

Crystal-field splitting of some quintet states of Tb^{3+} in aluminum garnets

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A detailed crystal-field splitting analysis is reported for the quintet states 5D_J , 5G_J , and 5L_J of $Tb^{3+}(4f^8)$ in the garnets $Y_3Al_5O_{12}$ (YAG) and $Tb_3Al_5O_{12}$ (TbAG). In both garnets we assume that Tb^{3+} ions occupy sites of D_2 symmetry in the cubic structure. We have analyzed the optical spectra of Tb^{3+} between 487 and 349 nm. The absorption spectrum consist of transitions from the ground-state multiplet manifold, 7F_6 , to individual energy (Stark) levels of the 5D_4 , 5D_3 , 5G_6 , ${}^5L_{10}$, 5G_5 , 5D_2 , 5G_4 , and 5L_9 multiplet manifolds. An algorithm used successfully by some of us earlier to analyze the spectra of $Tm^{3+}(4f^{12})$ in YAG is helpful in the present study to establish the crystal quantum labels, $\Gamma_n(n=1,2,3,4)$ for individual Stark levels. A lattice-sum model is used to determine an initial set of crystal-field splitting parameters, B_{nm} . A combined free-ion and crystal-field Hamiltonian is diagonalized for the quintet and septet states. Considerable crystal-field mixing is found among all the quintet states investigated. A least-squares fitting analysis between 130 experimental-to-calculated Stark levels for Tb^{3+} in YAG gave a rms deviation of 9 cm^{-1} . A least-squares fitting analysis between 136 experimental-to-calculated Stark levels for Tb^{3+} in TbAG gave a rms deviation of 10 cm^{-1} .

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I. INTRODUCTION

The magneto-optical properties of $Tb^{3+}(4f^8)$ in $Y_3Al_5O_{12}$ (YAG) and in the garnet $Tb_3Al_5O_{12}$ (TbAG) have received detailed attention in recent years since TbAG has been used with success as an optical Faraday device.¹⁻⁸ We and others have reported using $Tb_3Al_5O_{12}$ as a compact optical isolator having over 30 dB isolation with 0.2 dB forward loss and with an optical range from 470 to more than 530 nm.^{5,9} Further possible applications have led us to an indepth study of the crystal-field splittings of the energy levels of the ultraviolet (UV) quintet states of $Tb^{3+}(4f^8)$ in the garnet system, which have received relatively little attention over the years,¹⁰⁻¹⁵ except for an earlier analysis of the splitting of the 7F_J multiplet manifold by Bayerer *et al.*¹⁶

Different theoretical models have been advanced to explain the optical and magnetic behavior of the rare earth ions (R^{3+}) in $R_3Al_5O_{12}$ and the cooperative effects between the R^{3+} ions.¹⁷⁻²⁰ The electric field gradient at the R^{3+} site in $R_3Al_5O_{12}$ has been calculated and compared with experiment for a number of examples,¹⁷ and a superposition model of crystal fields was used by Newman and Stedman for $Er_3Al_5O_{12}$.¹⁸ Korolkov and Makhanev¹⁹ analyzed an overlap-local coordination model for $Tb_3Al_5O_{12}$ and $Dy_3Al_5O_{12}$, but obtained limited success. To this list we could add molecular orbital theory methods to interpret the effects of $5d$ orbitals on the UV spectra of R^{3+} ions in $R_3Al_5O_{12}$,⁶ but the fact remains that a detailed identification of individual energy (Stark) levels still needs to be done for the R^{3+} energy levels in the UV, especially for ions Gd^{3+} , Tb^{3+} , and Dy^{3+} in garnet hosts.

Recent studies reported on circular polarized lumines-

cence from Tb^{3+} :YAG in a magnetic field (MCPL)²⁰ and results obtained for Zeeman splittings of UV states of Tb^{3+} :YAG (Ref. 7) and Tb^{3+} : $Tb_3Al_5O_{12}$ (TbAG)²¹ have necessitated a detailed crystal-field analysis of the quintet states 5D_J , 5G_J , and 5L_J of $Tb^{3+}(4f^8)$. Of great assistance to this analysis has been the earlier work by Bayerer *et al.*¹⁶ on the interpretation of the splitting of the 7F_J multiplet of Tb^{3+} in YAG.

In the present study, we report the absorption spectra of Tb^{3+} in YAG and Tb^{3+} in TbAG between 487 and 349 nm that include the multiplet manifolds 5D_4 , 5D_3 , 5G_6 , ${}^5L_{10}$, 5G_5 , 5D_2 , 5G_4 , and 5L_9 of $Tb^{3+}(4f^8)$. Using a lattice-sum model to predict an initial set of crystal-field parameters, B_{nm} , we first calculated the splitting of the 7F_J multiplet manifolds as reported by Bayerer *et al.*¹⁶ With modest adjustment to the lattice-sum parameters, B_{nm} , we predicted both the Stark splitting and the symmetry label Γ_1 , Γ_2 , Γ_3 , or Γ_4 for each experimental Stark level they reported (see Table I). Using a transformation of coordinates, we find agreement between our symmetry label assignments and the B_{nm} parameters reported by Bayerer *et al.*¹⁶ We then expanded our analysis to include the Stark levels observed in the 5D_J , 5G_J , and 5L_J multiplet manifolds along with the observed splitting of the 7F_J manifolds. Using a combined free-ion and crystal-field Hamiltonian, the entire energy matrix for the septet and quintet states of $Tb^{3+}(4f^8)$ was then diagonalized. We carried out a least-squares fitting analysis for observed and calculated Stark levels and determined the symmetry label appropriate for each Stark level of Tb^{3+} in YAG and TbAG. The wave functions generated from these analyses have been used successfully to interpret the mag-

TABLE I. Splitting of 7F_J manifolds of $\text{Tb}^{3+}(4f^8)$ in $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Tb}_3\text{Al}_5\text{O}_{12}$.

