Comparative analysis of $Nd^{3+}(4f^3)$ energy levels in four garnet hosts

John B. Gruber
Department of Physics, San Jose State University, San Jose, California 95192

Marian E. Hills
Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555

Toomas H. Allik
Science Applications International Corporation, 1710 Goodridge Drive, P.O. Box 1303, McLean, Virginia 22102

C. K. Jayasankar, John R. Quagliano, and F. S. Richardson
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901
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As many as thirty-seven $^{2S+1}L_J$ multiplet manifolds of $Nd^{3+}(4f^3)$ have been analyzed in the garnets $Y_3Al_5O_{12}$ (YAG), $Y_3Sc_2Al_3O_{12}$ (YSAG), $Gd_3Sc_2Ga_3O_{12}$ (GSGG), and $La_3Lu_2Ga_3O_{12}$ (LLGG). The majority of Nd^{3+} ions substitute for Y^{3+}, Gd^{3+}, or La^{3+} ions in sites of D_2 point-group symmetry in the lattice. Individual Stark levels within each manifold have been identified experimentally up to 40 000 cm^{-1} and compared with results obtained from a theoretical calculation. The model Hamiltonian includes Coulombic, spin-orbit, and interconfiguration interaction terms for the $4f^3$ atomic configuration of Nd^{3+} and crystal-field terms in D_2 symmetry, including spin-correlated crystal-field (SCCF) contributions. The Hamiltonian was diagonalized within the complete $4f^3$ $SLJM_J$ basis set which includes 364 states. Comparison between 148 (Nd:YAG), 140 (Nd:YSAG), 143 (Nd:GSGG), and 107 (Nd:LLGG) observed and calculated Stark levels (without SCCF) yields rms deviations of 18, 19, 17, and 16 cm^{-1}, respectively. Results indicate that SCCF contributions yield modest improvement in the calculated value of the overall crystal-field splitting of the energy levels.

I. INTRODUCTION

The development of high-power diode arrays and the successful use of these arrays to pump solid-state laser materials[1-8] has reopened interest in the energy up-conversion process as a means to pump ultraviolet and/or visible tunable solid-state lasers. Potentially, laser diodes that operate in the near infrared can excite rare-earth ions to metastable states which can be further excited to higher energy levels. Macfarlane *et al.*[9] have demonstrated a 380-nm up-conversion laser operating between the $^4D_{3/2}$ and $^4I_{11/2}$ manifolds of Nd^{3+} in LaF_3. Kliewer and Powell[10] have shown that excited-state absorption of the pump photons can deter the generation of 1.06-μm radiation from Nd^{3+} in $Y_3Al_5O_{12}$ (YAG) when pumped by an alexandrite laser. In both cases, the knowledge of the ultraviolet and visible energy levels of Nd^{3+} in these well-known laser host materials was crucial in the analysis. It is timely now to examine in detail all the excited energy levels of Nd^{3+} in those garnets most used as solid-state lasers. Spectroscopic analysis leads to a characterization of atomic and crystal-field parameters needed to calculate energy levels and transition probabilities. These results can be expressed in terms of important laser parameters including transition wavelengths, cross sections, branching ratios, and efficiencies.

Many of the spectroscopic properties of Nd^{3+} in $Y_3Al_5O_{12}$ (YAG) have been reported earlier,[11-15] especially for the ^4I_J and $^4F_{3/2}$ multiplet manifolds. However, there remain different interpretations of the detailed splitting of $Nd^{3+}(4f^3)$ ion manifolds in the ultraviolet region.[16-18] Recently, Hua *et al.*[19] published a crystal-field splitting calculation for the entire $4f^3$ configuration of Nd:YAG. However, it is not clear how the authors analyzed and assigned their data in the calculation. For other garnets used as laser crystals, such as Nd^{3+} in $Y_3Sc_2Al_3O_{12}$ (YSAG), in $Gd_3Sc_2Ga_3O_{12}$ (GSGG), and in $La_3Lu_2Ga_3O_{12}$ (LLGG), there appear to be no reported detailed crystal-field splitting analyses of the energy levels in the visible and ultraviolet regions.[20-22]

