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Analysis of the optical spectrum of Tm^{3+} in $LiYF_4$

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Absorption and fluorescence spectra of Tm^{3+} in single-crystal $LiYF_4$ were recorded at temperatures between 5 and 77 K. The energy levels for the ground configuration were established from these data with the aid of theoretical calculations. Parameters were obtained that gave a least-squares deviation of 16.9 cm^{-1} between the experimental and calculated energy levels. These calculated levels were obtained by diagonalizing a Hamiltonian that describes the free-ion and crystal-field interactions in a basis of states spanning the $4f^{12}$ configuration. The free-ion parameters are $F_2 = 462.49$, $F_4 = 70.762$, $F_6 = 7.6265$, $\zeta = 2652.8$, $\alpha = 23.262$, $\beta = -761.64$, $M_0^{(0)} = 3.2459$, $M^{(0)} = 1.4608$, $M^{(2)} = 0.8202$, and $M^{(4)} = 0.5572$, and the crystal-field parameters are $B_{20} = 358.7$, $B_{40} = -607.8$, $B_{60} = -173.0$, $B_{44} = 844.2$, and $B_{64} = 629.2$ (all units are cm^{-1}). The calculated and crystal-field-split energy levels were in agreement to within 9 cm^{-1} after the calculated energy centroids were adjusted. The S_4 symmetry property of the ground state was determined to be Γ_2.

I. INTRODUCTION

An analysis of the optical absorption and fluorescence spectra of triply ionized thulium in lithium yttrium fluoride ($LiYF_4$) was made to determine the energy levels for the $4f^{12}$ configuration of Tm^{3+}. It is desirable to study this rare-earth ion because it is effectively the $4f^2$ configuration, which is easily handled theoretically and yet is sufficiently complicated to interact fully with the electrostatic field of the host material. Therefore this makes Tm^{3+} an effective probe and allows an analysis of the Tm^{3+} energy levels by a model in which the Tm^{3+} free-ion interactions and the crystal-field interactions can be separately described. The same crystal-field effects should influence other rare earths in $LiYF_4$ (also called YLF) that show promise[1–3] as useful laser materials. Also in this work, the theoretical model[4,5] mentioned above was examined. Earlier studies[4,5] of Tm^{3+} in $CaWO_4$ and YVO_4, which used this model yielded good agreement between theory and experiment, but were somewhat incomplete in that the smaller band gap in these materials did not allow absorption to the ^3P, ^1I, and ^1S terms to be observed experimentally. Because of the wider band gap of YLF, optical measurements were made for all but the $^1S_0$ state in the Tm^{3+} ground configuration. Therefore a more complete comparison of theory and experiment could be made.

An earlier experimental investigation[6] of YLF crystals containing several different rare earths gave the energy positions of many of the levels examined in this work. A reexamination of that Tm^{3+} data and an examination of additional experimental data within the framework of a complete theoretical description of the $4f^{12}$ configuration lead to a slightly different energy level scheme. This scheme is consistent with a Γ_2 ground state, where the levels are classified by irreducible representations[7] of the S_4 point group which is the symmetry of the Y^{3+} site. Several electric-dipole transitions from this state which are allowed by the selection rules are missing; this would also be the case if the ground state were assumed to be a Γ_1 level. A possible reason for these missing transitions can be given by considering electric-dipole selection rules in D_{2d} symmetry (S_4 is a subgroup of D_{2d}). A number of workers (see, for example, Ref. 8) studying rare earths in scheelite structures have interpreted their results by assuming D_{2d} point-group symmetry at the ion site. Our justification for this, however, is given in Sec. II.

II. THEORY

The Hamiltonian used here and the method of analysis have been described elsewhere.[4,5] Briefly, the method is to describe first the Tm^{3+} free-ion levels as completely as possible and then to determine the effects of the crystal on these energy levels. The Hamiltonian used and the associated parameters are

$$H = \sum_i H_i , \tag{1}$$

where in the notation of Judd[9] H_1 is the Coulomb interaction between the electrons, with the Slater parameters F_2, F_4, and F_6; and H_2 is the spin-orbit interaction, with the parameter ζ; H_3 is the crystal-field interaction, with the parameters B_{kq}; H_6 is the spin-spin interaction, with the Marvin integrals $M_0^{(0)}$, $M^{(0)}$, $M^{(2)}$, and $M^{(4)}$ as parameters, H_8 and H_9 are the spin-other-orbit and orbit-orbit interactions, with $M^{(0)}$, $M^{(2)}$, and $M^{(4)}$ parameters, as in H_6; and H_{10} is an effective Hamiltonian representing configuration interaction as given by Rajnak and Wybourne,[10] with parameters α, β, and γ.

The contact spin-spin interaction[11] has been included in H_6. The ratios of the Marvin integrals are assumed fixed at the values computed using Hartree-Fock wave functions[12] for Tm^{3+}, as in Refs. 4 and 5. We shall set $\gamma = 0$, as in the earlier work,[4,5] since the electrostatic interaction is overspecified without the $^1S_0$ multiplet and since γ has the least effect on the $L-S$ terms.

The Tm^{3+} free ion is described by the Hamiltonian (1), excluding H_3, which more explicitly is

$$H_3 = \sum_{i,k,q} B_{kq}^{\dagger} C_{kq}(i) , \qquad (2)$$

where C_{kq} is a spherical tensor of rank k and projection q, and the B_{kq} are the crystal-field parameters which describe the effect of the crystal on the free-ion energy levels. The i sum is over the $4f^{12}$ electrons. The S_4 point-group symmetry at the Y^{3+} sites in the crystal lattice limits the parameters for even k that can be non-zero in the expansion to B_{20}, B_{40}, B_{60}, B_{44}, and B_{64}. Although B_{44} and B_{64} can both be complex, one may choose a coordinate system where B_{44} is real and positive.