Manifold ^a	E (cm ⁻¹) obs. ^b Tb:YAG	E (cm ⁻¹) calc. ^c Tb:YAG	E (cm ⁻¹) obs. ^d TbAG	E (cm ⁻¹) calc. ^e TbAG	Γ_n^f TbAG	Percent mixing of free-ion states TbAG	
7F_6 (315)	0	0	0	2	1	$99.7{}^7F_6 + 0.16{}^7F_4 + 0.11{}^7F_5$	
	3	5	2	5	3	$99.7{}^7F_6 + 0.16{}^7F_5 + 0.15{}^7F_4$	
	65	60	74	71	4	$99.6{}^7F_6 + 0.38{}^7F_5 + 0.03{}^7F_3$	
	73	72	84	79	2	$99.5{}^7F_6 + 0.43{}^7F_5 + 0.03{}^7F_3$	
	211	212		186	1	$99.9{}^7F_6 + 0.03{}^7F_5 + 0.01{}^7F_2$	
	212	214		187	2	$99.9{}^7F_6 + 0.01{}^7F_1 + 0.01{}^7F_3$	
	263 ^g	260	263	270	1	$96.6{}^7F_6 + 3.03{}^7F_5 + 0.20{}^7F_3$	
	314 ^g	303	322	305	3	$96.7{}^7F_6 + 2.73{}^7F_5 + 0.27{}^7F_3$	
	375 ^g	372	373	384	4	$96.6{}^7F_6 + 2.56{}^7F_5 + 0.45{}^7F_4$	
		451		453	2	$97.2{}^7F_6 + 1.40{}^7F_5 + 1.20{}^7F_4$	
	458 ^g	465	460	455	3	$96.9{}^7F_6 + 2.53{}^7F_5 + 0.26{}^7F_4$	
	468 ^g	471	470	469	4	$96.8{}^7F_6 + 2.28{}^7F_5 + 0.43{}^7F_4$	
		488		496	1	$97.4{}^7F_6 + 2.19{}^7F_4 + 0.16{}^7F_5$	
	7F_5 (2338)	2116	2118	2119	2115	2	$99.5{}^7F_5 + 0.26{}^7F_6 + 0.18{}^7F_4$
2128		2129	2134	2138	4	$99.2{}^7F_5 + 0.58{}^7F_6 + 0.18{}^7F_3$	
2150		2148	2147	2145	1	$99.5{}^7F_5 + 0.34{}^7F_4 + 0.16{}^7F_6$	
2150		2149	2177	2182	3	$99.3{}^7F_5 + 0.24{}^7F_6 + 0.22{}^7F_4$	
2179		2173	2209	2203	2	$99.4{}^7F_5 + 0.27{}^7F_4 + 0.20{}^7F_6$	
2331		2331	2349	2347	2	$94.8{}^7F_5 + 2.23{}^7F_4 + 1.66{}^7F_3$	
2355		2363	2375	2377	4	$94.9{}^7F_5 + 1.90{}^7F_4 + 1.43{}^7F_6$	
2388		2391	2402	2408	3	$91.9{}^7F_5 + 4.73{}^7F_4 + 1.84{}^7F_6$	
		2475	2478	2495	1	$91.0{}^7F_5 + 3.14{}^7F_4 + 2.50{}^7F_6$	
		2583		2597	4	$93.0{}^7F_5 + 2.30{}^7F_4 + 2.09{}^7F_6$	
		2585	2618	2607	3	$94.2{}^7F_5 + 2.24{}^7F_6 + 2.09{}^7F_3$	
7F_4 (3587)	3368	3364	3375	3378	4	$95.5{}^7F_4 + 3.00{}^7F_3 + 0.80{}^7F_5$	
	3376	3367	3388	3385	3	$99.3{}^7F_4 + 0.29{}^7F_5 + 0.27{}^7F_3$	
	3392	3386	3399	3393	2	$97.9{}^7F_4 + 1.77{}^7F_3 + 0.30{}^7F_5$	
	3425	3416	3411	3410	1	$97.1{}^7F_4 + 1.94{}^7F_5 + 0.37{}^7F_3$	
	3493	3491	3517	3517	1	$99.0{}^7F_4 + 0.60{}^7F_5 + 0.21{}^7F_2$	
	3605	3615	3621	3626	4	$91.6{}^7F_4 + 3.79{}^7F_3 + 2.00{}^7F_1$	
	3683	3687	3703	3702	3	$83.4{}^7F_4 + 11.5{}^7F_3 + 3.04{}^7F_5$	
	3714	3719	3732	3736	2	$89.7{}^7F_4 + 7.24{}^7F_3 + 1.09{}^7F_5$	
	4036	4051	4043	4056	1	$84.7{}^7F_4 + 7.03{}^7F_3 + 5.47{}^7F_0$	
	7F_3 (4548)	4354	4345	4368	4367	2	$97.1{}^7F_3 + 2.66{}^7F_2 + 0.11{}^7F_4$
		4429	4451	4501	4487	1	$75.7{}^7F_3 + 16.2{}^7F_2 + 6.21{}^7F_4$
4502		4500	4519	4518	3	$84.2{}^7F_3 + 10.8{}^7F_2 + 3.51{}^7F_1$	
4544		4540	4554	4557	4	$84.2{}^7F_3 + 9.90{}^7F_2 + 4.39{}^7F_3$	
4609		4601	4617	4617	4	$87.4{}^7F_3 + 4.47{}^7F_2 + 3.55{}^7F_2$	
4649		4651	4677	4684	3	$84.6{}^7F_3 + 6.74{}^7F_1 + 4.56{}^7F_4$	
4674		4677	4688	4691	2	$79.8{}^7F_3 + 8.39{}^7F_4 + 8.36{}^7F_1$	
7F_2 (5231)		5020	5031	5030 ^f	5023	1	$98.2{}^7F_2 + 0.77{}^7F_4 + 0.60{}^7F_3$
	5029	5039	5062	5054	2	$94.5{}^7F_2 + 3.63{}^7F_3 + 1.44{}^7F_1$	
	5552	5543	5550	5552	1	$77.5{}^7F_2 + 14.3{}^7F_3 + 3.75{}^7F_0$	
	5595	5590	5593	5606	4	$83.7{}^7F_2 + 11.6{}^7F_3 + 2.66{}^7F_5$	
	5617	5604	5625	5621	3	$87.5{}^7F_2 + 9.78{}^7F_3 + 4.95{}^7F_1$	
	7F_1 (5662)	5742	5741	5738	5742	3	$81.4{}^7F_1 + 9.49{}^7F_3 + 3.86{}^7F_2$
5850		5852	5868	5858	2	$90.4{}^7F_1 + 5.17{}^7F_3 + 2.11{}^7F_4$	
5857		5856	5874	5880	4	$88.5{}^7F_1 + 6.48{}^7F_3 + 2.93{}^7F_4$	
7F_0 (5764)			5900 ^g	5911	1	$88.9{}^7F_0 + 5.56{}^7F_4 + 4.77{}^7F_2$	

^aMultiplet manifold of $\text{Tb}^{3+}(4f^8)$; number in parentheses is the centroid calculated for that manifold.^bEnergy levels obtained from Ref. 16.^cCalculated splitting based on B_{nm} reported in Table IV.^dEnergy levels obtained from Refs. 13 and J.A. Koningstein and G. Schaack, Phys. Rev. B 2, 1242 (1970).^eCalculated splitting based on B_{nm} reported in Table IV.^fPredicted Γ_n ($n=1,2,3,4$) for TbAG based on B_{nm} (Table IV).^gLevels obtained from data associated with the present study.

netic properties of the septet and quintet states of Tb^{3+} in both YAG and TbAG.^{22,23}

II. EXPERIMENTAL DETAILS

Single crystals of YAG doped with Tb^{3+} in different concentrations and single crystals of TbAG were grown either by spontaneous crystallization from flux⁷ or by the Czochralski method.²⁴ Yttrium aluminum garnet melts congruently at 1970 °C. The crystals grew parallel to the $\langle\langle\langle\rangle\rangle$ direction. Disks were cut so that the spectra could be measured along the crystallographic axes [001], or [011] of the cubic crystal.²⁵ Based on a distribution coefficient of 0.96 and a given dopant concentration in the melt, we obtained Tb^{3+} -doped YAG crystals containing various concentrations of Tb^{3+} .²⁶ The spectra reported here were obtained from single crystals of $\text{Tb}_{0.2}\text{Y}_{2.8}\text{Al}_5\text{O}_{12}$ (arbitrary direction) and $\text{Tb}_3\text{Al}_5\text{O}_{12}$ [001] direction.

