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Analysis of the ground configuration of Tm^{3+} in $CaWO_4$

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The energy levels of the ^1D, ^1G, ^3F, and ^3H terms of Tm^{3+} in $CaWO_4$ were established by an analysis of the absorption and fluorescence spectra. The absorption lines were used to establish most of the energy levels recorded over the wavelength range from 2.5 μm to the band edge at about 0.3 μm with crystals at temperatures from 2 to 300°K. Transitions to the levels of the $^3H_6$ ground multiplet were observed in fluorescence. An energy-level scheme was constructed by using electric dipole selection rules and by the aid of theoretical calculations. The ground state was identified as a singlet Γ_2; this is consistent with no electron paramagnetic resonance at 9 or 36 GHz, as reported by Kirton. The 1.911- and 1.916-μm laser lines reported by Johnson appear in fluorescence as transitions from a $^3F_4$ Γ_1 at 5594 cm^{-1} to $\Gamma_{3,4}$ and Γ_2 levels at 370 and 384 cm^{-1}. This is well above the energy position of 325 cm^{-1} for the terminal level reported by Johnson. The calculations were made by diagonalizing a Hamiltonian that describes the free ion and the crystal field in a basis of states spanning the entrie $4f^{12}$ configuration. In a least-squares calculation, an rms deviation of 6.7 cm^{-1} between the theoretical and experimental energy levels was obtained. Calculated energy levels are given for the entire Tm^{3+} ground configuration along with $g_\parallel$ factors for the doublet $\Gamma_{3,4}$ levels.

I. INTRODUCTION

The optical spectrum of trivalent thulium in single-crystal calcium tungstate has been examined. An analysis of these data was made by diagonalizing a Hamiltonian[1] describing the free-ion interactions and the crystal-field interaction in a basis of states spanning the entire $4f^{12}$ electronic configuration. Emphasis was placed on determining the parameters that describe the free-ion energy levels and the crystal-field parameters, which give the effect of the crystal on the free-ion energy levels. The free-ion parameters were then compared to free-ion parameters for Tm^{3+}-doped YVO_4 in a calculation using the same Hamiltonian.[1] Small differences between these parameters may be due to the difference in the dielectric constants of the two materials as described by Morrison *et al.*[2] In addition, these crystal-field parameters B_{kq} were shown to compare favorably with B_{kq} values reported[3-8] for other rare-earth ions in $CaWO_4$. An effective spin-orbit Hamiltonian[9] (ESOH) was used to describe the free-ion energy levels for these other rare earths.

Reasons for our interest in Tm^{3+}-doped $CaWO_4$ are the reported[10] laser actions of Tm^{3+}. Most of the energy levels of the $4f^{12}$ ground configuration, including those that take part in the laser action, have not previously been identified; and B_{kq} values obtained here can serve as a check on B_{kq} values obtained by interpolating from B_{kq} values reported for other rare earths[3-8] where the ESOH was used for the calculations.

The ESOH technique[9] is not useful for the analysis of Tm^{3+} since some of the low-lying terms are badly mixed by the spin-orbit interaction contrary to the ESOH assumption of nearly pure LS terms. Also, another widely used approach, the so-called operator-equivalent technique[11] which neglects J mixing, had been found to be poor for the analysis of Tm^{3+}, and perhaps for most other rare earths. In our earlier work,[1] it was noted that the effects of the Tm^{3+} free ion are not adequately described by the operator-equivalent method so that different sets of B_{kq} values consistent with different portions of the optical spectrum resulted. While term dependence of the B_{kq} is expected on a purely theoretical basis,[12] our results indicate that the term dependence of the crystal-field parameters is small.

II. THEORETICAL CONSIDERATIONS

In the method of analysis used here, one first describes the Tm^{3+} free-ion energy levels as completely as possible and then determines the effects of the crystal on these levels. The states of the free-ion Hamiltonian are labeled by the largest component of the wave function, and our labels for the $^3H_4$ and $^3F_4$ states do not correspond to those used by some authors since the spin-orbit interaction causes a large degree of mixing (ζ is large for Tm^{3+}). The free-ion Hamiltonian used is

$$H_{\text{free ion}} = \sum_i H_i \, , \tag{1}$$

where, in the notation of Judd,[13] H_1 is the Coulomb interaction, H_2 is the spin-orbit interaction, H_6 is the spin-spin interaction, H_8 is the spin-other-orbit interaction, H_9 is the orbit-orbit interaction, and H_{10} is an effective Hamiltonian representing configuration interaction, as given by Rajnak and Wybourne.[14]

The parameters contained in the above Hamiltonian are the Slater parameters F_2, F_4, and F_6; the