In the calculations, H of (1) was diagonalized in a $|JMLS\rangle$ basis spanning the entire $4f^{12}$ configuration. The eigenstates obtained transform[7] according to one of four irreducible representations (Γ_1, Γ_2, Γ_3, and Γ_4) of the S_4 point group. The levels characterized by wave functions transforming as Γ_3 and Γ_4 are degenerate and are designated $\Gamma_{3,4}$. The space is 91 dimensional and separates into a 25×25, a 24×24, and two 21×21 matrices. The first two, together with one of the latter, need to be diagonalized to determine, respectively, the energy levels for Γ_1, Γ_2, and $\Gamma_{3,4}$.

The classification of the experimental energy levels according to group properties can be made by determining the nature of the interaction governing the optical transitions; the energy levels are labeled in S_4 notation throughout the text. According to the group multiplication tables and the transformation properties of the electric-dipole operators,[7] identical axial and σ-polarized spectra (within a multiplicative factor) require the use of electric-dipole selection rules. Conversely, identical axial and π-polarized spectra require the use of magnetic-dipole selection rules. In this work it is found that the transitions are consistent with the electric-dipole operator.

As mentioned earlier, we also have considered[13] D_{2d} point-group symmetry in the analysis of these optical data. If the Tm^{3+} ion were in a site of D_{2d} symmetry, certain transitions would be forbidden, as shown in Table I. If, however, the local site symmetry is perturbed by a lower symmetry environment, such as S_4, some of the forbiddenness is lifted. Thus since the Tm^{3+} ion is in an S_4 symmetry site, which is almost D_{2d}, a large number of the low intensity lines can be explained. In the energy-level calculations, the imaginary component of B_{64} ($\mathrm{Im}B_{64}$) is a certain measure of the difference between D_{2d} and S_4. The odd-fold B_{kq} (odd k), however, enter the intensity calculations, and even if $\mathrm{Im}B_{64} = 0$, the imaginary B_{kq} for odd k are not necessarily small in S_4 (they are 0 in D_{2d}). Since we have considered both S_4 and D_{2d}, we have listed the corresponding identifications of the S_4 levels in D_{2d} notation in Table II. The full rotation-group compatibility tables for S_4 and D_{2d} are given in Table III, for each of the D_J^+ matrices used in labeling the Tm^{3+} energy levels.

III. EXPERIMENTAL PROCEDURE AND RESULTS

A. Experimental procedure

The same experimental procedures and apparatus were used in this investigation as have been reported elsewhere.[6] Optical spectra shown in the earlier report, in conjunction with additional data recorded at other wavelengths, were also used in this analysis and will therefore not be shown here. Instead, all the spectral lines will be described in tabular form.

The $LiYF_4$ (YLF) crystals used in this study were grown by a top-seeded-solution technique from a melt containing YF_3 and a slight excess of LiF over the stoichiometric amount.[14] The crystals were grown in a purified helium atmosphere. The anhydrous YF_3 and the rare-earth dopants were carefully dried and treated[15] in a hydrofluorination furnace just before being loaded into the crystal growth furnace. The trivalent rare-earth ions go in substitutionally for Y^{3+} and can be substituted up to 100% in the case of the heavier rare earths. The percentage dopant in the crystal is assumed to be the same as in the melt. In these crystals up to 2-at.% Tm was added to the melt. Samples ($5\times 5\times 8$ mm) were cut with two of the faces perpendicular to the optic axis of the crystal. All the faces were optically polished, and all the samples used were high-quality single crystals.

TABLE I. Selection rules for electric-dipole transitions in S_4 and in Γ_{2d}.

	S_4				D_{2d}				
	Γ_1	Γ_2	Γ_3	Γ_4	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Γ_1	···	π	σ	σ	···	···	π	···	σ
Γ_2	π	···	σ	σ	···	···	···	π	σ
Γ_3	σ	σ	···	π	π	···	···	···	σ
Γ_4	σ	σ	π	···	···	π	···	···	σ
Γ_5					σ	σ	σ	σ	π

TABLE II. Identifications of the irreducible representations of the D_{2d} point group in S_4 notation.

D_{2d}	S_4
Γ_1	Γ_1
Γ_2	
Γ_3	Γ_2
Γ_4	
Γ_5	$\Gamma_{3,4}$

The samples were mounted in a variable-temperature optical Dewar. Any temperature from liquid helium to room temperature could be obtained. A temperature controller was used to control the temperature to better than 1 K, as long as the helium flow was sufficient for the heat load.

Most of the absorption measurements were obtained using a Cary 14-R double-beam spectrophotometer with either a 0–2 or 0–0.2 absorbance-unit slide wire $[A = -\log_{10}(I/I_0)]$. The zero baseline of the instrument was not quite flat, but since the wavelength positions rather than the absolute strengths of the transitions are of interest, this was not serious. In the visible region (0.40–0.65 μm), the instrument has a resolution of about 1 Å. In the infrared region, the resolution was 10–30 Å, which is not good enough to resolve some of the closely spaced transitions. In this case, a McPherson 0.3-m spectrometer was used employing a grating with 600 grooves per millimeter and blazed at 1.6 μm. This instrument has a resolution of 1.5 Å in the wavelength range 1–2 μm when used in conjunction with the peripheral instrumentation described in the earlier report.[6] In every case the polarized spectra were obtained by using glan prisms. In the Cary 14-*R*, both the analyzing and reference beams were polarized.

