Origin of the Crystal Field in Ti³⁺-Substituted Alums

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An examination of the relationship between the crystal-field energy-level splittings and the crystal-structure details for several Ti³⁺-substituted alums is presented in an attempt to explain the peculiar paramagnetic-resonance behavior of these salts. With recently acquired data for $KAl(SO_4)_2 \cdot 12H_2O$ and $NaAl(SO_4)_2 \cdot 12H_2O$ added to the previously reported results for Rb, Tl, and Cs alums, a clear correlation is found to exist between the magnitude of the lower-symmetry crystal-field component and the respective aluminum-sulfur distances as determined by x-ray crystallography. After a careful study of the unit cell, it is concluded that the probable cause of the orthorhombic character of the crystal field is a displacement of the $(Ti \cdot 6H_2O)^{3+}$ ion from the trigonal symmetry axis. The reasons for the distortion are believed to be the positions of the surrounding $(SO_4)^{2-}$ groups and the radius of the Ti³⁺ ion, which is significantly larger than that of the host Al³⁺ ion.

I. INTRODUCTION

ONE of the most interesting but least studied ions of the iron group is trivalent titanium. With a single $3d$ electron, it has a ^2D orbital ground state which gives rise to a simple crystal-field energy-level structure. As a result, this ion in cubic and trigonal environments is frequently used as an example of the role played by the crystal field in quenching orbital angular momentum and producing spectroscopic splitting factors which approach the pure spin value of 2. More important from a diagnostic point of view, however, is the fact that the orbital angular momentum of Ti³⁺ is usually only partially quenched, with the result that the ion is potentially a sensitive probe of its immediate environment.

Because titanium strongly favors the tetravalent state, Ti³⁺ is considered to be a rare ion. In paramagnetic-resonance investigations, Ti³⁺ is usually studied as an impurity in a diamagnetic host lattice. However, an additional problem arises because it is substantially larger than Al³⁺ and other typical host ions, with the result that solid solutions or even moderate concentrations of Ti³⁺ are often impossible to obtain. Although paramagnetic-resonance experiments have been reported for Ti³⁺ in several host lattices, most of the available information has been obtained from the alum family of salts.

The first measurements of the paramagnetic-resonance spectrum of Ti³⁺ ions in an alum single crystal were reported by Bleaney *et al.*[1] in 1955. In this work, the sample studied was pure $CsTi(SO_4)_2 \cdot 12H_2O$, and the crystal field was found to have trigonal symmetry. More recently, investigations have been carried out on other members of the alum family with the Ti³⁺ ion substituted for Al³⁺ in small concentrations. The striking feature of the EPR spectra of these mixed crystals is the orthorhombic symmetry of the crystal field.[2]

In chronological order, it was in a Rb-alum host that the unusual Ti³⁺ spectrum was first observed[3] and interpreted in terms of an orthorhombic crystal field.[4] A similar behavior was later found for Tl alum[5] and, most recently, for K alum. In the case of the Cs alum host,[6] three distinct spectra were found. From theoretical considerations, it appears that they are related to the spectrum observed in pure CsTi alum. It is believed that the spectrum of Ti³⁺ in Na alum has been observed, but for reasons to be discussed in a later section, details are not available. The general appearance of the spectrum suggests that this host also provides an orthorhombic crystal field.

In this article, the symmetries and magnitudes of the crystal fields for this group of Ti³⁺-substituted salts are examined in relation to their individual crystal-structure details, with the intention of gaining further insight into the cause of the orthorhombic crystal-field symmetry.

II. CRYSTALLOGRAPHY

The crystal structure of the alums can be summarized as cubic with four molecules of the composition $R^{1+}R^{3+}(SO_4)_2 \cdot 12H_2O$ per unit cell. More specifically, the space group is $T_h^6(Pa3)$ and the metal cations

[1] 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).

[2] The fact that an orthorhombic model has been used to describe these fields does not eliminate the possibility of even lower symmetry. Experimental results indicate only that the fields have less than axial symmetry.

[3] G. F. Dionne, Can. J. Phys. **42**, 2419 (1964).

[4] G. F. Dionne, Phys. Rev. **137**, A743 (1965).

[5] J. A. MacKinnon and G. F. Dionne, Can. J. Phys. **44**, 2329 (1966).