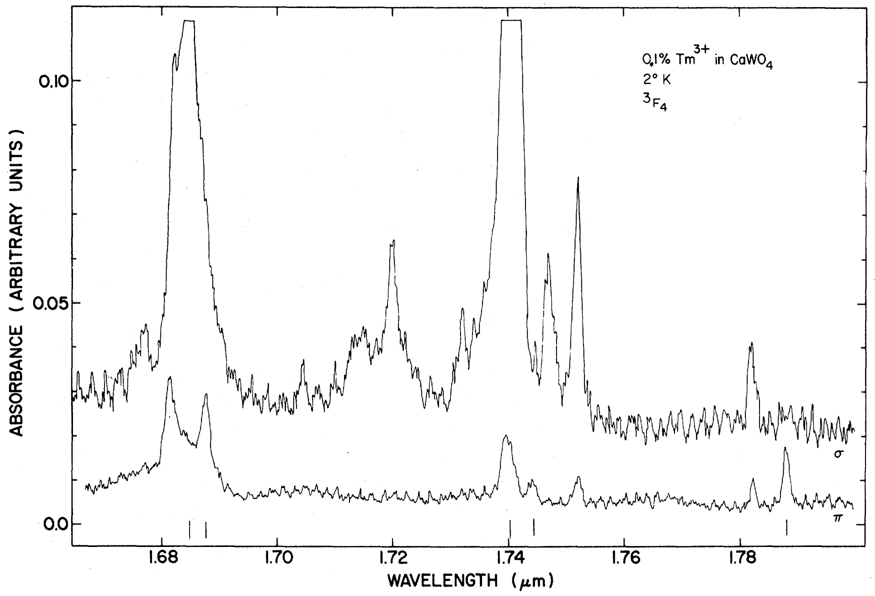

FIG. 1. Absorption transitions from the $^3H_6$ ground state to the $^3F_4$ energy levels for 0.1-at.% Tm^{3+} in $CaWO_4$. Data recorded with ir polarizers using a crystal immersed in liquid helium (at 2 °K).

TABLE I. Absorption lines of Tm^{3+} in $CaWO_4$ used to establish the energy levels of the $^3F_4$ multiplet.[a]

Line No.	Wavelength (μm)	Energy (cm^{-1})	Temperature (°K)	Relative intensity, polarization	S_4 symmetry property or other identification
1	1.6818	5946	2	22π, 30σ	
2	1.6845	5936	2	$>300\sigma$	$\Gamma_{3,4}$
3	1.6873	5927	2	20π	Γ_1
4	1.6916	5912	25	$>200\pi$	Line 2—24 cm^{-1}
5	1.6950	5900	25	165σ	Line 3—37 cm^{-1}, Γ_2 —26 cm^{-1}
6	1.7026	5873	25	π	Γ_2—53 cm^{-1}
7	1.7197	5815	2	30σ	
8	1.7285	5785	25	175σ	Γ_2—26 cm^{-1}
9	1.7405	5745	2	$>300\sigma$, 10π	$\Gamma_{3,4}$
10	1.7442	5733	2	5π	Γ_1
11	1.7479	5721	25	210σ	Line 9—24 cm^{-1}
12	1.7518	5708	2 25	50σ 140σ	Line 10—25 cm^{-1}
13	1.7557	5696	25	30π, 50σ	Line 9—49 cm^{-1}
14	1.7820	5612	2	6π, 20σ	
15	1.7849	5603	25	25σ	
16	1.7875	5594	2	13π	Γ_1
17	1.7962	5567	25	160σ	Line 16—27 cm^{-1}

[a] The wavelength, energy corresponding to the observed line, the temperature where first observed, relative intensity, and polarization are given. The identification of the corresponding energy level in S_4 notation, or other possible interpretation of the line, is also given.

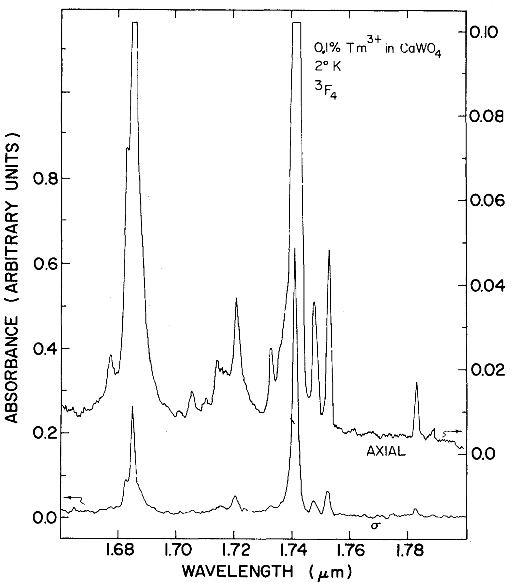

Fig. 2. Comparison of the axial and σ-polarized absorption spectra for 0.1-at.% Tm^{3+} in CaWO$_4$ at 2 °K in the wavelength region corresponding to ground state to $^3F_4$ transitions. The similarity of these spectra is consistent with the electric dipole selection rules. Different optical path lengths yield different intensities for the various absorptions. The axial spectrum therefore was recorded with a 0–0.2 absorbance unit slide wire (right-hand scale), and the σ spectrum was recorded with the 0–2 absorbance unit slide wire (left-hand scale).

spin-orbit parameter ζ; the Marvin integrals $M_0^{(0)}$, $M^{(0)}$, $M^{(2)}$, and $M^{(4)}$; and the interconfiguration mixing parameters α, β, and γ. The contact spin-spin interaction[15] has been included in H_6. The ratios of the Marvin integrals are assumed fixed at the values computed using interpolated Hartree-Fock wave functions[16] for Tm^{3+};

$$\begin{aligned} M^{(0)}/M_0^{(0)} &= 0.450\,053\ , \\ M^{(2)}/M_0^{(0)} &= 0.252\,685\ , \\ M^{(4)}/M_0^{(0)} &= 0.171\,668\ . \end{aligned} \tag{2}$$

As in the analysis[1] of Tm^{3+} in YVO$_4$, we shall set $\gamma = 0$ since the electrostatic interaction is overspecified without the $^1S_0$ multiplet and since γ has the least effect on the LS terms.