The fluorescence spectra were obtained using the McPherson 0.3-m spectrometer with interchangeable gratings. In the visible and near infrared up to 1 μm, a 1200-groves-per-millimeter grating blazed at 7500 Å was used, giving a maximum resolution of about 1 Å. In the 1–2-μm wavelength region, the 600-groves-per-millimeter grating mentioned above was used. For detection, an RCA C7164R photomultiplier was used for wavelengths up to 0.75 μm; a dry-ice-cooled RCA 7102 photomultiplier was used in the 0.75–1.1 μm region; and a liquid-nitrogen-cooled InAs diode detector was used in the 1.1–2.4 μm region. For wavelength calibration, the 5461-Å Hg line was used in first and second orders. Wavelength readings should be accurate to ± 2 Å for both gratings. For excitation a 1000-W xenon lamp was used in the visible and a 1000-W tungsten-iodide lamp in the infrared regions. In cases where overlapping fluorescence from different excited states occurs, monochromatic pump light from a Bausch and Lomb high-intensity monochromator was used. To reduce scattered pump light, where possible a level fluorescing to the ground multiplet was not pumped directly, and filters were used in every case.

B. Experimental results

A previous report[6] of the Tm^{3+} optical spectrum in $LiYF_4$ showed that the data were consistent with the choice of a Γ_1 ground state. Additional measurements and further analysis indicate that a Γ_2 ground state is more consistent with these data and the theoretical model. This will be discussed in more detail in the next section. In the tables that describe the absorption spectral lines, identifications are more consistent with electric-dipole selection rules and a Γ_2 ground state. These same assumptions are consistent with the fluorescence shown in Fig. 13 of Ref. 6 used to establish energy levels of the $^3H_6$ ground multiplet.

In this work we have labeled the states according to their largest L-S component. Mixing of the $^3F_4$, $^1G_4$, and $^3H_4$ states by the spin-orbit interaction causes the first multiplet above the $^3H_6$ to be predominantly $^3F_4$. The fluorescence shown in Fig. 13 of Ref. 6 and labeled $^3H_4$ in that work seems to be from the lowest $^3F_4$ energy level, in our notation. This fluorescing level is established here as a Γ_1 at 5605 cm^{-1}. A transition from this Γ_1 level to the Γ_2 ground state is not observed. Such a transition is allowed in S_4, but is not allowed by the selection rules in D_{2d} symmetry. The line in σ polarization at 1.794 μm seems to be from the 5605-cm^{-1} Γ_1 level to a $\Gamma_{3,4}$ level at about 30 cm^{-1}. The π line at this same wavelength may be due to incomplete polarization caused by the instrument. Two additional π lines seem to be from the 5605-cm^{-1} Γ_1 level to $^3H_6$ Γ_2 levels at about 282 and 310 cm^{-1}. A transition to a Γ_2 of possibly higher energy (calculated to be 400 cm^{-1} above the ground state) is outside the wavelength region over which these fluorescence data were recorded. A 5605-cm^{-1} σ transition to a possible $\Gamma_{3,4}$ level at about 347 cm^{-1} cannot definitely be established, but such a transition cannot

TABLE III. Full rotation-group compatibility tables for the groups S_4 and D_{2d}. The irreducible representations in the parentheses in S_4 relate to those in parentheses in D_{2d}, and likewise for the square brackets.

	S_4	D_{2d}
D_0^+	Γ_1	Γ_1
D_1^+	$\Gamma_1+(\Gamma_3+\Gamma_4)$	$\Gamma_2+(\Gamma_5)$
D_2^+	$\Gamma_1+2[\Gamma_2]+(\Gamma_3+\Gamma_4)$	$\Gamma_1+[\Gamma_3+\Gamma_4]+(\Gamma_5)$
D_3^+	$\Gamma_1+2[\Gamma_2]+2(\Gamma_3+\Gamma_4)$	$\Gamma_2+[\Gamma_3+\Gamma_4]+2(\Gamma_5)$
D_4^+	$3\Gamma_1+2[\Gamma_2]+2(\Gamma_3+\Gamma_4)$	$2\Gamma_1+\Gamma_2+[\Gamma_3+\Gamma_4]+2(\Gamma_5)$
D_5^+	$3\Gamma_1+2[\Gamma_2]+3(\Gamma_3+\Gamma_4)$	$\Gamma_1+2\Gamma_2+[\Gamma_3+\Gamma_4]+3(\Gamma_5)$
D_6^+	$3\Gamma_1+4[\Gamma_2]+3(\Gamma_3+\Gamma_4)$	$2\Gamma_1+\Gamma_2+2[\Gamma_3+\Gamma_4]+3(\Gamma_5)$

be ruled out; it would appear in σ at about 1.902 μm, where there is indeed a rise above the base line. A transition to a $\Gamma_{3,4}$ of higher energy (calculated to be about 370 cm^{-1}) would also be outside the range of the recorded data. A $^3H_6$ Γ_1 energy level is obtained from 77-K absorption spectra at an average value of 56 cm^{-1}; averaged 77-K absorption data give a value of 31 cm^{-1} for the $\Gamma_{3,4}$ level. This then gives one of three Γ_1 energy levels, three of four Γ_2 energy levels, and one (and perhaps two) of three $\Gamma_{3,4}$ energy levels for the $^3H_6$ ground multiplet.

