

Lawrence Berkeley National Laboratory

Recent Work

Title

ELECTRONIC ENERGY LEVELS AND CRYSTAL QUANTUM STATS OF Tm (IV)

Permalink

<https://escholarship.org/uc/item/26s2b309>

Authors

Gruber, John B.
Conway, John G.

Publication Date

1959-08-01

UNIVERSITY OF
CALIFORNIA
Ernest O. Lawrence
Radiation
Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-8839

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

ELECTRONIC ENERGY LEVELS AND CRYSTAL QUANTUM STATES OF Tm (IV)

John B. Gruber and John G. Conway

August 1959

Printed for the U. S. Atomic Energy Commission

ELECTRONIC ENERGY LEVELS AND CRYSTAL QUANTUM STATES OF Tm (IV)

John B. Gruber and John G. Conway

Lawrence Radiation Laboratory
University of California
Berkeley, California

August 1959

ABSTRACT

To date limited agreement has been obtained between theory and experiment for $4f \rightarrow 4f$ transitions for Tm (IV) ($4f^{12}$). It is clear from the considerations that have appeared so far in the literature that intermediate coupling is important in the case of Tm (IV). Solutions of the intermediate field equations yield $\zeta_{4f} = 2700 \text{ cm}^{-1}$, $F_2 = 450 \text{ cm}^{-1}$, and $\chi = \left(\frac{\zeta}{F_2}\right) = 3$. Experimental agreement to $\pm 200 \text{ cm}^{-1}$ was obtained.

ELECTRONIC ENERGY LEVELS AND CRYSTAL QUANTUM STATES OF Tm (IV)

John B. Gruber and John G. Conway

Lawrence Radiation Laboratory
University of California
Berkeley, California

August 1959

INTRODUCTION

Experimental investigations together with the theoretical considerations of Van Vleck¹ and Bethe² indicate that the sharp absorption lines of the rare-earth ions in the visible and near-infrared spectra are due to $4f \rightarrow 4f$ transitions. The case of Tm IV (Tm⁺³ ion) should yield to complete theoretical and experimental treatment, since it is a relatively simple problem of 12 f electrons. To date there have been many papers dealing with the absorption spectrum of Tm IV.³⁻⁹ Spedding has made the intermediate calculations for Tm IV using the ratios of F_4/F_2 and F_6/F_2 as derived from La II.⁶ The disagreement between Spedding's calculated and observed values averages about 1500 cm^{-1} . Jørgensen, who has made similar calculations, disagrees with Spedding on the assignments of the 3F_2 , 1I_6 , and 3P_2 levels.⁷ It would seem reasonable that better agreement should exist, particularly since very good agreement between theory and experiment has been obtained for Pr IV.¹⁰⁻¹³

A. GENERAL THEORY

The electronic configuration of Tm IV in the ground state is sometimes written as [Xe core] $4f^{12}$ where there are essentially two "holes" in the $4f$ shell. It is easily seen that Tm IV spectroscopically is quite similar to Pr IV, which has only two electrons in the $4f$ shell. According to the Pauli equivalence theorem, both ions should have the same number of electronic states. The only difference, as described by Hund's rules, would be that the multiplets are inverted.

Following the coupling scheme of Russell and Saunders, one may couple 12 equivalent f electrons to obtain

$$^1S^1P^1D^1F^1G^1H^1I^1.$$

The calculations for pure electrostatic interactions for Tm IV (f^{12}) are the same as for Pr IV (f^2). In an earlier paper¹⁴ the authors have developed in step-wise form the theory for the electronic energy levels of Tm IV in the intermediate coupling case,¹⁴ following the methods outlined by Condon and Shortley,¹⁵ and Spedding.⁶ The electrostatic results are given in Table I. In order to complete such calculations, it is necessary to consider which radial-wave equations should be put into the Slater integrals, F_k . The $4f$ hydrogenic wave functions will not describe very satisfactorily the f electrons in the Tm ion. A self-consistent field approximation would be necessary in order to obtain better radial functions. However, the ratio of F_k integrals is reasonably insensitive to the choice of the actual radial distribution function. One of the members of our group (John D. Axe) has calculated F_4/F_2 and F_6/F_2 ratios for the unlikely "square" radial distribution of $4f$ electrons and has obtained values that are not far from those obtained by Elliott, Judd, and Runciman¹⁶ for a hydrogenic distribution. We have calculated the ratios, F_4/F_2 and F_6/F_2 , using hydrogenic wave functions by straight integration methods and have obtained values identical with those of Judd.¹⁷ When the electrostatic equations in terms of F_2 were normalized to 3H as the ground state, the results were found to be in complete agreement with those obtained by Elliott, Judd, and Runciman.¹⁶

