PHYSICAL REVIEW B VOLUME 50, NUMBER 22 1 DECEMBER 1994-II

Energy-level and line-strength analysis of optical transitions between Stark levels in $Nd^{3+}:Y_3Al_5O_{12}$

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(Received 17 May 1994)

Results obtained from optical absorption measurements on $Nd^{3+}:Y_3Al_5O_{12}$ (Nd:YAG) at 10 and 295 K are reported and analyzed. The low-temperature (10 K) absorption spectrum shows transitions from the lowest Stark component of the $^4I_{9/2}$ (ground) multiplet to 133 of the 155 crystal-field (Stark) levels predicted to be located between 3900 and 40 000 cm^{-1}, spanning 35 excited multiplet manifolds of $Nd^{3+}(4f^3)$. Among the 133 transitions observed in the 10-K absorption spectrum, 97 are sufficiently well resolved to permit quantitative determination of transition line strengths. Energy levels for the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets are taken from previously obtained optical emission measurements, and the resulting 144-level data set is analyzed in terms of a model Hamiltonian that assumes D_2 site symmetry for the Nd^{3+} ions in Nd:YAG. Inclusion of two-electron correlation crystal-field (CCF) interaction terms in the model Hamiltonian explains the crystal-field splittings of several anomalous multiplets, and reduces the rms deviation between calculated and observed energies (for 144 levels) from 28 to 14 cm^{-1}. The optical line-strength data obtained in this study are analyzed in terms of an f-f transition intensity model developed by us in previous work. This model has broad applicability in analyses of f-f intensity data for transitions between Stark levels. Emission branching ratios for transitions from the $^4F_{3/2}$ multiplet are calculated and compared with literature values.

I. INTRODUCTION

The energy-level structures and optical properties of trivalent lanthanide ions (Ln^{3+}) in garnet hosts have been studied extensively over the past 25 years, and the applications of Ln^{3+}:garnet systems as laser materials are widely known.[1] Among these systems, $Nd^{3+}:Y_3Al_5O_{12}$ (Nd:YAG) has been exploited most fully in commercial optical technology applications, and is the basis of a major solid-state laser industry.

The spectroscopic properties and electronic energy-level structure of Nd:YAG and many other Ln^{3+}:garnet systems have been investigated by many workers, and the results obtained from these investigations have been analyzed at various levels of detail. The most detailed measurements and analyses have focused on (1) crystal-field energy-level structure associated with the $4f^N$ electronic configuration of the Ln^{3+} ions located at D_2 symmetry sites in the host (garnet) lattice, (2) total absorption cross sections associated with optical transitions between the ground and various excited $^{2S+1}L_J$ multiplet manifolds of the $4f^N(Ln^{3+})$ electronic configuration, and (3) branching ratios observed in optical emission from one or several excited multiplet levels.

Much of the energy-level data on Ln^{3+}:garnet systems have been analyzed in terms of model Hamiltonians constructed to represent the major interactions responsible for $4f^N$ electronic energy-level structure. These data are generally sufficient for supporting detailed parametric analyses of crystal-field energy-level structure, both within and among many $4f^N$ $[SL]J$ multiplet manifolds in any given system. In contrast, most of the optical absorption and emission data reported in the literature for Ln^{3+}:garnet systems are either inadequate or unsuitable for use in detailed analyses of transition intensities. Where intensity analyses have been performed, they have focused almost exclusively on *total* intensities associated with J-multiplet to J'-multiplet ($J \rightarrow J'$) transition manifolds, and they have been based on the phenomenological three-parameter form of the Judd-Ofelt theory for f-f transition intensities. The parameters derived from these intensity analyses (generally denoted by Ω_2, Ω_4, and Ω_6) are useful for characterizing $J \rightarrow J'$ intensity properties under room-temperature conditions at a phenomenological level, but they contain no information about how $J \rightarrow J'$ intensity is distributed among transitions between individual Stark levels, and they are of marginal value and questionable significance in dealing with low-temperature intensity data.

In the present study, we report measurements of optical line strengths for 97 transitions observed in the absorption spectrum of Nd:YAG at 10 K. All of these transitions originate from the lowest crystal-field level of the $^4I_{9/2}$ (ground) multiplet of $Nd^{3+}(4f^3)$, and they terminate on resolved crystal-field levels split out of 31 excited $[SL]J$ multiplets of $4f^3$.

The transition line-strength data obtained from our

0163-1829/94/50(22)/16309(17)/$06.00

absorption measurements are sufficient to support an intensity analysis considerably more detailed and definitive than those reported previously for Nd:YAG (and for other Ln^{3+}:garnet systems). The analysis is based on a parametric model that retains an explicit dependence on the *SLJ and* M_J compositions of the spectroscopic state vectors (as dictated by $4f$-electron–crystal-field interactions), allowing intensity distributions of transitions between Stark levels to be addressed. This model has been used with considerable success in analyzing optical line-strength data for transitions between Stark levels in a series of $Na_3[Ln(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ systems (where "oda" denotes an oxydiacetate dianion ligand),[2–9] and the parameters derived from those analyses have proved useful in sorting out various mechanistic contributions to $4f-4f$ transition intensities. Applications of this model to Nd:YAG intensity data are of interest for two reasons: (1) They provide further tests of the proposed general applicability of the model, and (2) the results may provide important insights into the mechanistic nature of $4f$-$4f$ optical processes in Ln^{3+}:garnet systems.

The parametric intensity analyses performed in the present study require as input both empirical line-strength data and crystal-field state vectors (expressed in an f^3SLJM_J angular momentum basis). The latter are obtained as the eigenvectors of a model Hamiltonian parametrized to give optimum fits between calculated and observed locations of crystal-field energy levels. Standard one-electron crystal-field interactions cannot account for the crystal-field splittings observed within certain multiplet manifolds of $4f^3(Nd^{3+})$.[10,11] These discrepancies between calculated and observed splittings are resolved by including certain correlation crystal-field (CCF) interaction terms in the model Hamiltonian. These CCF terms not only alter the calculated splitting energies within the problematic multiplet manifolds, but also alter the state vectors calculated for the affected crystal-field levels. The latter has important consequences in our intensity calculations and analyses, which, for comparison, we performed both *with* and *without* inclusion of CCF effects.

Finally, we note that branching ratios for ${}^4F_{3/2} \rightarrow {}^4I_J$ emission processes in Nd:YAG have been reported by several workers.[12–14] These branching ratios were measured at sample temperatures of 77 and 300 K, but they are well resolved with respect to crystal-field component transitions. These data are also considered in our intensity analyses, and are compared with predicted emission branching ratios based upon our calculated absorption parametrization.

II. OPTICAL ABSORPTION MEASUREMENTS

All of the optical absorption measurements performed in the present study were carried out on a Nd^{3+}:$Y_3Al_5O_{12}$ (Nd:YAG) crystal with a 0.092 mol concentration of Nd^{3+} ions. If it is assumed that all of the Nd^{3+} ions are located at erstwhile Y^{3+} sites in the host lattice, then a 0.092 mol concentration of Nd^{3+} corresponds to a 0.41% occupancy of Y^{3+} sites by Nd^{3+} ions. The crystal thickness along the optical path in our absorption measurements was 0.50 cm.

All absorption measurements were carried out using a Cary Model 2415 UV-Vis-NIR spectrophotometer, and spectra were recorded over the 250–2600 nm wavelength range. Measurements were performed at sample temperatures of 10 and 295 K, with the crystal sample mounted at the cold station of a CTI-Cryogenics closed-cycle helium refrigerator/cryostat. The temperature of the cold station in this refrigerator/cryostat was controlled using a Lake Shores Cryogenics, Inc. temperature controller (model DRC-70).

The ground and first-excited crystal-field levels of the ${}^4I_{9/2}(4f^3)$ ground multiplet of Nd:YAG are separated by $\sim$133 cm^{-1}, and at 10 K, all transitions observed in the optical absorption spectra originate from the ground crystal-field level of ${}^4I_{9/2}$. The 250–2600 nm wavelength range of our absorption measurements spans 35 excited multiplet manifolds of $Nd^{3+}(4f^3)$. These excited multiplet manifolds contain a total of 155 crystal-field levels (each a Kramer's doublet), and transitions to 133 of these levels were observed in our 10-K absorption spectra.

Among the 133 observed transitions, 97 showed spectral line shapes sufficiently well resolved (and well defined) to permit quantitative determinations of transition line strengths. Line strengths were determined by integrating observed absorbances over transition line profiles and then evaluating

$$S_{i\rightarrow f}(D^2) = \frac{9.174\times 10^{-3} g_i}{c_m\ \ell\ \chi_\lambda}\int_{i\rightarrow f}\frac{A(\bar\nu)d\bar\nu}{\bar\nu}, \tag{1}$$

where $S_{i\rightarrow f}(D^2)$ denotes the line strength of a transition $i \rightarrow f$, expressed in units of D^2 (D $\equiv$ 1 debye unit = 10^{-18} esu cm = 3.3356×10^{-30} C m); g_i is the degeneracy of level i; c_m is the molar concentration of Nd^{3+} ions in the sample; ℓ is the sample thickness (in cm); χ_λ is a correction factor for bulk sample refractivity at the transition wavelength λ; $A(\bar\nu)$ denotes the decadic absorbance of the sample at wave number $\bar\nu$; and the integration is over the absorbance profile of the $i \rightarrow f$ transition. In all of our experiments, $c_m = 0.092$ mol and $\ell = 0.50$ cm, and for all transitions, $g_i = 2$. In evaluating the χ_λ factors, we assumed the predominance of electric-dipole contributions to transition intensities, and defined χ_λ according to

$$\chi_\lambda = \frac{(n_\lambda^2+2)^2}{9n_\lambda}, \tag{2}$$

where n_λ is the refractive index of the sample at wavelength λ. The wavelength dependence of n_λ was calculated from the Sellmeier dispersion equation

$$n_\lambda = \left[1 + \frac{A\lambda^2}{\lambda^2 - B}\right]^{1/2}, \tag{3}$$

where $A = 2.2779$ and $B = 11\,420$ nm^2.[15]

At 295 K, *four* of the five crystal-field levels split out of the ${}^4I_{9/2}$ ground multiplet of Nd:YAG have significant thermal populations, and transitions originating from each of these levels are observed in the 295-K absorption spectra. These transitions are too congested and their lines are too poorly resolved to permit quantitative line-strength determinations for individual transitions between Stark levels. However, integrated intensities over complete $^4I_{9/2}$ (multiplet) to excited multiplet transition manifolds were determined, and the results compared to those obtained from similar measurements reported previously by Krupke[16] and Kaminskii and Li.[17]