All the energy levels of the $^3F_4$ multiplet can be established from the absorption measurements recorded at different temperatures. These data are summarized in Table IV. Polarization measurements made at 77 K are shown in Fig. 11 of Ref. 6. Some magnetic-dipole transitions cannot be ruled out from the data, but transitions obeying the electric-dipole rules predominate. By considering electric-dipole selection rules and S_4 symmetry, transitions from a Γ_2 ground state to three Γ_1 energy levels might be expected in the π spectrum taken at 5 K. Only two of these π lines are observed at 5757 and at 5967 cm^{-1}. Further, the line at 5757 cm^{-1} is about 6 times more intense than the 5967-cm^{-1} line. By use of the electric-dipole selection rules in D_{2d} symmetry, only a transition to the 5757-cm^{-1} level is allowed (see Table II). Hence a slight distortion of D_{2d} symmetry would allow the other π transitions. Absorption to the Γ_1 energy level at 5605 cm^{-1} from the ground state was not observed. However, a transition from the $\Gamma_{3,4}$ level at 31 cm^{-1} to this Γ_1 was seen at 77 K; evidence for this Γ_1 level also comes from the fluorescence to the $^3H_6$ multiplet, as described above. Transitions to the Γ_2 energy levels are not seen at 5 K, and are not expected, but these Γ_2 levels are established from warm-up measurements.

The $^3H_5$ energy levels were established from the absorption measurements recorded at 77 K and are given in Table V. These polarized absorption spectra are also shown in Fig. 12 of Ref. 6, and additional data were recorded at 5 and 20 K. The $^3H_5$ splits into three Γ_1, two Γ_2, and three $\Gamma_{3,4}$ energy levels. Absorption lines are seen in the π spectrum that correspond to transitions from the ground state to two Γ_1 levels allowed in D_{2d} symmetry (three are expected in S_4, see Table III). However, from all these data, the three Γ_1 levels, two Γ_2 levels, and one of the three $\Gamma_{3,4}$ levels are identified. The σ line at 8500 cm^{-1} may be used to establish either the first or the second highest $\Gamma_{3,4}$ level. Since this ambiguity exists, the 8500-cm^{-1} line was not used in the calculations.

The $^3H_4$ energy levels were established from the absorption measurements listed in Table VI. The $^3H_4$ multiplet splits into three Γ_1, two Γ_2, and two $\Gamma_{3,4}$ energy levels. Three transitions from the Γ_2 ground state to the Γ_1 levels might therefore be expected, and these are seen at 12 621, 12 741, and, possibly, 12 825 cm^{-1}. The π line at 12 741 cm^{-1} is at least 10 times more intense than the other π lines at 5 K in this wavelength region. In D_{2d}, only a transition to this line is expected in the π spectrum. Transitions to the $^3H_4$ energy levels from the 31-cm^{-1} line were seen in the π spectrum recorded at higher temperatures.

Absorption lines shown in Fig. 9 of Ref. 6 and summarized in Table VII were used to establish all the $^3F_3$ energy levels. The $^3F_3$ splits into one Γ_1, two Γ_2, and two $\Gamma_{3,4}$ energy levels. The π transition from the ground state is allowed in D_{2d} as well as in S_4 and appears as a rather intense π line at 14 616 cm^{-1}. Absorption to the $^3F_2$ energy levels (one Γ_1,

TABLE IV. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^3F_4$ multiplet. The wavelength, energy, polarization, and intensity corresponding to the observed line are given. The crystal temperature at which the absorption line was measured is also given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity σ	Intensity[a] π	Temperature (K)	Identification
1	17 940	5574	10	···	77	$\Gamma_1 - 31$ cm^{-1}
2	17 520	5708	10	3	77	No. 6 − 52 cm^{-1}
3	17 450	5731	···	6, >100	5, 77	No. 6 − 29 cm^{-1}
4	17 440	5734	90	···	77	No. 5 − 23 cm^{-1}
5	17 370	5757	···	60	5	Γ_1
6	17 360	5760	68	···	5	$\Gamma_{3,4}$
7	17 250	5796	40	8	77	$\Gamma_2 - 31$ cm^{-1}
8	17 190	5877	···	b	5	extra
9	16 910	5913	···	10	77	$\Gamma_2 - 31$ cm^{-1}
10	16 830	5942	50	>100	77	No. 12 − 35 cm^{-1}, No. 11 − 25 cm^{-1}
11	16 760	5967	···	10	5	Γ_1
12	16 730	5977	30	···	5	$\Gamma_{3,4}$
13	16 510	6057	···	b	5	extra

[a] b means small bump.

TABLE V. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^3H_5$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity σ	Intensity π	Temperature (K)	Identification
1	12155	8227	···	18	77	$\Gamma_2 - 56\ cm^{-1}$
2	12115	8254	20	18	77	$\Gamma_2 - 31\ cm^{-1}$, No. $5 - 31\ cm^{-1}$
3	12100	8264	100	70	77	No. $6 - 31\ cm^{-1}$
4	12080	8278	3	···	77	extra
5	12070	8285	25	5	77	$\Gamma_{3,4}$
6	12055	8295	4	5	77	Γ_1
7	11810	8467	10	75	77	No. $9 - 33\ cm^{-1}$, $\Gamma_1 - 30\ cm^{-1}$
8	11795	8477	10	···	77	$\Gamma_2 - 31\ cm^{-1}$
9	11765	8500	7	···	77	No. $10 - 32\ cm^{-1}$, $\Gamma_{3,4}$
10	11720	8532	···	5	77	Γ_1

two Γ_2, and one $\Gamma_{3,4}$) are also given in Fig. 9 of Ref. 6. From these measurements, only the $\Gamma_{3,4}$ level at 15218 cm^{-1} and the Γ_2 level at 15104 cm^{-1} can be determined, as shown in Table VIII. A transition from the ground state to the $^3F_2$ Γ_1 level (S_4 notation) is not allowed in D_{2d}. Small lines are observed in the π spectrum between the $^3F_2$ and $^3F_3$ wavelength regions. These lines can be attributed to vibronic transitions accompanying the intense π line at 14 616 cm^{-1}.