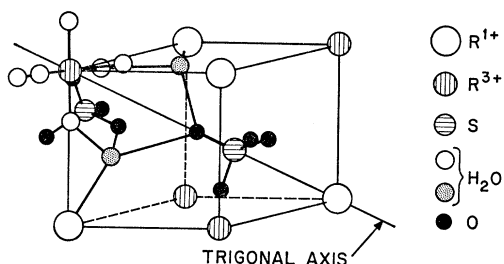[6] G. A. Woonton and J. A. Mackinnon, Can. J. Phys. **46**, 59 (1968).

FIG. 1. Structure details of one octant of an α-type alum are shown together with the axis of trigonal symmetry.

occupy alternate sites on the cube corners (see Fig. 1). In all known cases, six H_2O molecules are octahedrally coordinated with the small trivalent cations. The distribution of the other six H_2O molecules depends on the size of the monovalent ions,[7] and to some extent, characterizes the α, β, and γ alum types.[8] The eight $(SO_4)^{2-}$ groups are dispersed equally through the different octants of the unit cell and consist of a single sulfur atom surrounded by four tetrahedrally coordinated oxygens. The bonding arrangement in a single octant, shown in Fig. 1, is typical for an α or β alum.

Since the crystal field at the R^{3+} site is determined by the disposition of the various ligands, it is appropriate to list the different neighbors in order of proximity:

six H_2O	at 2.0 Å,
six $(SO_4)^{2-}$	at 5.0 Å,
six R^{1+}	at 6.0 Å,
two $(SO_4)^{2-}$	at 6.5 Å.

The above distances are approximate since slight variations exist among the different members of the alum family. In general, the six H_2O molecules form a near-regular octahedron which is assumed to produce a cubic crystal field. In some cases, a small trigonal distortion has been found and is considered to contribute to a trigonal-field component which appears to have its main origin in the positions of the $(SO_4)^{2-}$ groups. Before describing the locations of the sulfate ions, which represent the second and fourth neighbors, it will be pointed out that the third neighbor R^{1+} ions occupy the face centers of the unit cell with R^{3+} at the center and thus form a regular octahedron of pure cubic symmetry. As a result, in their normal positions, they do not contribute to the lower-symmetry components of the crystal field.

In Fig. 2, the positions of the sulfur atoms are shown schematically. The six second neighbors lie in $\{110\}$

[7] R. W. G. Wyckoff, *Crystal Structures III* (Interscience Publishers, Inc., New York, 1960).
[8] H. Lipson and C. A. Beevers, Proc. Roy. Soc. (London) **A148**, 664 (1935).

planes approximately at the intersections of the line through R^{3+}, which forms a 90° angle with the two parallel octant body diagonals. In each case, the distance d_0 from R^{3+} to S is equal and is given for the three different alum types by the following:

$$d_0 = 0.409a_0, \quad (\beta \text{ type})$$
$$= 0.407a_0, \quad (\alpha \text{ type})$$
$$= 0.412a_0, \quad (\gamma \text{ type})$$

where $a_0 =$ lattice constant.

As indicated in Fig. 3, these six $(SO_4)^{2-}$ groups form a trigonally distorted octahedron around R^{3+}, with the threefold axis of symmetry along a unit cell $\langle 111 \rangle$ direction. On this same axis but outside of the distorted octahedron, the remaining two sulfates lie at a distance d_0', given by

$$d_0' = 0.572a_0, \quad (\beta \text{ type})$$
$$= 0.537a_0, \quad (\alpha \text{ type})$$
$$= 0.470a_0, \quad (\gamma \text{ type}).$$

In order to illustrate how the eight sulfate groups provide a threefold axis of symmetry along one body diagonal, a view of the unit cell along this axis is presented in Fig. 4, where the second neighbor $(SO_4)^{2-}$ groups are arranged in a manner which features the necessary threefold symmetry. In Table I, the actual values of a_0, d_0, and d_0' are listed for the alum crystals discussed in subsequent sections. A compilation of the available crystal-field data derived from paramagnetic
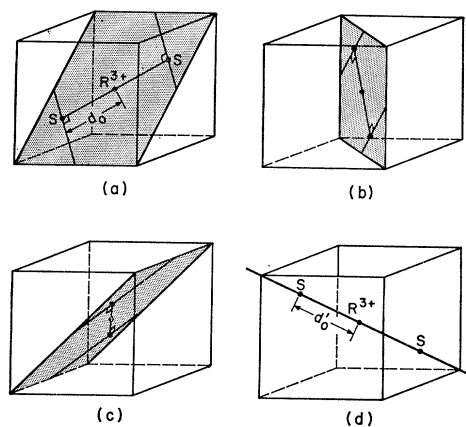