III. METHODS OF ANALYSIS

A. Energy levels

The energy levels analyzed in this study span 37 (of the 41 total) $^{2S+1}L_J$ multiplet manifolds of the $4f^3(\mathrm{Nd}^{3+})$ electronic configuration, and they include 144 of the 166 crystal-field levels predicted to be split out of these multiplets. The locations of 133 levels were determined from our optical absorption measurements carried out at a sample temperature of 10 K (see Sec. II), and the locations of the remaining levels, within the $^4I_{9/2}$ and $^4I_{11/2}$ multiplet manifolds, were taken from previous emission studies of Nd:YAG.[18]

Our analysis of crystal-field energy-level structure in Nd:YAG is based on the use of a model Hamiltonian defined to operate entirely *within* the $4f^3$ electronic configuration of Nd^{3+}. All parts of the Hamiltonian that depend on $4f$-electron radial coordinates, or describe the intermixing from states of opposite parity, are represented as parameters that may be used as variables in performing experimental-to-calculated energy-level data fits. For convenience of discussion, the model Hamiltonian may be partitioned as follows:

$$\hat{H} = \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{CF}} + \hat{H}_{\mathrm{CCF}}, \qquad (4)$$

where $\hat{H}_{\mathrm{A}}$ denotes an "atomic" Hamiltonian defined to include all relevant interactions *except* those associated with nonisotropic components of the crystal-field potential, and $\hat{H}_{\mathrm{CF}}$ and $\hat{H}_{\mathrm{CCF}}$ are crystal-field interaction operators that are defined below. The atomic Hamiltonian is expressed explicitly as

$$\hat{H}_{\mathrm{A}} = E_{\mathrm{avg}} + \sum_k F^k \hat{f}_k + \alpha \hat{L}(\hat{L}+1) + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7) + \sum_i T^i \hat{t}_i + \zeta_{\mathrm{s.o.}} \hat{A}_{\mathrm{s.o.}} + \sum_k P^k \hat{p}_k + \sum_j M^j \hat{m}_j, \qquad (5)$$

where $k = 2, 4, 6$; $i = 2, 3, 4, 6, 7, 8$; and $j = 0, 2, 4$. Both the notation and meanings of the various operators and parameters in this expression are defined according to standard practice.[19,20]

The $\hat{H}_{\mathrm{CF}}$ operator is defined to represent the *anisotropic* components of the *one-electron* crystal-field interactions, and may be expressed in the following form:

$$\hat{H}_{\mathrm{CF}} = \sum_{kq} B_q^k \hat{C}_q^{(k)}, \qquad (6)$$

where the B_q^k parameters contain the radially dependent parts of the one-electron crystal-field interactions, and the $\hat{C}_q^{(k)}$ are many-electron spherical tensor operators acting within the $4f^N$ electronic configuration. Only the *even-parity* parts of this operator are relevant to our $4f^3(\mathrm{Nd}^{3+})$ energy-level calculations, thus limiting allowed values of k to 2, 4, and 6. Further, if we assume D_2 symmetry for the crystal-field potential at the Nd^{3+} sites in Nd:YAG, the allowed values of q are limited to 0, ±2, ±4, and ±6.

The $\hat{H}_{\mathrm{CCF}}$ operator in Eq. (4) is defined according to the prescriptions of Judd[21] and Li and Reid[10,22] to include contributions from correlated two-electron crystal-field interactions. This Hamiltonian contains a large number of terms, but previous studies have shown that just a few of these terms are needed in treating crystal-field splitting problems in Nd^{3+} systems.[10,11,23] Following this previous work, we use the following highly restricted form of the $\hat{H}_{\mathrm{CCF}}$ operator in the present study:

$$\hat{H}_{\mathrm{CCF}} = \sum_i G_i^4 \left[\hat{g}_{i0}^{(4)} + \frac{B_2^4}{B_0^4}\left(\hat{g}_{i2}^{(4)} + \hat{g}_{i-2}^{(4)}\right) + \frac{B_4^4}{B_0^4}\left(\hat{g}_{i4}^{(4)} + \hat{g}_{i-4}^{(4)}\right) \right], \qquad (7)$$

where the summation is restricted to terms labeled as $i = 2$, $10A$, and $10B$ in the general formal representation of $\hat{H}_{\mathrm{CCF}}$ (see Refs. 10 and 22 for details of notation). Note that in writing Eq. (7), it is assumed that the q dependence of the G_{iq}^4 CCF parameters follows that of the one-electron CF parameters B_q^4 according to

$$G_{iq}^4 = G_i^4 \left(\frac{B_q^4}{B_0^4} \right). \qquad (8)$$

Therefore, the $\hat{H}_{\mathrm{CCF}}$ operator used in the present study contains just three independent parameters G_2^4, G_{10A}^4, and G_{10B}^4. For more detailed discussion of the $\hat{H}_{\mathrm{CCF}}$ Hamiltonian and its use in crystal-field energy-level analyses, the reader is referred to Refs. 10, 11, 21, 22, and 24.

B. Transition line strengths

In our parametric analyses of optical line strengths for transitions between crystal-field (Stark) levels, we employ methodologies that have been described in considerable detail elsewhere.[2–9,25–28] It is assumed that observed line strengths derive entirely from electric- and magnetic-dipole transition mechanisms, and that these line strengths may be calculated by evaluating

$$S_{i \to f} = |\langle \psi_i | \hat{\mu}_{\mathrm{eff}} | \psi_f \rangle|^2 + |\langle \psi_i | \hat{\mathbf{m}} | \psi_f \rangle|^2 , \qquad (9)$$

where $\hat{\mu}_{\mathrm{eff}}$ denotes an "effective" electric-dipole moment operator (defined below), $\hat{\mathbf{m}}$ denotes the magnetic-dipole moment operator, ψ_i and ψ_f are state vectors for the initial and final levels in the $i \to f$ transition, and all degeneracies pertinent to levels i and f are contained *implic-*

itly in the transition matrix elements. The radial dependence of the electric-dipole matrix element is absorbed entirely into the $\hat{\mu}_{\text{eff}}$ operator in parametric form, and $\hat{\mu}_{\text{eff}}$ is defined as an *even-parity* operator that operates *within* the $4f^N$ electronic configuration. This operator effectively represents the combined perturbations of odd-parity crystal-field interactions *and* odd-parity electric-dipolar radiation field interactions on the $4f$ electrons of the system.

Expressed in explicit form, the qth (spherical) component of $\hat{\mu}_{\text{eff}}$ is given by[2–9,25–28]

$$(\hat{\mu}_{\text{eff}})_q = -e(-1)^q \sum_{\lambda tp} A^{\lambda}_{tp} \sum_{\ell} \langle \lambda\ell, 1-q|tp\rangle \hat{U}^{(\lambda)}_{\ell}, \quad (10)$$

where $\lambda = 2, 4, 6$; $t = \lambda, \lambda{\pm}1$; $p = 0, \pm1, \pm2, ..., \pm t$; and $\ell = q+p$. The $\hat{U}^{(\lambda)}_{\ell}$ are intraconfigurational many-electron unit tensor operators that act within the $4f^N$ electronic configuration, and the A^{λ}_{tp} are parameters that contain structural and mechanistic details regarding interactions of the odd-parity crystal field *and* the electric-dipolar radiation field with the $4f$ electrons of the system.

The $\{A^{\lambda}_{tp}\}$ parameter set must reflect the site symmetry of the lanthanide ions, which places restrictions on the permissible pairs of (t,p) values for each value of λ.[25,26] For D_2 site symmetry, there are 5 A^2_{tp} parameters, with (t,p) = (2,0), (2,±2), and (3,±2); 11 A^4_{tp} parameters, with (t,p) = (3,±2), (4,0), (4,±2), (4,±4), (5,±2), and (5,±4); and 17 A^6_{tp} parameters, with (t,p) = (5,±2), (5,±4), (6,0), (6,±2), (6,±4), (6,±6), (7,±2), (7,±4), and (7,±6). However, we also have the relationship $(A^{\lambda}_{tp})^* = (-1)^{t+p+1} A^{\lambda}_{t-p}$, and the total number of *independent* parameters in the $\{A^{\lambda}_{tp}\}$ set for D_2 symmetry is 18: 3 with λ=2, 6 with λ=4, and 9 with λ=6.

Insertion of Eq. (10) into Eq. (9) yields

$$S_{i\to f} = e^2 \left| \sum_{\lambda tp} A^{\lambda}_{tp} \sum_{\ell q} \langle \lambda\ell, 1-q|tp\rangle (-1)^q \langle \psi_i|\hat{U}^{(\lambda)}_{\ell}|\psi_f\rangle \right|^2 + |\langle \psi_i|\hat{\mathbf{m}}|\psi_f\rangle|^2, \quad (11)$$

where q = 0, ±1. In performing our transition line-strength calculations, the $\langle \psi_i|\hat{U}^{(\lambda)}_{\ell}|\psi_f\rangle$ and $\langle \psi_i|\hat{\mathbf{m}}|\psi_f\rangle$ matrix elements are evaluated directly, using ψ_i and ψ_f state vectors generated from the energy-level calculations described in Sec. III A, and the A^{λ}_{tp} parameters are treated as variables in fitting calculated line strengths to the observed line strengths [as determined from Eq. (1) given in Sec. II].

The *total* line strength associated with a particular multiplet-to-multiplet transition manifold may be obtained by summing over all the $S_{i\to f}$ line strengths that contribute to the transition manifold of interest. Under the very special conditions in which both the initial and final multiplet levels derive entirely from $4f^N$ $[SL]J$ states of well-defined J character, *and* in which all of the crystal-field (or M_J) sublevels within each multiplet can be assumed to be essentially degenerate, it is readily shown that the electric-dipole (ED) contributions to the total line strength can be evaluated from[3,5,25,26]

$$S^{\text{ED}}_{\psi J\to\psi' J'} = e^2 \sum_{\lambda} \frac{1}{(2\lambda+1)} \sum_{tp} \left|A^{\lambda}_{tp}\right|^2 \langle \psi J\|\hat{\mathbf{U}}^{(\lambda)}\|\psi' J'\rangle^2, \quad (12)$$

where ψJ and $\psi' J'$ are intermediate-coupled wave functions that are eigenvectors of the atomic Hamiltonian defined by Eq. (5). Making the following identification between the A^{λ}_{tp} parameters and the Judd-Ofelt Ω_{λ} intensity parameters,

$$\Omega_{\lambda} = \frac{1}{(2\lambda+1)} \sum_{tp} \left|A^{\lambda}_{tp}\right|^2, \quad (13)$$

we note that Eq. (12) *exactly* matches the famous Judd-Ofelt expression for multiplet-to-multiplet ($\psi J \to \psi' J'$) transition line strengths:

$$S^{\text{ED}}_{\psi J\to\psi' J'} = e^2 \sum_{\lambda} \Omega_{\lambda} \langle \psi J\|\hat{\mathbf{U}}^{(\lambda)}\|\psi' J'\rangle^2. \quad (14)$$

This expression has been widely used, with considerable success, in analyses of $\psi J \to \psi' J'$ transition intensity data, and the Ω_{λ} intensity parameters derived from these analyses are often used as diagnostic indicators of f-f electric-dipole transition intensity mechanisms.[29]

However, the special conditions on which the rigorous validity of Eqs. (12) and (14) is based are never fully met in real systems. These conditions require the absence of crystal-field-induced mixings *among* different J multiplets, and the absence of crystal-field-induced splittings *within* J multiplets.