The $^1G_4$ multiplet splits into three Γ_1, two Γ_2, and two $\Gamma_{3,4}$ energy levels. Absorption transitions from the Γ_2 ground state to the Γ_1 and $\Gamma_{3,4}$ levels might be expected at 5 K. Transitions to both the $\Gamma_{3,4}$ energy levels are observed at 21195 and 21 561 cm^{-1}, but only one Γ_1 level at 21 322 cm^{-1} can be established from the 5-K spectra. In D_{2d} only this transition observed in the π-polarized spectrum would be allowed. The additional data, summarized in Table IX and recorded at warmer crystal temperatures, allow us to establish all but one Γ_2 level of the $^1G_4$ multiplet.

Absorption lines recorded at various crystal temperatures over the wavelength region of the $^1D_2$ multiplet are given in Table X. This multiplet splits into one Γ_1, two Γ_2, and one $\Gamma_{3,4}$ energy levels. A Γ_2 ground state transition to the Γ_1 level (S_4 notation) would not be allowed in D_{2d}. No such π line is seen that would establish the Γ_1 level; however, the two Γ_2 levels and the $\Gamma_{3,4}$ level of the $^1D_2$ multiplet are established.

Absorption lines recorded at 5 K that correspond to transitions from the ground state to energy levels of the $^3P_1$, $^3P_2$, and $^1I_6$ multiplets are given in Table XI. A π-polarized line might be expected in S_4 corresponding to a transition from the Γ_2 ground state to the $^3P_0$ Γ_1 energy level. Such a transition is forbidden in D_{2d}, and no such transition could be established from these data. At 5 K, transitions from higher energy levels in the $^3H_6$ would be frozen out due to the Boltzmann factor. However, transitions to the other Γ_1 and $\Gamma_{3,4}$ levels might be expected. The $^1I_6$ splits into three Γ_1, four Γ_2, and three $\Gamma_{3,4}$ levels; the $^3P_2$ splits into one Γ_1, two Γ_2, and one $\Gamma_{3,4}$; and the $^3P_1$ splits into one Γ_1 and $\Gamma_{3,4}$ level. From these data, two $^1I_6$ energy levels (a Γ_1 at 34928 cm^{-1} and a $\Gamma_{3,4}$ at 34728 cm^{-1}), two $^3P_1$ (a Γ_1 at 36443 and a $\Gamma_{3,4}$ at 36530 cm^{-1}) and one $^3P_2$ (a $\Gamma_{3,4}$ at 38219 cm^{-1}) are established. Thus there are several missing levels when electric-dipole selection rules and S_4 symmetry are considered. However, all the transitions allowed in D_{2d} from the Γ_2 ground state to Γ_1 levels (S_4 notation) in these multiplets are observed. Some of the other levels are

TABLE VI. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^3H_4$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity σ	Intensity[a] π	Temperature (K)	Identification
1	7797	12825	···	b	5	(Γ_1)
2	7812	12800	···	2, 17	5, 20	$\Gamma_{3,4} - 31\ cm^{-1}$
3	7849	12741	···	80	5	Γ_1
4	7911	12641	···	2	5	extra
5	7923	12621	···	8	5	Γ_1
6	7928	12613	···	20	20	$\Gamma_{3,4} - 31\ cm^{-1}$

[a] b means small bump.

TABLE VII. Absorption lines of Tm^{3+} in $\mathrm{LiYF_4}$ in energy region of the ${}^3F_3$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity[a] σ	Intensity π	Temperature (K)	Identification
1	6909	14 474	12	...	77	No. 4 − 57 cm^{-1}
2	6898	14 497	...	9	20	No. 4 − 34 cm^{-1}
3	6896	14 501	b	...	77	extra
4	6882	14 531	32, >100	...	5, 77	$\Gamma_{3,4}$, $\Gamma_2 - 30\ \mathrm{cm}^{-1}$
5	6863	14 571	...	33	20	No. 7 − 34 cm^{-1}
6	6861	14 574	25	...	20	$\Gamma_2 - 31\ \mathrm{cm}^{-1}$
7	6847	14 605	24	...	5	$\Gamma_{3,4}$
8	6842	14 616	...	45	5	Γ_1
9	6831	14 639	...	3	5	extra

[a] b means small bump

not established, perhaps because of the relatively low intensity of the transitions in this wavelength region. Additional energy levels that are consistent with the calculations and that cannot be ruled out are given in parentheses in Table XII; these levels are not used in the calculations. Extra lines of relatively low intensity are observed between 33 440 and 33 852 cm^{-1}.