FIG. 2. The locations of the eight sulfur atoms which surround R^{3+} in a unit cell are shown schematically. In (a) through (c), the three pairs of second-neighbor sulfurs are presented as lying in $\{110\}$ planes at the intersections of $\langle 111 \rangle$ axes in their respective octants and the line approximately perpendicular to these axes passing through R^{3+} at the center of the unit cell. The distance from R^{3+} to each of these six S atoms is denoted by d_0. In (d), the two fourth-neighbor sulfurs are shown as lying on the main body diagonal at a distance from R^{3+} denoted by d_0'.
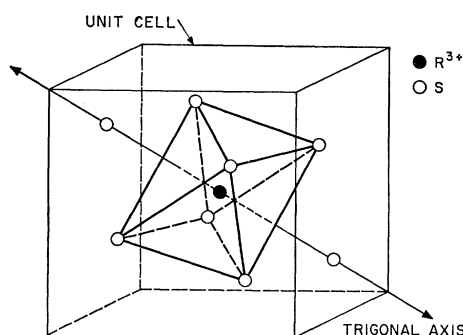
Fig. 3. The second-neighbor sulfur atoms are presented as forming a trigonally distorted octahedron which surrounds R^{3+}. Outside of this octahedron and on the axis of trigonal symmetry lie the fourth-neighbor sulfurs.

resonance will now be undertaken in order to establish a correlation with the pertinent crystal-structure details.

III. SUMMARY OF CRYSTAL-FIELD DATA

From the results of investigations reported earlier,[4] the crystal-field energy-level structure of the Ti^{3+} ion for orthorhombic (D_{2h}) symmetry may be represented by Fig. 5. Since the nearest-neighbor H_2O dipoles form a near-regular octahedron, it is customary to represent the basic symmetry as cubic (O_h). With a cubic field, the ^2D orbital ground state is split into a lower triplet T_{2g} and upper doublet E_g, separated by $10Dq\sim20\,000$ cm⁻¹. In fields of axial symmetry, T_{2g} is further split into a singlet and a doublet, with this final orbital degeneracy removed by spin–orbit coupling. For the case of orthorhombic symmetry, T_{2g} is split into three singlets. Although the upper doublet E_g is not of immediate importance, it should be mentioned that its degeneracy will not be removed by a trigonal field;
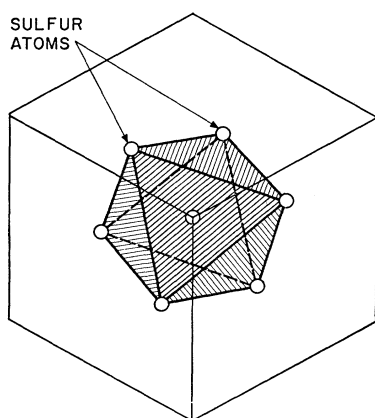

Fig. 4. The unit cell of the alum lattice is sketched as viewed along a $\langle 111 \rangle$ axis. The presence of the threefold symmetry of the sulfate groups is clearly evident.

Table I. Crystal-structure data for selected alums.

Alum	Type	a_0 Å	d_0 Å	d_0' Å
$CsAl(SO_4)_2\cdot12H_2O$	β	12.333	5.044	7.054
$RbAl(SO_4)_2\cdot12H_2O$	α	12.220	4.974	6.562
$TlAl(SO_4)_2\cdot12H_2O$	α	12.206	4.968	6.555
$KAl(SO_4)_2\cdot12H_2O$	α	12.133	4.938	6.515
$NaAl(SO_4)_2\cdot12H_2O$	γ	12.190	5.022	5.729

fields of both tetragonal and orthorhombic symmetry split the doublet and would undoubtedly affect optical-absorption spectra.