C. Superposition model and intrinsic intensity parameters

The A^{λ}_{tp} parametrization scheme described above applies only to the electric-dipole intensities of *one-photon–one-electron* f-f transition processes, but it is otherwise free of any detailed mechanistic assumptions about these processes.[25,26] However, information regarding specific mechanistic contributions to electric-dipole intensity is contained *implicitly* in the relative signs and magnitudes of the A^{λ}_{tp} parameters.[2,3,5–8,29–32]

Perhaps the most notable mechanistic differentiation provided by the A^{λ}_{tp} parameters is that obtained from comparisons between the $t = \lambda \pm 1$ and $t = \lambda$ subsets of these parameters. For all mechanisms based on pairwise lanthanide-ligand (Ln-L) interactions that are assumed to be cylindrically symmetric *and* independent, the $t = \lambda$ parameters $\{A^{\lambda}_{\lambda p}\}$ must vanish. Therefore, the relative magnitude of the $t = \lambda$ parameters versus the $t = \lambda \pm 1$ parameters can provide information about the local symmetry and pairwise independence of the Ln-L interactions that contribute to f-f electric-dipole intensity.

Crystal-field interaction models based on the assumption of pairwise independent and cylindrically symmetric Ln-L interactions are often referred to as "superposition models," reflecting the representation of total (or global) interactions as "superpositions" of local (Ln-L) pairwise interactions.[33–37] These models may be expected to work best for systems in which the first coordination sphere of the lanthanide ion is comprised entirely of monatomic ligands. This condition is met in Nd:YAG, where each Nd^{3+} ion in a Y^{3+} (D_2 symmetry) lattice site has eight oxygen atoms in its first coordination sphere. Detailed superposition model (SM) analyses of crystal-field energy parameters for Nd:YAG have been reported by Nekvasil.[38]

In order to test the validity of the superposition model (SM) assumptions in treating Nd:YAG intensity data, we performed two sets of line-strength analyses: one in which all 18 members of the $\{A_{tp}^{\lambda}\}$ parameter set were used in fitting calculated line strengths to observed line strengths, and another in which only the nine $t = \lambda \pm 1$ members of this parameter set were incorporated into our calculations. Hereafter, we shall refer to the general, 18-parameter analyses as "GP" fits, and to the superposition-model-restricted, 9-parameter analyses as "SMP" fits. Similar, comparative analyses of f-f intensity data have been reported previously for other systems.[2,5–8,27,28,30–32,39]

According to the basic tenets of the superposition model, the crystal-field energy parameters (B_q^k) and electric-dipole intensity parameters (A_{tp}^{λ}) should be expressible as summations over individual ligand contributions to Ln-L and Ln-L-$h\nu$ (radiation field) interaction strengths. This notion leads to expressions of the form[27,28,32,37]

$$B_q^k = \sum_L \bar{B}_k(L) C_{-q}^k(L)(-1)^q (R_0/R_L)^{\tau_k(L)}, \qquad (15)$$

$$A_{tp}^{\lambda} = \sum_L \bar{A}_t^{\lambda}(L) C_{-p}^t(L)(-1)^p (R_0/R_L)^{\tau_t^{\lambda}(L)}, \qquad (16)$$

where $C_{-q}^k(L)$ and $C_{-p}^t(L)$ are normalized spherical harmonic functions that together with R_L locate the position of ligand L in the coordination environment of the Ln atom; R_0 is the radial distance between Ln and some (real or pseudo) reference ligand located on the Z axis of the system; $\tau_k(L)$ and $\tau_t^{\lambda}(L)$ are power-law exponents that reflect the falloff of crystal-field interaction strengths with distance; and $\bar{B}_k(L)$ and $\bar{A}_t^{\lambda}(L)$ are commonly referred to as *intrinsic* Ln-L interaction parameters. If all the ligands of interest are *chemically* identical, it may be presumed that the $\bar{B}_k$ and $\bar{A}_t^{\lambda}$ intrinsic parameters and the τ_k and τ_t^{λ} power-law exponents are independent of L labels, and Eqs. (15) and (16) may be rewritten as

$$B_q^k = \bar{B}_k \sum_L C_{-q}^k(L)(-1)^q (R_0/R_L)^{\tau_k}, \qquad (17)$$

$$A_{tp}^{\lambda} = \bar{A}_t^{\lambda} \sum_L C_{-p}^t(L)(-1)^p (R_0/R_L)^{\tau_t^{\lambda}}. \qquad (18)$$

Given empirically determined values of B_q^k and A_{tp}^{λ} parameters and detailed structural information about the coordination environment of the Ln atom, these equations can be used to determine values for the $\bar{B}_k$ and $\bar{A}_t^{\lambda}$ *intrinsic* parameters and the τ_k and τ_t^{λ} power-law exponents.

As noted earlier, superposition model analyses of Nd:YAG crystal-field energy parameters have been reported in the literature.[38] In the present study, we performed similar analyses with the A_{tp}^{λ} intensity parameters derived from our SMP fits of transition line-strength data.

IV. RESULTS AND DISCUSSION

A. Energy levels

Parameters for the model Hamiltonian, defined in Eqs. (5) – (7), were calculated using a least-squares fitting to 144 experimentally resolved $4f^3(\mathrm{Nd}^{3+})$ Stark component energy levels. Sixteen of the 20 atomic Hamiltonian parameters [see Eq. (5)] were freely varied in the energy-level fittings. The remaining four parameters were constrained by Hartree-Fock-determined fixed ratios: M^2 and M^4 to M^0, and P^4 and P^6 to P^2.

An ambiguity arises when determining crystal-field and correlation crystal-field parameter values, due to the three possible choices of the Z axis in D_2 symmetry for the $\mathrm{Nd}^{3+}(\mathrm{Y}^{3+})$ sites of the YAG crystal. For each of these three choices, there are two possible orientations, which only affect the signs of the $q = \pm 2$, ± 6 components. In order to emphasize the approximate O_h and D_4 character of the Nd^{3+} site, and to facilitate comparison with Nekvasil's[38] superposition model analysis, we will emphasize the Morrison-Leavitt[40] "set 3" orientation.

However, since most of the reported crystal-field parameters in the literature utilize a differing orientation, we present our crystal-field and correlation crystal-field parameters in each of the three possible Z-axis orientations in Table I. The first three numerical columns of this table present our optimized crystal-field parameter set (CF) neglecting correlation, and the last three columns present the optimized parameter set (CCF) including correlation crystal-field parameters. Individual parameter values vary widely between the three orientations. However, for each value of k and i, the magnitudes of $\sum_q |B_q^k|^2$ and $\sum_q |G_{iq}^k|^2$ are invariant with respect to Z-axis orientation. The ratios of the different q components of the correlation crystal-field G_{iq}^k parameters were not freely varied; rather, they were constrained according to Eq. (8).

Table II presents the complete parameter sets generated in the CF and CCF fittings. Crystal-field and correlation crystal-field parameters are presented in the Morrison-Leavitt "set 3" orientation. Uncertainties for each parameter were generated by multiplying the square roots of the diagonal elements of the error matrix by the overall standard deviation, and they represent a factor of 2 increase in the square of the standard deviation. All parameters, uncertainties, and standard deviations in this table are given in units of cm^{-1}. As can be seen from the bottom line of this table, inclusion of the three CCF operators greatly improves the overall fit to the experimental levels, with a factor of 2 reduction in the overall

TABLE I. Crystal-field and correlation crystal-field energy parameters (in cm^{-1}) for three different D$_2$ symmetry orientations of the Nd^{3+}(Y^{3+}) sites in Nd:YAG. See Ref. 40 for definition of set numbers 1–3.

	CF			CCF		
Parameter	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3
B_0^2	422	−17	−405	405	−17	−387
B_2^2	158	−337	179	151	−323	172
B_0^4	−183	659	−2823	−122	714	−2766
B_2^4	−2199	1667	540	−2202	1672	529
B_4^4	−971	−1674	1239	−937	−1637	1275
B_0^6	−1949	−907	955	−1865	−1003	972
B_2^6	−591	573	−390	−605	569	−333
B_4^6	833	1111	1610	853	1083	1611
B_6^6	−583	1143	−281	−632	1110	−229
G_{20}^4				−36	208	−804
G_{22}^4				−640	486	154
G_{24}^4				−272	−476	371
G_{10A0}^4				57	−333	1290
G_{10A2}^4				1026	−780	−247
G_{10A4}^4				437	763	−594
G_{10B0}^4				27	−157	609
G_{10B2}^4				485	−368	−117
G_{10B4}^4				206	361	−281

standard deviation from 31 cm^{-1} down to 15 cm^{-1} (rms deviation reduced from 28 cm^{-1} down to 14 cm^{-1}).

Calculated energy levels using the two sets of Hamiltonian parameters of Table II are compared with experiment in the first columns of Table III. Root mean square deviations are given for each multiplet. The addition of the three CCF parameters G_{10A}^4, G_{10B}^4, and G_2^4 vastly improves the fits to several multiplets that are not well explained by the CF fitting. For example, the total crystal-field splitting of the $^2H(2)_{11/2}$ multiplet (levels 48–53), which is *underestimated* by 203 cm^{-1} in the CF fit, is well explained by the CCF fit. The crystal-field splitting of the $^2G_{7/2}$ multiplet (levels 57–60) is *overestimated* by more than 60 cm^{-1} in the CF fit, but is explained much better by the CCF fit. Two other prominent multiplets not well explained by the CF fit are the high-energy multiplets $^2F(2)_{5/2}$ (levels 160–162) and $^2F(2)_{7/2}$ (levels 163–166). The CF fit underestimates the crystal-field splittings of these two multiplets by about 180 cm^{-1} and 160 cm^{-1}, respectively, while the CCF fit is significantly closer, with a respective underestimation of about 50 cm^{-1} and overestimation of 12 cm^{-1}.