The purpose of this paper is several fold. First, we report the experimentally determined energy (Stark) levels of $Nd^{3+}(4f^3)$ in YSAG, LLGG, and GSGG up to 40 000, 35 000, and 34 000 cm^{-1}, respectively. To the list of energy levels already reported for Nd:YAG, we include additional levels up to 40 000 cm^{-1} deduced from our spectroscopic studies. Second, the energy-level data are analyzed in terms of a model Hamiltonian that assumes D_2 site symmetry for the Nd^{3+} ions in the garnet lattice. Both the atomic ("free-ion") and crystal-field interaction terms in the model Hamiltonian are parametrized, and both the atomic and crystal-field interaction parameters are used in fitting calculated to experimental energy-level data. The crystal-field part of the model Hamiltonian is defined to include the standard one-electron interaction terms as well as additional terms

TABLE I. Hamiltonian parameters derived from analyses *without* inclusion of SCCF. See Sec. III of text. Parameters are defined according to Eqs. (1)–(3).

Parameter	Parameter values (cm^{-1}) Nd:YAG	Nd:YSAG	Nd:GSGG	Nd:LLGG
E_{av}	24 117(40)[a]	24 163(40)	23 988(40)	24 144(40)
F^2	71 090(45)	71 554(66)	69 551(93)	71 248(65)
F^4	50 917(65)	52 564(109)	47 440(150)	48 201(100)
F^6	34 173(45)	35 361(105)	33 756(160)	32 403(92)
α	20.8(2.1)	20.9(2.3)	16.8(2.2)	18.0(2.5)
β	−651(16)	−661(16)	−547(15)	−585(16)
γ	1868(24)	1419(60)	2406(89)	2598(52)
T^2	231(27)	207(30)	660(28)	173(35)
T^3	46(9)	47(10)	49(9)	44(9)
T^4	39(11)	51(11)	122(10)	56(11)
T^6	−236(14)	−259(15)	−222(14)	−203(16)
T^7	237(20)	231(21)	350(21)	197(24)
T^8	174(23)	204(25)	749(24)	115(32)
ζ	875(7)	878(8)	886(7)	885(7)
M^0	2.58(1.32)	2.36(1.58)	2.95(1.36)	2.55(1.33)
P^2	275(35)	233(36)	198(35)	163(36)
B_{20}	−690(23)	−819(26)	−467(22)	−1265(30)
B_{22}	−158(21)	−224(23)	−117(20)	−361(26)
B_{40}	−343(39)	−206(41)	−907(36)	−114(42)
B_{42}	−2401(29)	−2473(31)	−2482(25)	−2006(30)
B_{44}	−1094(33)	−988(34)	−652(34)	−819(35)
B_{60}	2315(44)	2040(45)	1734(41)	1729(42)
B_{62}	922(36)	878(36)	567(34)	792(37)
B_{64}	−1124(35)	−1087(35)	−1035(31)	−811(34)
B_{66}	836(38)	824(39)	1030(36)	830(37)
N[b]	148	140	143	107
σ (cm^{-1})[c]	18.4	18.8	17.0	16.4

[a]Numbers in parentheses represent an estimate of the uncertainty defined as the change required to double the standard deviation.
[b]Number of experimental levels included in data fits.
[c]rms deviation between calculated and experimental energies.

TABLE II. Crystal-field and restricted SCCF parameters. See Sec. III of text. The B_{km} parameters are defined according to Eq. (3) and the c_k parameters are defined by $c_k = b_{km}/B_{km}$.

Parameter	Parameter values (cm^{-1}) Nd:YAG	Nd:YSAG	Nd:GSGG	Nd:LLGG
B_{20}	−696(22)[a]	−848(29)	−478(20)	−1309(28)
B_{22}	−158(20)	−225(24)	−119(18)	−350(24)
B_{40}	−341(37)	−152(44)	−905(32)	−142(39)
B_{42}	−2415(28)	−2555(32)	−2503(24)	−1996(33)
B_{44}	−1098(31)	−1058(37)	−682(31)	−817(33)
B_{60}	2309(43)	1994(50)	1888(39)	1756(42)
B_{62}	915(34)	899(40)	608(31)	793(36)
B_{64}	−1116(34)	−1046(41)	−1119(30)	−831(33)
B_{66}	820(37)	822(44)	1070(34)	826(37)
c_2	−0.049	0.039	−0.130	−0.069
c_4	−0.005	−0.066	−0.014	0.009
c_6	0.007	0.038	−0.066	−0.009
N[b]	148	140	143	107
σ (cm^{-1})[c]	18.3	18.3	16.2	16.2