Absorption spectra between 487 and 349 nm were obtained from a double-diffraction monochromator, model MDR-23 grating monochromator, having a spectral resolution better than 3 cm^{-1} over the wavelength investigated. A calibrated photomultiplier tube with feedback on the light flux was used as a detector. To eliminate temperature-dependent transitions (hot bands), we compared the 78 K absorption spectra with the 300 K spectra and eliminated the hot bands from the tables of the 78 K absorption spectrum.

Knowing the splitting of the ground-state manifold 7F_6 given in Table I, we are able to establish that all the spectra reported in Tables II and III are due to transitions only from $Z_1=0\text{ cm}^{-1}$ (Γ_1), and $Z_2=3\text{ cm}^{-1}$ (Γ_3) of 7F_6 to excited Stark levels of the quintet states. Given the limitation in resolution of our spectrometer we could not fully resolve the transitions originating from both Z_1 and Z_2 at 78 K. Since Z_1 and Z_2 are nearly equally populated at that temperature, selection rules predict transitions to all $2J+1$ Stark components of the quintet states. Thus Table II (Tb^{3+} :YAG) and Table III (Tb^{3+} :TbAG) only list the predicted Γ_n for each Stark level. However, since the calculation predicts the splitting and the Γ_n for the 7F_J multiplet so well, we include the Γ_n assignments for the quintet states since these predictions have already been useful for recently reported studies on the MCPL and observed Zeeman effect between Stark levels within the quintet states.^{22,23}

III. MODELING THE CRYSTAL-FIELD SPLITTING

The parametrized Hamiltonian for Tb^{3+} in the garnet structure includes the Coulombic, spin-orbit, and interconfiguration interaction terms associated with the free-ion Hamiltonian and the crystal-field terms that lift the degeneracy of the free-ion multiplets, ${}^{2S+1}L_J$, into energy levels that are designated as Stark levels. The free-ion part of the Hamiltonian is written as

$$H_{\text{FI}} = \sum_k E^k e_k + \zeta \sum_{i=1}^8 l_i \cdot s_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7), \quad (1)$$

with values for electronic repulsion between $4f$ electrons, spin-orbit, and interconfiguration interaction terms taken from earlier work on $\text{Tb}^{3+}(4f^8)$ reported by Carnall *et al.*²⁷ The parameters are listed in Table IV of this work. With these parameters we obtain a set of free-ion wave functions used in the calculation of the matrix elements of the crystal-field splitting of the multiplet manifolds.

The crystal-field terms in the Hamiltonian are given as

$$H_{\text{CF}} = \sum_{m=-n}^n B_{nm}^* \sum_{i=1}^8 C_{nm}(\hat{r}_i), \quad (2)$$

where the B_{nm} represent the crystal-field parameters with $n=2, 4$, and 6 , the index i runs over the eight $4f$ electrons in the ground state of $\text{Tb}^{3+}(4f^8)$, and where $B_{nm}^* = (-1)^m B_{n,-m}$. The one-electron operators $C_{nm}(\hat{r}_i)$ are related to the standard spherical harmonics¹ as

$$C_{nm}(\hat{r}_i) = [4\pi/(2n+1)]^{1/2} Y_{n,m}. \quad (3)$$

The Tb^{3+} ion occupies dodecahedral sites having D_2 symmetry in the garnet lattice. The D_2 point-group symmetry contains four one-dimensional irreducible representations Γ_1 , Γ_2 , Γ_3 , and Γ_4 . In a non-Kramers system like $\text{Tb}^{3+}(4f^8)$, containing an even-number of $4f$ electrons, each multiplet is split into $2J+1$ Stark-level components labeled according to a symmetry designation, Γ_n . The full-rotation compatibility table for the D_2 group and the algorithm used to make symmetry label assignments have been reported earlier²⁴ for Tm^{3+} :YAG, TmAG, and is found to work equally well for the Tb^{3+} garnet systems.

While the B_{nm} can be chosen so that all are real, this by itself does not uniquely define the system since there are six ways to choose B_{nm} real. Morrison *et al.*¹ have expanded on this topic and have provided the reader with equivalent sets of B_{nm} for Nd^{3+} :YAG as an example. In the local coordinate system for Tb^{3+} :YAG, Bayerer *et al.*¹⁶ chose X' parallel to the [001] axis, perpendicular to the $Y'Z'$ plane, while Gruber *et al.*^{24,25} chose Z parallel to the [001] axis, perpendicular to the XY plane. Thus we have two different sets of symmetry labels to reconcile when comparing the results from these two groups. However, by transformation of coordinates the Bayerer *et al.*¹⁶ labels Γ_1 , Γ_3 , Γ_4 , and Γ_2 become the Gruber *et al.*^{24,25} labels Γ_1 , Γ_2 , Γ_3 , and Γ_4 , respectively, and so one can match both the calculated crystal-field splitting and the symmetry labels of the Bayerer *et al.*¹⁶ data for Tb^{3+} :YAG very well with the calculated splitting and symmetry labels of the Stark levels reported in the present study. This analysis provides a level of confidence in analyzing the Tb^{3+} multiplets in the ultraviolet, where crystal-field mixing plays an important role (see Tables II and III). There are nine crystal-field parameters for Tb^{3+} in D_2 sites, all real: B_{20} , B_{22} , B_{40} , B_{42} , B_{44} , B_{60} , B_{62} , B_{64} , and B_{66} reported in units of cm^{-1} .

To establish the lattice-sum components, A_{nm} , for the garnet structure, we carried out a point-charge lattice-sum calculation that included point-charge, point-dipole, and self-induced contributions. The lattice-sum components are given as

TABLE II. Absorption spectra of 5D_J , 5G_J , and 5L_J states of $\text{Tb}^{3+}(4f^8)$ in $\text{Y}_3\text{Al}_5\text{O}_{12}$.^a