The crystal Hamiltonian is[17]

$$H_3 = \sum_{i,k,q} B_{kq}^{\dagger} C_{kq}(i)\ , \tag{3}$$

where C_{kq} is the spherical tensor of rank k and projection q, and the B_{kq} are the crystal-field parameters. The parameters B_{20}, B_{40}, B_{60}, B_{44}, Real B_{64}, and Imaginary B_{64} in (3) are the only nonzero B_{kq} entering the calculations because of the S_4 symmetry at the site of the thulium ion in the crystal and the choice of the coordinate system. That is, both B_{44} and B_{64} can be complex, but it simplifies the calculations to choose the coordinate system so that B_{44} is real and positive.

The Hamiltonian $H_{\text{free ion}} + H_3$ was diagonalized in a $|JMLS\rangle$ basis spanning the entire $4f^{12}$ configuration. The eigenstates thus obtained transform according to one of four irreducible representations[18] of the point group S_4, namely $\mathbf{\Gamma}_1$, $\mathbf{\Gamma}_2$, $\mathbf{\Gamma}_3$, and $\mathbf{\Gamma}_4$. The levels characterized by wave functions transforming as $\mathbf{\Gamma}_3$ are degenerate with those transforming as $\mathbf{\Gamma}_4$ and are designated $\mathbf{\Gamma}_{3,4}$.

The classification of the experimental energy levels according to group properties can be made from the recorded spectra by first determining the nature of the interaction governing these optical transitions. In the interaction matrix, states coupled by the electric dipole and magnetic dipole components of the radiation are usually the dominant terms. These components are identified by considering first that CaWO$_4$ has three mutually perpendicular axes; two are equivalent a axes and one is the unique c axis. When light is propagated along an a axis, the component of the electric or magnetic dipole operator parallel to the c axis

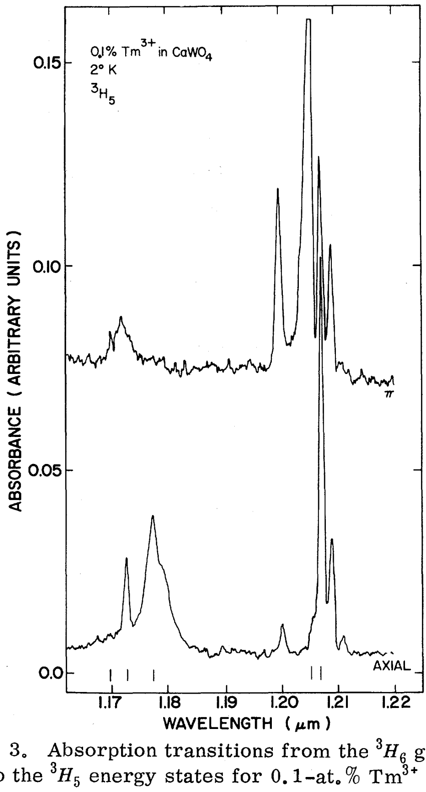

FIG. 3. Absorption transitions from the $^3H_6$ ground state to the $^3H_5$ energy states for 0.1-at.% Tm^{3+} in CaWO$_4$. Axial and π-polarized absorption lines were recorded at 2 °K. σ-spectrum recorded over this wavelength region is similar to the axial spectrum but is of less quality.

TABLE II. Absorption lines of Tm^{3+} in $CaWO_4$ used to establish the energy levels of the $^3H_5$ multiplet.[a]

Line No.	Wavelength (μm)	Energy (cm^{-1})	Temperature (°K)	Relative intensity, polarization	S_4 symmetry property or other identification
1	1.1696	8550	2	6π	Γ_1
2	1.1716	8535	2	11π	Γ_1
3	1.1722	8531	2	19σ	$\Gamma_{3,4}$
4	1.1759	8504	25	60π	Line 3—27 cm^{-1}
5	1.1766	8499	2	38σ	$\Gamma_{3,4}$
6	1.1798	8476	2	10σ	Line 3—55 cm^{-1}
7	1.1821	8460	25	15σ	(Γ_2—26 cm^{-1})
8	1.1838	8447	25	15σ	Line 5—52 cm^{-1}
8	1.1995	8337	2	43π	
10	1.2049	8299	2	250π	Γ_1
11	1.2066	8288	2	100σ, 50π	$\Gamma_{3,4}$
12	1.2087	8273	2 25	25π, 45σ 70π, 160σ	Line 10—26 cm^{-1}
13	1.2103	8262	25	200π, 100σ	Line 11—26 cm^{-1}
14	1.2117	8253	25	90σ	(Γ_2—26 cm^{-1})
15	1.2143	8235	25	30σ	Line 11—53 cm^{-1}

[a] The wavelength, energy corresponding to the observed line, the temperature where first observed, relative intensity, and polarization are given. The identification of the corresponding energy level in S_4 notation, or other possible interpretation of the line, is also given.