C. Calculations

Initial energy levels for the ground configuration of Tm^{3+} in YLF were calculated and compared with experimental values. The parameters used in (1) for these calculations were the free-ion parameters obtained[4] by fitting Tm^{3+} energy levels in $\mathrm{CaWO_4}$, and crystal-field parameters obtained by extrapolating from reported [16,17] B_{kq} values for Nd^{3+} and Er^{3+} in YLF. This calculation yielded a Γ_2 ground state, a $\Gamma_{3,4}$ level as the next-higher energy level, and a Γ_1 level above this $\Gamma_{3,4}$. Since it had been reported[6] that a Γ_1 ground state is consistent with the measurements, the following calculation was made.

If the ground state is either a Γ_1 or a Γ_2 in S_4, only ground-state-to-$\Gamma_{3,4}$ transitions might be expected in the σ-polarized spectrum at 5 K. Thus the $\Gamma_{3,4}$ energy levels determined in the preceding section could be compared with calculated $\Gamma_{3,4}$ levels; the same calculation yields also the Γ_1 and Γ_2 levels. The parameters in (1) were therefore varied until a least-rms deviation between the experimental and calculated $\Gamma_{3,4}$ levels was obtained. A result of this calculation was that the Γ_2 remained the lowest level, a $\Gamma_{3,4}$ the second-higher level, and a Γ_1 as the next-higher level.

The above calculations suggest that the ground state is Γ_2 rather than Γ_1, and the rms deviation between the calculated and measured energy levels is much smaller by assuming a Γ_2 ground state. This does not explain, however, why many of the allowed transitions in S_4 are not observed.

Since S_4 is a subgroup of D_{2d}, the use of irreducible representations of D_{2d} rather than S_4 may be considered. In D_{2d}, the electric-dipole transitions from the ground state, denoted Γ_2 in S_4, which are allowed by the selection rules (see Table I) are indeed observed as the strongest π lines. Many of the smaller π lines that might not be expected in D_{2d} can then be accounted for by a small nonzero value of $\mathrm{Im}B_{64}$. Imaginary components of B_{kq} for odd k would affect the intensities but would not enter the energy-level calculations.

Additional support for this proposed energy-level scheme and for arguments using electric-dipole selection rules in D_{2d} come from absorption measure-

TABLE VIII. Absorption lines of Tm^{3+} in $\mathrm{LiYF_4}$ in energy region of the ${}^3F_2$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity[a] σ	Intensity[a] π	Temperature (K)	Identification
1	6646	15 047	..., b	b, 15	20, 77	$\Gamma_2 - 57\ \mathrm{cm}^{-1}$
2	6634	15 073	4	...	20	$\Gamma_2 - 31\ \mathrm{cm}^{-1}$
3	6595	15 163	2	...	77	No. 5 − 55 cm^{-1}
4	6587	15 181	3	22	20	No. 5 − 37 cm^{-1}
5	6571	15 218	40	2	5	$\Gamma_{3,4}$

[a] b means small bump.

TABLE IX. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^1G_4$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity[a] σ	Intensity[a] π	Temperature (K)	Identification
1	4773	20 950	8	...	77	$\Gamma_2 - 31\ cm^{-1}$
2	4731	21 137	1	...	77	No. $5 - 58\ cm^{-1}$
3	4726	21 160	b	...	77	extra
4	4723	21 173	...	3	20	No. $5 - 22\ cm^{-1}$
5	4718	21 195	15	...	5	$\Gamma_{3,4}$
6	4714	21 213	...	3	5	extra
7	4706	21 248	5	...	77	$\Gamma_2 - 31\ cm^{-1}$
8	4699	21 281	2	6	77	No. $9 - 41\ cm^{-1}$
9	4690	21 322	...	15	5	Γ_1
10	4659	21 464	...	12	77	extra
11	4653	21 491	2	3	20	extra
12	4644	21 533	5	5	77	No. $13 - 28\ cm^{-1}$
13	4638	21 561	10	b	5	$\Gamma_{3,4}$, Γ_1

[a] b means small bump.

ments recorded at warmer crystal temperatures. At 77 K, for example, three π lines corresponding to transitions from a Γ_1 at 56 cm^{-1} to higher-energy Γ_2 levels are recorded. Each of these transitions is allowed in D_{2d} as well as in S_4. Other π lines that are not allowed in D_{2d} were not observed. In addition, use of D_{2d} was made earlier to account for the lines observed in the $^3F_4$-to-$^3H_6$ fluorescence spectrum.

After establishing an energy-level scheme for the Tm^{3+} $4f^{12}$ configuration, we made a least-squares calculation to determine parameters that describe the Tm^{3+} free-ion interactions and the crystal-field parameters that describe the perturbation on the free-ion levels. The parameters in (1) were varied until a least-rms value of 16.9 cm^{-1} between calculated and experimental energy levels was obtained. In the least-squares calculation, it was found that the calculated energy levels were not nearly as sensitive to $\mathrm{Im}B_{64}$ as to the other B_{kq}. This component also tended to approach zero. Therefore it was decided to set it ($\mathrm{Im}B_{64}$) arbitrarily equal to zero rather than rediagonalize the large matrices in order to vary this parameter. A rapid method of obtaining a least-rms deviation between calculated and experimental energy levels (using perturbation theory) could then be used in which such diagonalization was required a minimal number of times. The calculated and experimental energy levels thus obtained are listed in Table XII in S_4 notation. The calculated $g_\parallel$ values are also given for the $\Gamma_{3,4}$ doublets (all $g_\perp$ values are zero). For completeness, D_{2d} identifications of the energy levels are also given in the table.