It has been found for many of the +3 rare-earth ions that intermediate coupling is important. Qualitatively the L-S coupling scheme may predict the proper order of levels from the ground state in some cases where one is not too far out into intermediate coupling. In the case of Tm IV, certain levels such as the 1G_4 and 3F_2 are greatly effected by other levels of the same j value. In the crystal lattice, crystal quantum levels having the same quantum numbers or levels related to one another by selection rules will also be affected to a lesser extent. It is therefore necessary to introduce the spin-orbit interaction term (ζ) into the secular equations. The addition of the crystal-field interaction to the secular equations will be considered in a later paper.

Spedding has given the secular equations for f^2 .⁶ For the f^{12} configuration, one need only change the sign in front of each ζ value.¹⁵ The authors divided each term and ζ value in Spedding's equation by F_2 and used the variable $\chi = \zeta/F_2$. The secular equations may be solved for energy/ F_2 as a

Table I

Pure Electrostatic Energy Levels - f^{12} Configuration			
Level	Electrostatic equations in terms of Slater integrals	Electrostatic equations in terms of F_2 (a)	Energy levels normalized to $3_H = 0$
3_H	$F_0 - 25 F_2 - 51 F_4 - 13 F_6$	$F_0 - 32.3 F_2$	$0.00 F_2$
3_F	$F_0 - 10 F_2 - 33 F_4 - 286 F_6$	$F_0 - 18.9 F_2$	$13.4 F_2$
1_G	$F_0 - 30 F_2 + 97 F_4 + 78 F_6$	$F_0 - 15.5 F_2$	$16.8 F_2$
1_D	$F_0 + 19 F_2 - 99 F_4 + 715 F_6$	$F_0 + 16.3 F_2$	$48.4 F_2$
1_I	$F_0 + 25 F_2 + 9 F_4 + F_6$	$F_0 + 26.3 F_2$	$58.6 F_2$
3_P	$F_0 + 45 F_2 + 33 F_4 - 1287 F_6$	$F_0 + 30.3 F_2$	$62.6 F_2$
1_S	$F_0 + 60 F_2 + 198 F_4 + 1716 F_6$	$F_0 + 113.2 F_2$	$145.5 F_2$

(a) $F_4 = 0.138 F_2$, and $F_6 = 0.0151 F_2$.

function of χ . Since all except the three-by-three equations were solved by hand, it is possible to give complete analytical expressions (see Table II). The values for the three-by-three equations were obtained from an IBM-650 program. The results of the calculations appear in Fig. 1.

B. EXPERIMENTAL STUDIES

Spectrographic Equipment

The spectra were taken on a Wadsworth spectrograph. Two gratings were used in this instrument -- one with 30,000 lines-per-inch and another with 15,000 lines-per-inch -- giving dispersions of 2.46 Å per mm and 5.25 Å per mm.

The light sources employed were an air-cooled high-pressure mercury lamp (BH6) and a commercially available Kistiakowsky-type hydrogen discharge lamp.¹⁸ Quartz and pyrex dewars were used. Three types of polarizers were employed -- a Nicol, an Ahrein with ultraviolet-transmitting cement, and a Wollaston. Iron and mercury lines served as wavelength references. The plates were measured on a precision screw-type comparator.