$2S+1L_J^b$	λ (Å) ^c	α (cm ⁻¹) ^d	E (cm ⁻¹) ^e obs.	E (cm ⁻¹) ^f calc.	Γ_n calc. ^g	Percent mixing of free-ion states
5D_4 (20 596)	4873.2	0.43	20 515 ^h	20 514	1	$99.8^5D_4 + 0.11^5L_{10} + 0.02^5G_4$
	4872.8	0.10	20 516.3 ^h	20 516	3	$99.8^5D_4 + 0.12^5L_{10} + 0.02^5G_6$
	4867.8	0.47	20 537.3 ^h	20 530	4	$99.7^5D_4 + 0.13^5L_{10} + 0.03^5D_3$
	4866.4	0.94	20 543.3 ^h	20 545	2	$99.7^5D_4 + 0.09^5L_{10} + 0.08^5G_4$
	4857.2	1.80	20 582.2 ^h	20 585	4	$99.7^5D_4 + 0.11^5L_{10} + 0.09^5G_4$
	4856.8	1.37	20 583.8 ^h	20 587	1	$99.6^5D_4 + 0.15^5G_6 + 0.11^5L_{10}$
	4854.6	0.39	20 593.3 ^h	20 594	3	$99.6^5D_4 + 0.14^5G_6 + 0.09^5L_{10}$
	4844.1	2.35	20 637.7 ^h	20 638	2	$99.6^5D_4 + 0.16^5G_6 + 0.10^5G_5$
	4839.8	0.15	20 656.5 ^h	20 649	1	$99.3^5D_4 + 0.39^5G_6 + 0.10^5D_4$
	5D_3 (26 336)	3823.0	0.95	26 145	26 144	3
3823.2		1.97	26 149	26 151	1	$70.3^5G_6 + 25.9^5D_3 + 1.73^5L_{10}$
3819.7		0.27	26 173	26 188	4	$61.9^5D_3 + 35.9^5G_6 + 0.97^5L_{10}$
5G_6 (26 520)	3815.6	0.36	26 200	26 210	2	$82.2^5D_3 + 15.1^5G_6 + 1.09^5L_{10}$
	3815.9	0.25	26 208	26 212	4	$65.9^5D_3 + 31.9^5G_6 + 1.02^5L_{10}$
	3812.0	0.30	26 226	26 229	3	$71.3^5D_3 + 26.0^5G_6 + 1.47^5L_{10}$
	3802.5	0.46	26 291	26 280	1	$73.2^5G_6 + 22.9^5D_3 + 2.37^5L_{10}$
	3798.8	1.10	26 317	26 323	2	$96.4^5D_3 + 2.58^5G_6 + 0.82^5L_9$
	3796.9	0.05	26 330	26 326	3	$66.6^5D_3 + 29.4^5G_6 + 2.17^5G_5$
	3790.8	0.96	26 372	26 376	2	$92.9^5G_6 + 4.33^5L_{10} + 1.23^5G_5$
	3788.1	0.90	26 391	26 381	4	$57.9^5G_6 + 36.6^5D_3 + 2.97^5G_5$
	3785.4	2.32	26 410	26 429	1	$47.5^5G_6 + 47.2^5D_3 + 2.61^5G_5$
	3777.6	2.37	26 464	26 482	1	$77.1^5G_6 + 20.1^5L_{10} + 1.55^5L_9$
	3771.9	0.08	26 504	26 508	3	$63.4^5G_6 + 21.1^5D_3 + 12.0^5L_{10}$
	3771.1	0.06	26 510	26 514	4	$70.9^5G_6 + 13.8^5D_3 + 12.6^5L_{10}$
	3769.6	0.10	26 520	26 526	2	$65.2^5G_6 + 17.5^5L_{10} + 14.1^5D_3$
	3764.8	1.62	26 554	26 562	3	$78.6^5G_6 + 9.20^5D_3 + 9.2^5L_{10}$
	${}^5L_{10}$ (27 146)	3730.8	1.96	26 790	26 787	3
3730.5		3.27	26 798	26 794	4	$83.5^5G_6 + 13.4^5L_{10} + 1.35^5D_3$
3729		2.89	26 802	26 800	1	$91.2^5G_6 + 5.90^5L_{10} + 2.48^5D_3$
3728.5		2.00	26 813	26 807	2	$91.0^5L_{10} + 7.89^5G_6 + 0.31^5D_3$
				26 869	1	$90.4^5L_{10} + 8.15^5G_6 + 0.50^5D_3$
				26 889	2	$91.9^5L_{10} + 6.54^5G_6 + 0.59^5L_9$
				26 895	2	$90.7^5L_{10} + 6.85^5G_6 + 1.13^5G_5$
				26 915	4	$92.2^5L_{10} + 5.25^5G_6 + 1.21^5G_5$
				26 923	3	$85.4^5L_{10} + 11.3^5G_6 + 1.26^5G_5$
				26 971	1	$84.5^5L_{10} + 12.2^5G_6 + 1.08^5G_5$
				27 025	4	$87.5^5L_{10} + 9.18^5G_6 + 1.36^5G_5$
				27 044	4	$79.6^5L_{10} + 19.5^5G_6 + 0.34^5G_4$
				27 051	3	$91.8^5L_{10} + 3.49^5G_6 + 3.37^5G_5$
				27 055	3	$91.9^5L_{10} + 3.91^5G_5 + 2.56^5G_6$
				27 067	4	$89.1^5L_{10} + 5.33^5G_5 + 4.25^5G_6$
				27 073	4	$88.8^5L_{10} + 5.39^5G_5 + 4.29^5G_6$
				27 077	3	$91.9^5L_{10} + 4.45^5G_5 + 2.38^5G_6$
				27 515	1	$92.4^5L_{10} + 3.85^5G_5 + 2.54^5G_6$
	3633.3	1.22	27 515	27 528	1	$92.9^5L_{10} + 4.81^5G_5 + 1.34^5G_6$
	3632.5	1.20	27 521	27 533	3	$94.4^5L_{10} + 2.72^5G_5 + 2.03^5G_6$
5G_5 (27 795)	3620.4	0.32	27 613	27 639	4	$84.6^5L_{10} + 11.8^5G_5 + 1.52^5G_4$
	3613.3	0.36	27 668	27 664	4	$93.5^5L_{10} + 3.50^5G_5 + 2.06^5G_6$
	3610.6	0.29	27 688	27 679	2	$83.8^5G_5 + 7.53^5G_4 + 6.25^5L_{10}$
	3607.2	0.43	27 714	27 713	3	$71.8^5G_5 + 18.0^5L_{10} + 6.20^5G_4$
	3606	0.29	27 728	27 726	2	$80.4^5G_5 + 10.6^5G_4 + 5.58^5L_{10}$
					2	$49.2^5G_5 + 43.2^5L_{10} + 5.51^5G_4$

TABLE II. (Continued).