In Table II, the measured g factors and calculated lower-symmetry crystal-field energy-level separations are presented for the Ti^{3+}-doped alum lattices that have been studied to date. With the exception of Cs alum, there appears to be little doubt that the lower-symmetry field is orthorhombic. In every case, the g factors were determined from analyses of the paramagnetic-resonance spectrum at liquid-helium temperatures. Energy-level splittings for the orthorhombic fields were determined from the perturbation-theory approach of Dionne.[4] For Cs alum, the value of the trigonal splitting was estimated from the computed curves of Gladney and Swalen.[9] Although the Na alum spectrum has not been analyzed in detail because the combination of large natural linewidth, small range of g factors, and the apparent large number of lines makes resolution virtually impossible, there is ample evidence to suggest the presence of a lower-than-trigonal field. A spectrum of more than four lines must immediately eliminate the possibility of a trigonal field. In this case,
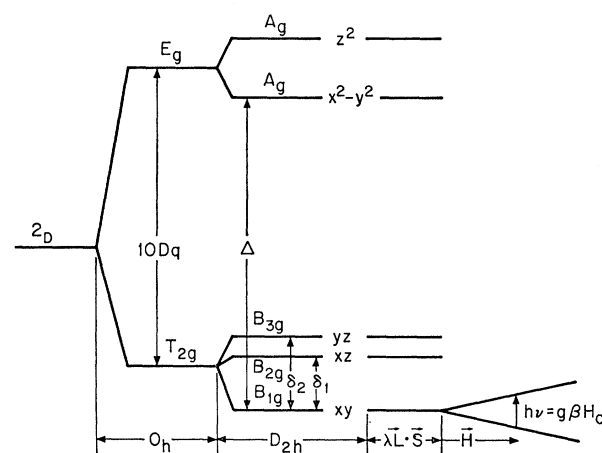

Fig. 5. Energy-level structure of Ti^{3+} in an alum lattice having a crystal field of orthorhombic (D_{2h}) symmetry.

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

TABLE II. Paramagnetic-resonance and crystal-field data for Ti^{3+} in alum lattices.

Alum	g_z	g_x	g_y	δ_1 [a] (cm^{-1})	δ_2 [a] (cm^{-1})	ϵ	Reference
$CsTi(SO_4)_2 \cdot 12H_2O$	1.25	1.14	1.14				1, 9
$Cs\{AlTi\}(SO_4)_2 \cdot 12H_2O$	1.241	0.931	0.931				6, 9
	1.192	0.696	0.696	$\sim$500	$\sim$500	0	6, 9
	1.166	0.230	0.230				6, 9
$Rb\{AlTi\}(SO_4)_2 \cdot 12H_2O$	1.895	1.715	1.767	1070	1310	0.20	3, 4
$Tl\{AlTi\}(SO_4)_2 \cdot 12H_2O$	1.938	1.790	1.834	1462	1843	0.23	5
$K\{AlTi\}(SO_4)_2 \cdot 12H_2O$	1.975	1.828	1.897	1780	2947	0.49	New data
$Na\{AlTi\}(SO_4)_2 \cdot 12H O$	$g_{max}=2.00$; $g_{min}=1.86$			>2000 [b]	>3000 [b]	$\cdot\cdot$	New data

[a] δ_1 and δ_2 were calculated for $\lambda = 154$ cm^{-1}.   [b] These numbers are rough estimates based on the theoretical work mentioned in the text.

an average value for the splitting has been estimated from the relation

$$\delta \simeq \lambda(1-\tfrac{1}{2}g)^{-1}, \qquad (1)$$

which has been shown to be a good approximation in the case of both Rb and Tl alum,[5] where it was used to obtain δ_1 and δ_2 from g_x and g_y, respectively.

Because the question of covalent bonding must be considered, particularly in the samples where sizeable orthorhombic fields are present, the above equation was used to compute the curves presented in Figs. 6(a) and 6(b), which show the variation in δ_1 and δ_2 with a decreasing average spin-orbit coupling constant λ. Based on the data in Table II, it is certain that Cs alum lies far below Rb alum and Na alum well above K alum, in both graphs.

From the foregoing, it is very evident that a strong correlation exists between the magnitudes of the crystal-field splittings and the corresponding aluminum-to-sulfur separations (Table I) in the respective lattices. This fact will now be examined in conjunction with other phenomena in an attempt to clarify the nature of the Ti^{3+} environment in these crystals.