transforms as a Γ_2 or Γ_1, respectively, and that component of these operators perpendicular to the *c* axis transforms as a $\Gamma_{3,4}$. When the crystal is reoriented so that light is passed along the *c* axis, the electric and magnetic dipole operators transform as the Γ_3 (or Γ_4) irreducible representation. The spectrum recorded in this geometry is called the axial spectrum. The σ-polarized and π-polarized spectra are recorded where the electric vector is oriented perpendicular and parallel, respectively, to the *c* axis of the crystal and the light is propagated along an *a* axis. Using the transformation properties of the electric and magnetic dipole operators and the S_4 group multiplication table,[18] one is able to construct an energy-level scheme for the recorded data, and it is found that the transitions are consistent with the electric dipole operator.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The measurements were made using single crystals of $CaWO_4$ grown by the Czochralski method from melts containing 0.05-, 0.1-, or 0.5-at. % thulium with sodium added for charge compensation in the melt ratio of 4:1 Na:Tm. The same experimental procedures were used as reported[5–7] earlier for other rare earths in recording these data at crystal temperatures estimated to be 2, 25, 85, and 300 °K. These estimated temperatures were obtained by placing a calibrated germanium resistance thermometer in the same configuration as the crystal.

Most of the absorption measurements were made with the crystals at temperatures from 25 to 300 °K over the wavelength range from 0.3 to 2.5 μm with a Cary 14 spectrophotometer using either a 0–2 or 0–0.2 absorbance unit slide wire. The relative intensities of the lines corresponding to transitions to the various multiplets in this wavelength range are similar to those published by Johnson[19] using a 0.8-at. % crystal at 77 °K. Also, earlier measurements made at 2 °K, in the attempt to identify what was considered to be the ^3H energy levels for analysis using the ESOH, supplemented these data of the $^1G_4$, $^3H_5$, and $^3F_4$ energy levels. At this lower temperature only the ground state should be populated appreciably. Hence, transitions from the energy levels above the ground state to the states of these *J* multiplets, which cannot always be definitely separated from ground-state transitions, are frozen out. Though this 2 °K data aided the analysis, parts of the

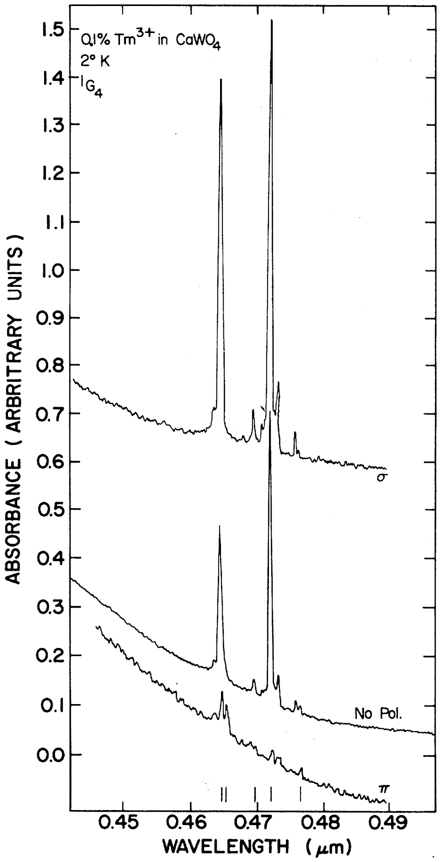

FIG. 4. Absorption transitions from the $^3H_6$ ground to the $^1G_4$ energy levels for 0.1-at.% Tm^{3+} in $CaWO_4$ at 2 °K. Data were recorded with film polarizers using the crystal at 2 °K.

spectra were still complicated by extra lines. Polarizers and various crystal orientations were tried for the purpose of identifying the transitions by their transformation properties. Attention was paid to the polarization characteristics[5] of the Cary 14 and to the slight difference in the instrument's response to light polarized parallel to, rather than perpendicular to, the entrance slit. The crystal orientations were sometimes hard to determine visually, but no line-shape differences were noted when small changes were made in crystal orientation from the best estimate of the proper orientation. Also, some line broadening was observed using the crystal at 85 °K, but no significant differences from the lower temperature data were established for wavelength positions. In the spectra using heavier concentrations of Tm^{3+} in the crystals some changes in the widths of the lines were found and extra lines were seen; however, no significant changes in the positions of the peaks of the absorption lines were found.

The fluorescence lines served mostly to verify the identifications made of the absorption transitions. Fluorescence from the $^3F_4$ multiplet (denoted $^3H_4$ elsewhere[19]) to the $^3H_6$ ground multiplet that were recorded using a 0.5-at. %-Tm^{3+} doped $CaWO_4$ crystal at 85 °K were similar to earlier published data[19] recorded using 0.8-at. % Tm^{3+} in uncompensated $CaWO_4$ crystals at 77 °K. This fluorescence was recorded on the Cary 14 operated in the more sensitive transmission mode; i.e., 10% transmission represents full scale on the recording chart. This emission was stimulated by using a 100-W xenon pump. Fluorescence spectra were also recorded on a half-meter spectrometer, using a photomultiplier tube with an S-20 surface as the detector, over the wavelength range corresponding to transitions from the $^1D_2$ to the $^3H_5$ and $^3F_4$ multiplets and from the $^1G_4$ to the $^3H_6$ multiplet. The fluorescing levels were not pumped directly so that background radiation that might have complicated the emission data was reduced. A 500-W Hg arc lamp was used for the excitation. The wavelengths of the absorption and fluorescence were adjusted so that energies corresponding to the same wavelengths seen in both measurements would match in the region of the 5460.7-Å Hg calibration line. The measurements normalized in this manner are reproducible to about 1 Å over the entire wavelength region. Some uncertainty in the position of the peaks (~3Å) of the weaker $^1D_2$ and $^1G_4$ absorption lines, however, results in a greater over-all uncertainty in the measurements.