[a]Numbers in parentheses represent an estimate of the uncertainty defined as the change required to double the standard deviation.
[b]Number of experimental levels included in the data fits.
[c]rms deviation between calculated and experimental energies.

that provide some partial (phenomenological) consideration of electron-correlation effects in the $4f$-electron–crystal-field interactions. In our model, these additional terms are related to the *spin-correlated crystal-field* (SCCF) interactions described and used in previous analyses of lanthanide $4f^N$ energy-level structures.[23–24] Third, the results of calculated-versus-experimental energy-level fits are reported for analyses carried out both *with* and *without* inclusion of SCCF terms in the model Hamiltonian.

Comparisons between calculated and observed energy levels include the following numbers of Stark levels: 148 (Nd:YAG), 140 (Nd:YSAG), 143 (Nd:GSGG), and 107 (Nd:LLGG), with respective rms deviations of 18, 19, 17, and 16 cm^{-1} (from calculations performed *without* inclusion of SCCF effects). Inclusion of SCCF terms in the parametric energy-level analyses yields modest improvements in the data fits, but the results are inconclusive regarding the possible importance of SCCF effects in the neodymium garnet systems examined in this study. The data sets for the respective systems contain a sufficient representation of free-ion ($4f^3SLJ$) parent states to support a reasonably good characterization of the atomic parameters in our model Hamiltonian, and the values determined for these parameters show interesting differences among the four garnet hosts. This is the first comparative study of neodymium garnet systems in which energy-level analyses are carried out within commensurate parametrization schemes (for the atomic *and* crystal-field parts of the $4f$-electron Hamiltonian).

II. EXPERIMENTAL DETAILS

Part of the absorption and emission spectra of Nd:YSAG, Nd:LLGG, and Nd:GSGG was reported earlier by several authors.[20–22] That work is extended here to include an analysis of the spectra observed in the visible and the ultraviolet regions. The spectra were obtained between 10 and 15 K, using the same techniques and instrumentation described earlier.[20–22] The same crystals were used with Nd^{3+} ion concentrations of 1.8 (YSAG), 1.0 (LLGG), and 1.6 (GSGG) at. wt. % based on ions in D_2 lattice sites. The crystals were grown by Kokta.[35] To the energy levels already reported for Nd:YAG,[14,15] we add new levels obtained from our analysis of the absorption spectrum between 350 and 210 nm. The Nd:YAG crystal contained 1.1 at. wt. % Nd. The GSGG crystal also contained 1.2 at. wt. % Cr.

Most of the Nd^{3+} ions substitute for Y^{3+}, Gd^{3+}, or La^{3+} ions in lattice sites having D_2 symmetry. The size of the Nd^{3+} ions, however, causes the formation of numerous microstrains throughout the lattice[35–37] and limits the maximum concentration of Nd^{3+} to several percent in the garnet structures.[38] Strain broadening of observed emission and absorption peaks has been the topic of several investigations.[14,15,21,39,40] Weak spectra appearing in the vicinity of strong emission or absorption from Nd^{3+} ions in D_2 sites have been attributed in several cases as coming from Nd^{3+} ions that experience a slightly different crystal field due to lattice strains and defects that arise during the growth of the crystal.[20–22,39]

Our approach in analyzing the spectra has been to identify the strongest transitions associated with an isolated manifold as representative of Nd^{3+} ions in D_2 sites. Wherever possible, Stark levels identified by an analysis of hot-band data are confirmed from emission spectra obtained by selectively exciting Stark levels of Nd^{3+} ions in D_2 sites using various lasers as the excitation source.[20–22] We observe electronic transitions from the ground level to nearly all $J+\frac{1}{2}$ Stark levels associated with isolated multiplet manifolds. Where several of these multiplets overlap, we identify individual Stark levels with the aid of the crystal-field splitting calculations. All Stark levels are represented by the same symmetry label ($^2\Gamma_5$) and electronic electric-dipole and magnetic-dipole transitions are allowed between all Stark levels of Nd^{3+} ions in D_2 symmetry.[15]