The parameters of (1) obtained in the least-squares fit described above are shown in column A of Table XIII. Earlier calculations[4,5] for Tm^{3+} in $CaWO_4$ and YVO_4 yielded rms values of 6.7 and 10.6 cm^{-1}, respectively, between calculated and measured energy levels. However, in the earlier calculations, fewer multiplets were included with the same number of parameters. In this work, we have introduced energy levels of the $^3P_2$, $^3P_1$, and $^1I_6$ multiplets, and, as a result, the Hamiltonian of (1) does not have enough parameters to fit the energy centroids adequately. The calculated crystal-field splittings are in good agreement, however, with the measurements. By matching the energy centroids of the calculated and measured energy levels, an rms deviation of 9 cm^{-1} between calcu-

TABLE X. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^1D_2$ multiplet. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity σ	Intensity π	Temperature (K)	Identification
1	3584	27 901	22	10	77	$\Gamma_2 - 31\ cm^{-1}$, $\Gamma_2 - 62\ cm^{-1}$
2	3580	27 932	5	...	77	$\Gamma_2 - 31\ cm^{-1}$
3	3576	27 964	16	...	77	No. $5 - 55\ cm^{-1}$
4	3574	27 980	...	10	20	No. $5 - 39\ cm^{-1}$
5	3569	28 019	25	2	5	$\Gamma_{3,4}$

TABLE XI. Absorption lines of Tm^{3+} in $LiYF_4$ in energy region of the $^3P_0$; $^3P_1$, and $^2P_2$ multiplets. The same quantities described in Table IV are given.

Line	Wavelength (Å)	Frequency (cm^{-1})	Intensity[a] σ	Intensity[a] π	Temperature (K)	Identification
1	2994	33 400	7	7	5	extra
2	2987	33 478	...	b	5	extra
3	2973	33 636	2	2	5	extra
4	2967	33 704	1	1	5	extra
5	2963	33 749	1	1	5	extra
6	2954	33 852	1	1	5	extra
7	2879.5	34 728	6	6	5	$^1I_6\ \Gamma_{3,4}$, ($^1I_6\ \Gamma_1$)
8	2866	34 891	...	s[b]	5	extra
9	2863	34 928	...	3	5	$^1I_6\ \Gamma_1$
10	2861	34 953	...	s	5	extra
11	2852	35 063	b	...	5	$^1I_6\ \Gamma_{3,4}$
12	2744	36 443	...	2	5	$^3P_1\ \Gamma_1$
13	2737.5	36 530	4	b	5	$^3P_1\ \Gamma_{3,4}$
14	2724	36 711	...	b	5	extra
15	2616.5	38 219	37	6	5	$^3P_2\ \Gamma_{3,4}$
16	2609	38 329	3	...	5	extra
17	2596	38 521	b	1	5	extra
18	2588	38 640	...	2	5	extra

[a] b means small bump.

[b] s means shoulder on line.

lated and measured crystal-field-split levels is obtained, and this compares favorably with similar calculations for Tm^{3+} in $CaWO_4$ and in YVO_4.

Since we have established energy levels for the ground configuration of Tm^{3+} in YLF, we can now determine how reliable are the parameters that were found to be consistent with the ground configuration[4,5] of Tm^{3+} in $CaWO_4$ and YVO_4. In these earlier studies, the $^3P_1$, $^3P_2$, and $^1I_6$ multiplets could not be obtained experimentally owing to the smaller band gaps of these crystals. A least-squares calculation was therefore made excluding these higher multiplets for Tm^{3+} in YLF and again setting $\mathrm{Im}B_{64} = 0$. These parameters, given in column B of Table XIII are compared with the parameters which are consistent with all the measured energy levels (column A of Table XIII). It is noted that the largest changes occur in α, β, and $M^{(k)}$, that the $M^{(k)}$ tend toward nonphysical values (negative $M^{(k)}$ — Judd *et al.*[18] observed this behavior in fitting spectra in earlier work), and that the B_{kq} are somewhat less sensitive. It is possible then that the B_{kq} which are consistent with the measurements of Tm^{3+} in $CaWO_4$ and in YVO_4 would likewise be reliable. The calculated crystal-field splittings are within 1 or 2 cm^{-1} from each other using B_{kq} from either column A or column B of this table.

IV. CONCLUSIONS

In this study of the fluorescence and absorption spectra of Tm^{3+} in single-crystal YLF ($LiYF_4$), energy levels for the $4f^{12}$ configuration were established. The relatively large band gap of YLF permitted measurements in wavelength regions corresponding to electronic transitions including all but the $^1S_0$ energy level. An energy level scheme for the Tm^{3+} ground configuration resulted; this is given in Table XII. In the analysis of the experimental data, the use of electric-dipole selection rules in D_{2d} was made to account for some of the missing lines and for the relative intensities of the observed lines. A Hamiltonian meant to describe the free-ion interactions and the crystal-field interaction was diagonalized in a basis of states spanning the $4f^{12}$ electronic configuration. The parameters in this Hamiltonian were varied until a least-rms deviation of 16.9 cm^{-1} resulted between calculated and experimental energy levels. The B_{kq} values, given in Table XIII, describe the crystal-field splittings of the various J multiplets to within 9 cm^{-1} rms; this value is attained by matching the energy centroids for each J multiplet with experimental values. Even though the free-ion Hamiltonian could not fit the energy centroids exactly, the B_{kq} describe accurately the crystal-field splittings and ought to be reliable for use in future intensity and energy-level calculations for other rare earths in YLF.