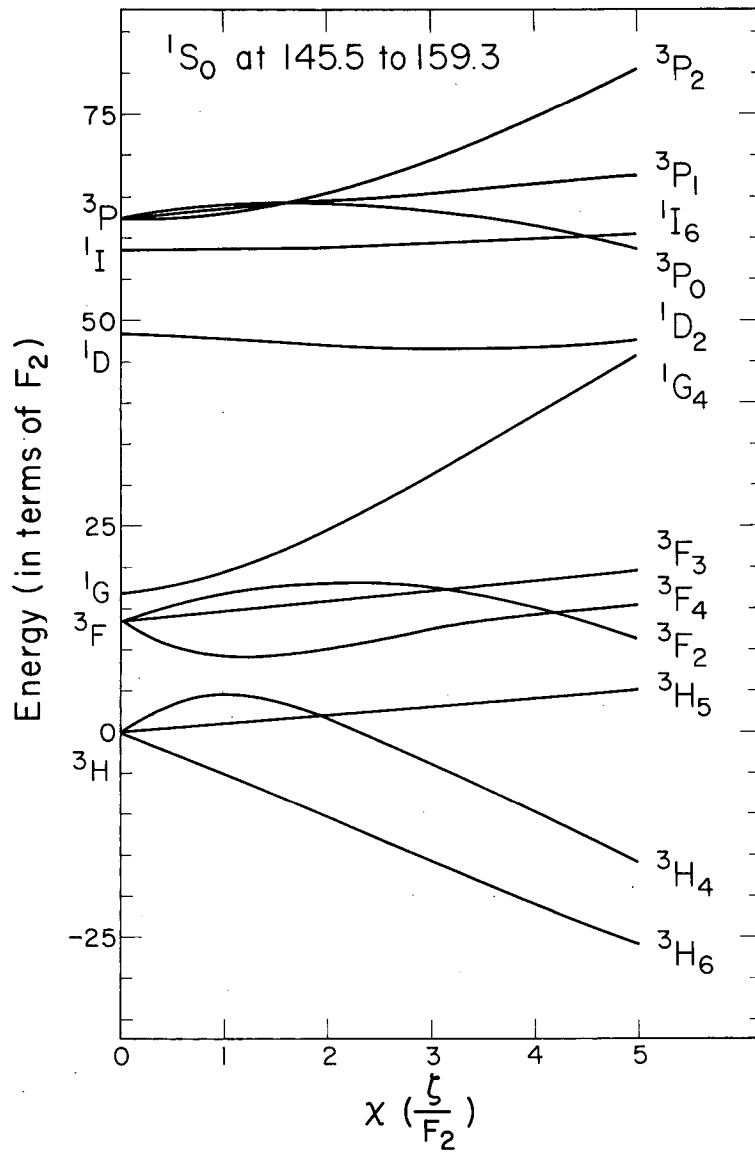
Crystals

The spectra of three crystals have been observed: $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$, $\text{TmCl}_3 \cdot 6 \text{H}_2\text{O}$, and TmCl_3 in LaCl_3 . The ethylsulfate was prepared by mixing stoichiometric amounts of thulium sulfate and barium ethylsulfate. After the solutions were centrifuged to remove the BaSO_4 , they were allowed to evaporate slowly at room temperature.

The hydrated chloride was grown by slow evaporation of a 6.0 N HCl solution. The TmCl_3 in anhydrous LaCl_3 crystal was prepared by sublimation of the mixed chlorides in vacuum. The purified mixture was melted into quartz crystal-growing tubes, sealed under vacuum, and slowly lowered through a furnace.¹⁹ X-ray analysis of several of these crystals showed that the crystal would remain predominantly hexagonal when as much as 10% TmCl_3 could be incorporated into the LaCl_3 matrix. The crystal structure of TmCl_3 is tetragonal and the compositions above 10% did not give a single crystal. The Tm^{+3} in

Table II

Analytical Expressions for $E/F_2 = f(X)$	
Levels	$E/F_2 = f(X)$
3H_5	X
3F_3	$13.4 + X$
3P_1	$62.5 + X$
1S_0	$104 + X + 1/2\sqrt{196X^2 - 332X + 6824}$
3P_0	$104 + X - 1/2\sqrt{196X^2 - 332X + 6824}$
1I_6	$29.3 - 2.5X + 1/2\sqrt{49X^2 + 586X + 3440}$
3H_6	$29.3 - 2.5X - 1/2\sqrt{49X^2 + 586X + 3440}$



MU-17077

Fig. 1. Energy-level diagram for Tm IV in intermediate coupling. The 1S_0 varies from 145.5 $X = 0$ to 159.3 for $X = 5$.

LaCl_3 crystals showed strong continuous absorption below 3000 Å, completely masking the ^3P levels. The other crystals, however, were transparent in this region. Jørgensen notes a similar opacity for Tm^{+3} in HClO_4 and attributes this to f-d transitions.²⁰

$^3\text{H}_4$ and $^3\text{H}_5$ levels

The spectrum of 203.0 mg of anhydrous TmCl_3 in 10.0 ml of 0.10 M DCl in > 98.5% D_2O was measured between 1 and 2 μ on a recording Cary 14 spectrophotometer. An acid solution was necessary in order to prevent the hydrolysis of the Tm^{+3} ion. Ordinary-water absorption bands appear around 1.4 μ and 1.8 μ , making it difficult to employ H_2O as a solvent for absorption studies in the region from 1 to 2 μ . In the case of D_2O , the isotope shift is far enough to the red (to about 2.2 μ) to make D_2O a useful solvent for studies in the region where the $^3\text{H}_5$ and $^3\text{H}_4$ levels are expected. Two peaks (1.175 μ and 1.206 μ) and one shoulder (1.217 μ) were found for the $^3\text{H}_5$, and one peak (1.668 μ) and one shoulder (1.715 μ) were found for the $^3\text{H}_4$ (see Fig. 4). The theoretical values calculated for $^3\text{H}_5$ and $^3\text{H}_4$ are 8520 cm^{-1} and 5320 cm^{-1} , which may be compared with the mean experimental values 8,390 cm^{-1} and 5,900 cm^{-1} , respectively.