The construction of the energy-level scheme from the measurements was greatly facilitated by a theoretical calculation of the energy levels by B_{kq} values interpolated from results[3–8] of other rare earths in $CaWO_4$. This calculation yielded a ground state that has Γ_2 transformation properties, and this is in agreement with Kirton's epr measurements[20] and theoretical calculations of the magnetic properties of some rare earths by Shekun.[21] A Γ_2 ground state is also consistent with the polarization measurements that allowed the following identifications for the energy levels of the various J multiplets.

Absorption measurements made with a $CaWO_4$: 0.1-at. %-Tm^{3+} crystal at 2 °K over the wavelength region corresponding to ground state to $^3F_4$ transitions are shown in Fig. 1. Both σ- and π-polarized spectra are complicated with extra lines. Wavelength positions corresponding to Γ_1 and $\Gamma_{3,4}$ energy levels (established as electric dipole transitions from the ground state to these $^3F_4$ levels) are denoted by hash marks along the abscissa. Confirmation of these identifications comes from the 25–85 °K data which show absorption lines corresponding to electric dipole transi-

TABLE III. Absorption lines of Tm^{3+} in $CaWO_4$ used to establish the energy levels of the $^1G_4$ multiplet.[a]

Line No.	Wavelength (μm)	Energy (cm^{-1})	Temperature (°K)	Relative intensity, polarization	S_4 symmetry property or other identification
1	0.4647	21 520	2	75σ, 6π	$\Gamma_{3,4}$
2	0.4653	21 492	2	4π	Γ_1 and
			85	5σ, 13π	Line 1—28 cm^{-1}
3	0.4662	21 450	85	6σ	Γ_2—26 cm^{-1}
4	0.4668	21 423	85	12π	Γ_2—53 cm^{-1}
5	0.4697	21 292	2	3π, 3σ	Γ_1
6	0.4706	21 249	85	12σ	Γ_2—26 cm^{-1}
7	0.4722	21 180	2	85σ	$\Gamma_{3,4}$
8	0.4727	21 154	85	11π	Line 7—26 cm^{-1}
9	0.4733	21 129	2	8σ	Line 7—51 cm^{-1}
			85	8σ	
10	0.4759	21 013	2	5σ	
11	0.4765	20 986	2	2π, 2σ	Γ_1
12	0.4771	20 960	85	20σ	Line 11—26 cm^{-1}

[a] The wavelength, energy corresponding to the observed line, the crystal temperature when first observed, relative intensity, and polarization are given. The identification of the corresponding energy level in S_4 notation, or other possible interpretation of the line, is also given.

tions from a possible $\Gamma_{3,4}$ level at 26 cm^{-1} above the ground state to these same energy levels. Electric dipole transitions from a Γ_2 ground state to the $^3F_4$ Γ_2 energy levels are forbidden by the selection rules and apparently do not show up in the 2 °K data. Sufficient lines are present, however, to suggest magnetic dipole Γ_2 to Γ_2 transitions. For the most part, this does not seem to be the case when spectra recorded at higher temperatures are considered. Lines corresponding to electric dipole transitions are observed in the σ spectrum at 25 and 85 °K that seem to be from a 26-cm^{-1} $\Gamma_{3,4}$ level to the $^3F_4$ Γ_1 and Γ_2 energy levels, and π lines are observed from this $\Gamma_{3,4}$ level to the $^3F_4$ $\Gamma_{3,4}$ energy levels. Thus a self-consistent energy-level scheme can be constructed by using electric dipole selection rules and not by using magnetic dipole selection rules. These absorption lines and their interpretations are given in Table I. The similarity of the axial and σ spectra are shown for comparison in Fig. 2.

Absorption measurements made with this same crystal at 2 °K over the wavelength region corresponding to transitions to the $^3H_5$ energy levels are shown in Fig. 3. The axial spectrum shows more detail than the σ spectrum and is therefore shown for comparison with the π spectrum. Wavelength positions corresponding to possible Γ_1 (π lines) and $\Gamma_{3,4}$ (σ lines) energy levels of the $^3H_5$ multiplet are denoted by hash marks along the abscissa. Again the σ and axial spectrum are similar, as they are over every wavelength region from 0.3 to 2.5 μm, indicating electric dipole transitions. The $^3H_5$ energy levels established from these data and from the spectra recorded at 25 and 85 °K are given in Table II.

Absorption measurements were also recorded with crystals of various Tm^{3+} concentrations at 2 °K over the wavelength region corresponding to ground state to $^1G_4$ transitions. Data recorded with the 0.1-at.%-Tm doped crystal in this wavelength region are shown in Fig. 4. Energy levels established from these data and data recorded at warmer temperatures are given in Table III. Of the $^1G_4$ levels a Γ_1 level lies lowest and seems to be the primary fluorescing level to the $^3H_6$ multiplet at 25 and 85 °K.