The energy-level data set analyzed in this study corresponds closely to that investigated previously by Gruber *et al.*,[18] although there are some differences in the locations and assignments of levels in a few multiplet regions. As expected, the *atomic* and *one-electron crystal-field* Hamiltonian parameter values derived in the present study are quite similar to those obtained by Gruber and co-workers, but the treatment of *correlation crystal-field* effects is entirely different in the two studies. Gruber *et al.* employed a highly restrictive variant of CCF theory, commonly referred to as the *spin-correlated crystal-field* (SCCF) model. However, inclusion of SCCF terms in the model Hamiltonian could not resolve the large discrepancies between calculated and observed crystal-field splittings in the problematic $^2H(2)_{11/2}$, $^2G_{7/2}$, and $^2F(2)_{5/2}$ multiplet manifolds, and did not produce any significant improvement in calculated-to-observed energy-level fits.[18]

B. Transition line strengths

As was the case for the crystal-field and correlation crystal-field energy parameters, values of the calculated intensity parameters are dependent upon which choice of Z-axis orientation is selected. Transition intensity parameters are presented in Table IV for each of the three possible Z-axis orientations. Each column in this table corresponds to the crystal-field energy parameter set given in the respective column of Table I.

For the CF and CCF fittings given in Table IV, all 18 parameters in the general intensity parametrization were freely varied. However, many of the intensity parameters have uncertainties greater than their magnitudes, and therefore have values that are not statistically significant. Parameters with statistically insignificant values (given within parentheses in Table IV) were removed, and the remaining parameters were refit to the experimental data, significantly decreasing the statistical standard deviations of the fittings, while only negligibly increasing respective root mean square deviations.

Final results of the fittings that include only those intensity parameters with statistically significant values are given in Table V for the Morrison-Leavitt "set 3" orientation. The first two numerical columns of Table V present fittings for superposition-model-restricted intensity parametrization using CF and CCF wave functions. Only six of the nine allowed parameters of the superposition model are included in these fittings, as values determined for the A^2_{32}, A^6_{74}, and A^6_{76} parameters are not statistically significant. Similarly, the last two columns of this table present fittings for the general intensity parametrization, where all statistically significant parameters are included.

The intensity parameters and uncertainties in Table V are given in units of $i \times 10^{-12}$ cm. Uncertainties for individual parameters are generated by multiplying the square roots of the diagonal elements of the error matrix by σ, and represent a factor of 2 increase in the square of the overall standard deviation. The 97 experimentally resolved line strengths were fit using a differential least-squares fitting which minimizes $|(\text{expt}-\text{calc})/(\text{expt}+\text{calc})|^2$, and a unitless standard deviation σ is given in terms of this differential weighting. Thus, for example, the $\sigma = 0.369$ represents an $(\text{expt}/\text{calc}) = (1+\sigma)/(1-\sigma) = 2.17$ uncertainty factor in the predicted intensities. We see from the fits in this table that the use of CCF wave functions and the addition of intensity parameters predicted by the superposition model to be zero both give improvements to the intensity fits.

TABLE II. Hamiltonian parameters (in cm^{-1}) obtained from crystal-field (CF) and correlation crystal-field (CCF) analyses of Nd:YAG energy-level data.

Parameter[a]	CF	CCF
E_{avg}	24097 ± 11	24095 ± 6
F^2	70845 ± 156	70809 ± 78
F^4	51235 ± 338	51132 ± 175
F^6	34717 ± 145	34819 ± 71
α	21.1 ± 0.4	20.8 ± 0.2
β	−645 ± 19	−629 ± 10
γ	1660 ± 43	1656 ± 22
T^2	345 ± 57	366 ± 29
T^3	46 ± 7	46 ± 3
T^4	61 ± 9	66 ± 5
T^6	−272 ± 17	−270 ± 8
T^7	318 ± 30	324 ± 15
T^8	271 ± 38	307 ± 18
$\zeta_{\text{s.o.}}$	876 ± 4	873 ± 2
M^0	1.62 ± 0.41	1.76 ± 0.22
M^2	0.558 M_0	0.558 M_0
M^4	0.377 M_0	0.377 M_0
P^2	107 ± 85	209 ± 44
P^4	0.75 P_2	0.75 P_2
P^6	0.50 P_2	0.50 P_2
B^2_0	−405 ± 29	−387 ± 15
B^2_2	179 ± 25	172 ± 12
B^4_0	−2823 ± 84	−2766 ± 45
B^4_2	540 ± 93	529 ± 45
B^4_4	1239 ± 67	1275 ± 36
B^6_0	955 ± 101	972 ± 51
B^6_2	−390 ± 87	−333 ± 45
B^6_4	1610 ± 56	1611 ± 27
B^6_6	−281 ± 78	−229 ± 39
G^4_2		−804 ± 135
G^4_{10A}		1290 ± 80
G^4_{10B}		609 ± 108
N[b]	144	144
n[c]	25	28
σ[d]	31.1	15.3

[a] Parameter notation follows that of Eqs. (5) – (7) of the text. See Sec. IV A in the text for further descriptions of the $\{B^k_q\}$ and $\{G^k_i\}$ parameter sets used.

[b] Total number of energy levels used in the parametric data analyses.

[c] Total number of freely varied parameters.

[d] Standard deviations (in cm^{-1}) calculated for least-squares energy-level fits.

Assuming the superposition model holds, we can use the calculated parameters of Table V to generate *intrinsic* intensity parameters analogous to the intrinsic crystal-field parameters generated by Nekvasil.[38] If we assume that only the coordinated ligands give significant contributions, then Eq. (18) can be used to determine values for the intrinsic parameters. The quantities associated with the sets of identical ligands (L') at the same distance,

$$\sum_{L'} C^t_{-p}(L')(-1)^p, \tag{19}$$

are referred to as "coordination factors." Coordination factors relevant to the intensity parameters for Nd:YAG are calculated and presented in Table VI. Multiplying the coordination factors by the radial terms, and summing over the sets of ligands, we get a total geometric factor,

$$\sum_{L} C^t_{-p}(L)(-1)^p(R_0/R_L)^{\tau^\lambda_t}, \tag{20}$$

which relates the empirically determined A^λ_{tp} intensity parameters to the intrinsic parameters $\bar{A}^\lambda_t$ [see Eq. (18)]. Total geometric factors and intrinsic parameters for Nd:YAG are presented in the last two columns of Table VI.

Previous work that includes both empirical fits[27,32] and detailed calculations[41] found that the intrinsic parameters $\bar{A}^2_1$, $\bar{A}^2_3$, $\bar{A}^6_5$, and $\bar{A}^6_7$ tend to be positive, and $\bar{A}^4_3$ and $\bar{A}^4_5$ tend to be negative. Except for $\bar{A}^2_1$ and $\bar{A}^2_3$, which were not determined in this calculation, all intrinsic parameters given in the last column of Table VI follow this trend. However, we see there is quite poor internal agreement regarding magnitudes of the intrinsic parameters $\bar{A}^4_5$ (determined from A^4_{52} and A^4_{54}) and $\bar{A}^6_5$ (determined from A^6_{52} and A^6_{54}). These discrepancies cannot be removed by reasonable choices of the power-law exponents, or by reasonable distortions of the site geometry.

If we consider the calculated geometric factors presented in Table VI to be essentially correct, we can fit the $\bar{A}^\lambda_t$ intrinsic intensity parameters directly to the experimental data. Results of this new fitting are presented in Table VII. The two columns on the left of this table present the fitted intrinsic intensity parameter values and uncertainties, while the right-hand columns give resultant calculated A^λ_{tp} intensity parameters. There is reasonable agreement between the large A^4_{54} and A^6_{54} parameters calculated in Table VII and fitted in column SMP/CCF of Table V, but differences between the other intensity parameters are more pronounced. Even so, the intrinsic intensity parameter fitting presented in Ta-

TABLE III. Calculated and experimentally observed energy-level data and transition line strengths for Nd:YAG.[a]

		Energy (cm^{-1})					Line strengths (10^{-7} D^2) [b]				
	Level		CF		CCF			CF		CCF	
Multiplet	No.	Expt.	Calc.	Δ	Calc.	Δ	Expt.[c]	Calc.[d]	$\frac{E-C}{E+C}$	Calc.[e]	$\frac{E-C}{E+C}$
$^4I_{9/2}$	1	0	−6	6	6	−6					
	2	133	138	−5	134	−1	—	4349		5227	
	3	199	205	−6	205	−6	—	7737		7240	
	4	310	338	−28	327	−17	—	12418		12202	
	5	859	872	−13	870	−11	—	13272		11281	
	Total [f]							37777		35951	
	σ[g]			*14*		*10*			—		—
$^4I_{11/2}$	6	2002	2002	0	2003	−1	—	7200		6246	
	7	2029	2020	9	2023	6	—	10387		6478	
	8	2110	2087	23	2086	24	—	3987		3526	
	9	2147	2147	0	2142	5	—	17330		15403	
	10	2468	2470	−2	2467	1	—	2298		2014	
	11	2521	2526	−5	2518	3	—	8872		6762	
	Total							50073		40429	
	σ			*10*		*10*			—		—
$^4I_{13/2}$	12	3926	3922	4	3927	−1	1009	2597	−0.440	2317	−0.393
	13	3936	3925	11	3930	6	2688	3396	−0.116	4165	−0.215
	14	4035	4009	26	4011	24	1668	2652	−0.228	3927	−0.404
	15	4050	4045	5	4042	8	2779	5438	−0.324	4386	−0.224
	16	—	4431		4428		—	62		104	
	17	4437	4438	−1	4438	−1	1247	593	0.355	697	0.283
	18	4501	4509	−8	4498	3	2320	3576	−0.213	3747	−0.235
	Total						11712	18315	−0.220	19344	−0.246
	σ			*12*		*11*			*0.299*		*0.303*
$^4I_{15/2}$	19	5762	5750	12	5765	−3	438	511	−0.077	821	−0.304
	20	5817	5835	−18	5838	−21	375	501	−0.144	475	−0.118
	21	5938	5926	12	5940	−2	637	339	0.304	580	0.047
	22	5971	5969	2	5966	5	427	325	0.136	389	0.047
	23	6578	6568	10	6569	9	230	230	0.002	138	0.250
	24	6594	6605	−11	6601	−7	406	261	0.217	292	0.163
	25	6647	6657	−10	6651	−4	399	246	0.237	314	0.120
	26	6735	6743	−8	6744	−9	1217	771	0.224	953	0.122
	Total						4129	3184	0.129	3962	0.021
	σ			*11*		*9*			*0.191*		*0.169*
$^4F_{3/2}$	27	11435	11413	22	11421	14	367	424	−0.072	526	−0.178
	28	11519	11479	40	11484	35	1069	5656	−0.682	6681	−0.724
	Total						1436	6079	−0.618	7206	−0.668
	σ			*32*		*26*			*0.485*		*0.527*
$^4F_{5/2}$, $^2H(2)_{9/2}$	29	12367	12354	13	12343	24	2261	8758	−0.590	9958	−0.630
	30	12433	12432	1	12413	20	639	2352	−0.573	4654	−0.759
	31	12516	12448	68	12519	−3	620	7742	−0.852	4005	−0.732
	32	12571	12598	−27	12567	4	4801	3902	0.103	6659	−0.162
	33	12604	12650	−46	12616	−12	1389	1413	−0.009	1579	−0.064
	34	12620	12670	−50	12645	−25	1945	1385	0.168	1872	0.019
	35	12825	12800	25	12834	−9	565	1673	−0.495	1122	−0.330
	36	12851	12843	8	12848	3	1137	1182	−0.019	884	0.125
	Total						13355	28407	−0.360	30734	−0.394
	σ			*37*		*15*			*0.459*		*0.456*
$^4F_{7/2}$, $^4S_{3/2}$	37	13359	13378	−19	13374	−15	6271	6587	−0.025	9803	−0.220
	38	13425	13436	−11	13426	−1	653	2360	−0.567	1245	−0.312
	39	13561	13553	8	13554	7	—	1768		1150	
	40	13567	13566	1	13566	1	—	5168		6292	
	41	13592	13599	−7	13600	−8	4330	2497	0.269	2334	0.300
	42	13629	13649	−20	13637	−8	5755	8391	−0.186	9432	−0.242
	Total							26771		30255	
	σ			*13*		*8*			*0.327*		*0.271*
$^4F_{9/2}$	43	14620	14641	−21	14618	2	522	789	−0.204	604	−0.073
	44	14672	14685	−13	14661	11	336	861	−0.438	704	−0.353
	45	14788	14776	12	14788	0	350	445	−0.119	451	−0.125
	46	14814	14822	−8	14837	−23	412	388	0.031	306	0.149
	47	14911	14918	−7	14936	−25	457	427	0.033	379	0.093
	Total						2078	2911	−0.167	2444	−0.081
	σ			*13*		*16*			*0.223*		*0.188*
$^2H(2)_{11/2}$	48	15741	15862	−121	15757	−16	16	50	−0.516	18	−0.065
	49	15831	15882	−51	15842	−11	50	47	0.034	42	0.088
	50	15865	15909	−44	15864	1	67	35	0.306	58	0.073
	51	15950	15920	30	15945	5	75	58	0.125	68	0.052
	52	16088	16005	83	16087	1	75	30	0.434	43	0.275
	53	16104	16022	82	16119	−15	14	23	−0.264	24	−0.273
	Total						297	244	0.098	252	0.081
	σ			*75*		*10*			*0.325*		*0.168*
$^4G_{5/2}$	54	16842	16864	−22	16848	−6	618	1014	−0.243	916	−0.194
	55	16982	16982	0	16984	−2	4151	18956	−0.641	9892	−0.409
	56	17038	17057	−19	17071	−33	1459	9497	−0.734	7621	−0.679
	Total						6229	29467	−0.651	18429	−0.495

