STUDIES ON THE MAGNETIC SUSCEPTIBILITY OF SOME V³⁺ ALUMS AND Ti³⁺ CAESIUM ALUM IN THE RANGE 300°K TO 100°K

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ABSTRACT The paper describes the details of the difficult process of obtaining large single crystals of four alums of V³⁺ and one of Ti³⁺ and the measurements of their magnetic susceptibility in the range 300° to 100°K All the salts are apparently found to obey Curie law very well But a theoretical analysis of the data on modern lines shows that in all the salts variations of the effective mean moment square P_f^2 with temperature are to be expected owing to (1) change in the trigonal crystalline splitting with temperature and (2) change in the Boltzmann distribution of the population of the different close lying levels with temperature. Evidently, the variations in the liquid air range are not sufficient to produce a deviation from linearity of P_f^2 - T curves, though deviations in their slopes against T axis as also the intercepts with P_f^2 axis from the theoretical expectations are observed. In Ti³⁺ the change in crystalline field with temperature is considerable at very low temperatures. In V³⁺ alums there is also an appreciable change in crystalline fields from one salt to another.

1. INTRODUCTION

In an earlier paper, one of us (Dutta-Roy, 1956) has discussed the dependence of the crystalline electric fields on the change in structure, in a large number of Cr³⁺ alums. It was found that the mean susceptibility at room temperature changed quite appreciably from one class of alum to another and in a given alum with temperature owing to a phase change of some sort taking place.

The isomorphous V³⁺ and Ti³⁺ alums are expected to behave in a much more complicated way than the Cr³⁺ alums, since in both the former cases triplet orbital states lie lowest in the crystalline Stark pattern as against a singlet for Cr³⁺. As such, in the former the additional *induced* distortion of the Jahn-Teller cluster arising from distant atoms should be of about the same importance as the primary Jahn-Teller distortion itself, in producing the anisotropy of the cluster (Van Vleck, 1939) whereas, in Cr³⁺ the effect of the distant atoms is practically the only one.

In the present paper we have measured very accurately the mean susceptibilities of four V³⁺ alums containing the alkali cations NH_4^+, Rb^+, Tl^+ and Cs^+ and the Cs⁺ alum of Ti³⁺, all with SO_4^{2-} as acid radicals, with the help of the refined techniques of magnetic measurements described in details in an earlier paper

(Dutta-Ray, 1955 ; also Thesis 1958). Only a summary of the main points of inte g st in the experiments are given here and also the details of the rather difficult technique of preparation of the salts.

2. METHOD OF PREPARATION OF THE ALUMS

(a) V^{3+} *alums.* A solution of $V_2(SO_4)_3$ in water when exposed to air is very easily oxidised to vanadyl sulphate, so that the usual method of crystallisation, by evaporation of aqueous solutions of equimolecular proportions of component salts in air, cannot be adopted. Even the product sold in bottles as vanadic sulphate really consists nearly entirely of vanadyl sulphate. Hence, we have adopted the electrolytic method for reducing V^{4+} to V^{3+} in an electrolytic cell modified to suit our requirements The electrolytic cell consisting of a 250 c.c. pyrex beaker is divided into an inner anode and an outer cathode chamber by a small unglazed porcelain pot passing through a stopper closing the mouth of the beaker. A platinum strip about 6 cm. ×2 cm. and a closely wound platinum spiral of $\frac{1}{2}$ mm. diam   wire, 1 cm. spiral diameter and 6 cm. length are used as cathode and anode respectively. A continuous stream of CO_2 is circulated in the cathode chamber throughout the entire operations following. The anode chamber contains dilute H_2SO_4 (100 c c of water and 25 c.c. of 50% acid) and the cathode chamber contains a nearly saturated solution of equimolecular proportion of vanadyl sulphate and an alkali sulphate (NH_4, Rb, Tl or Cs as the case may be) very carefully prepared in oxygen free water, filtered and acidulated with about 1 c.c. of dilute H_2SO_4 (same strength as above). The electrolytic cell is kept inside an ice bath and during the whole operation the temperature is never allowed to rise above 5°C. About 0 4 amps. of current taken from a 6 volt storage cell is passed through the cell.