The absorption to the $^3H_4$, $^3F_3$, $^3F_2$, and $^1D_2$ multiplets were also recorded using these crystals at temperatures of 25 and 85 °K. These data are

TABLE IV. Absorption lines of Tm^{3+} in $CaWO_4$ used TO establish the energy levels of the $^1D_2$, $^3F_2$, $^3F_3$, and $^3H_4$ multiplets.[a]

Line No.	Wavelength (μm)	Energy (cm^{-1})	Temperature (°K)	Relative intensity, polarization	S_4 symmetry property or other identification
1	3580.5	27 929	25	38σ	$\Gamma_{3,4}$
2	3583.7	27 904	85	12π	Line 1—25 cm^{-1}
3	3587.1	27 878	85	5σ	Line 1—51 cm^{-1}
4	3599.5	27 782	85	14σ, 8π	Γ_2—26 cm^{-1}
5	6598	15 156	25, 85	5σ, 3σ	$\Gamma_{3,4}$
6	6609	15 131	25, 85	15π	$\Gamma_{3,4}$—25 cm^{-1}
7	6661	15 013	85	3σ	Γ_2—26 cm^{-1}
8	6673	14 986	25, 85	10π, 10π	Γ_2—53 cm^{-1}
9	6861	14 575	25	220π	Γ_1
10	6862	14 572	25	45σ	$\Gamma_{3,4}$
11	6877	14 541	25	105π	Line 10—31 cm^{-1}
12	6879	14 537	25	34σ	Γ_2—26 cm^{-1}
13	6892	14 509	25, 85	5σ, 8σ	Line 10—63 cm^{-1}
14	6905	14 483	25, 85	5σ, 60σ	Γ_2—26 cm^{-1}
15	6906	14 481	25, 85	50σ, 60σ	$\Gamma_{3,4}$
16	6917	14 457	25	4π	Line 15—24 cm^{-1}
17	6930	14 430	85	12σ	Line 15—51 cm^{-1}
18	7791	12 835	25	10π	Γ_1
19	7793	12 832	25	10σ	$\Gamma_{3,4}$
20	7806	12 811	25	20σ	Line 18—24 cm^{-1}
21	7809	12 806	25	40π	Line 19—26 cm^{-1}
22	7819	12 789	25	30π	
23	7824	12 781	25	30σ	Line 19—51 cm^{-1}
24	7838	12 759	25	85π	Γ_1
25	7850	12 739	25	25σ	Line 24—20 cm^{-1}
26	7902	12 655	25	15π	
27	7919	12 628	25	200σ	$\Gamma_{3,4}$
28	7936	12 600	25	140π	Γ_1, line 27—28 cm^{-1}
29	7952	12 576	25	150σ	Line 28—24 cm^{-1}, 27—52 cm^{-1}
30	7964	12 557	25	100σ	Γ_2—26 cm^{-1}

[a] The wavelength, energy corresponding to the observed line, the temperature, relative intensity, and polarization are given. Lines numbered 1–4 correspond to transition to $^1D_2$ levels, 5–8 to ^3F, levels, 9–17 to $^3F_3$ levels, 18–29 to $^3H_4$ energy levels.

listed in Table IV along with the energy levels established from these measurements. Some extra lines complicate the measurements, and this could lead to certain ambiguities. However, most levels are established by transitions from at least two low-lying energy levels in these cases.

Only the Γ_2 ground state, the $\Gamma_{3,4}$ energy level at 26 cm^{-1} and the Γ_1 level at 53 cm^{-1} of the $^3H_6$ multiplet were established from the absorption data. Additional levels might be established by

TABLE V. Fluorescence lines observed in the energy region corresponding to radiative transitions from energy levels of the $^3F_4$ and $^1G_4$ multiplets to the ground $^3H_6$ multiplet of Tm^{3+} in $CaWO_4$.[a]

A (cm^{-1})	*B* (5602 cm^{-1} − *A*)	*C* (cm^{-1})	*D* (5599 cm^{-1} − *C*)	*E* (cm^{-1})	*F* (5603 cm^{-1} − *E*)	*G* (cm^{-1})	*H* (20 986 cm^{-1} − *G*)	*I* (cm^{-1})
(4)5745	$\Gamma^+_{3,4} \to 0$							
(4)5719	$\Gamma^+_{3,4} \to 26$							
				5706.5				
(5)5692	$\Gamma^+_{3,4} \to 53$	(4)5694	$\Gamma^+_{3,4} \to 53$					
		(4)5630.6						
(sh)5602	0	(7)5599	0	5603.2	0	(6)20986	0	0
(52)5568	34	(19)5565.4	33.6	5566.4	36.8	(33)20946	40	26 from absorption
				5558.6				
		(7)5537		5538		(b)20898		
		(4)5460		5453.5		(b)20699		
(3)5385				5386	217.2			
		(5)5370.5	228.5					
(3)5357	245							245
		(6)5281	318	5275.4	327.8			328
(sh)5264	338			5254.3	348.9			338
(sh)5244	358	(13)5242.4	356.6					
(28)5230	372			5233.4	369.8	(23)20612	374	370
(sh)5208	394			5219	384.2	(b)20525		384
(b)5164								