C. RESULTS

Johnsen has identified the 0 and ± 1 crystal quantum levels of the $^3\text{H}_6$ ground-state multiplet and the upper multiplets of $^3\text{F}_{2,3,4}$ and $^1\text{G}_4$. Our work confirms these ground-state assignments for transitions to the ultraviolet multiplets of $^3\text{P}_{0,1,2}$ and $^1\text{D}_2$.

The symmetry of the Tm^{+3} ion in the ethylsulfate crystal is C_{3h} as given by Johnsen⁹ and Ketelaar.²¹ The crystal-quantum selection rules for this symmetry have been discussed previously.¹⁰ The ultraviolet multiplets appear sharper than the $^3\text{F}_{2,3,4}$ group. As a result, one observes transitions from additional ground-state crystal quantum levels to excited states. At 77°K, 194°K, and 273°K, the 3 and ± 2 crystal quantum levels of the $^3\text{H}_6$ are populated. Transitions from these levels appear more intense as one goes from N_2 temperature

(77°K) to CO₂ temperature (194°K). From the 3 and ±2 crystal quantum states the position of the $\mu = 0$ level in 1G_4 was determined.

Figure 2 is the energy level diagrams for the 3P_0 , 3P_1 , 3P_2 multiplets; Fig. 3 is the diagram for the 1D_2 and 1G_4 . The $^3F_{2,3,4}$ lines are too broad to permit an extension of the analysis. Polarized lines are observed between the 3P_0 and 3P_1 multiplets which are not due to impurities. These lines are probably due to the 1I_6 multiplet. The lines are faint and difficult to distinguish from vibrational lines of the 3P_0 and 3P_1 . As many as 10 vibrational lines per multiplet appear to the violet of the 3P_2 and 1D_2 .

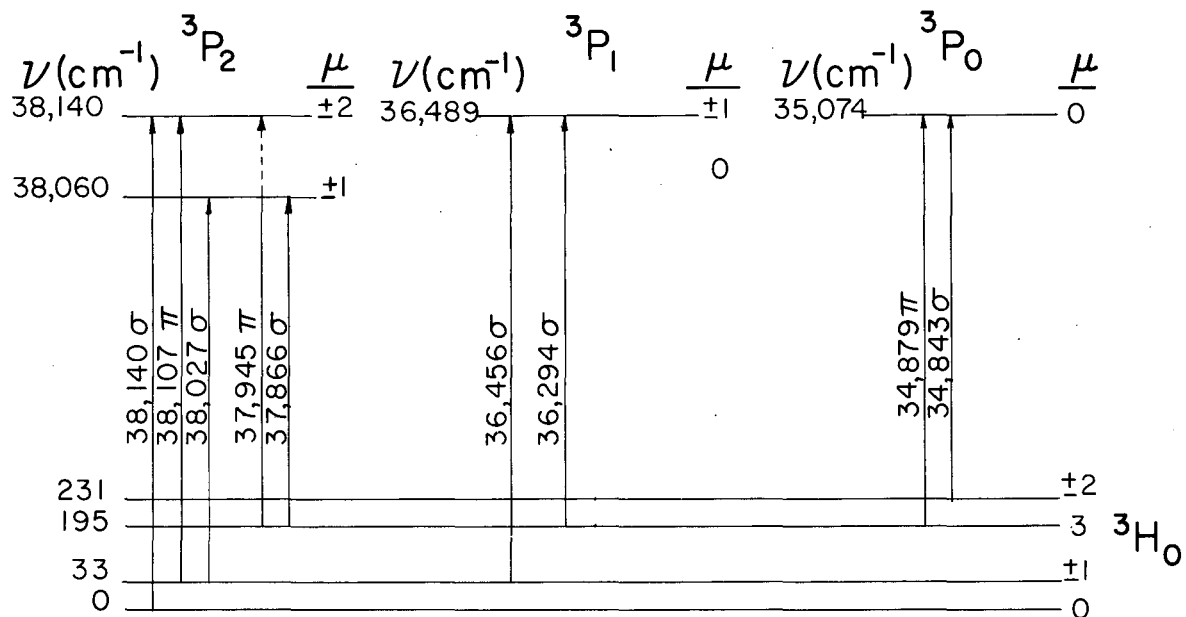
Holmium and erbium ethylsulfate crystals were prepared and polarization spectra taken to determine if these impurities appeared in the Tm spectra. No lines of Er or Ho were observed in the Tm spectra taken.