$2S+1L_J^b$	λ (Å) ^c	α (cm ⁻¹) ^d	E (cm ⁻¹) ^e obs.	E (cm ⁻¹) ^f calc.	Γ_n calc. ^g	Percent mixing of free-ion states
				27 729	1	$89.0^5L_{10} + 7.15^5G_5 + 1.79^5G_6$
	3600.0	1.23	27 760	27 745	2	$52.1^5L_{10} + 41.6^5G_5 + 2.71^5G_6$
	3599.1	3.32	27 777	27 768	1	$77.6^5G_5 + 8.79^5L_{10} + 6.23^5D_2$
	3592.5	0.91	27 815	27 812	1	$70.1^5G_5 + 14.5^5D_2 + 8.73^5L_{10}$
	3592.1	0.87	27 831	27 827	3	$90.5^5G_5 + 3.81^5D_2 + 2.89^5L_{10}$
				27 828	2	$92.4^5G_5 + 2.84^5L_{10} + 2.12^5D_2$
	3589.0	0.68	27 830	27 837	4	$92.5^5G_5 + 2.66^5L_{10} + 1.93^5D_2$
	3580.0	0.20	27 880	27 884	4	$77.0^5G_5 + 17.3^5D_2 + 2.47^5L_{10}$
	3579.3	0.60	27 930	27 906	3	$81.4^5G_5 + 12.7^5D_2 + 2.20^5L_{10}$
5D_2	3567	0.14	28 026	28 040	2	$90.5^5D_2 + 6.46^8G_4 + 2.20^5G_5$
(28 150)	3555	0.14	28 122	28 132	1	$91.7^5D_2 + 4.75^5G_5 + 3.11^5G_4$
5G_4				28 163	1	$49.7^5G_4 + 30.1^5D_2 + 18.8^5L_9$
(28 307)				28 164	4	$53.5^5G_4 + 26.1^5D_2 + 13.6^5L_9$
				28 167	3	$64.9^5G_4 + 20.4^5L_9 + 11.4^5D_2$
5L_9	3545.9	0.73	28 194	28 237	2	$96.5^5L_9 + 1.49^5G_4 + 0.68^5D_3$
(28 503)	3542.3	0.61	28 222	28 254	3	$97.2^5L_9 + 0.98^5G_5 + 0.88^5G_4$
	3538.2	1.14	28 255	28 255	1	$68.7^5L_9 + 13.5^5D_2 + 12.9^5G_4$
	3538.0	1.63	28 258	28 257	4	$83.6^5L_9 + 9.67^5D_2 + 3.22^5G_4$
	3536.5	1.68	28 268	28 262	1	$61.5^5G_4 + 34.0^5L_9 + 2.53^5D_2$
	3534.2	0.63	28 287	28 299	4	$64.2^5L_9 + 28.1^5G_4 + 4.24^5G_5$
	3534.0	0.30	28 300	28 313	2	$56.5^5L_9 + 36.9^5G_4 + 4.50^5G_5$
				28 316	3	$42.3^5G_4 + 41.2^5L_9 + 7.27^5G_5$
	3529.8	0.41	28 322	28 327	3	$41.4^5L_9 + 37.6^5D_2 + 10.6^5G_5$
				28 332	4	$63.6^5L_9 + 26.3^5G_4 + 5.83^5D_2$
				28 337	2	$77.9^5L_9 + 17.8^5G_4 + 2.87^5G_5$
				28 347	1	$47.9^5L_9 + 39.3^5G_4 + 6.29^5D_2$
				28 357	2	$54.2^5L_9 + 37.3^5G_4 + 4.29^5G_5$
				28 360	3	$36.3^5L_9 + 32.8^5G_4 + 23.4^5D_2$
	3524.1	1.64	28 368	28 371	1	$45.9^5G_4 + 31.1^5D_2 + 13.5^5G_5$
	3518.7	0.23	28 411	28 410	4	$39.3^5G_4 + 35.6^5D_2 + 13.3^5L_9$
	3504.5	0.40	28 527	28 547	1	$54.9^5L_9 + 40.4^5G_4 + 3.08^5G_5$
	3499.5	0.64	28 567	28 559	2	$58.2^5L_9 + 36.7^5G_4 + 3.85^5G_5$
	3499.0	0.36	28 570	28 562	3	$58.8^5L_9 + 37.0^5G_4 + 2.98^5G_5$
	3496.0	0.30	28 595	28 589	2	$57.8^5L_9 + 44.8^5G_4 + 3.19^5G_5$
	3495.4	0.41	28 601	28 594	1	$50.9^5L_9 + 34.0^5G_4 + 3.17^5G_5$

^aSpectrum obtained at 78 K; hot bands removed from the table based on comparison with 300 K absorption spectrum; transitions from 7F_6 ($\Gamma_1=0$ cm⁻¹ and $\Gamma_3=3$ cm⁻¹) are partially resolved as transitions to excited Stark levels.

^bMultiplet manifold of Tb³⁺(4f⁸); number in parentheses is the centroid calculated for the manifold.

^cWavelength in angstroms.

^dAbsorption coefficient in cm⁻¹.

^eEnergy in vacuum wave numbers.

^fCalculated splitting based on B_{nm} given in Table IV.

^gCalculated symmetry label for Γ_1 , Γ_2 , Γ_3 , or Γ_4 for calculated splitting.

^hReference 16; data reported between 1.2 and 4.2 K.

$$A_{nm} = -e^2 \sum_j q_j C_{nm}(\hat{R}_j) / R_j^{n+1}, \quad (4)$$

where q_j is the effective charge on the ion at R_j , e is the electrostatic charge in esu, and the sum extends over all ions in the lattice. The ion positions, effective ionic charges, and the oxygen ion polarizabilities have been reported earlier.²⁴

Our coordinate system involved the Z axis parallel to [001]. In the XY plane the X axis is parallel to [110] and the Y axis is parallel to [110] of the cubic garnet lattice. The calculated A_{nm} for the D_2 sites in YAG are as follows: $A_{20}=1451.8$, $A_{22}=2218.4$, $A_{40}=-614.93$, $A_{42}=-2809.3$, $A_{44}=-4934.3$, $A_{60}=-1477.9$, $A_{62}=-567.93$, $A_{64}=645.13$, and $A_{66}=-501.61$, all in units of cm⁻¹/Å ^{n} . These compo-

TABLE III. Absorption spectra of 5D_J , 5G_J , and 5L_J states of $\text{Tb}^{3+}(4f^8)$ in $\text{Tb}_3\text{Al}_5\text{O}_{12}$.^a