[a] The fluorescence listed in columns *A* and *G* were recorded here using a 0.5 at.%-Tm^{3+} doped $CaWO_4$ crystal at 85 °K. The energy positions given in columns *C* and *E* were obtained using uncompensated 0.3- and 0.8-at.%-Tm^{3+} doped $CaWO_4$ crystals, respectively, at 77 °K. These data were supplied to us by L. F. Johnson of Bell Labs. In each the $^3F_4$ and $^1G_4$ multiplets, a Γ_1 level lies lowest and seems to be the predominant fluorescing level. This allows possible Γ_2 and $\Gamma_{3,4}$ energy levels of the $^3H_6$ multiplet given in column *I* to be established. Columns, *B*, *D*, and *F* give positions of $^3H_6$ energy levels that might be established by subtracting values given in *A*, *C*, and *E* from the possible fluorescing Γ_1 levels or from a fluorescing $\Gamma^+_{3,4}$ level at about 5745 cm^{-1}. Relative intensities, where available, are given in parentheses and the notation b means bump and sh means shoulder on a more intense line.

the fluorescence from the $^1G_4$ to the $^3H_6$ which coincides with levels that might be established from Johnson's reported[10] fluorescence measurements; that fluorescence originates from the lowest Γ_1 level of the $^3F_4$ multiplet (which he designates $^3H_4$). All these fluorescence lines to the $^3H_6$ multiplet are given in Table V along with Johnson's fluorescence data.

IV. CALCULATIONS

The calculations played an important role in the analysis of these experimental data, which were complicated by many extra lines, since a good description of the energy levels was initially obtained. The initial parameters were the free-ion parameters reported[1] for Tm^{3+} in YVO_4 and the crystal-field parameters obtained by interpolating B_{kq} values reported[3–8] for other rare earths in $CaWO_4$. The calculations thus aided the identification of energy levels for a nearly complete energy-level scheme that resulted in an rms deviation of 6.7 cm^{-1} between the theoretical and experimental energy levels in the least-squares-fitting procedure. Of fifty-two possible nondegenerate energy levels in the ^3H, ^3F, ^1G, and ^1D terms, forty were established, and there was evidence for eight additional energy levels consistent with the calculations. There was no experimental evidence of four of the predicted energy levels. The experimental energy levels are given in Table VI together with the final calculated energy levels. In addition, calculated $g_{\parallel}$ values are listed for the $\Gamma_{3,4}$ levels ($g_{\perp} = 0$ in every case). The final parameters giving this fit to 6.7 cm^{-1} are shown in

TABLE VI. Experimental and theoretical energy levels of Tm^{3+} in $CaWO_4$.[a]

Multiplet	Representation	Experimental energy (cm^{-1})	Theoretical energy (cm^{-1})	$g_{\parallel}$
$^3H_6$	Γ_2	0	−11	
	$\Gamma_{3,4}$	26	21	−0.119
	Γ_1	53	53	
	Γ_2	(245)	255	
	Γ_2	(328)	315	
	$\Gamma_{3,4}$	(338)	336	−1.689
	Γ_1		338	
	Γ_1		379	
	$\Gamma_{3,4}$	(370)	392	8.786
	Γ_2	(384)	395	
$^3F_4$	Γ_1	5594	5588	
	Γ_1	5733	5744	
	$\Gamma_{3,4}$	5745	5744	0.224
	Γ_2	5811	5809	
	Γ_2	5926	5935	
	Γ_1	5927	5923	
	$\Gamma_{3,4}$	5936	5936	−4.777
$^3H_5$	Γ_2	8279	8276	
	$\Gamma_{3,4}$	8288	8283	0.729
	Γ_1	8299	8297	
	Γ_2	8486	8501	
	$\Gamma_{3,4}$	8499	8506	6.015
	$\Gamma_{3,4}$	8531	8524	−0.539
	Γ_1	8535	8541	
	Γ_1	8550	8557	
$^3H_4$	Γ_2	12 583	12 594	
	Γ_1	12 600	12 594	
	$\Gamma_{3,4}$	12 628	12 636	0.572
	Γ_1	12 759	12 760	
	$\Gamma_{3,4}$	12 832	12 834	−4.305
	Γ_1	12 835	12 827	
	Γ_2		12 881	
$^3F_3$	$\Gamma_{3,4}$	14 481	14 487	−5.111
	Γ_2	14 509	14 508	
	Γ_2	14 563	14 565	
	$\Gamma_{3,4}$	14 572	14 564	0.918
	Γ_1	14 575	14 569	
$^3F_2$	Γ_2	15 039	15 047	
	$\Gamma_{3,4}$	15 156	15 147	1.286
	Γ_2	(15 152)	15 158	
	Γ_1		15 227	
$^1G_4$	Γ_1	20 986	20 988	
	$\Gamma_{3,4}$	21 180	21 185	0.569
	Γ_2	21 275	21 273	
	Γ_1	21 292	21 301	
	Γ_2	21 476	21 469	
	Γ_1	21 492	21 490	
	$\Gamma_{3,4}$	21 520	21 506	−4.395
$^1D_2$	Γ_2	27 808	27 811	
	Γ_2	(27 855)	27 851	
	$\Gamma_{3,4}$	27 929	27 927	2.270
	Γ_1	(27 940)	27 941	
$^1I_6$	Γ_2		34 436	
	$\Gamma_{3,4}$		34 455	−2.102
	Γ_1		34 484	
	Γ_1		34 642	
	$\Gamma_{3,4}$		34 743	3.610
	Γ_2		34 804	
	Γ_1		34 829	
	$\Gamma_{3,4}$		34 851	4.489
	Γ_2		35 137	
	Γ_2		35 138	
$^3P_0$	Γ_1		35 379	
$^3P_1$	Γ_1		35 943	
	$\Gamma_{3,4}$		36 068	2.962
$^3P_2$	Γ_2		37 772	
	$\Gamma_{3,4}$		37 977	2.612
	Γ_2		38 030	
	Γ_1		38 154	
$^1S_0$	Γ_1		79 396	