The experimental data, including Johnsen's were fitted to Fig. 1 and a good fit was obtained for $\chi = 3$, $F_2 = 450 \text{ cm}^{-1}$, and $\zeta_{4f} = 2700 \text{ cm}^{-1}$. The spin-orbit interaction term, ζ , as used in Fig. 1 and in Spedding's work is one half this value. From these parameters the calculated positions were obtained and are tabulated in Table III. Table IV includes the measured wave lengths, their intensity and polarization, and the crystal quantum transitions for the ethylsulfate.

Table V gives the wave length and intensity for the lines appearing in the spectrum of $\text{TmCl}_3 \cdot 6 \text{ H}_2\text{O}$. The similarity in the spectra of the hydrated chloride and the ethylsulfate allows us to assign the multiplets, but the crystal quantum assignment cannot be made because the point symmetry of the Tm^{+3} ion is not known. Table VI gives the wave lengths and intensities for the TmCl_3 in LaCl_3 . The only multiplets seen are the 1D_2 and 1G_4 . The continuous absorption in the ultraviolet masks the 3P levels, and the 3F levels are too weak for good measurements.

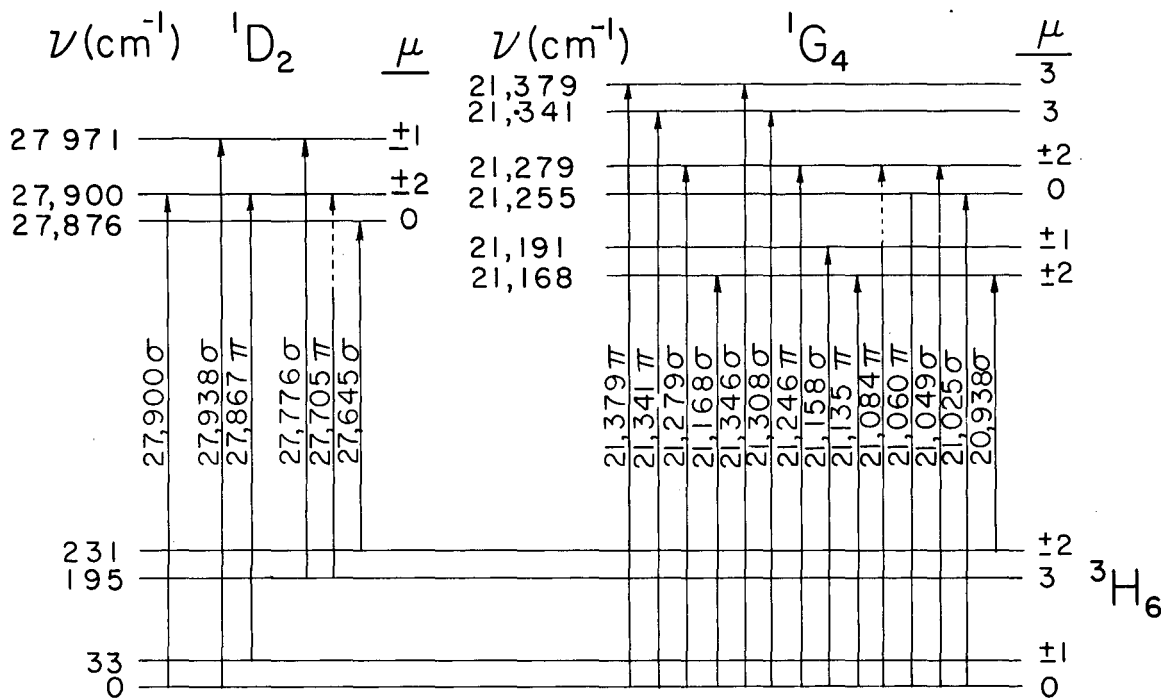
DISCUSSION OF ERRORS

The spectral lines of the $^3P_{0,1,2}$ and 1D_2 groups are measured to $\pm 0.1 \text{ \AA}$; the 1G_4 lines are measured to $\pm 0.2 \text{ \AA}$. It is not possible to measure the positions of lines more accurately than this because line widths are considerable in many cases. In some cases the calculated energy levels (Table III)