Soon reddish violet crystals of the alum as observed in transmitted light, appear in the cathode chamber, and after about 4 hours of operation sufficient quantity of microcrystals for our purpose is deposited. These are removed from the solution and washed with ice-cold acetone. The crystals are dried and then dissolved in oxygen free cold water at about 10°C, just below saturation. The solution is transferred to two or three small clean crystallizing dishes and allowed to crystallize in a desiccator filled with CO_2 using conc. H_2SO_4 as desiccant, placed in a vibration free ice-box in which the temperature is maintained at about 5°C. After about 24 hours a few large (5 mm across) well developed octahedral single crystals of the alum may be picked up from the solution The crystals are washed with ice cold acetone and after drying dipped in a dilute solution of collodion for protection. The crystals are tested under polarizing microscope and immediately used for magnetic measurements in the cryostat. It is noted that the NH_4 and Tl alum crystals show a tendency to melt in their water of crystallization near room temperature and also of decomposing comparatively quickly, and hence the collodion coating and quick action in measurements are essential near this

temperature. The Rb and Cs salts are much more stable and can be preserved in CO_2 atmosphere even at room temperatures and without coating for a few months. The crystals can be preserved indefinitely in sealed tubes containing CO_2 in a refrigerator. With due precautions no change in the crystals have been observed in the course of several hours, which are needed to finish a series of magnetic measurements, as shown by the reproducibility of the curves for the data with falling and rising temperatures.

(b) Ti^{3+} *alums.* We could prepare only one of these, namely, the titanium caesium sulphate alum. For the preparation of this alum, the basic material required is titanic acid hydrate, which is prepared by precipitation from a solution of $TiCl_4$ in dilute HCl with NH_4OH. The precipitate of $Ti(OH)_4$ is carefully washed several times with warm water to ensure complete removal of NH_4Cl. The precipitate is then heated to about 80°C and dried in a vacuum desiccator and a weighed quantity of it is dissolved in $(4N).H_2SO_4$. The reduction of Ti^{4+} to Ti^{3+} is done in an electrolytic cell as in the case of V^{3+} alums in CO_2 atmosphere, using a current of 0.2 amperes for about 12 hours, keeping the temperature at about 0°C with a low salt content freezing mixture. The complete reduction is marked by the change of the colourless solution to violet and also a rapid fall in the cell current.

The alum is prepared by adding equimolecular proportion of Cs_2SO_4 to the reduced solution. A slow current of CO_2 is passed through the solution to prevent oxidation. The alum is then precipitated from the solution with ice-cold acetone and filtered in a suction filter. The precipitate is next boiled in dilute H_2SO_4 (100 c c of water in 25 c.c. of 20% H_2SO_4) in CO_2 atmosphere. The precipitate is thus dissolved and CO_2 bubbled through solution till the solution is clear violet. The solution is then transferred back to the electrolytic cell and a small current is passed for 2 to 3 hours to ensure complete reduction in case some titanyl salt had been formed during previous operations. The solution is then transferred to a flat bottom conical flask and CO_2 bubbled through it for a little while. The flask is then put in a CO_2 filled desiccator with conc. H_2SO_4 as desiccant and the whole put away in the ice box for crystallisation. After about 48 hours small shining deep violet crystals of the alum appear at the bottom The bigger crystals about 3mm. across are picked out, washed with acetone, coated with a thin layer of collodion and are immediately used for magnetic measurements. The time required for a complete low temperature run for magnetic measurements did not decompose the crystals appreciably, as shown by the reversibility and reproducibility of the data curve

3. A SUMMARY OF THE EXPERIMENTAL TECHNIQUES FOR SUSCEPTIBILITY MEASUREMENT

A modified form of Curie balance, consisting of a light thin horizontal glass tube suspended near the middle with a fine vertical quartz fibre attached at the

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upper end to a graduated vernier torsion head (reading to 0.1°), is used to balance the horizontal magnetic translational force on the specimen, attached to one end of the balance arm.   The electromagnet is turned on its side so that the pole pieces are horizontal and one above the other.   The pole-gap is shaped, following Sucksmith (1939), with about 6° inclination in the central one-third portion of the pole-pieces, while the remaining two-thirds, one portion on either end, are parallel, giving a vertical field in the central region and a horizontal gradient along the length of the pole-pieces.   The balance arm with the specimen goes into the central region at right angles to the length of the pole-pieces (Dutta Roy, 1955).   An   automatic liquid air cryostat developed in this laboratory (Bose, 1947) placed horizontally enclosing the specimen, provides temperatures accurate to more than 0.1°K (measured with a calibrated Cu-constantan thermocouple) for magentic measurements.