The results of our analyses lead to the Hamiltonian parameters and crystal-field energy levels reported in Tables I–V. In Table IV experimental energy levels for

TABLE III. Crystal-field and unrestricted SCCF parameters. See Sec. III of text. The B_{km} and b_{km} parameters are defined according to Eq. (3). The values listed for c_{km} were calculated from fitted values of B_{km} and b_{km} according to $c_{km}=b_{km}/B_{km}$.

Parameter	Parameter values (cm^{-1}) Nd:YSAG	Nd:GSGG	Nd:LLGG
B_{20}	−794(29)[a]	−509(18)	−1242(28)
B_{22}	−307(26)	−65(17)	−426(24)
B_{40}	−182(41)	−819(36)	−193(37)
B_{42}	−2505(34)	−2587(22)	−1941(36)
B_{44}	−1196(43)	−399(34)	−980(40)
B_{60}	2219(55)	2158(40)	1588(49)
B_{62}	755(52)	555(40)	915(44)
B_{64}	−1029(47)	−958(36)	−822(43)
B_{66}	665(58)	878(42)	944(48)
b_{20}	−152(37)	80(27)	45(31)
b_{22}	149(33)	−30(23)	139(30)
b_{40}	−18(27)	−54(33)	−19(34)
b_{42}	111(36)	126(24)	−123(35)
b_{44}	203(43)	−289(31)	212(39)
b_{60}	−190(50)	−328(36)	61(42)
b_{62}	113(46)	51(34)	−173(37)
b_{64}	−86(42)	−42(32)	−65(39)
b_{66}	238(52)	68(37)	−71(42)
c_{20}	0.191	−0.157	−0.036
c_{22}	−0.485	0.461	−0.326
c_{40}	0.099	0.066	0.098
c_{42}	−0.044	−0.049	0.063
c_{44}	−0.169	0.724	−0.216
c_{60}	−0.086	−0.152	0.039
c_{62}	0.149	0.092	−0.189
c_{64}	0.083	0.044	0.079
c_{66}	0.358	0.077	−0.075
N[b]	140	143	107
σ (cm^{-1})[c]	15.7	14.6	15.3

[a]Numbers in parentheses represent an estimate of the uncertainty defined as the change required to double the standard deviation.

[b]Number of experimental levels included in the data fits.

[c]rms deviation between calculated and experimental energies.

TABLE IV. Energy levels of Nd^{3+} in YAG and YSAG.