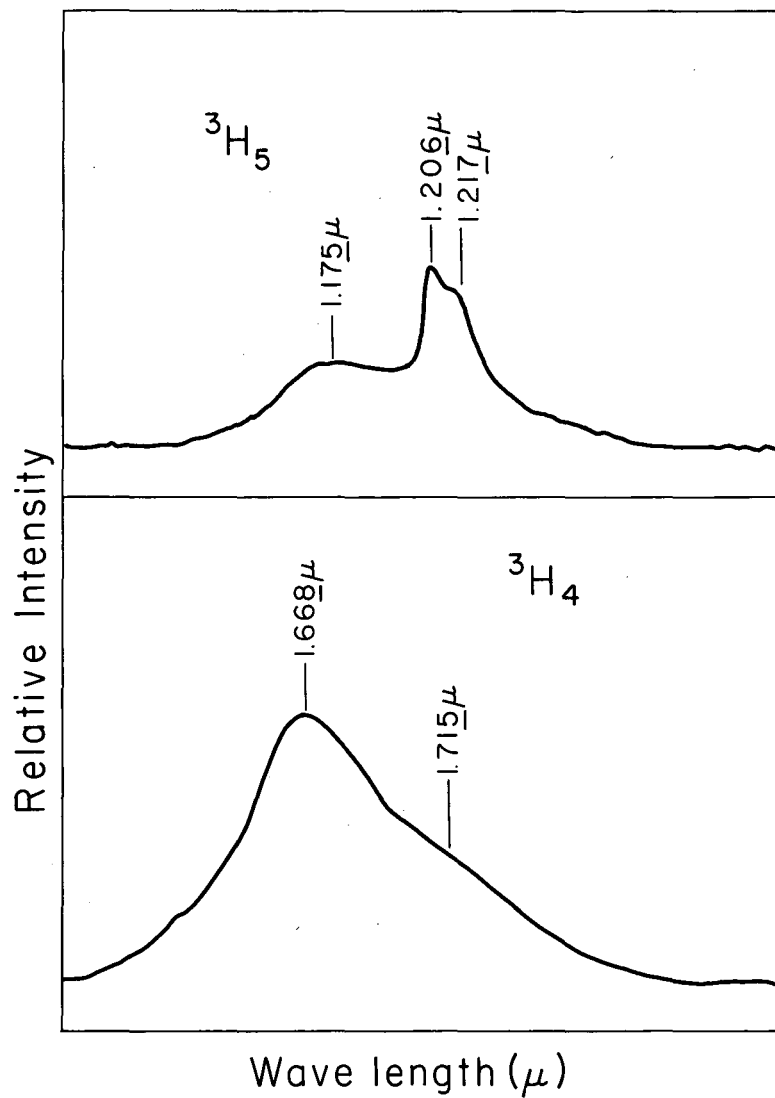
MU-17817

Fig. 2. Transitions from ground states to $3\text{P}_{2,1,0}$ of $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. Spectra of single crystal at 77°K ; electromagnetic radiation transmitted perpendicular to unique Z axis of crystal. Forbidden transition $3 \rightarrow \pm 2$ observed in 3P_2 group.



MU-17818

Fig. 3. Transitions from ground states to 1D_2 and 1G_4 of $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. Spectra of single crystal at 77°K; electromagnetic radiation transmitted perpendicular to unique Z axis of crystal. Forbidden transition 3 → ± 2 observed in 1D_2 and 1G_4 groups.



MU-17819

Fig. 4. The 3H_5 and 3H_4 multiplets in D_2O .

Table III

Comparison of Theory with Experiment		
Levels	Values for energy levels (cm^{-1})	
	Theory	Experiment
$^3\text{H}_6$	100	105
$^3\text{H}_4$	5320	5900
$^3\text{H}_5$	8520	8390
$^3\text{F}_4$	12730	12673 ⁹
$^3\text{F}_3$	14550	14446 ⁹
$^3\text{F}_2$	15000	15092 ⁹
$^1\text{G}_4$	21120	21275 ⁹
$^1\text{D}_2$	28090	27926
$^1\text{I}_6$	33850	--
$^3\text{P}_0$	35600	35074
$^3\text{P}_1$	36640	36443
$^3\text{P}_2$	38440	38100
$^1\text{S}_0$	75030	--