The translational motion of the specimen is optically magnified with the help of a bifilar mirror provided with a suitable oil damping arrangement, attached to the other end of the balance beam, and a telescope and scale arrangement. The force on the specimen is balanced accurately to more than 0.1% by twisting the quartz fibre suspension till the zero position of the image of the scale in the telescope is restored.   With the Sucksmith shape of pole-gap the uniformity of the force is within 0.1% over a volume of about 1 c.c. in the central region so that the mounting and positioning of the specimens and standard substance (chromium potassium alum already standardised by earlier experiments; Dutta Roy, 1955) of smaller volumes need not be very critical.   The arrangement gives the susceptibility along the field direction, i.e. the vertical.   But in the present the alums being of the cubic class the mode of orientation of crystal in the field is immaterial The balance is enclosed within a suitable draught and moisture proof box, with a side tube to cryostat, a top tube to enclose the fibre suspension and a front glass panel for the observation of the image of the scale from the bifilar mirror.   Details of measurement are omitted.   Under the conditions of measurement described at room temperature 300°K, we have

$$\chi - \frac{\theta}{\theta_s} \cdot \frac{m}{m_s} \left(\chi_s - \frac{k_a}{\rho_s} \right) + \frac{k_a}{\rho} \qquad - \qquad \ldots \ (1)$$

in which χ's are the mass susceptibilities of crystal along the field direction, θ's the angles of twist of torsion fibre to balance the magnetic force on specimen, m's the masses, ρ's densities, symbols with and without the subscript 's' referring to the standard and the unknown crystal specimen respectively, and k_a is the volume susceptibility of surrounding air.   At any other temperature T (degrees Kelvin),

$$\chi_T = \chi \cdot \frac{\theta_T}{\theta} / \left[1 + \frac{k_a}{k} \left(1 - \gamma \cdot 300 \right) \left(1 - \frac{300}{T} \right) \right] \qquad \ldots \ (2)$$

in which k is the volume susceptibility of the crystal at 300°K, and γ is its volume coefficient of expansion. The measurements are taken at 15° or 20°K intervals or even closer in the range 300°K to 100°K The treatment of the results is as in the earlier papers and the final values for mean susceptibilities are given at 20° intervals, being obtained from the mean curve for the product $\theta_T \times T$ against T. The individual values for three different specimens of each salt do not deviate by more than 0.2% from the mean curve. The gm. molecular susceptibilities χ_M corrected for diamagnetism of the molecule, the squares of

the effective moments in Bohr magneton $p_f{}^2$ the (using $p_f{}^2 = \dfrac{3k\chi_M \, T}{N\beta^2}$

$= 7.995 . \chi_M \, T)^*$ at different temperatures, which are same as the mean ionic values $P_f{}^2$, are given in the Tables 1–V.

TABLE I

V.NH$_4$(SO$_4$)$_2$,12H$_2$O

Temp °K	$\chi_M \times 10^6$	$P_f{}^2$ (Obs.)	$P_f{}^2$ (Calc.)
300	3025	7.254	7.264
280	3234	7 240	7.243
260	3476	7.226	7.222
240	3759	7.211	7.201
220	4084	7 183	7.180
200	4482	7 167	7.160
180	4967	7.148	7.138
160	5569	7 124	7 117
140	6334	7.089	7.096
120	7364	7 054	7.072
100	8780	7.020	7.040

TABLE II

V.Rb(SO$_4$)$_2$,12H$_2$O

Temp °K	$\chi_M \times 10^6$	$P_f{}^2$ (Obs.)	$P_f{}^2$ (Calc.)
300	3080	7.387	7.387
280	3293	7.372	7.362
260	3533	7.340	7.335
240	3812	7.313	7 309
220	4140	7.281	7.282
200	4533	7.247	7.257
180	5015	7.216	7 229
160	5627	7.191	7.203
140	6391	7.157	7.176
120	7440	7.139	7.150
100	8912	7.125	7.125

* Using values of the physical constant by Dumond & Cohen, (1948).