$2S+1L_J^b$	λ (Å) ^c	α (cm ⁻¹) ^d	E (cm ⁻¹) ^e obs.	E (cm ⁻¹) ^f calc.	Γ_n calc. ^g	Percent mixing of free-ion states	
5D_4 (20 605)	4873.6	24	20 513	20 505	1	$99.8^5D_4 + 0.11^5L_{10} + 0.09^5G_4$	
	4873	10	20 515	20 507	3	$99.8^5D_4 + 0.12^5L_{10} + 0.02^5G_6$	
	4870	29	20 528	20 520	4	$99.8^5D_4 + 0.13^5L_{10} + 0.03^5G_6$	
	4867.2	13	20 540	20 548	2	$99.7^5D_4 + 0.09^5L_{10} + 0.09^5G_4$	
	4855.3	36	20 590	20 602	4	$99.7^5D_4 + 0.13^5L_{10} + 0.08^5G_4$	
	4854.1	14	20 595	20 607	1	$99.6^5D_4 + 0.14^5G_6 + 0.13^5L_{10}$	
	4850.6	16	20 610	20 618	3	$99.6^5D_4 + 0.14^5G_6 + 0.10^5L_{10}$	
	4841	33	20 651	20 654	2	$99.6^5D_4 + 0.16^5G_6 + 0.11^5G_5$	
	4835.4	10	20 675	20 683	1	$99.3^5D_4 + 0.40^5G_6 + 0.09^5G_4$	
	5D_3 (26 302)	3821(sh)	6	26 160	26 152	3	$51.9^5G_6 + 44.5^5D_3 + 1.94^5L_{10}$
3820(sh)		16	26 170	26 170	1	$58.0^5G_6 + 38.2^5D_3 + 1.92^5L_{10}$	
5G_6 (26 566)	3820	36	26 175	26 173	4	$81.7^5D_3 + 16.5^5G_6 + 0.71^5L_{10}$	
	3817.4	5.2	26 188	26 183	2	$86.1^5D_3 + 11.2^5G_6 + 1.12^5G_5$	
	3817(sh)	3.3	26 194	26 190	4	$65.6^5D_3 + 32.1^5G_6 + 1.08^5L_{10}$	
	3811.4	11.3	26 225	26 214	3	$73.9^5D_3 + 23.2^5G_6 + 1.50^5L_{10}$	
	3805	25	26 274	26 290	2	$97.2^5D_3 + 1.74^5G_6 + 0.85^5L_9$	
	3799.4	11.5	26 312	26 297	1	$61.8^5G_6 + 33.6^5D_3 + 2.50^5L_{10}$	
	3797	11	26 324	26 314	3	$55.4^5D_3 + 39.6^5G_6 + 2.39^5G_5$	
	3786.1	32	26 405	26 407	4	$66.8^5G_6 + 26.4^5D_3 + 3.06^5G_5$	
	3785.1	24.5	26 412	26 413	2	$90.1^5G_6 + 7.38^5L_{10} + 1.32^5G_5$	
	3781.4	53	26 438	26 436	1	$67.5^5G_6 + 24.8^5D_3 + 2.87^5L_{10}$	
	3775.1	49	26 483	26 493	1	$71.2^5G_6 + 26.5^5L_{10} + 1.61^5L_9$	
	3775(sh)	10	26 493	26 497	3	$64.3^5G_6 + 17.4^5L_{10} + 14.8^5D_3$	
	3770(b)	10	26 520	26 527	4	$65.6^5G_6 + 23.7^5L_{10} + 8.31^5D_3$	
				26 534	2	$59.2^5G_6 + 27.9^5L_{10} + 9.94^5D_3$	
	3760.4	39	26 585	26 594	3	$70.7^5G_6 + 21.0^5L_{10} + 5.49^5D_3$	
	3757(sh)	8	26 610	26 616	1	$69.3^5G_6 + 27.9^5L_{10} + 1.00^5D_3$	
				26 617	4	$56.3^5G_6 + 28.8^5L_{10} + 11.4^5D_3$	
	3742.8	7	26 710	26 700	2	$76.9^5G_6 + 20.7^5L_{10} + 1.56^5D_3$	
	${}^5L_{10}$ (27 094)	3738.8	6.4	26 739	26 739	3	$79.7^5L_{10} + 18.1^5G_6 + 0.94^5D_3$
					26 751	4	$80.1^5L_{10} + 17.1^5G_6 + 1.39^5D_3$
3736(b)		5.1	26 753	26 753	1	$85.0^5L_{10} + 13.1^5G_6 + 0.82^5L_9$	
3735.4		7.8	26 763	26 769	2	$72.9^5L_{10} + 24.5^5G_6 + 0.97^5G_5$	
3727.1		56	26 823	26 827	1	$85.1^5L_{10} + 12.1^5G_6 + 1.23^5G_5$	
3724.8		45	26 839	26 843	2	$80.0^5L_{10} + 15.9^5G_6 + 1.43^5G_5$	
3719.1(sh)		10	26 880	26 887	3	$83.6^5L_{10} + 13.0^5G_6 + 1.25^5G_5$	
3717(sh)		6	26 890	26 896	4	$76.7^5L_{10} + 19.4^5G_6 + 1.10^5D_3$	
3710.8		34	26 941	26 961	1	$71.8^5L_{10} + 27.3^5G_6 + 0.40^5D_4$	
3705.5		18	26 979	26 993	3	$90.8^5L_{10} + 3.94^5G_6 + 3.63^5G_5$	
3705(sh)		10	26 985	26 994	4	$89.4^5L_{10} + 5.48^5G_6 + 3.67^5G_5$	
				27 020	2	$85.8^5L_{10} + 8.32^5G_6 + 4.84^5G_5$	
3699(sh)		10	27 026	27 026	3	$91.6^5L_{10} + 4.40^5G_5 + 2.93^5G_6$	
				27 027	4	$86.5^5L_{10} + 7.72^5G_6 + 4.72^5G_5$	
3696.5		55	27 045	27 030	1	$91.9^5L_{10} + 3.81^5G_5 + 3.11^5G_6$	
3631.9		40	27 526	27 546	1	$92.7^5L_{10} + 4.70^5G_5 + 1.73^5G_6$	
3630.9		31	27 534	27 553	3	$95.0^5L_{10} + 2.51^5G_6 + 1.82^5G_5$	
3625(b)	6	27 580	27 590	4	$96.3^5L_{10} + 3.06^5G_5 + 0.29^5L_9$		
3619.6	9.2	27 619	27 591	2	$94.2^5L_{10} + 2.65^5G_5 + 2.11^5G_5$		
5G_5 (27 783)	3616.2	9.8	27 645	27 646	4	$88.0^5G_5 + 6.38^5G_4 + 2.30^5L_{10}$	
	3615(sh)	6.3	27 655	27 659	2	$72.7^5G_5 + 16.5^5L_{10} + 5.30^5G_4$	
				27 692	1	$82.3^5L_{10} + 12.4^5G_5 + 2.27^5D_2$	
	3608.9	12	27 701	27 702	3	$78.5^5G_5 + 9.41^5G_4 + 6.75^5D_2$	

TABLE III. (Continued).