TABLE III. *(Continued).*

	Level	Energy (cm^{-1})					Line strengths (10^{-7} D^2) [b]				
			CF		CCF			CF		CCF	
Multiplet	No.	Expt.	Calc.	Δ	Calc.	Δ	Expt.[c]	Calc.[d]	$\frac{E-C}{E+C}$	Calc.[e]	$\frac{E-C}{E+C}$
	σ			*17*		*19*			*0.580*		*0.471*
$^2G_{7/2}$	57	17237	17203	34	17230	7	845	1351	−0.230	627	0.148
	58	17257	17264	−7	17270	−13	2675	716	0.578	1404	0.312
	59	17316	17294	22	17305	11	309	1489	−0.656	472	−0.208
	60	17565	17595	−30	17564	1	5548	10217	−0.296	6842	−0.104
	Total						9377	13772	−0.190	9345	0.002
	σ			*25*		*9*			*0.476*		*0.208*
$^4G_{7/2}$	61	18719	18698	21	18726	−7	395	292	0.150	220	0.285
	62	18821	18819	2	18811	10	1645	1478	0.054	2404	−0.187
	63	18839	18852	−13	18842	−3	1614	3862	−0.410	2403	−0.196
	64	18979	18991	−12	18961	18	2808	2904	−0.017	2683	0.023
	Total						6462	8535	−0.138	7709	−0.088
	σ			*14*		*11*			*0.220*		*0.197*
$^2K_{13/2}$, $^4G_{9/2}$	65	19157	19142	15	19165	−8	290	443	−0.208	439	−0.204
	66	19290	19275	15	19294	−4	320	305	0.023	470	−0.190
	67	19320	19323	−3	19326	−6	—	129		192	
	68	—	19429		19445		—	264		265	
	69	19468	19465	3	19478	−10	588	520	0.061	543	0.040
	70	19542	19519	23	19538	4	—	318		334	
	71	19569	19576	−7	19558	11	1361	1665	−0.100	1347	0.005
	72	19612	19588	24	19594	18	279	256	0.042	140	0.330
	73	19650	19656	−6	19657	−7	277	419	−0.205	226	0.102
	74	19816	19814	2	19814	2	254	218	0.077	358	−0.170
	75	—	19866		19874		—	162		104	
	76	20046	20027	19	20024	22	948	590	0.233	573	0.247
	Total						4318	5290	−0.101	4989	−0.072
	σ			*14*		*11*			*0.142*		*0.190*
$^2G(1)_{9/2}$, $^2D(1)_{3/2}$, $^4G_{11/2}$, $^2K_{15/2}$	77	20721	20703	18	20717	4	299	108	0.472	224	0.144
	78	20762	20780	−18	20760	2	590	235	0.431	545	0.040
	79	20781	20805	−24	20770	11	—	643		244	
	80	20794	20819	−25	20785	9	—	192		179	
	81	20968	20957	11	20971	−3	130	149	−0.069	216	−0.250
	82	21036	21004	32	21012	24	103	208	−0.340	144	−0.170
	83	21083	21046	37	21090	−7	213	110	0.318	41	0.677
	84	21116	21096	20	21107	9	76	152	−0.334	181	−0.408
	85	21159	21144	15	21160	−1	546	167	0.532	177	0.510
	86	21163	21166	−3	21172	−9	—	62		75	
	87	—	21505		21513		—	169		220	
	88	21549	21526	23	21526	23	—	103		56	
	89	21602	21616	−14	21616	−14	—	8		15	
	90	21667	21661	6	21671	−4	—	53		52	
	91	21695	21716	−21	21731	−36	—	157		250	
	92	21766	21766	0	21765	1	—	275		177	
	93	21792	21811	−19	21793	−1	—	78		79	
	94	—	21866		21869		—	188		279	
	95	21870	21901	−31	21883	−13	—	84		44	
	96	21959	21927	32	21913	46	—	95		107	
	97	22036	22049	−13	22033	3	717	308	0.399	289	0.425
	Total							3545		3595	
	σ			*21*		*17*			*0.385*		*0.384*
$^2P_{1/2}$	98	23148	23130	18	23124	24	247	1792	−0.757	2005	−0.780
	Total						247	1792	−0.757	2005	−0.780
	σ			*18*		*24*			*0.757*		*0.780*
$^2D(1)_{5/2}$	99	23662	23676	−14	23666	−4	37	41	−0.045	47	−0.112
	100	23743	23759	−16	23759	−16	45	18	0.431	26	0.260
	101	23835	23816	19	23808	27	17	13	0.128	9	0.315
	Total						99	72	0.160	82	0.096
	σ			*16*		*18*			*0.261*		*0.245*
$^2P_{3/2}$	102	25980	26009	−29	25998	−18	70	76	−0.041	71	−0.011
	103	26061	26063	−2	26060	1	—	1		7	
	Total						70	77	−0.049	78	−0.058
	σ			*21*		*13*			*0.041*		*0.011*
$^4D_{3/2}$, $^4D_{5/2}$, $^4D_{1/2}$	104	27561	27537	24	27547	14	801	2005	−0.429	2219	−0.470
	105	27659	27684	−25	27675	−16	1230	2539	−0.347	2677	−0.370
	106	27797	27800	−3	27791	6	725	713	0.009	842	−0.075
	107	28177	28176	1	28193	−16	—	1703		1629	
	108	28271	28276	−5	28287	−16	—	5138		7240	
	109	28385	28376	9	28361	24	—	6549		5920	
	Total							18648		20528	
	σ			*15*		*16*			*0.319*		*0.348*
$^2I_{11/2}$	110	28553	28567	−14	28578	−25	166	47	0.559	45	0.572
	111	28745	28761	−16	28753	−8	83	56	0.195	90	−0.043
	112	28917	28927	−10	28919	−2	836	516	0.237	457	0.293
	113	—	29079		29089		—	42		56	

TABLE III. *(Continued).*

Multiplet	Level No.	Energy (cm^{-1}) Expt.	CF Calc.	Δ	CCF Calc.	Δ	Line strengths (10^{-7} D^2)^b Expt.^{c}	CF Calc.^{d}	$\frac{E-C}{E+C}$	CCF Calc.^{e}	$\frac{E-C}{E+C}$
	114	29223	29231	−8	29245	−22	151	240	−0.229	298	−0.328
	115	—	29333		29343		—	64		64	
	Total						1236	966	0.123	1012	0.100
	σ			*13*		*17*			*0.338*		*0.361*
$^2L_{15/2}$, $^4D_{7/2}$, $^2I_{13/2}$	116	29729	29733	−4	29733	−4	—	30		18	
	117	—	29855		29843		—	133		209	
	118	29889	29866	23	29875	14	—	16		27	
	119	—	29898		29894		—	48		43	
	120	29955	29940	15	29945	10	—	317		337	
	121	29993	30012	−19	30009	−16	—	155		191	
	122	30088	30071	17	30073	15	—	104		84	
	123	—	30087		30105		—	65		39	
	124	30133	30124	9	30124	9	—	33		36	
	125	—	30165		30164		—	95		38	
	126	30209	30215	−6	30215	−6	—	328		391	
	127	—	30245		30232		—	3		10	
	128	—	30319		30295		—	26		33	
	129	—	30353		30351		—	23		44	
	130	30414	30416	−2	30428	−14	—	164		185	
	131	—	30488		30486		—	61		84	
	132	30539	30545	−6	30538	1	—	23		22	
	133	—	30576		30568		—	17		12	
	134	—	30591		30590		—	11		15	
	Total							1652		1817	
	σ			*13*		*11*			—		—
$^2L_{17/2}$	135	31304	31285	19	31278	26	—	13		16	
	136	—	31400		31399		—	31		36	
	137	31459	31464	−5	31460	−1	—	9		2	
	138	31488	31512	−24	31493	−5	—	4		2	
	139	31534	31539	−5	31530	4	—	4		8	
	140	31560	31556	4	31568	−8	—	2		4	
	141	31613	31625	−12	31614	−1	—	10		3	
	142	31751	31771	−20	31754	−3	—	13		12	
	143	31895	31865	30	31882	13	—	13		13	
	Total							100		97	
	σ			*18*		*11*			—		—
$^2H(1)_{9/2}$	144	32555	32564	−9	32558	−3	45	30	0.199	43	0.017
	145	32606	32577	29	32595	11	29	52	−0.278	31	−0.024
	146	32655	32650	5	32652	3	32	49	−0.206	54	−0.253
	147	32713	32715	−2	32705	8	24	152	−0.723	170	−0.749
	148	32739	32749	−10	32736	3	72	5	0.876	16	0.642
	Total						203	287	−0.173	314	−0.216
	σ			*14*		*7*			*0.538*		*0.456*
$^2D(2)_{3/2}$	149	32972	32960	12	32970	2	95	74	0.123	84	0.059
	150	33035	33039	−4	33031	4	161	98	0.242	81	0.328
	Total						256	172	0.195	166	0.213
	σ			*9*		*3*			*0.192*		*0.236*
$^2D(2)_{5/2}$, $^2H(1)_{11/2}$	151	33687	33698	−11	33684	3	14	4	0.588	11	0.151
	152	—	33749		33767		—	28		12	
	153	33831	33820	11	33827	4	148	76	0.319	65	0.390
	154	34047	34026	21	34054	−7	11	38	−0.540	12	−0.030
	155	—	34066		34087		—	8		35	
	156	34138	34141	−3	34164	−26	77	36	0.360	13	0.719
	157	—	34215		34216		—	4		10	
	158	34282	34300	−18	34281	1	299	74	0.603	109	0.467
	159	—	34413		34439		—	6		5	
	Total						551	274	0.335	272	0.340
	σ			*14*		*12*			*0.496*		*0.427*
$^2F(2)_{5/2}$	160	37777	37909	−132	37826	−49	172	88	0.323	54	0.523
	161	38077	38018	59	38061	16	412	102	0.603	100	0.611
	162	38192	38145	47	38193	−1	28	20	0.155	16	0.270
	Total						612	211	0.488	170	0.566
	σ			*88*		*29*			*0.405*		*0.490*
$^2F(2)_{7/2}$	163	39202	39293	−91	39187	15	86	17	0.664	23	0.577
	164	39333	39325	8	39332	1	17	4	0.615	6	0.462
	165	39417	39378	39	39401	16	102	9	0.836	14	0.751
	166	39690	39621	69	39687	3	33	20	0.244	13	0.419
	Total						238	51	0.650	57	0.612
	σ			*60*		*11*			*0.628*		*0.567*
$^2G(2)_{9/2}$	167	—	46818		46791		—	1		15	
	168	—	46840		46807		—	23		14	
	169	—	46985		46963		—	9		8	
	170	—	47064		47046		—	1		1	
	171	—	47074		47097		—	1		2	
	Total							36		40	