IV. SOURCE OF THE CRYSTAL FIELD

A. Trigonal Symmetry

The first description of the crystal field of the alums in terms of their crystal structure was published by Van Vleck in 1939.[10,11] In his estimation of the trigonal-field splitting of Ti^{3+}, V^{3+}, and Cr^{3+}, the basic source of this lower-symmetry component was logically attributed to the positions of the next-nearest-neighbor sulfate ions. This concept is analogous to that which is prevalent in considerations of magnetic anisotropy in ferrites and other magnetic materials, and is based on the normal positions of the various atoms or ions in the lattice without appealing to local distortions, vacancies, or other imperfections.

It is the electric field produced by the trigonally symmetric $(SO_4)^{2-}$ ions that was referred to as the

"direct effect of distant atoms." Because they bond directly to the H_2O molecules which constitute the octahedra surrounding the trivalent cation sites, there is ample reason to expect the octahedra to have a natural trigonal distortion; this was referred to as the "indirect effect of distant atoms." A third mechanism examined by Van Vleck was the Jahn-Teller effect, which was shown to be theoretically capable of causing crystal-field splittings comparable to those of the two other mechanisms. For a dipole model of the H_2O molecules the total splitting from all three effects was computed as 1075 cm^{-1} [12] of which 400 cm^{-1} was attributed to the $(SO_4)^{2-}$ ions directly. Although these
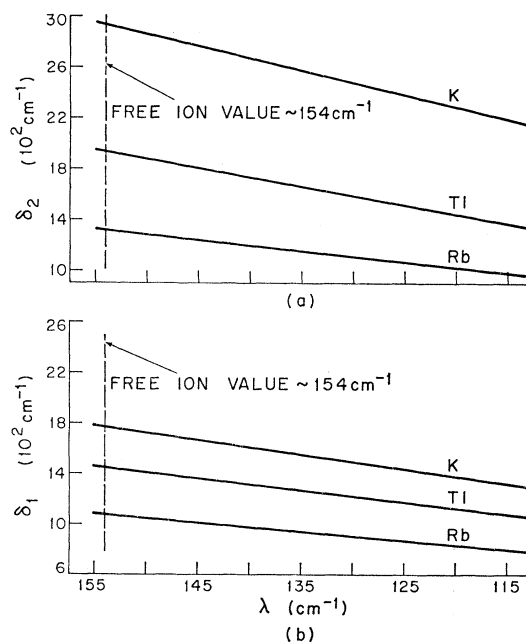

FIG. 6. In (a) and (b), the values of the crystal-field splitting parameters δ_2 and δ_1 are presented as a function of the spin-orbit coupling constant λ for Ti^{3+} in Rb, Tl, and K alum. The results for Cs and Na alum are not suitable for this type of presentation, but as indicated in Table II, would undoubtedly lie below Rb for Cs and above K in the case of Na.

[10] J. H. Van Vleck, J. Chem. Phys. **7**, 61 (1939).
[11] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[12] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940), Ref. 14.

numbers can only be considered as estimates some insight may be gained by comparing them with the quantities derived from experiments.
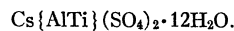
Cs Alum

The results cited in Table II for CsTi alum and Cs{AlTi} alum suggest that δ (here considered as an average of δ_1 and δ_2 since the level above the ground state is an orbital doublet) is considerably less than 1075 cm⁻¹. From the Gladney and Swalen analysis for a singlet ground state,[13] the best value for splitting of each site is about 500 cm⁻¹. A qualitative examination of these calculated curves indicates that this splitting value should vary monotonically among the four spectra, with the largest value occurring for the Cs{AlTi} alum site with $g_{\parallel} = 1.166$ and $g_{\perp} = 0.230$ and the smallest for the case of pure CsTi alum with $g_{\parallel} = 1.25$ and $g_{\perp} = 1.14$. Since the lattice constant of CsTi alum should be larger than that of Cs alum or any Cs{AlTi} alum, the above result is probably consistent with the crystallography. A direct correlation should exist between the respective d_0 and d_0' values and energy-level separations δ.