$2S+1L_J^b$	λ (Å) ^c	α (cm ⁻¹) ^d	E (cm ⁻¹) ^e obs.	E (cm ⁻¹) ^f calc.	Γ_n calc. ^g	Percent mixing of free-ion states
5D_2 (28 001)	3606.6	15	27 719	27 702	2	$80.6^5L_{10} + 14.8^5G_5 + 2.79^5G_6$
				27 724	2	$87.0^5G_5 + 6.32^5G_4 + 3.99^5L_{10}$
				27 725	1	$65.3^5G_5 + 16.4^5L_{10} + 12.6^5D_2$
	3596.3	52	27 793	27 787	1	$63.6^5G_5 + 24.9^5D_2 + 6.67^5L_{10}$
				27 812	3	$83.5^5G_5 + 9.16^5D_2 + 3.37^5L_{10}$
	3594(sh)	32	27 813	27 814	2	$81.1^5G_5 + 12.7^5D_2 + 3.67^5L_{10}$
				27 817	4	$67.0^5G_5 + 29.6^5D_2 + 1.73^5L_{10}$
	3592(sh)	14	27 830	27 831	4	$89.6^5G_5 + 3.49^5D_2 + 3.04^4L_{10}$
				27 874	3	$80.5^5G_5 + 14.5^5D_2 + 1.41^5L_{10}$
	3590.6	26	27 843	27 954	2	$80.8^5D_2 + 13.9^5G_5 + 4.30^5G_4$
				27 975	1	$86.1^5D_2 + 11.4^5G_5 + 1.89^5G_4$
	3586.6	29	27 874	28 110	1	$52.2^5D_2 + 26.6^5G_4 + 11.0^5G_5$
28 125				4	$42.0^5D_2 + 27.1^5G_4 + 22.5^5G_5$	
3576.3	18	27 954	28 204	3	$42.4^5D_2 + 25.5^5G_4 + 17.2^5G_5$	
			28 215	2	$97.7^5L_9 + 0.66^5L_{10} + 0.66^5G_4$	
(28 001)	3573.6	10.4	28 208	2	$91.0^5L_9 + 5.20^5D_2 + 2.21^5G_5$	
			28 220	4	$91.0^5L_9 + 5.20^5D_2 + 2.21^5G_5$	
3556.4	5.9	28 110	28 221	1	$87.1^5L_9 + 6.08^5D_2 + 2.63^5G_5$	
			28 229	3	$95.9^5L_9 + 1.61^5G_5 + 1.47^5D_2$	
3554.7	6.3	28 125	28 258	3	$43.8^5L_9 + 24.6^5G_4 + 20.5^5D_2$	
			28 289	4	$89.3^5L_9 + 7.27^5G_4 + 1.60^5G_5$	
3544.6	19	28 204	28 292	1	$59.4^5G_4 + 37.7^5L_9 + 1.53^5G_6$	
			28 313	2	$83.5^5L_9 + 13.9^5G_4 + 1.71^5G_5$	
5L_9 (28 486)	3544(sh)	6	28 336	4	$45.4^5L_9 + 45.0^5G_5 + 3.95^5G_5$	
			28 336	3	$49.9^5L_9 + 39.2^5G_4 + 7.86^5G_5$	
3542(b)	16	28 225	28 336	2	$63.5^5L_9 + 31.4^5G_4 + 3.65^5G_5$	
			28 342	1	$46.1^5L_9 + 35.7^5G_4 + 8.20^5G_5$	
3536	35	28 268	28 366	2	$65.4^5L_9 + 28.6^5G_4 + 3.34^5G_5$	
			28 375	3	$49.5^5G_4 + 46.2^5L_9 + 1.84^5D_2$	
3534.7	40.4	28 283	28 382	1	$65.8^5G_4 + 23.0^5L_9 + 5.58^5G_5$	
			28 411	4	$59.4^5G_4 + 20.8^5L_9 + 12.2^5D_2$	
5G_4 (28 359)	3532.3	28	28 541	1	$53.8^5G_4 + 41.4^5L_9 + 3.51^5G_5$	
			28 559	1	$53.8^5G_4 + 41.4^5L_9 + 3.51^5G_5$	
3528(sh)	5.7	28 336	28 581	2	$48.5^5L_9 + 46.5^5G_4 + 4.22^5G_5$	
			28 583	3	$47.8^5G_4 + 47.4^5L_9 + 3.69^5G_5$	
3527	14.4	28 345	28 588	4	$50.2^5G_4 + 44.5^5L_9 + 3.85^5G_5$	
			28 600	2	$58.9^5G_4 + 36.0^5L_9 + 3.83^5G_5$	
3523(sh)	23	28 375	28 603	1	$53.2^5L_9 + 44.8^5G_4 + 0.98^5G_5$	
			28 382	1		
3522.3	40	28 382				
3515.7	14	28 436				
3502.7	17	28 541				
3498.4	23	28 576				
3498(sh)	4.7	28 585				
3495(sh)	5.7	28 605				
3493.7	16.5	28 615				

^aSpectrum obtained at 78 K; hot bands removed based on comparison with 300 K absorption spectrum; transitions from 7F_6 ($\Gamma_1 = 0 \text{ cm}^{-1}$ and $\Gamma_3 = 3 \text{ cm}^{-1}$) to excited Stark levels are unresolved.

^bMultiplet manifold for $\text{Tb}^{3+}(4f^8)$; number in parentheses is the centroid calculated for the manifold.

^cWavelength in angstroms; sh denotes shoulder; b denotes broad.

^dAbsorption coefficient in cm^{-1} .

^eEnergy in vacuum wave numbers.

^fCalculated splitting based on B_{nm} given in Table IV.

^gCalculated symmetry label for Γ_1 , Γ_2 , Γ_3 , or Γ_4 for the calculated splitting.

nents are converted into crystal-field parameters, B_{nm} , through the theory developed by Morrison and his colleagues²⁸⁻³⁰ where

$$B_{nm} = \rho_n A_{nm}, \quad (5)$$

and where the ρ_n parameters account for shielding and other effects that change the values of $\langle r^n \rangle$ when the Tb^{3+} free-ion

is placed in the lattice environment. For Tb^{3+} , $\rho_2 = 0.1673$, $\rho_4 = 0.4990$, and $\rho_6 = 1.1232$, in units of Å^n . The B_{nm} parameters obtained for Tb^{3+} :YAG from the lattice-sum calculations are given in Table IV.

The predicted splitting for the Stark levels of the 7F_J multiplet, using the B_{nm} parameters determined from the lattice-sum calculations and varying only the centroids of

TABLE IV. Crystal-field splitting parameters B_{nm} for $\text{Tb}^{3+}(4f^8)$.^a

Calculation	B_{20} (cm^{-1})	B_{22} (cm^{-1})	B_{40} (cm^{-1})	B_{42} (cm^{-1})	B_{44} (cm^{-1})	B_{60} (cm^{-1})	B_{62} (cm^{-1})	B_{64} (cm^{-1})	B_{66} (cm^{-1})
$\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ^b	461	165	-169	-1720	-900	-1324	-621	599	-561
$\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ^c	464	126	-16.9	-1811	-999	-1228	-470	642	-491
$\text{Tb}^{3+}:\text{Tb}_3\text{Al}_5\text{O}_{12}$ ^d	551	36	-156	-1651	-922	-1288	-432	541	-426
$\text{Tb}^{3+}:\text{Tb}_3\text{Al}_5\text{O}_{12}$ ^e	509	52	-54.4	-1826	-1013	-1347	-465	553	-516

^aFree-ion parameters for $\text{Tb}^{3+}(4f^8)$: $E^1 = 6022$, $E^2 = 29.03$, $E^3 = 608.5$, $\zeta = 1710$, $\alpha = 20.1$, $\beta = -370$, and $\gamma = 1256$, in units of cm^{-1} .

^bParameters B_{nm} obtained from lattice-sum calculation for YAG.

^cParameters B_{nm} obtained from fitting 130 experimental-to-calculated levels; rms = 9 cm^{-1} ; Tb:YAG.

^dParameters B_{nm} obtained from lattice-sum calculation for TbAG.