$^{2S+1}L_J$ [a]	Level number	Nd:YAG E (cm^{-1}) Expt. [b]	Calc. [c]	Δ (cm^{-1})	Nd:YSAG E (cm^{-1}) Expt. [d]	Calc. [c]	Δ (cm^{-1})
$^4I_{9/2}$	1	0	−4	4	0	9	−9
	2	130	142	−12	114	118	−4
	3	199	205	−6	183	195	−12
	4	308	328	−20	301	310	−9
	5	857	870	−13	823	838	−15
$^4I_{11/2}$	6	2002	1990	12	1979	1972	7
	7	2029	2017	12	2022	2003	19
	8	2110	2102	8	2101	2090	11
	9	2147	2140	7	2136	2134	2
	10	2468	2465	3	2437	2439	−2
	11	2521	2524	−3	2495	2502	−7
$^4I_{13/2}$	12	3922	3908	14	3905	3895	10
	13	3930	3916	14	3929	3908	21
	14	4032	4026	6	4029	4021	8
	15	4047	4041	6	4044	4039	5
	16	4435	4421	14		4396	
	17	4442	4441	1	4419	4423	−4
	18	4498	4504	−6	4478	4487	−9
$^4I_{15/2}$	19	5758	5756	2	5766	5766	0
	20	5814	5804	10	5797	5802	−5
	21	5936	5939	−3	5927	5939	−12
	22	5970	5971	−1	5981	5975	6
	23	6570	6557	13	6544	6526	18
	24	6583	6596	−13	6560	6578	−18
	25	6639	6659	−20	6622	6632	−10
	26	6734	6758	−24	6711	6713	−2
$^4F_{3/2}$	27	11 427	11 421	6	11 423	11 409	14
	28	11 512	11 493	19	11 523	11 491	32
$^4F_{5/2}$	29	12 370	12 359	11	12 382	12 359	23
and	30	12 432	12 436	−4	12 441	12 449	−8
$^2H_{9/2}(2)$	31	12 519	12 451	68	12 538	12 460	78
	32	12 575	12 610	−35	12 583	12 613	−30
	33	12 607	12 650	−43	12 621	12 653	−32
	34	12 623	12 693	−70	12 637	12 696	−59
	35	12 819	12 811	8	12 825	12 807	18
	36	12 840	12 856	−16	12 860	12 845	15
$^4F_{7/2}$	37	13 363	13 364	−1	13 367	13 373	−6
and	38	13 433	13 440	−7	13 441	13 448	−7
$^4S_{3/2}$	39	13 563	13 555	8	13 570	13 563	7
	40	13 572	13 572	0	13 580	13 580	0
	41	13 596	13 596	0	13 602	13 602	0
	42	13 633	13 646	−13	13 642	13 650	−8
$^4F_{9/2}$	43	14 626	14 643	−17	14 630	14 641	−11
	44	14 678	14 685	−7	14 695	14 693	2
	45	14 793	14 779	14	14 786	14 770	16
	46	14 819	14 815	4	14 834	14 830	4
	47	14 916	14 914	2	14 939	14 935	4
$^2H_{11/2}(2)$	48	15 838	15 898	−60	15 860	15 901	−41
	49	15 870	15 920	−50	15 886	15 924	−38
	50		15 946			15 950	
	51	15 957	15 956	1	15 960	15 957	3
	52	16 103	16 037	66	16 093	16 033	60
	53	16 119	16 067	52	16 124	16 065	59
$^4G_{5/2}$	54	16 849	16 848	1	16 880	16 880	0

TABLE IV. (*Continued*).

		Nd:YAG			Nd:YSAG		
	Level	E (cm^{-1})			E (cm^{-1})		
$^{2S+1}L_J$ [a]	number	Expt. [b]	Calc. [c]	Δ (cm^{-1})	Expt. [d]	Calc. [c]	Δ (cm^{-1})
	55	16 992	16 978	14	17 010	16 985	25
	56	17 047	17 054	−7	17 065	17 069	−4
$^2G_{7/2}$	57	17 241	17 220	21	17 262	17 244	18
	58	17 268	17 275	−7	17 286	17 292	−6
	59	17 322	17 302	20	17 331	17 319	12
	60	17 575	17 594	−19	17 587	17 612	−25
$^4G_{7/2}$	61	18 723	18 709	14	18 755	18 741	14
	62	18 822	18 831	−9	18 839	18 844	−5
	63	18 843	18 863	−20	18 864	18 872	−8
	64	18 986	18 987	−1	18 997	19 006	−9
$^2K_{13/2}$	65	19 154	19 133	21	19 179	19 148	31
and	66		19 262		19 309	19 285	24
$^4G_{9/2}$	67	19 294	19 317	−23	19 350	19 336	14
	68		19 421			19 429	
	69	19 470	19 448	22	19 455	19 442	13
	70		19 499		19 513	19 521	−8
	71	19 543	19 555	−12	19 589	19 564	25
	72	19 596	19 593	3	19 627	19 614	13
	73	19 651	19 660	−9	19 677	19 678	−1
	74	19 814	19 823	−9	19 810	19 818	−8
	75		19 870		19 892	19 867	25
	76	20 048	20 026	22	20 088	20 065	23
$^2G_{9/2}(1)$,	77	20 730	20 719	11	20 747	20 745	2
$^2D_{3/2}(1)$,	78	20 773	20 797	−24	20 790	20 817	−27
$^4G_{11/2}$,	79	20 790	20 819	−29	20 812	20 844	−32
and	80	20 803	20 833	−30	20 825	20 849	−24
$^2K_{15/2}$	81	20 962	20 954	8	20 995	20 977	18
	82	21 029	21 011	18		21 016	
	83		21 057		21 057	21 077	−20
	84	21 080	21 072	8	21 110	21 099	11
	85	21 159	21 141	18	21 133	21 151	−18
	86	21 162	21 152	10	21 177	21 162	15
	87		21 491		21 492	21 483	9
	88	21 522	21 514	8	21 528	21 510	18
	89	21 593	21 608	−15	21 608	21 618	−10
	90	21 661	21 664	−3	21 697	21 687	10
	91	21 697	21 709	−12	21 706	21 719	−13
	92	21 767	21 754	13	21 772	21 775	−3
	93	21 791	21 782	9	21 801	21 798	3
	94		21 851			21 866	
	95	21 872	21 866	6	21 877	21 879	−2
	96	21 906	21 906	0	21 925	21 912	13
	97	22 036	22 043	−7	22 070	22 079	−9
$^2P_{1/2}$	98	23 155	23 135	20	23 170	23 160	10
$^2D_{5/2}(1)$	99	23 674	23 685	−11	23 663	23 670	−7
	100	23 764	23 764	0	23 759	23 766	−7
	101	23 849	23 838	11	23 878	23 857	21
$^2P_{3/2}$	102	25 994	26 026	−32	25 981	26 017	−36
	103		26 085			26 098	
$^4D_{3/2}$,	104	27 571	27 550	21	27 594	27 555	39
$^4D_{5/2}$	105	27 670	27 683	−13	27 708	27 703	5
	106	27 809	27 818	−9	27 855	27 836	19
	107	28 183	28 182	1	28 201	28 185	16
	108	28 263	28 272	−9	28 280	28 304	−24