It should be pointed out that the possibility of the orbital doublet lying lowest cannot be eliminated, particularly for the site with $g_{\parallel} = 1.166$ and $g_{\perp} = 0.230$. In this case, the spectrum bears a strong resemblance to that of Ti³⁺ in Al₂O₃ ($g_{\parallel} = 1.067$, $g_{\perp} < 0.1$), which was interpreted as resulting from a lower-than-axial field component.[14] However, in the work of Van Vleck cited earlier, a careful examination of this question has concluded that the orbital singlet should be lowest. For the Al₂O₃ host, the situation is probably reversed because the trigonal field is produced mainly by positively charged Al³⁺ ions, in contrast to the negative (SO₄)²⁻ groups in Cs alum.

With a lower-symmetry splitting value of 500 cm⁻¹, it should also be pointed out that the major part of the trigonal field could be attributed to the direct effect of the (SO₄)²⁻ ions. Although this result does not rule out the possibility of contributions from the other two mechanisms, it does suggest that their effects might be smaller than predicted.

With regard to the existence of different sites for Ti³⁺ in Cs alum, it would appear that inhomogeneities of the Ti³⁺ concentration are probably the cause. Evidence of this effect may be seen from the manner in which the

g factors gradually approach those of pure CsTi alum, thus suggesting that the lowest g factors are found for the site of lowest local Ti³⁺ concentration. In crystals grown from aqueous solution, it is not unusual to find that concentration gradients and clustering effects produce compositional variations.

B. Orthorhombic Symmetry

From the first observation of the orthorhombic behavior of the Ti³⁺ spectrum in Rb alum,[3] it was believed that its main cause was in some way related to relative the radii of the two trivalent cations involved in the substitution. Accepted values of these quantities are 0.76 Å for Ti³⁺ and 0.51 Å for Al³⁺. Based on the description of the crystal structure presented earlier, it is clear that ligand displacements must take place when the significantly larger Ti³⁺ ion is substituted for the host Al³⁺. The real question concerns the mechanism by which the natural trigonal symmetry is reduced to orthorhombic.

It is important to recall that both the nearest- or first-neighbor H₂O dipoles and the third neighbor R^{1+} ions are octahedrally coordinated around R^{3+}. As a result, although substitution of Ti³⁺ for Al³⁺ will reduce bond lengths and raise the total energy, the position of minimum energy will remain at the center and no loss of symmetry should be expected.

In order to reduce some of the confusion that may occur because the bonding between Ti³⁺ and the (SO₄)²⁻ ions is indirect via the H₂O molecules, it might be better to continue this discussion in terms of the (Ti·6H₂O)³⁺ ion. With this model, the arrangement of the (SO₄)²⁻ ions in Fig. 3 may now be examined.

Since (Ti·6H₂O)³⁺ is at the center of the trigonally distorted octahedron of sulfate ions, there is still no reason to expect a loss of symmetry, since a displacement in any direction would only further increase the energy. However, the two fourth-neighbor sulfates which lie along the trigonal axis can provide a cause for a displacement. If these (SO₄)²⁻ ions are considered as fixed, the substitution of the larger Ti³⁺ ion will again decrease the normal bond lengths and raise the total energy. However, in this case, the energy can be lowered if the (Ti·6HO)³⁺ group moves perpendicular to this axis, with the result that a new equilibrium position may be established off of the ⟨111⟩ axis but remaining in the {111} plane. Since the symmetry is threefold, as indicated by Fig. 4, there would be at least three different directions in which the displacement could occur. However, as argued in earlier work,[3] the point group T_h will permit only 12 different crystal-field orientations and the occurrence of three magnetically distinguishable displacements in the {111} plane, in combination with the four trigonal axes, appears to be the most probable situation.

Before discussing the individual alum host lattices it should be mentioned that this mechanism for the

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[13] In Figs. 4(a) and 4(b) of Ref. 9, dashed-line curve 6 appears to fit best this particular situation. In this case, $v = -500$ cm⁻¹ (corresponding to our $\delta = +500$ cm⁻¹) and $v \sim -3000$ cm⁻¹. It should be pointed out that the slope of the variation of $|g_{\perp}|$ versus $|v'|$ is very high at $v \sim -3000$ cm⁻¹, and this can account for the wide variation in $g_{\perp}$ among the different spectra in

$$\text{Cs\{AlTi\}(SO}_4)_2 \cdot 12\text{H}_2\text{O}.$$

[14] L. S. Kornienko and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **38**, 1651 (1960) [English transl.: Soviet Phys.—JETP **11**, 1189 (1960)].