[a] The theoretical levels were computed using the parameter values given in table VII, and are within an rms deviation of 6.7 cm^{-1} from the experimental energy levels. The levels listed in parentheses were not used in the calculations. Calculated $g_{\parallel}$ values are also given for the $\Gamma_{3,4}$ levels (all $g_{\perp}$ values are zero).

column A of Table VII. Also given in Table VII, column B, are the initial values of the parameters.

V. DISCUSSION OF RESULTS

In this study of Tm^{3+} in $CaWO_4$, many extra lines complicated the optical spectrum in the wavelength region accessible (the band edge is near 3000 Å, and this prohibits obtaining absorption to energy levels above the $^1D_2$ multiplet). These added complications had prevented an earlier analysis by the ESOH technique[9] which ought not be nearly so good for Tm^{3+} as for other rare earths owing to term mixing. A smooth variation in the B_{kq} for other rare earths was obtainable[3–8] using ESOH, however, and it was of interest to see how well the interpolated results compare with B_{kq} values obtained by considering the full Hamiltonian for Tm^{3+}. The latter B_{kq} values are shown for comparison in Table VII, column A, where it is noted that the interpolated values (column B) are in reasonable agreement; this corroborates the reliability of the ESOH. The comparison of the free-ion parameters of Tm^{3+} in YVO_4 and $CaWO_4$ is also seen here. The small discrepancies in the F_k, of columns A and B, for example, might be explained[2] by the different dielectric constants of the two materials, This is only conjecture, however, since the dielectric constant for YVO_4 has not been reported in the literature and since larger variations of α, β, and $M_0^{(0)}$ for Tm^{3+} in the different host crystals add to the uncertainties in F_k values.

In addition to obtaining parameters consistent with the entire optical spectrum of Tm^{3+} in $CaWO_4$, calculated energy levels and $g_{\parallel}$ factors for the entire $4f^{12}$ configuration are given. The ground state is identified as a Γ_2 and mixing of the $^3H_4$, $^3F_4$, and $^1G_4$ energy levels by the spin-orbit interaction caused the first multiplet above the ground multiplet to be predominantly $^3F_4$. The extra lines in the optical spectrum are not understood in detail. However, many extra lines oc-

TABLE VII. Free-ion and crystal-field parameters for Tm^{3+} in $CaWO_4$.[a]

	A (cm^{-1})	B (cm^{-1})
F_2	458.798	463.35
F_4	70.004	71.19
F_6	7.845	8.063
ζ	2641.825	2641.662
$M_0^{(0)}$	2.139	2.644
$M^{(0)}$	0.962	1.190
$M^{(2)}$	0.540	0.668
$M^{(4)}$	0.367	0.454
α	17.411	28.03
β	−747.465	−1053.266
B_{20}	417.7	459.6
B_{40}	−687.7	−620.9
B_{60}	17.1	10.5
B_{44}	753.6	733.0
Real B_{64}	504.3	562.8
Imag. B_{64}	359.2	97.2

[a] The parameters given in column A give an rms deviation between the experimental and calculated energy levels of 6.7 cm^{-1}. Those in column B are the initial values used in the calculations, which facilitated this analysis.

cur[8,22] in the optical spectrum of the next heavier rare-earth ion (Yb^{3+}) in $CaWO_4$. This suggests several different mechanisms including vibronic transitions (electronic effects coupling with the crystal lattice) and stronger perturbations due to more local distortion by the impurity ion for these ions near the full $4f^N$ shell. The reported[10,19] laser transitions are from a Γ_1 level of the $^3F_4$ multiplet at 5594 cm^{-1}. The terminal level for the 1.911-μm laser line is at 370 cm^{-1}, and the terminal level for the 1.916-μm laser line is at 384 cm^{-1}. The calculations suggest the 370-cm^{-1} level to be a $\Gamma_{3,4}$ and the 384-cm^{-1} level to be a Γ_2 though the polarization measurements are ambiguous. For both transitions the terminal level lies well above the approximate value of 325 cm^{-1} for the terminal level that had previously been reported.[10,19] The terminal level would therefore not be thermally populated so readily, and four-level laser action for Tm^{3+} is more understandable. Also the identification of these levels suggests that a Tm^{3+} in $CaWO_4$ laser, using a laser crystal grown along an a axis, can have either a σ- or π-polarized output at nearly the same frequency, and this might be useful for modulation of the laser output. In addition to the results above, the establishment of a Γ_2 ground state would now explain Kirton's not finding epr at 9 and 36 GHz. Our calculated $g_{\parallel}$ factor for the $\Gamma_{3,4}$ level at 26 cm^{-1}, which is very small, indicates that an experimental $g_{\parallel}$ factor would also be difficult to establish. Many of the other excited-state $g_{\parallel}$ factors could be measured, however, and this would be an excellent check of our results. Intensity calculations, which we are presently attempting should also serve as a check on these results and indicate the reasons that certain of the transitions are extremely weak.

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