Table IV

Spectra, polarization, and crystal quantum transitions of $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$													
Term assignment	Crystal quantum trans.	Wavelengths, intensities, and polarization								Wave numbers (in vacuum)			
		77°K (in air)	I.	P.	194°K (in air)	I.	P.	273°K (in air)	I.	P.	77°K	194°K	273°K
$^3\text{P}_2$	0 → ±2	2621.1	8 ^b	σ	2621.7	6 ^c	σ				38,140	38,132	
	±1 → ±2	2623.4	8 ^a	π	2624.0	6 ^b	π				38,107	38,099	
	±1 → ±1	2629.0	4 ^b	σ	2629.3	6 ^b	σ	2629.6	4 ^d	σ	38,027	38,022	38,017
	3 → ±2	2634.6	4 ^b	π	2635.1	6 ^b	π	2635.4	5 ^d	π	37,945	37,938	37,934
	3 → ±1	2640.0	1 ^a	σ	2639.8	6 ^b	σ	2640.1	6 ^d	σ	37,866	37,870	37,866
$^3\text{P}_1$	±1 → ±1	2742.2	8 ^a	σ	2743.1	5 ^b	σ	2743.9	4 ^c	σ	36,456	36,444	36,434
	3 → ±1,0	2754.4	3 ^a	σ	2755.5	5 ^b	σ				36,294	36,280	
$^3\text{P}_0$	3 → 0	2866.2	6 ^c	π	2867.6	5 ^c	π	2867.5	5 ^d	π	34,879	34,863	34,862
	±2 → 0	2869.1	6 ^c	σ	2870.4	5 ^d	σ	2870.6	5 ^d	σ	34,843	34,828	34,825
$^1\text{D}_2$	±1 → ±1	3578.3	9 ^d	σ	3578.9	6 ^d	σ	3579.0	6 ^d	σ	27,938	27,934	27,933
	0 → ±2	3583.2	9 ^d	σ							27,900		
	±1 → ±2	3587.4	9 ^c	π	3587.9	6 ^c	π	3589.7	4 ^d	π	27,867	27,864	27,850
	3 → ±1	3599.2	5 ^b	σ							27,776		
	3 → ±2	3608.6	4 ^b	π	3608.7	6 ^b	π	3608.4	8 ^b	π	27,705	27,704	27,705
	±2 → 0	3616.2	3 ^b	σ	3616.4	6 ^b	σ	3616.9	8 ^b	σ	27,645	27,644	27,640
$^1\text{G}_4$	0 → 3	4676.3	7 ^a	π							21,379		
	±1 → 3	4683.4	7 ^b	σ							21,346		
	0 → 3	4684.6	8 ^b	π	4685.0	5 ^c	π				21,341	21,339	
	±1 → 3	4691.8	6 ^d	σ							21,308		
	0 → ±2	4698.2	5 ^d	σ	4698.0	3 ^d	σ				21,279	21,277	
	±1 → ±2	4705.5	6 ^a	π	4708.7	3 ^d	π				21,246	21,231	
	0 → ±2	4723.0	6 ^b	σ							21,168		
	±1 → ±1	4725.0	6 ^b	σ	4724.6	5 ^d	σ				21,158	21,160	
	±1 → ±2	4730.2	6 ^b	π							21,135		
	3 → ±2	4741.7	3 ^a	π	4745.2	5 ^b	π				21,084	21,068	
	3 → 0	4747.1	3 ^b	π							21,060		
	±2 → ±2	4749.3	2 ^c	σ							21,049		
	±2 → 0	4754.8	2 ^b	σ							21,025		
±2 → ±2	4774.5	1 ^a	σ							20,938			

^aLine width; 0.1 A to 0.5 A.

^bLine width; 0.5 A to 1.0 A.

^cLine width; 1.0 A to 2.0 A.

^dLine width; 2.0 to 4.0 A.

Table IV.

Table V

Spectra of $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$							
Term assignment	$\lambda(\text{Å})$ 77°K (in air)	$\lambda(\text{cm}^{-1})$ 77°K (in vac.)	I	Term assignment	$\lambda(\text{Å})$ 77°K (in air)	$\lambda(\text{cm}^{-1})$ 77°K (in vac.)	I
$^3\text{P}_2$	2590.9	38,585	8 ^c	$^1\text{G}_4$	4629.2	21,596	8 ^b
	2602.7	38,410	9 ^d		4645.9	21,518	6 ^b
	2611.5	38,281	8 ^c		4649.5	21,502	9 ^d
	2613.7	38,249	5 ^b		4680.5	21,359	3 ^c
	2622.0	38,127	4 ^b		4709.8	21,226	4 ^b
	2626.2	38,066	4		4716.5	21,196	2 ^c
$^3\text{F}_1$	2734.3	36,562	4 ^b	$^3\text{F}_2^e$	4719.8	21,181	1
	2743.5	36,439	6 ^a		6567	15,220	5 ^d
	2747.1	36,391	6 ^a		6586	15,180	5 ^c
$^3\text{P}_0$	2879.3	34,721	5 ^c	$^3\text{F}_3$	7058	14,160	6 ^c
$^1\text{D}_2$	3552.7 3556.5 3560.0 3569.3 3573.2 3579.1	28,140 28,110 28,082 28,008 27,978 27,932	6 ^b 9 ^c 9 ^c 6 ^a 6 ^a 3		$^3\text{F}_4$	7064	14,150
				7104		14,070	7 ^b
				7116		14,050	7 ^b
				7140		14,020	4 ^b
				7147		13,990	3 ^c
				7159		13,970	3 ^c
				7709		12,970	3 ^d
				7781		12,850	3 ^d
7793	12,830	2					
7828	12,770	2					
7910	12,640	2					
7922	12,620	1					