TABLE III. *(Continued).*

		Energy (cm^{-1})					Line strengths (10^{-7} D^2) [b]				
	Level		CF		CCF			CF		CCF	
Multiplet	No.	Expt.	Calc.	Δ	Calc.	Δ	Expt.[c]	Calc.[d]	$\frac{E-C}{E+C}$	Calc.[e]	$\frac{E-C}{E+C}$
	σ			—		—			—		—
$^2G(2)_{7/2}$	172	—	47746		47714		—	3		5	
	173	—	47793		47778		—	25		32	
	174	—	47966		47919		—	14		13	
	175	—	48114		48141		—	16		15	
	Total							58		64	
	σ			—		—			—		—
$^2F(1)_{7/2}$	176	—	64518		64530		—	2		2	
	177	—	64925		64903		—	11		6	
	178	—	65031		65009		—	3		3	
	179	—	65297		65213		—	4		6	
	Total							20		18	
	σ			—		—			—		—
$^2F(1)_{5/2}$	180	—	65991		65923		—	22		18	
	181	—	66292		66201		—	4		4	
	182	—	66566		66433		—	24		20	
	Total							50		42	
	σ			—		—			—		—

[a] All experimental data obtained from absorption measurements carried out at 10 K.

[b] All line strengths are for transitions originating from the lowest crystal-field level of the $^4I_{9/2}$ (ground) multiplet manifold.

[c] Experimental line strengths determined according to Eq. (1) of the text.

[d] Calculated line strengths from evaluation of Eq. (11), using A_{tp}^{λ} parameters given in the GP/CF column of Table V.

[e] Calculated line strengths from evaluation of Eq. (11), using A_{tp}^{λ} parameters given in the GP/CCF column of Table V.

[f] Total summed intensities and deviations $[(E_{\text{tot}} - C_{\text{tot}})/(E_{\text{tot}} + C_{\text{tot}})]$ given for transitions from the ground (Stark) level to all levels of each excited multiplet manifold.

[g] Root mean square energy level and intensity deviations given for each multiplet.

ble VII yields an rms fitted error only about 4% greater than that of the SMP/CCF fit. We conclude that the superposition model seems to be only approximately correct for analysis of $4f$-$4f$ transitions in Nd:YAG, and thus we use the general parameter fits in our detailed intensity analysis.

Detailed results of the two general parameter intensity fits are presented in the right-hand columns of Table III. Experimental absorption line strengths at 10 K for transitions from the ground (Stark) component of the $^4I_{9/2}$ ground multiplet were determined as described in Sec. II. Calculated line strengths were determined from evalua-

TABLE IV. Electric-dipole intensity parameters (in $i \times 10^{-12}$ cm) for three different D_2 symmetry orientations of the $Nd^{3+}(Y^{3+})$ sites in Nd:YAG. See Ref. 40 for definition of set numbers 1–3. Parameters with statistically insignificant values (given in parentheses) were removed, and the remaining parameters were refit to experiment to generate final line-strength fittings given in Table V.

		CF			CCF	
Parameter	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3
A_{20}^2	(22)	282	261	(−73)	−149	221
A_{22}^2	222	(97)	(124)	−151	(120)	(31)
A_{32}^2	(−106)	(−106)	(−106)	(−42)	(−42)	(−42)
A_{32}^4	−216	−216	−216	−180	−180	−180
A_{40}^4	334	175	117	263	168	75
A_{42}^4	(−37)	137	(−100)	(−59)	119	(−60)
A_{44}^4	(20)	152	201	(22)	101	179
A_{52}^4	−424	202	222	−473	173	300
A_{54}^4	(−12)	373	−362	(−73)	446	−373
A_{52}^6	683	−571	(−112)	682	−595	(−87)
A_{54}^6	−265	−459	724	−293	−444	737
A_{60}^6	(−11)	(85)	(−45)	(33)	118	−112
A_{62}^6	−110	−150	−165	(−16)	−107	−92
A_{64}^6	(−23)	(2)	(−32)	(−18)	(4)	(−57)
A_{66}^6	143	(83)	(61)	132	(−4)	(18)
A_{72}^6	(−13)	(−61)	(−56)	(−23)	(−80)	−156
A_{74}^6	(5)	(37)	(−42)	(−65)	113	(−48)
A_{76}^6	(−73)	(−20)	(−26)	−148	(−86)	(−3)

TABLE V. Values of electric-dipole intensity parameters (in $i \times 10^{-12}$ cm) derived from analyses of Nd:YAG absorption line-strength data (obtained at a sample temperature of 10 K).

A^{λ}_{tp}	SMP/CF[a]	SMP/CCF[b]	GP/CF[c]	GP/CCF[d]
A^2_{20}			348 ± 92	199 ± 74
A^2_{22}			—[e]	—[e]
A^2_{32}	—[e]	—[e]	—[e]	—[e]
A^4_{32}	−212 ± 65	−170 ± 58	−151 ± 58	−164 ± 62
A^4_{40}			98 ± 62	97 ± 59
A^4_{42}			—[e]	—[e]
A^4_{44}			238 ± 66	213 ± 56
A^4_{52}	439 ± 45	415 ± 41	280 ± 64	316 ± 52
A^4_{54}	−403 ± 54	−400 ± 47	−346 ± 59	−374 ± 50
A^6_{52}	−99 ± 78	−115 ± 70	—[e]	—[e]
A^6_{54}	748 ± 59	749 ± 54	739 ± 54	749 ± 55
A^6_{60}			—[e]	−101 ± 77
A^6_{62}			−230 ± 54	−109 ± 52
A^6_{64}			—[e]	—[e]
A^6_{66}			—[e]	—[e]
A^6_{72}	−119 ± 74	−190 ± 73	—[e]	−149 ± 72
A^6_{74}	—[e]	—[e]	—[e]	—[e]
A^6_{76}	—[e]	—[e]	—[e]	—[e]
N[f]	97	97	97	97
n[g]	6	6	8	10
σ[h]	0.416	0.389	0.398	0.369

[a] Superposition-model-restricted intensity parametrization using wave functions from crystal-field (CF) energy-level fits.

[b] Superposition-model-restricted intensity parametrization using wave functions from correlation crystal-field (CCF) energy-level fits.

[c] General intensity parametrization using wave functions from CF energy-level fits.

[d] General intensity parametrization using wave functions from CCF energy-level fits.

[e] Parameters with statistically insignificant values omitted.

[f] Total number of experimentally determined line strengths used in the parametric data analyses.

[g] Total number of freely varied parameters.

[h] Unitless standard deviations given for a differential least-squares weighting, which minimizes the values $|(\text{expt}-\text{calc})/(\text{expt}+\text{calc})|^2$.

TABLE VI. Calculation of coordination factors and intrinsic parameters for Nd:YAG.

		Coordination factors					
A^{λ}_{tp}	Value[a]	Ligand set 1[b]	Ligand set 2[c]	τ^{λ}_{t}[d]	Total[e]	$\bar{A}^{\lambda}_{t}$	Value[f]
A^2_{32}	—	0.891	−0.634	5	0.409	$\bar{A}^2_3$	—
A^4_{32}	−170	0.891	−0.634	5	0.409	$\bar{A}^4_3$	−416
A^4_{52}	415	−0.081	−0.029	7	−0.101	$\bar{A}^4_5$	−4109
A^4_{54}	−400	1.275	0.909	7	1.900	$\bar{A}^4_5$	−210
A^6_{52}	−115	−0.081	−0.029	7	−0.101	$\bar{A}^6_5$	1138
A^6_{54}	749	1.275	0.909	7	1.900	$\bar{A}^6_5$	394
A^6_{72}	−190	−0.500	0.393	9	−0.260	$\bar{A}^6_7$	731
A^6_{74}	—	0.565	0.575	9	0.917	$\bar{A}^6_7$	—
A^6_{76}	—	1.209	−0.900	9	0.658	$\bar{A}^6_7$	—

[a] From column SMP/CCF of Table V (in $i \times 10^{-12}$ cm).

[b] From Nekvasil (Ref. 38), four O^{2-} ligands at coordinates $(R_1,\theta_1,\phi_1) = (2.303\ \text{Å}, 123.86°, -192.52°)$ plus D_2 symmetry operations.

[c] From Nekvasil (Ref. 38), four O^{2-} ligands at coordinates $(R_2,\theta_2,\phi_2) = (2.4323\ \text{Å}, 125.94°, 81.24°)$ plus D_2 symmetry operations.

[d] Power-law exponents from simple electrostatic mechanism.