TABLE III

$V.Tl(SO_4)_2,12H_2O$

Temp °K	$\chi_M \times 10^6$	P_f^2 (Obs.)	P_f^2 (Calc)
300	3083	7.394	7.394
280	3292	7.370	7 384
260	3542	7 362	7 375
240	3834	7 357	7 365
220	4181	7.353	7.355
200	4596	7.348	7.348
180	5104	7 345	7.339
160	5736	7 336	7.330
140	6545	7 324	7.321
120	7625	7.314	7 311
100	9141	7 308	7 302

TABLE IV

$V.Cs(SO_4)_2,12H_2O$

Temp. °K	$\chi_M \times 10^6$	P_f^2 (Obs.)	P_f^2 (Calc.)
300	3078	7 382	7 397
280	3295	7 372	7 372
260	3536	7 350	7.347
240	3281	7 331	7 322
220	4152	7.310	7.296
200	4552	7.278	7 271
180	5034	7.244	7.245
160	5643	7.218	7.219
140	6425	7.191	7 194
120	7471	7.168	7 169
100	8921	7.132	7.143

TABLE V

$Cs.Ti (SO_4)_2,12H_2O$

Temp. °K	$\chi_M \times 10^6$	P_f^2 (Obs.)	P_f^2 (Calc.)
300	1188	2.848	2 855
280	1270	2.843	2.943
260	1357	2.832	2 829
240	1456	2.819	2 815
220	1581	2 803	2.801
200	1728	2.787	2.787
180	1911	2.775	2 773
160	2142	2.764	2.760
140	2434	2.748	2.745
120	2822	2.731	2.731
100	3369	2.717	2.718

4. DISCUSSION OF THE RESULTS ON V^{3+} ALUMS

(a) *Variation of P_f^2 from salt to salt and with temperature.*

It will be seen on a general survey of the table of values of P_f^2 in V^{3+} alums that the values are about 8 to 12% less than the "spin only" value of 8 squared Bohr magnetons. The values of P_f^2 for Rb, Cs and Tl alums at 300°K are practically the same, whereas, the value for NH_4 alum at 300°K is about 2% less than the previous group. It can be seen from figures 1(a(and (b) that the temperature
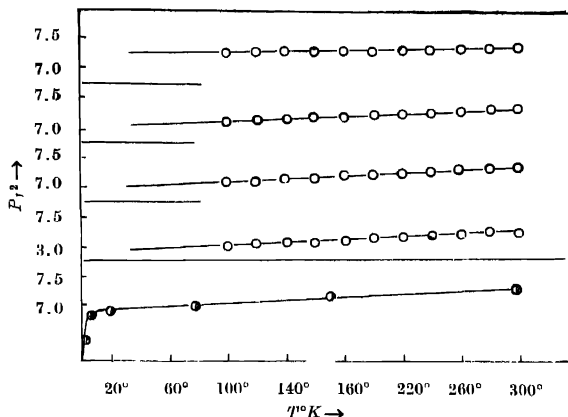
Fig. 1a . $P_f^2 - T$ curves for V^{3+} sulphate alums
O   present measurements by Dutta Roy
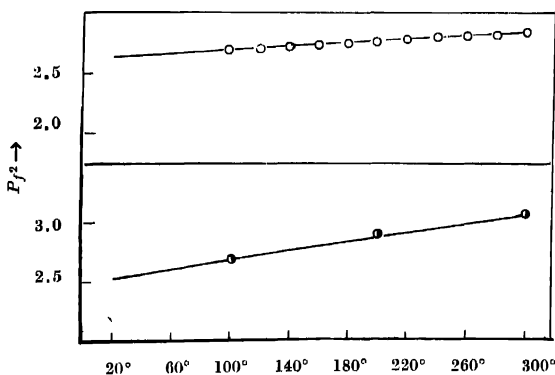● Leiden measurements.

Fig. 1b : $P_f^2 - T$ curves for Ti^{3x} sulphate alum.
O   present measurements by Dutta Roy
● Leiden measurements,

variation curve of P_f^2 for all the alums in our range of temperatures are rectilinear with appreciable slopes against temperature axis, which are very nearly the same for Rb and Cs alums as also for the NH_4 alum though the room temperature value lies lower for the latter. In Tl alum the slope is appreciably smaller than the others though the room tempera ture value is the same as Rb and Cs alums

P_f^2 values for all the salts in this range appear to obey a Curie Law of the form $P_f^2 = AT + B$ quite well, but with somewhat different A and B values as indicated in the table 6 below. Measurements on V^{3+} ammonium alum by Van den Handel & Siegert (1937) give P_f^2 as 7.290 at $297.4°K$, 7 169 at 169 8°K and 7.002 at 77.7°K, and agree well with our values in this range.