^eParameters B_{nm} obtained from fitting 136 experimental-to-calculated levels; rms = 10.0 cm^{-1} ; TbAG.

each manifold, agrees well with the observed splitting and the symmetry label (Γ_n) assignments. Only in cases where neighboring Stark levels are predicted within several wave numbers of each other is there an occasional overlap of assignments, such as we find in 7F_5 . By transformation of coordinates, the Bayerer *et al.* B_{nm} parameters can be compared to the lattice-sum parameters as well as to the final set of B_{nm} parameters obtained by including experimental Stark levels from the 5D_J , 5G_J , and 5L_J manifolds reported in Tables II and III. The experimental Stark levels and the symmetry label assignments given in Tables I–III are based on a single set of B_{nm} for each garnet given in Table IV. From a final least-squares fitting of all the data for $\text{Tb}^{3+}:\text{YAG}$ that included 130 Stark levels, we obtained a rms of 9 cm^{-1} between calculated and experimentally assigned levels. The calculated splitting is reported in Tables I and II. Many of the predicted Γ_n have been confirmed experimentally by reported studies on Zeeman effects and features of magnetopolarized luminescence.^{22–26}

Since a solid-solution phase exists between YAG and TbAG, one can follow the spectral details of individual transitions and the relatively small energy shifts in Stark levels as the $\text{Tb}^{3+}(4f^8)$ ion moves from the dilute YAG matrix to the pure compound TbAG.^{1–3} Given the similarity in local site symmetry of Tb^{3+} in both YAG and TbAG, we can model the splitting of the ${}^{2S+1}L_J$ multiplets in the pure garnet, TbAG, with a lattice-sum calculation for a starting set of B_{nm} , or we can use the final set of B_{nm} for $\text{Tb}^{3+}:\text{YAG}$ given in Table IV as the starting set for TbAG. Either way, we obtain a final set of B_{nm} for Tb^{3+} in TbAG also reported in

Table IV. The calculated Stark levels and Γ_n assignments are listed in Tables I and III. The final set of B_{nm} parameters for Tb^{3+} in TbAG is sufficiently close to the lattice-sum B_{nm} values, also listed in Table IV, that it is not likely that false minima are involved in the fitting analyses for Tb^{3+} in either host matrix. A total of 136 Stark levels were involved in analyzing the TbAG spectrum, giving an rms deviation of 10 cm^{-1} between calculated and observed levels. The wave functions for individual Stark levels predicted for Tb^{3+} in TbAG have been used successfully in describing the magnetic properties of the quintet states of Tb^{3+} in TbAG.^{22,23}

In summary, we report a detailed crystal-field splitting analysis of those quintet states of $\text{Tb}^{3+}(4f^8)$ whose energies are determined from the absorption spectra observed between 487 and 349 nm in the garnet hosts YAG and TbAG. In most cases the expected $2J+1$ Stark levels of a given multiplet manifold are identified from the 78 K absorption spectrum since the ground-state Stark level Γ_1 and the first excited Stark level, Γ_3 , at 3 cm^{-1} permit between the two levels, transitions to all excited Stark levels, Γ_1 , Γ_2 , Γ_3 , or Γ_4 . A least-squares fitting analysis between 130 experimental-to-calculated Stark levels for Tb^{3+} in YAG gave a rms deviation of 9 cm^{-1} . A similar analysis for the Stark levels of Tb^{3+} in TbAG, involving 136 experimental-to-calculated levels, gave a rms deviation of 10 cm^{-1} . Individual wave functions obtained from this calculation in a simple $|JM_J\rangle$ basis have been used successfully to interpret the MCPL and the Zeeman splitting of Tb^{3+} states in YAG and TbAG.

¹C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, New York, 1982), Vol. 5.

²A. K. Zvezdin, V. K. Matveev, A. A. Mukhin, and A. I. Popov, *Rare-Earth Ions in Magnetically Ordered Crystals* (Nauka, Moscow, 1985).

³A. A. Kaminskii, *Laser Crystals* (Springer, New York, 1981).

⁴W. De Sorbo, *Phys. Rev.* **158**, 839 (1967).

⁵F. J. Sansalone, *Appl. Opt.* **10**, 2329 (1971).

⁶U. V. Valiev, A. A. Klochkov, and V. Nekvasil, *Opt. Spectrosc.* **75**, 33 (1993).

⁷U. V. Valiev, V. Nekvasil, Sh. I. Mukhamedhanova, D. R. Dzhuraev, and K. S. Saidov, *Phys. Status Solidi B* **213**, 493 (1999).

⁸Sh. U. Abdullaev, U. V. Valiev, D. R. Dzhuraev, and V. Nekvasil, *Opt. Spectrosc.* **84**, 412 (1998).

⁹J. B. Gruber, C. K. Jensen, and M. L. Boling, *Optical Faraday Devices: Uses and Applications* (SPIE, Bellingham, WA, 2001).

- ¹⁰C. B. Rubenstein, L. G. Van Uitert, and W. H. Grodkiewicz, *J. Appl. Phys.* **35**, 3069 (1964).
- ¹¹C. A. Morrison, D. E. Wortmann, and N. Karayianis, *Phys. C: Solid State Phys.* **9**, L191 (1976).
- ¹²J. A. Koningstein, *Phys. Rev.* **136**, A717 (1964).
- ¹³D. Boal, P. Grünberg, and J. A. Koningstein, *Phys. Rev. B* **7**, 4757 (1973).
- ¹⁴P. Grünberg, S. Hufner, E. Orlich, and J. Schmitt, *Phys. Rev.* **184**, 285 (1969).
- ¹⁵J. A. Koningstein and C. J. Kane-Maguire, *Can. J. Chem.* **52**, 3445 (1974).
- ¹⁶R. Bayerer, J. Heber, and D. Mateika, *Z. Phys. B: Condens. Matter* **64**, 201 (1986).
- ¹⁷M. Wojcik, *J. Magn. Magn. Mater.* **15**, 21 (1980).
- ¹⁸D. J. Newman and G. E. Stedman, *J. Chem. Phys.* **51**, 3013 (1969).
- ¹⁹V. S. Korolkov and A. G. Makhanev, *Phys. Status Solidi B* **81**, 387 (1977).
- ²⁰U. V. Valiev, U. R. Rustamov, B. Yu. Sokolov, V. Nekvasil, R. A. Rupp, M. Fally, and I. Amin, *Phys. Status Solidi B* **231**, 98 (2002).
- ²¹N. P. Kolmakova, S. V. Koptsik, G. S. Krinchik, and A. Ya. Sarantsev, *Fiz. Tverd. Tela (Leningrad)* **33**, 2674 (1991) [*Sov. Phys. Solid State* **33**, 1510 (1991)].
- ²²U. V. Valiev, J. B. Gruber, U. R. Rustamov, K. S. Saidov, and B. Yu. Sokolov, *Pis'ma Zh. Tekh. Fiz.* **29**, 7 (2003).
- ²³U. V. Valiev, J. B. Gruber, B. Zandi, D. R. Djuraev, K. M. Mukimov, and N. M. Narzullaev (unpublished).
- ²⁴J. B. Gruber, M. E. Hills, R. M. Macfarlane, C. A. Morrison, G. A. Turner, G. J. Quarles, G. J. Kintz, and L. Esterowitz, *Phys. Rev. B* **40**, 9464 (1989).
- ²⁵J. B. Gruber, M. D. Seltzer, V. J. Pugh, and F. S. Richardson, *J. Appl. Phys.* **77**, 5882 (1995).
- ²⁶J. B. Gruber, *Tunable Lasers for Engineering and Biological Applications* (SPIE, Bellingham, WA, 1992).
- ²⁷W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.* **49**, 4424 (1968).
- ²⁸R. P. Leavitt and C. A. Morrison, *J. Chem. Phys.* **73**, 749 (1980).
- ²⁹C. A. Morrison, R. P. Leavitt, and D. E. Wortman, *J. Chem. Phys.* **73**, 2580 (1980).
- ³⁰C. A. Morrison and R. P. Leavitt, *J. Chem. Phys.* **71**, 2366 (1979).