superconducting state. At  $T \leq 0.8^\circ\text{K}$ ,  $C_n = 0.00101T^{-2} + 1.69T + 1.42T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$  and at  $T \leq 0.35^\circ\text{K}$ ,  $C_s = 1.22T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ . The absence of the hyperfine contribution to  $C_s$  is a consequence of the long spin-lattice relaxation time. Below  $0.35^\circ\text{K}$ , where the superconducting-state lattice heat capacity can be measured, the normal-state lattice heat capacity is only a small part of  $C_n$  and calorimetric measurements alone cannot exclude the possibility that the lattice heat capacities in the two states are equal. However, the excellent agreement between the elastic constants and the apparent normal-state lattice heat capacity supports the conclusion that they are not. The apparent discrepancy in the lattice heat capacities is less than that reported by Bryant and Keesom but the difference is largely accounted for by differences in analysis of the normal-state data and by their assumption that the measured  $C_s$  included the nuclear quadrupole term. The measurements of  $C_s$  extend to temperatures well below that at which the electronic contribution becomes negligible and therefore permit a comparison with theoretical studies of the superconducting-state lattice heat capacity. The heat capacity of tin was measured only below  $1^\circ\text{K}$ . Below  $0.45^\circ\text{K}$ ,  $C_s = 0.246T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ , in good agreement with the elastic constants. Within the experimental error,  $C_n = 1.78T + 0.246T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ .

### I. INTRODUCTION

PRIOR to the report by Bryant and Keesom on the heat capacity of indium,<sup>1,2</sup> the heat capacity of superconducting metals had generally been interpreted as the sum of separable electronic and lattice contributions, the latter of which was assumed to be unchanged by the superconducting transition. This interpretation

can be summarized by the equations

$$C_n = \gamma T + C_{ln}, \quad (1)$$

$$C_s = C_{es} + C_{ls}, \quad (2)$$

and

$$C_{ln} = C_{ls}, \quad (3)$$

in which  $C_n$  and  $C_s$  are the heat capacities in the normal and superconducting states,  $C_{ln}$  and  $C_{ls}$  are the lattice contributions,  $C_{es}$  is the superconducting-state electronic heat capacity, and the electronic heat capacity in the normal state is the product of the constant  $\gamma$  and the temperature  $T$ . At low temperatures the lattice heat capacity can be expressed as a series in odd powers of  $T$ . The first term is the  $T^3$  term and its coefficient is

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<sup>1</sup> C. A. Bryant and P. H. Keesom, *Phys. Rev. Letters* **4**, 460 (1960).

<sup>2</sup> C. A. Bryant and P. H. Keesom, *Phys. Rev.* **123**, 491 (1961).