TABLE VI

Empirical $P_f^2 - T$ parameters for the different alums

	Vanadium alum				Titanium alum
	NH_4	Rb	Cs	Tl	Cs
B	6 949 (6 921)	6 995	7 015	7.136	2.650
$A \times 10^4$	11 4 (13.1)	13 1	12 5	8.2	6 6
g	1.864 (1.860)	1 870	1.872	1.888	1.880

The values in the parantheses are from Van den Handel's data.

The measurements of Van den Handel for the NH_4 salt extend down to $1.465°K$ and the $P_f^2 - T$ curve here is found to deviate from Curie Law slowly at first above $20°K$ and then more quickly and then very rapidly at $4°K$ tending towards a very low value near $0°K$. This is shown in figure 1(a). The curvature at low temperatures apparently does not seem to have an appreciable effect on the behaviour in the liquid air range. Significance of all these facts is to be fitted into a satisfactory scheme.

(b) Crystalline field theory of V^{3+} alum.

In order to explain the experimental results of Van den Handel and Siegert on V^{3+} ammonium alum (1937) mentioned in the previous section, Siegert (1937) postulated a breakdown of the Russel-Saunders coupling between the individual orbital and spin moments of the $3d$ electrons in the V^{3+} ion (free ion ground state $3d^2\ ^3F$) under the influence of the major cubic component of the crystalline field arising from the trigonally elongated octahedron formed by the six water molecules immediately surrounding the V^{3+} ion (Beevers and Lipson, 1935). Since

the separations of the energy levels under the cubic field are of the order of 10^4 cm^{-1} Siegert considered only the lowest orbital triplet level Γ_4 (figure 2a) and fur-
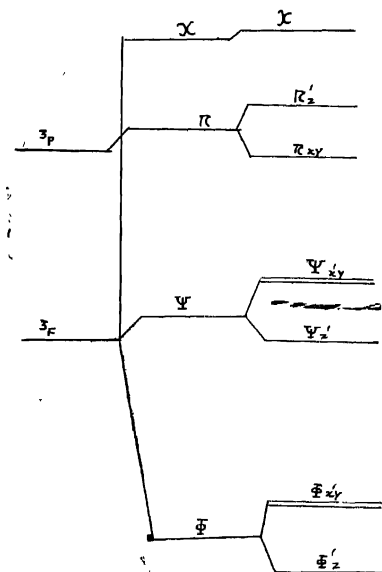

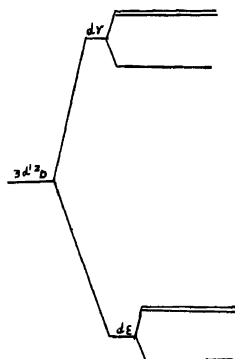Fig. 2a : Energy level diagram for V^{3+} (not drawn to scale).

Fig. 2b : Energy level diagram for Ti^{3+} (not drawn to scale).

ther assumed that under the trigonal field and the spin-orbit perturbation this level is split up so as to make a nonmagnetic singlet state lie lowest, with a doublet close above it and other levels at several hundred cm⁻¹ above. Thus assuming the trigonal splitting coefficient $\Delta = -700$ cm⁻¹, the spin splitting, $D = 4.76$ cm⁻¹, but the spin-orbit coupling coefficient $\zeta = +64$ cm⁻¹ instead of the free ion value of $+104$ cm⁻¹ (Laporte, 1928) he obtained a fairly good fit (a) with the experimental deviation of P_f^2 from the spin only value, (b) with the nearly linear form of the $P_f^2 - T$ curve above 20°K and (c) with the quick drop in this curve near liquid helium temperatures, tending to very low values of P_f^2. Then, his theoretical high frequency term came out as $3.63 \times 10^{-3}.T$ as against the experimental value $1.31 \times 10^{-3}.T$ (obtained from the straight portion of the $P_f^2 - T$ curve at high temperatures, see Table VI).

The basic objections to the above theory appear to be the *ad hoc* assumption of the complete breakdown of R–S coupling (Van Vleck, 1939; Owen. 1955) and the neglect of the upper cubic levels and also the components of the ^3P multiplet which are sufficiently close to the ground level to affect its contributions to the effective magnetic moment.