[e] Total geometric factors from Eq. (20).

[f] Intrinsic parameters (in $i \times 10^{-12}$ cm) calculated by dividing the A^{λ}_{tp} parameters by the total geometric factors [see Eq. (18)].

TABLE VII. Calculation of intensity parameters from fitted intrinsic intensity parameters for Nd:YAG.

$\bar{A}_t^\lambda$	Value[a]	Geometric factor[b]	A_{tp}^λ	Value[c]
$\bar{A}_3^2$	110 ± 184	0.409	A_{32}^2	45
$\bar{A}_3^4$	−192 ± 158	0.409	A_{32}^4	−78
$\bar{A}_5^4$	−271 ± 22	−0.101	A_{52}^4	27
$\bar{A}_5^4$	−271 ± 22	1.900	A_{54}^4	−515
$\bar{A}_5^6$	429 ± 29	−0.101	A_{52}^6	−43
$\bar{A}_5^6$	429 ± 29	1.900	A_{54}^6	815
$\bar{A}_7^6$	103 ± 87	−0.260	A_{72}^6	−27
$\bar{A}_7^6$	103 ± 87	0.917	A_{74}^6	95
$\bar{A}_7^6$	103 ± 87	0.658	A_{76}^6	68

[a] Intrinsic intensity parameters (in $i\times10^{-12}$ cm) fitted directly. Statistical standard deviation, $\sigma = 0.402$ (rms = 0.391).
[b] Total geometric factors from Table VI.
[c] Intensity parameters (in $i \times 10^{-12}$ cm) calculated from Eq. (18).

tion of Eq. (11), using the A_{tp}^λ parameter sets given in the GP/CF and GP/CCF columns of Table V. Calculated magnetic-dipole contributions are negligible for all transitions *except* those to levels in the ground ($^4I_{9/2}$) and first excited ($^4I_{11/2}$) multiplets. Along with the experimental and calculated line strengths are presented the differential deviation (expt−calc)/(expt+calc) for each transition. Total multiplet intensities and unitless differential root mean square deviations are presented for each multiplet.

The use of CCF wave functions provides a modest (about 9%) improvement in the overall line-strength fitting over the use of the CF wave functions. However, for selected multiplets that have large eigenvector modifications due to inclusion of CCF operators, a much greater improvement can be seen. Examining those multiplets in which the CCF wave functions have the greatest effect upon the energy levels, we find that the CCF intensity fitting reduces the rms line-strength deviation by a factor of 2 for the $^2H(2)_{11/2}$ and $^2G_{7/2}$ multiplets. In contrast, we do not see an equivalent improvement for transitions to the high-lying $^2F(2)_{5/2}$ and $^2F(2)_{7/2}$ multiplets. This lack of improvement in calculated transition line strengths to high-energy multiplets perhaps can be rationalized by a partial breakdown of the Judd-Ofelt closure approximation, which is foundational to our transition line-strength calculations. Due to the small energy difference between energies of the final transition states and low-lying states of the first excited configuration $4f^25d$, errors introduced from the Judd-Ofelt closure approximation for these high-energy transitions can be expected to be much larger than for transitions to lower-energy levels.

TABLE VIII. Experimental line strengths determined for several ground- ($^4I_{9/2}$) to-excited multiplet transition manifolds of Nd:YAG at room temperature.

		Line strengths (10^{-6} D^2)	
Excited multiplet	λ[a]	Krupke[b]	Present work
$^4F_{3/2}$	880	1640	1710
$^4F_{5/2}$, $^2H_{9/2}$	790	8070	7570
$^4F_{7/2}$, $^4S_{3/2}$	750	7610	7300
$^4F_{9/2}$	680	623	646
$^2P_{1/2}$	430	171	173
$^2P_{3/2}$	385	140	140

[a] Approximate centroid of absorption band (in nm).
[b] See Table 1 of Ref. 16.

TABLE IX. Comparison of Ω_λ intensity parameters (in 10^{-20} cm^2).

	Ω_2	Ω_4	Ω_6
SMP/CF[a]	—[c]	8.9	8.9
SMP/CCF[a]	—[c]	8.0	9.4
GP/CF[a]	2.4	6.3	9.3
GP/CCF[a]	0.79	7.1	9.3
Krupke[b] (Ref. 16)	0.2	2.7	5.0
Kaminskii and Li[b] (Ref. 17)	0.37	2.29	5.97

[a] Ω_λ parameters calculated according to Eq. (13) of the text.
[b] Ω_λ parameters obtained from fits of room-temperature intensity data to the phenomenological Judd-Ofelt intensity formula [see Eq. (14) of the text].
[c] Ω_2 parameter indeterminate for this fit.

Total multiplet-to-multiplet absorption line strengths were measured at 295 K, and are presented in Table VIII. The last two columns of this table show that the published measurements of Krupke[16] at room temperature are virtually identical to our measurements.

Table IX presents the derived effective Ω_λ parameters from the four fittings of Table V for comparison with those obtained by Krupke[16] and Kaminskii and Li.[17] The Ω_2 parameters are poorly determined, as illustrated by the broad differences between parameter values for the different fits. There is reasonable agreement between the effective Ω_4 and Ω_6 parameters for the four fittings of Table V, but these parameter values are far from the literature values. These differences in parameter values should not be surprising. The literature values were determined at room temperature, while the parameters of Table V were generated for experimental measurements at 10 K. The derivation of Eq. (13) assumes that all Stark components of the initial state multiplet are equally occupied. However, even at room temperature, only *four* of the five ground-state Stark components have significant population, and at 10 K, only the lowest component is populated.

C. Emission branching ratios

Branching ratios for $^4F_{3/2} \rightarrow {}^4I_J$ emission processes in Nd:YAG were calculated for emission at 300 and 77 K. We converted our calculated emission line strengths into branching ratios that can be compared to published experimental data by calculating the relative populations of the two levels of the excited $^4F_{3/2}$ multiplet at the relevant temperatures (assuming a Boltzman distribution) and converting line strengths into Einstein A coefficients. To compare our results with the tables of Watts,[12] it was necessary to multiply our results by the photon energy and renormalize, in order to calculate the relative power (*not* the number of photons) radiated into each line. These calculated branching ratios are compared with the experimental data of Watts[12] in Table X for emission at 300 K and in Table XI for emission at 77 K.

Calculated values presented in Tables X and XI were not fit to the experimental data. Rather, the A_{tp}^{λ} intensity parameters determined from the absorption intensity fittings (given in the GP/CF and GP/CCF columns of Table V) were used directly in the branching ratio calculations. However, the agreement between calculated values and experimental data is comparable to that of the absorption fitting.

Comparison of calculated vs experimental branching ratios in Tables X and XI shows a reversal of the two lowest-lying Stark components of $^4I_{13/2}$ (level numbers 12 and 13) in the 77- and 300-K data as compared to our 10-K data. This reversal is reasonable, as these two Stark components are split by at most 10 cm^{-1}.

V. CONCLUSION

The energy-level data analyzed in this study does not differ significantly from that reported and analyzed in previous studies of Nd:YAG.[1,18,38,40,42] However, the method of analysis employed in the present study differs

TABLE X. Calculated and experimentally determined branching ratios for emission from the two Stark components of the $^4F_{3/2}$ multiplet of Nd:YAG at 300 K.

		Energy	Branching ratios				
	Level	(cm^{-1})		CF		CCF	
Transition[a]	No.[b]	Expt.[c]	Expt.[c]	Calc.[d]	$\frac{E-C}{E+C}$	Calc.[e]	$\frac{E-C}{E+C}$
$^4F_{3/2}a \rightarrow {}^4I_{13/2}$	18	6930	0.0093	0.0073	0.118	0.0072	0.127
	17	6993	0.0064	0.0051	0.116	0.0046	0.162
	16	—	—	0.0019		0.0026	
	15	7373	0.016	0.0068	0.403	0.0082	0.323
	14	7389	0.0036	0.0047	−0.133	0.0020	0.284
	13	7503	0.0071	0.0053	0.148	0.0032	0.383
	12	7493	0.013	0.0121	0.037	0.0160	−0.103
	Total		0.055	0.043	0.124	0.044	0.118
	σ				*0.196*		*0.253*
$^4F_{3/2}a \rightarrow {}^4I_{11/2}$	11	8908	0.033	0.0195	0.256	0.0171	0.318
	10	8961	0.050	0.0202	0.425	0.0208	0.412
	9	9275	0.057	0.0426	0.144	0.0396	0.180
	8	9312	0.071	0.0933	−0.136	0.0647	0.047
	7	9396	0.046	0.0434	0.029	0.0392	0.079
	6	9420	0.088	0.1044	−0.085	0.1113	−0.117
	Total		0.345	0.323	0.032	0.293	0.082
	σ				*0.221*		*0.233*
$^4F_{3/2}a \rightarrow {}^4I_{9/2}$	5	10569	0.039	0.0638	−0.242	0.0708	−0.289
	4	11107	0.026	0.0355	−0.155	0.0398	−0.210
	3	11220	0.029	0.0636	−0.374	0.0695	−0.411
	2	11294	0.043	0.0783	−0.291	0.0593	−0.159
	1	11425	0.0096	0.0061	0.224	0.0072	0.145
	Total		0.147	0.247	−0.256	0.247	−0.254
	σ				*0.267*		*0.262*
$^4F_{3/2}b \rightarrow {}^4I_{13/2}$	18	—	—	0.0002		0.0001	
	17	7077	0.010	0.0012	0.790	0.0020	0.673
	16	—	—	0.0059		0.0045	
	15	7458	0.0076	0.0074	0.016	0.0051	0.196
	14	7474	0.020	0.0127	0.222	0.0101	0.330
	13	7586	0.018	0.0144	0.110	0.0131	0.159
	12	7580	0.0057	0.0048	0.089	0.0054	0.031
	Total		0.061	0.046	0.137	0.040	0.209
	σ				*0.373*		*0.354*
$^4F_{3/2}b \rightarrow {}^4I_{11/2}$	11	8990	0.040	0.0272	0.190	0.0325	0.104
	10	9045	0.017	0.0280	−0.244	0.0283	−0.249
	9	9360	0.048	0.0209	0.395	0.0176	0.464
	8	9399	0.14	0.0635	0.376	0.0741	0.308
	7	9478	0.0033	0.0082	−0.425	0.0054	−0.244
	6	9506	0.049	0.0409	0.090	0.0429	0.067
	Total		0.297	0.189	0.224	0.201	0.194
	σ				*0.311*		*0.273*
$^4F_{3/2}b \rightarrow {}^4I_{9/2}$	5	10654	0.033	0.0208	0.226	0.0223	0.193
	4	11193	0.0046	0.0128	−0.472	0.0100	−0.370
	3	11307	0.023	0.0421	−0.293	0.0556	−0.415
	2	11375	0.014	0.0195	−0.164	0.0258	−0.297
	1	11509	0.015	0.0557	−0.576	0.0624	−0.612
	Total		0.090	0.151	−0.255	0.176	−0.326
	σ				*0.379*		*0.402*

[a] Initial state designators *a* and *b* refer to the first and second Stark components, respectively, of the $^4F_{3/2}$ multiplet (level numbers 27 and 28 in Table III).