occurrence of orthorhombic symmetry might easily be applied to the behavior of Cr^{3+} in $(NH_3CH_3)Al(SO_4)_2 \cdot 12H_2O$ at temperatures below 170°K, where an orthorhombic spectrum has been observed.[15]

Rb, Tl, and K Alum

As indicated in Table I, these three salts are α-type and have proportionately smaller d_0 and d_0' separations than the β-type Cs alum. In addition, because of the different ionic radii of Rb^{1+} (1.48 A), Tl^{1+} (1.40 Å), and K^{1+} (1.33 Å) the lattice constant varies within the group with the result that the actual separations vary slightly among the three compounds. From the relative magnitudes of δ_1 and δ_2 in the three salts, as indicated in Table II, it is evident that the degree of distortion is in accord with the aforementioned unit-cell dimensions. This fact is further reflected by the degree of departure from axial symmetry, defined as

$$\epsilon = 2(\delta_2 - \delta_1)/(\delta_1 + \delta_2), \qquad (2)$$

which also increases as d_0 and d_0' become smaller. From observations of the physical appearance of these crystals there are further indications that titanium substitutions cause local distortions. Only $Cs\{AlTi\}(SO_4)_2 \cdot 12H_2O$ retains a high degree of transparency and gives any indication that a complete range of solid solutions may be possible.

Na Alum

Of all the known members of the alum family, $Na\,Al(SO_4)_2 \cdot 12H_2O$ is the only example of the γ structure. Since this features a small monovalent cation, it is not surprising to find the small Al^{3+} as the trivalent cation when it is recalled that the monovalent site is always larger than the trivalent one. As a result, the occurrence of substituted Na alum crystals is rare because most of the other trivalent ions of interest are larger than Al^{3+}. When the large Ti^{3+} ion is considered, the chances for undistorted substitution are substantially worse, both from the above argument and the previous one involving the magnitudes of d_0 and d_0', which are about 15% smaller than in the α-type discussed earlier.

Paramagnetic-resonance absorptions from Na alum have been attributed to the presence of Ti^{3+} ions but have not been analyzed because the individual lines

could not be resolved. It appears that many lines are present, thus ruling out the possibility of the natural trigonal symmetry, with the g factor ranging from 1.86 to 2.00. As a result it seems probable that there is a very large splitting of the lower orbital levels (see Table II) caused by a severe local distortion. From x-ray crystallographic analysis, it has been shown that some monoclinic phase accompanies titanium additions,[16] a result which suggests that perhaps all of the previously discussed orthorhombic crystal fields are in reality monoclinic. Unfortunately, the g tensors upon which the crystal-field interpretations are based cannot distinguish between any of the symmetries which are lower than axial, and the answer to this question must await the acquisition of additional information.

V. CONCLUSIONS

From the analysis of the results of paramagnetic-resonance experiments with several members of the alum family containing small amounts of Ti^{3+} ions, it is believed that the lower-than-trigonal component of the crystal field is caused by an effective displacement of the $(Ti \cdot 6H_2O)^{3+}$ ion perpendicular to the crystal-field axis of trigonal symmetry. This conclusion is suggested by the positions of the surrounding $(SO_4)^{2-}$ ions which should not readily accommodate the large Ti^{3+} ion without a distortion that lowers the local symmetry. The thesis is supported by a strong correlation which exists between the Al^{3+} to S separations of the various lattices and the experimentally derived orthorhombic crystal-field energy-level splittings.

In the β-type Cs alum, Ti^{3+} may be substituted more freely than in the other cases and it is only in this host that the natural trigonal symmetry is observed. For the α-type Rb, Tl, and K alum, only an orthorhombic component of the field is present, and its magnitude increases as d_0 and d_0' become smaller. Finally, in the case of Na alum, which is the only known example of the γ type, severe distortions are judged to exist as a result of its small lattice dimensions. From x-ray examination, a monoclinic phase was detected when titanium was added and it is expected that further details of this lattice as well as other general information concerning the chemistry and crystallography will be reported in the near future.

[15] K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 338 (1955).

[16] A. J. Frueh (private communication).