In a recent paper one of us (Chakravarty. 1959) has applied the method of Abragam and Pryce (1951) to the problem of V^{3+} alums, without recourse to any special postulate regarding R–S breakdown and, taking into consideration the contributions of all the upper levels, has obtained for the square of the effective moment,

$$P_f^2 = \frac{2A^2 + 16B^2 kT/D[\exp(D/kT)-1]}{2+\exp(D/kT)} + \frac{3kT}{N\beta^2} K_e$$

$$= \frac{3kT}{N\beta^2} K_e + 2g_\parallel^2 + \frac{2D}{3kT}(g^2-g_\perp^2) \qquad \ldots (3)$$

degree of approximation, in which $A^2 = g_\parallel{}^2$, $B^2 = g_\perp^2/4$ and $g = \sqrt{\frac{1}{3}(g_\parallel^2 + 2g_\perp^2)}$, is the mean spectroscopic splitting factor and K_e is the high frequency susceptibility, D, the spin splitting and other symbols have the usual meanings. the complicated functions of Δ, ζ and α and α' the Lande splitting g, D and K_e are contained in (Chakravarty, 1959). Expression (3) gives good fit with the factors in the crystal field (Van den Handel *et al* (1937) and Datta-Roy (1958) on NH₄ experimental results of over the range of temperatures (Table VII) taking by trial and error alum, over the entire range of the $\Delta = -1350$ cm⁻¹, $\alpha = 1.10$, $\alpha' = 1.35$, $\zeta = +64$ cm⁻¹ the values of the parameters of $t = 1.820$, $g = 1.870$ as against the experimental leading to $g_\parallel = 1.960$, $g_\perp$ below cm⁻¹ and $\frac{3k}{N\beta^2} K_e = 1.98 \times 10^{-3}$ as against the mean value $g = 1.864$, $D = 4.80$

TABLE VII

V.NH$_4$(SO$_4$)$_2$,12H$_2$O.

T°K.	P_f^2 (Theo.)	P_f^2 (Expl.)*
100	7.016	7.040
200	7.062	7.160
300	7.128	7.264

* Fit with Van den Handel's results are not shown because these have been discussed in details by Chakravarty (1959).

experimental value 1.23×10^{-3} (Table VI). It is further found that in the range 300°K to 100°K the contribution of the term of the order $1/T$ (equation (3)) is below the limit of experimental errors of ±0.2%. In fact, even at 10°K this contribution amounts to a little over 1% only. The other two terms in equation (3) are of the form $AT + B$, which explains why the empirical curve in the high temperature range is appreciably a straight line. It is to be remarked, however, that the theoretical slope of the line given by $\dfrac{3k}{N\beta^2}$. K_e is somewhat different from the experimental, even considering the comparatively large error in determining this small term (about ±5%). This is probably due to the fact that g and hence Δ the trigonal field splitting coefficient changes *a little* with temperature which is not sufficient to produce a deviation from linearity but effectively causes an appreciable change in the experimental slope. Thus, evidently the theoretical g value taken to fit the empirical straight line represents really the average value in the given temperature range.

It would be very nice if the actual values of g and D could be determined directly by paramagnetic resonance at each temperature, so that we could account for even the small misfit in K_e value. But, unfortunately, the large spin-splitting $D = 4.8$ cm^{-1} makes it impossible to induce transitions between the lowest levels unless microwaves of 2 mm. or less wavelengths are used, which has not been as yet done.

(c) *The crystal field parameters*

In the paper mentioned earlier, Chakravarty has shown that the values of parameters $g_{\parallel}$, $g_{\perp}$, D and K_e, Δ, α, α' and ζ must be chosen so as to be consistent with the cubic field coefficient $G = 39000$ cm^{-1} and ^3P multiplet separation in crystal, $E_p = 9300$ cm^{-1} obtained from optical absorption measurements (Hartmann and Schlafer, 1951) and with a reasonable set of values of the second order and fourth order trigonal field coefficients H and I, namely, 3500 cm^{-1} and 3400 cm^{-1} respectively (Abragam and Pryce 1951). It is worth noticing that