The limitations of the model used in this analysis and earlier analyses[4,5] were also examined here. Since the smaller band gap of $CaWO_4$ and YVO_4 did not allow measurement of the ^3P, ^1I, and ^1S energy levels in the Tm^{3+} ground configuration, parameters were reported earlier that were consistent with the

TABLE XII. Experimental and theoretical energy levels of Tm^{3+} in single-crystal $LiYF_4$. The theoretical levels were calculated using the parameter values given in column A of Table XIII and give a rms deviation of 16.9 cm^{-1} from the experimental energy levels. The calculated Stark splittings of the individual multiplets are within 9 cm^{-1} rms of the measured splittings. Calculated g values are also given for the $\Gamma_{3,4}$ levels, and the symmetry is S_4; D_{2d} identifications of the levels are also shown.

Multiplet	S_4	D_{2d}	Experimental energy (cm^{-1})	Calculated energy (cm^{-1})	$g_\parallel$
$^3H_6$	2	4	0	−13	
	3,4	5	31	13	−0.340
	1	1	56	39	
	2	3	282	268	
	2	4	310	302	
	1	2	...	324	
	3,4	5	...	327	11.513
	1	1	...	374	
	3,4	5	...	375	−4.182
	2	3	...	409	
$^3F_4$	1	1	5605	5613	
	3,4	5	5760	5770	0.110
	1	2	5757	5776	
	2	4	5827	5828	
	2	3	5944	5936	
	1	1	5967	5985	
	3,4	5	5977	5976	−4.632
$^3H_5$	2	3	8285	8274	
	3,4	5	8285	8287	0.193
	1	2	8295	8307	
	3,4	5	(8500)	8500	10.121
	1	1	8497	8518	
	3,4	5	(8500)	8534	−4.144
	2	4	8508	8531	
	1	2	8532	8537	
$^3H_4$	2	4	...	12 621	
	1	1	12 621	12 619	
	3,4	5	12 644	12 648	−0.087
	1	2	12 741	12 765	
	1	1	12 825	12 826	
	3,4	5	12 831	12 841	−3.677
	2	3	...	12 938	
$^3F_3$	3,4	5	14 531	14 531	−4.385
	2	4	14 561	14560.	
	3,4	5	14 605	14 605	0.237
	2	3	14 605	14 611	
	1	2	14 616	14 629	
$^3F_2$	2	3	15 104	15 067	
	2	4	...	15 189	
	3,4	5	15 218	15 166	1.278
	1	1	...	15 235	
$^1G_4$	1	1	20 981	20 997	
	3,4	5	21 195	21 199	0.381
	2	4	21 279	21 271	
	1	2	21 322	21 317	
	2	3	...	21 448	
	3,4	5	21 561	21 536	−4.219
	1	1	21 561	21 548	

TABLE XII. (*continued*)

Multiplet	S_4	D_{2d}	Experimental energy (cm^{-1})	Calculated energy (cm^{-1})	$g_\parallel$
$^1D_2$	2	4	27 932	27 952	
	2	3	27 963	27 987	
	1	1	...	28 067	
	3,4	5	28 019	28 048	2.243
$^1I_6$	2	3	...	34 705	
	3,4	5	34 728	34 727	−2.160
	1	1	...	34 759	
	1	2	34 928	34 930	
	3,4	5	(35 063)	35 034	5.290
	2	4	...	35 120	
	1	1	...	35 142	
	3,4	5	...	35 155	2.863
	2	3	...	35 357	
	2	4	...	35 359	
$^3P_0$	1	1	...	35 834	
$^3P_1$	1	2	36 443	36 431	
	3,4	5	36 530	36 536	2.954
$^3P_2$	2	3	...	37 978	
	3,4	5	38 219	38 186	2.647
	2	4	...	38 258	
	1	1	...	38 334	
$^1S_0$	1	1	...	79 428	

lower-lying energy levels. The fact that the crystal-field parameters are insensitive to the inclusion of the higher energy levels for Tm^{3+} in YLF suggests that these parameters reported for Tm^{3+} in $CaWO_4$ and in YVO_4 would likewise accurately describe the crystal-field interaction. Furthermore, the importance of this result is that it indicates that the crystal-field parameters are relatively term independent. Larger changes in the magnetic interactions indicate a need for the inclusion of additional parameters[18] in the free-ion Hamiltonian. Inclusion of the P_k parameters described by Judd[18] in the model should improve the fit to the energy centroids considerably, but is not expected to affect the description of the crystal field signifi-

TABLE XIII. Free-ion and crystal-field parameters for Tm^{3+} in $LiYF_4$. The parameters given in column A were obtained by fitting all the experimental data given in Table XII. The parameters given in column B neglect the $3P$ and ^1I energy levels.

Parameter	A (cm^{-1})	B (cm^{-1})
F_2	462.49	465.45
F_4	70.762	70.885
F_6	7.6265	8.1047
ζ	2652.8	2620.0
$M_0^{(0)}$	3.2459	−0.5382
$M^{(0)}$	1.4608	−0.2422
$M^{(2)}$	0.8202	−0.1360
$M^{(4)}$	0.5572	−0.0924
α	23.262	22.189
β	−761.64	−999.05
B_{20}	358.7	344.7
B_{40}	−607.8	−641.0
B_{60}	−173.0	−152.2
B_{44}	844.2	868.3
$\mathrm{Re}B_{64}$	629.2	626.5
$\mathrm{Im}B_{64}$	0.0	0.0

cantly; this will be the subject of a future investigation.

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