[b] Final state Stark component level numbers correspond to level numbers given in Table III.

[c] Experimental energies and branching ratios taken from Watts (Ref. 12).

[d] Branching ratios calculated using the A_{tp}^{λ} parameters listed in the GP/CF column of Table V.

[e] Branching ratios calculated using the A_{tp}^{λ} parameters listed in the GP/CCF column of Table V.

from the previous studies with respect to inclusion of correlation crystal-field (CCF) interaction terms in the $4f^3(\mathrm{Nd}^{3+})$ model Hamiltonian. In the present study, we found that some partial consideration of CCF effects is *essential* to achieving satisfactory agreement between calculated and observed crystal-field splitting energies within certain $^{2S+1}L_J$ multiplet manifolds. Inclusion of just three CCF interaction terms in the model Hamiltonian produced results in excellent overall agreement with experiment. The three CCF interaction terms found to be important in our analysis of Nd:YAG energy-level data (G_2^4, G_{10A}^4, and G_{10B}^4) have been identified previously as important contributors to $\mathrm{Nd}^{3+}(4f^3)$ energy-level structure in other systems.[10,11,23] One of these CCF terms (parametrized as G_{10A}^4) also has significant effects on the crystal-field energy-level structure of $\mathrm{Er}^{3+}(4f^{11})$ in YAG, and in $\mathrm{Y_3Sc_2Al_3O_{12}}$ and $\mathrm{Y_3Sc_2Ga_3O_{12}}$ garnet hosts.[43]

Previous studies of $4f$-$4f$ absorption intensities in Nd:YAG have focused almost exclusively on the measurement and analysis of *total* intensities associated with ground-multiplet ($^4I_{9/2}$) to excited-multiplet transition manifolds, under room-temperature conditions. The results obtained from these studies have practical value and they can be organized and interpreted at a general phe-

TABLE XI. Calculated and experimentally observed branching ratios for emission from the two Stark components of the $^4F_{3/2}$ multiplet of Nd:YAG at 77 K.

Transition[a]	Level No.[b]	Energy (cm^{-1}) Expt.[c]	Branching ratios	CF		CCF	
			Expt.[c]	Calc.[d]	$\frac{E-C}{E+C}$	Calc.[e]	$\frac{E-C}{E+C}$
$^4F_{3/2}a \rightarrow {}^4I_{13/2}$	18	6927	0.016	0.0101	0.227	0.0102	0.220
	17	6993	0.012	0.0070	0.265	0.0066	0.293
	16	—	—	0.0027		0.0037	
	15	7378	0.031	0.0094	0.534	0.0117	0.452
	14	7394	0.0043	0.0065	−0.204	0.0029	0.199
	13	7502	0.010	0.0073	0.158	0.0045	0.378
	12	7495	0.020	0.0166	0.093	0.0227	−0.063
	Total		0.093	0.060	0.221	0.062	0.199
	σ				*0.283*		*0.296*
$^4F_{3/2}a \rightarrow {}^4I_{11/2}$	11	8905	0.042	0.0269	0.220	0.0243	0.268
	10	8961	0.066	0.0279	0.406	0.0297	0.379
	9	9298	0.085	0.0594	0.177	0.0571	0.196
	8	9320	0.10	0.1293	−0.128	0.0926	0.039
	7	9397	0.080	0.0598	0.144	0.0559	0.177
	6	9424	0.11	0.1444	−0.135	0.1591	−0.183
	Total		0.483	0.448	0.038	0.419	0.071
	σ				*0.224*		*0.231*
$^4F_{3/2}a \rightarrow {}^4I_{9/2}$	5	10573	0.061	0.0882	−0.183	0.1011	−0.247
	4	11112	0.039	0.0491	−0.114	0.0568	−0.186
	3	11226	0.058	0.0880	−0.205	0.0994	−0.263
	2	11298	0.090	0.1083	−0.092	0.0846	0.031
	1	11429	0.012	0.0084	0.176	0.0102	0.080
	Total		0.260	0.342	−0.136	0.352	−0.150
	σ				*0.160*		*0.185*
$^4F_{3/2}b \rightarrow {}^4I_{13/2}$	18	—	—	0.0001		0.0000	
	17	7077	0.0032	0.0005	0.733	0.0009	0.580
	16	—	—	0.0025		0.0019	
	15	7463	0.0030	0.0031	−0.020	0.0022	0.144
	14	7479	0.0097	0.0054	0.282	0.0044	0.371
	13	7587	0.0098	0.0061	0.233	0.0057	0.264
	12	7576	0.0020	0.0020	−0.005	0.0023	−0.079
	Total		0.028	0.020	0.168	0.018	0.224
	σ				*0.366*		*0.338*
$^4F_{3/2}b \rightarrow {}^4I_{11/2}$	11	8990	0.022	0.0115	0.312	0.0142	0.216
	10	9046	0.0084	0.0118	−0.170	0.0124	−0.190
	9	9366	0.020	0.0089	0.386	0.0077	0.442
	8	9403	0.047	0.0270	0.271	0.0325	0.182
	7	—	—	0.0035		0.0024	
	6	9509	0.015	0.0173	−0.072	0.0188	−0.112
	Total		0.112	0.080	0.169	0.088	0.122
	σ				*0.266*		*0.255*
$^4F_{3/2}b \rightarrow {}^4I_{9/2}$	5	10656	0.020	0.0088	0.388	0.0098	0.344
	4	—	—	0.0045		0.0036	
	3	—	—	0.0140		0.0191	
	2	—	—	0.0064		0.0087	
	1	—	—	0.0174		0.0201	
	Total		0.020	0.051	−0.437	0.061	−0.508
	σ				*0.388*		*0.344*

[a] Initial state designators a and b refer to the first and second Stark components, respectively, of the $^4F_{3/2}$ multiplet (level numbers 27 and 28 in Table III).

[b] Final state Stark component level numbers correspond to level numbers given in Table III.

[c] Experimental energies and branching ratios taken from Watts (Ref. 12).

[d] Branching ratios calculated using the A_{tp}^{λ} parameters listed in the GP/CF column of Table V.

[e] Branching ratios calculated using the A_{tp}^{λ} parameters listed in the GP/CCF column of Table V.

nomenological level. However, they contain no information about the underlying crystal-field component structure of the absorption intensity spectra, and they have limited utility for characterizing intensity mechanisms. The absorption line-strength data obtained in the present study, for transitions between Stark levels, contain considerably more information about intensity distributions and how the distributions are related to (and determined by) the detailed $SLJM_J$ compositions of the crystal-field state vectors. For electric-dipole intensity, this information is embodied in the $\langle\psi_i|\hat{U}_\ell^{(\lambda)}|\psi_f\rangle$ matrix elements and A_{tp}^{λ} parameters of the expressions used in our analysis of transition line-strength data [see Eq. (11) in Sec. III B].

The absorption line-strength analyses performed in the present study are the first to be reported for transitions between individual Stark levels in Nd:YAG (or for *any* Ln^{3+}:garnet system). The only truly comparable intensity analyses reported in the literature are those carried out on the Nd^{3+},[6,7] Sm^{3+},[2,3] Eu^{3+},[5] and Ho^{3+}[8,9] members of the $Na_3[Ln(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ series of compounds (where oda $\equiv$ oxydiacetate $\equiv$ $^{-}OOCCH_2OCH_2COO^{-}$). In these compounds, the Ln^{3+} ions are located at sites with D_3 symmetry, and they are coordinated to six negatively charged carboxylate oxygen atoms and three neutral ether oxygen atoms. Therefore, although the site symmetry (D_3) and coordination number (9) of the Ln^{3+} ions in these compounds differ from those found at the Y^{3+} substitutional sites in YAG, the *chemical* nature of the immediate Ln^{3+} coordination environment in these compounds is similar to that in Ln^{3+}:YAG.

Overall, the $4f$-$4f$ transition intensities observed for Nd:YAG are somewhat stronger than those observed for $Na_3[Nd(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ (denoted hereafter as NdODA), and the intensity distributions observed within most multiplet-to-multiplet transition manifolds are also different for Nd:YAG *versus* NdODA. These observations are reflected in the respective $\{A_{tp}^{\lambda}\}$ intensity parameter sets derived for the two systems (see Refs. 6 and 7 for results on NdODA). The stronger $4f$-$4f$ intensities observed for Nd:YAG *versus* NdODA can be attributed to stronger crystal-field perturbations exerted by the eight O^{2-} donor atoms in Nd:YAG relative to the weaker perturbations expected from the six O^{-} and three O (neutral) donor atoms in NdODA. Differences between the intensity distributions observed in Nd:YAG *versus* NdODA spectra reflect differences in the crystal-field anisotropies at the D_2 *versus* D_3 symmetry sites in the respective systems.

The transition line-strength analyses carried out in the present study go far beyond any previous treatments of Nd:YAG intensity data. The results obtained from these analyses provide a useful parametric representation of line intensities associated with transitions between individual Stark levels. Comparisons between the calculated and experimental line strengths listed in Table III show that this representation falls short of complete *quantitative* accuracy, but it provides a reasonably good basis for rationalizing the data at a semiquantitative level. Moreover, the parameters that define this representation are sufficiently well characterized to be useful calibration points for future theoretical work and detailed computational studies on lanthanide $4f$-$4f$ transition intensities. The intensity parameters derived from our previous analyses of LnODA line-strength data have served a similar purpose.[31,44]

Finally, we note that while the superposition model may not be fully justified in analysis of $4f$-$4f$ intensities in Nd:YAG, it does work better than for NdODA. This is not surprising given the nature of the immediate coordination environment around each Nd^{3+} ion, which is comprised of eight negatively charged monatomic O^{2-} ligands. The distortions of our intensity parameters away from reasonable superposition values suggests that lattice ions outside the NdO_8 coordination clusters are effective in distorting the local symmetry of Nd-O pairwise interactions away from $C_{\infty v}$. Analyses of intensity data for Nd^{3+} in other garnet hosts may help clarify this issue. Unfortunately, very little quantitative intensity data for transitions between Stark levels are currently available in the literature, and what *are* available are insufficient for carrying out parametric analyses of the type described in the present study. As more quantitative intensity data become available for detailed analysis, detailed mechanistic interpretations of the A_{tp}^{λ} intensity parameters are likely to emerge.

ACKNOWLEDGMENTS

We thank Dr. Stephen Payne (Lawrence Livermore Laboratory) for providing the Nd:YAG crystal used in this study. This work was supported by the U.S. National Science Foundation through a research grant (CHE-9213473) to F.S.R.

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