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experimental parameters g_1 and $g_\perp$ are uniquely fixed, at least in theory, even from mean susceptibility when D is fixed from the low temperature measurements and g and K_c are found from the intercept and the slope of the high temperature curve where the effect of D may be considered zero, provided the value of ζ, has been fixed. In view of what has been said earlier the values of g and K_c have to be slightly adjusted and a number of trials with different ζ values made till the values of Δ, α and α' correspond to reasonable values of H and I. It is found in this way that though there may be other sets of values of ζ, Δ, α and α' which satisfy the experimental parameters g, D and K_c, H and I are rather sensitive to changes in these and become quite unreasonable if these values are changed to any considerable extent, and the best set of values are found as given above. It would have saved much trouble in finding $g_{\parallel}$, $g_\perp$ and D by trial and error if these could have been obtained directly from paramagnetic resonance data. But these are not available for the reasons already mentioned. It is interesting to remark that the 40% reduction in the value of ζ from free ion value, also needed in Siegert's theory, suggests that a fairly large overlap, $f^2 = 0.60$ of the $3d$ wave functions of V^{3+} with both the s-and p-wave functions of attached water-oxygens, exists in these alums (Owen, 1955). On the other hand, the value of Δ found by us is about double than that obtained by Siegert, namely, -700 cm^{-1}.

Now it is very probable that the covalency factor of 0.60 and hence ζ is practically the same in all these alums, since this arises from the semi covalent bond between the 6 water molecules surrounding the V^{3+} ion in everyone of the alums and may not be much influenced by the long range lattice structure; moreover, the values of α and α' representing effect of upper levels, also should not be very different. Then we may make an attempt to estimate the values of Δ, D, g and K_c for the three alums other than NH_4 alum. Of these the Rb and Cs alums appear to behave practically identically and only a little different from NH$_4$, whereas the Tl alum is appreciably different. In view of the roughness in the trial and error calculations and the labour involved, it may not be worthwhile to perform these for Rb and Cs salts separately.

We find that for the Tl alum the parameters $\Delta = -1440$ cm^{-1}, $\bar{\zeta} = +64$ cm^{-1}, $\alpha = 1.084$, $\alpha' = 1.380$ give $D = 4.812$ cm^{-1}, $g_\parallel = 1.990$, $g_\perp = 1.819$,

$g = 1.878$ and $\dfrac{3k}{N\beta^2} K_c = 1.759 \times 10^{-3}$. The theoretical values of P_f^2 calculated from the above and the experimental values are given for comparison below. The g value gives good fit with experimental value of 1.886 and the contribution of the $1/T$ term is quite negligible as required by the linearity of the $P_f^2 - T$ curve in our range. The large difference with the experimental $\dfrac{3k}{N\beta^2}$. K_e term 0.82×10^{-3}

TABLE VIII

V.Tl(SO$_4$)$_2$,12H$_2$O

T°K.	P²$_f$ (Theo.)	P²$_f$ (Expl.)
300	7.506	7.394
200	7.365	7.348
100	7.230	7.308

indicates the effect of the appreciable variation of g value with temperature. Δ value in Tl alum is appreciably larger than the NH_4 alum and is the main reason for the observed larger g value. It is evident qualitatively that the parameters for the Rb and Cs alums are intermediate between the NH_4 and Tl alums.

5. (a) *Variation of $P_f{}^2$ for Ti^{3+} alum with temperature*

It will appear from the table 5 that $P_f{}^2$ for Ti^{3+} alum at 300°K is ∼ 5% less than the spin only value and falls linearly to ∼ 9% less than the spin only value 3, at 100°K, so that the data may be very well represented by the empirical formula

$$P_f{}^2 = 6.6 \times 10^{-4} \times T + 2.650 \qquad \ldots \quad (4)$$

It wil be seen from our expression (4) above that the A term contributes about 5% of the total $P_f{}^2$ at 300°K while B contributes the bulk of ∼ 95%. There is no trace of any nonlinear term.

The Leiden measurements on mean susceptibility of this alum by Van den Handel (Thesis 1940) for four different samples in the range 300°K to 1.2°K are so inconsistent amongst one another that it is difficult to put much reliance upon them (see also remarks by Van Vleck, 1940). Even for one of the samples for which the room temperature value is fairly close to ours the entire temperature variation of $P_f{}^2$ is of the form $P_f{}^2 = 14.6 \times 10^{-4}T + 2.784 - 42.3/T$ ... (5) Apart from the fact that the Leiden high frequency term is too large the $1/T$ term also cannot be fitted with any theory as will be seen later.