^aLine width; 0.1 Å to 0.3 Å.
^bLine width; 0.3 Å to 0.8 Å.
^cLine width; 0.8 Å to 1.5 Å.
^dBroad complex of unresolved vibrational and electronic lines.
^e $\text{F}_{2,3,4}$ measured to nearest 1 Å.

Table VI

Spectra and Polarization of Anhydrous TmCl_3 in LaCl_3				
Term assignment	λ (Å) 77°K (in air)	λ (cm^{-1}) 77°K (in vac.)	P	I
1D_2	3609.3	27,689	σ	5 ^b
	3614.2	27,661	σ	5 ^b
	3618.2	27,630	π	4 ^a
	3621.6	27,604	σ	3 ^c
	3626.3	27,569	σ	3 ^c
	3630.9	27,534	π	4 ^b
1G_4	4708.0	21,234	π	4 ^b
	4714.1	21,207	π	4 ^b
	4733.0	21,122	σ	2 ^c
	4636.1	21,109	σ	2 ^c
	4740.6	21,088	π	3 ^a
	4743.7	21,075	π	3 ^a
	4752.0	21,038	σ	1 ^b
^a Line width less than 0.1 Å. ^b Line width; 0.1 Å to 0.5 Å. ^c Line width; 0.5 Å to 1.5 Å.				

differ from the experimental value by as much as 200 cm^{-1} . This lack of agreement is due to (a) the theoretical calculations for the field-free ion are good only to 100 cm^{-1} , (b) the perturbing influence of the neighboring ligands in the crystal will shift the centers of the stark-split j-levels from the field-free j-level calculations, and (c) the center of gravity of the crystal-field split levels cannot be known without a detailed calculation of the crystal-field splitting.

ACKNOWLEDGMENT

We wish to acknowledge the help of B. B. Cunningham, R. D. McLaughlin, K. S. Pitzer, and J. D. Axe. This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. J. H. Van Vleck, J. Phys. Chem. 41, 67 (1937).
2. H. Bethe, Z. Physik 60, 218 (1930).
3. W. Prandtl and K. Scheiner, Z. Anorg. u. allgen. Chem. 220, 107 (1934).
4. H. Gabrecht, Ann. Physik, Ser. 5, 31, 600 (1935).
5. H. Bethe and F. H. Spedding, Phys. Rev. 52, 545 (1937).
6. F. H. Spedding, Phys. Rev. 58, 255 (1940).
7. C. K. Jørgensen, Acta. Chem. Scand. 9, 540 (1955).
8. D. C. Stewart, Absorption Spectra of Lanthanide and Actinide Rare Earths. III. The Heavier Lanthanide Elements in Aqueous Perchloric Acid Solution, Argonne National Laboratory Report, ANL-5624 (Oct. 1956).
9. U. Johnsen, Z. Physik 152, 454 (1958).
10. Sayre, Sancier, and Freed, J. Chem. Phys. 23, 2060 (1955); ibid. 29, 242 (1958).
11. B. R. Judd, Proc. Roy. Soc. (London) A241, 414 (1957).
12. G. H. Dieke and R. Sarup, J. Chem. Phys. 29, 741 (1958).
13. W. A. Ranciman and B. G. Wybourn, University of Canterbury, Christ Church, New Zealand, private communication (to be published) 1959.
14. J. B. Gruber and J. G. Conway, Electronic Energy for Tm IV, UCRL-8666, March 1959.
15. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, (University Press, Cambridge, 1953).

16. Elliott, Judd, and Runciman, Proc. Roy. Soc. (London) A240, 509 (1957).
17. B. R. Judd, Proc. Roy. Soc. (London) A228, 123 (1955).
18. G. B. Kistiakowsky, Rev. Sci. Instr. 2, 549 (1931).
19. Gruen, Conway, and McLaughlin, J. Chem. Phys. 25, 1102 (1956).
20. C. K. Jørgensen, Acta Chemica Scandinavica 9, 540 (1955).
21. J. A. A. Ketelaar, Physica (Haag) 4, 619 (1937).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.