(b) *Theory for Ti^{3+} ion in crystalline fields of trigonal symmetry*

Under a crystalline field of cubic symmetry with a small superposed trigonal component as occurrs in the alums the original $3d^1$ ^2D ground state of a free Ti^{3+} ion together with the spin orbit coupling is split as shown in figure 2b. Each orbital level has a twofold Kramers degeneracy which is slightly split to ∼ 0.002 cm^{-1} only, by the effect of the very small exchange and dipole coupling existing even in these highly magnetically diluted salts, as shown by adiabatic demagnetization experiments (Kurti and Simon, 1935). But we may neglect this for our present purpose. The Kramers doublet can be further split appreciably only by the magnetic field and thus $P_f{}^2$ should strictly obey a Curie Law between 1°K to 300°K,

unless the trigonal field separation Δ between the basic orbital singlet and the next higher doublet is comparable to any value of kT in this range

Bleaney *et al* (1955) have found from paramagnetic resonance measurements that $g - 1.25$, $g_\perp - 1.14$, so that $g = 1.176$, at helium temperature only, since at higher temperature the spin lattice relaxation time is of the order of 10^{-6} – 10^{-10}sec. making measurements impossible. In order to reconcile this abnormally low value of g and also the departure of Leiden $P_f{}^2$ from Curie law shown by eqn (5) these workers assume a high degree of charge overlap, between the d-orbitals of Ti^{3+} and s and p orbitals of the surrounding water-oxygens, represented by a factor $K = 0.7$ and find that $\Delta \approx 30$ cm^{-1}. On the other hand, the paramagnetic absorption measurements at 90°K and 2°K give relaxation times $\sim 10^{-9}$ and $\sim 10^{-3}$ sec. respectively (de Haas *et al* 1938: Gorter *et al*, 1938), from which assuming the usual structural model of the alums (Beevers and Lipson, 1935) Van Vleck (1940) has shown that "Raman Process" is predominant for relaxation phenomenon in Ti^{3+} alum and Δ is ~ 1000 cm^{-1} and ~ 200 cm^{-1} at 90°K and 2°K respectively.

TABLE IX

Ti.Cs(SO$_4$)$_2$,12H$_2$O

T°K.	$P^2{}_f$ (Theo.)	$P^2{}_f$ (Expl.)
300	2.849	2.875
240	2.793	2.807
200	2.763	2.775
140	2.724	2.680
100	2.693	2.625

We have shown in an earlier note (1959) that starting with the molecular orbital theory, as applied by Van Vleck (1935), Stevens (1953) and others (Pryce *et al*, 1958) in many transition group salts, and assuming that the Ti^{3+} and O^{2-} charge overlap is anisotropic in character, Bleaney *et al*'s (1955) abnormal g value at low temperatures and our own $P_f{}^2$ value at high temperatures may be fitted into a scheme consistent with the picture given by the paramagnetic absorption as well as optical absorption measurements.

We find that in the liquid air range $g_\parallel = 1.919$, $g_\perp = 1.775$, $g = 1.823$ as against experimental value 1.880, and $\Delta = 800$ cm^{-1}, $k_\parallel = 0.800$, $k_\perp = 0.580$, (anisotropic overlap factors). $\dfrac{3k}{N\beta^2}$. $K_c = 15.3 \times 10^{-4}$ as against experimental value 6.6×10^{-4}, give fairly good fit with the experimental $P_f{}^2$ values (Table IX), while any value of $\Delta = 200$ cm^{-1} to 30 cm^{-1} may be fitted with the resonance g values, in liquid helium

range, other parameters remaining about the same. The fitting is not improved much by readjusting the parameters within reasonable limits. The whole expla - nation of the magnetic behaviour thus lies in the fact that Δ decreases rather quickly from below 100°K, owing to decrease in the spin lattice interaction. But the consequent curvature of the $P_f{}^2$ curve is to a considerable extent balanced by the variation of the moment caused by thermal depopulation of the upper orbital levels as the temperature falls, so that the $P_f{}^2$ curve is apparently straight except perhaps much below liquid air range. These variations, though much smaller in the liquid air range, influence the observed slope of the line as also its intercept

on $P_f{}^2$ axis and makes them different from the theoretical values given by $\dfrac{3k}{N\beta^2}$. K,

and g respectively. These are also the reasons why there is a small persistent deviation of the theoretical and experimental $P_f{}^2$ values Whether this is a purely thermal expansion effect or due to a change in crystal phase cannot be ascertained for the lack of suitable data

Measurements below liquid air temperatures are in progress in order to verify all the details of the theory which have been communicated in a separate paper.

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