TABLE IV. (*Continued*).

		Nd:YAG			Nd:YSAG		
	Level	E (cm^{-1})			E (cm^{-1})		
$^{2S+1}L_J$[a]	number	Expt.[b]	Calc.[c]	Δ (cm^{-1})	Expt.[d]	Calc.[c]	Δ (cm^{-1})
$^4D_{1/2}$	109	28 359	28 374	−15	28 417	28 410	7
$^2I_{11/2}$	110	28 580	28 601	−21	28 571	28 573	−2
	111	28 800	28 819	−19	28 794	28 821	−27
	112	28 930	28 957	−27	28 986	28 989	−3
	113	29 140	29 124	16	29 104	29 108	−4
	114	29 270	29 258	12	29 282	29 289	−7
	115	29 360	29 366	−6	29 377	29 364	13
$^2L_{15/2}$,	116	29 715	29 712	3	29 709	29 679	30
$^4D_{7/2}$,	117	29 876	29 867	9		29 826	
and	118	29 880	29 881	−1	29 878	29 883	−5
$^2I_{13/2}$	119	29 920	29 917	3		29 918	
	120	29 953	29 952	1	29 940	29 947	−7
	121		30 048			30 026	
	122	30 070	30 057	13	30 048	30 042	6
	123	30 140	30 121	19		30 100	
	124	30 160	30 147	13	30 157	30 162	−5
	125	30 190	30 198	−8		30 203	
	126	30 230	30 233	−3		30 287	
	127	30 289	30 283	6	30 294	30 298	−4
	128	30 360	30 350	10	30 340	30 367	−27
	129	30 400	30 389	11		30 416	
	130	30 464	30 442	22		30 479	
	131	30 495	30 495	0	30 534	30 519	15
	132	30 547	30 550	−3	30 581	30 583	−2
	133	30 611	30 593	18		30 606	
	134	30 620	30 611	9	30 665	30 624	41
$^2L_{17/2}$	135		31 247			31 220	
	136		31 393			31 336	
	137	31 440	31 459	−19	31 437	31 458	−21
	138	31 530	31 525	5	31 516	31 512	4
	139	31 570	31 567	3	31 546	31 545	1
	140	31 585	31 583	2	31 586	31 572	14
	141	31 665	31 667	−2	31 676	31 678	−2
	142		31 795			31 820	
	143		31 885			31 927	
$^2H_{9/2}(1)$	144	32 613	32 621	−8	32 584	32 580	4
	145	32 662	32 662	0	32 658	32 653	5
	146	32 745	32 730	15	32 701	32 708	−7
	147	32 802	32 801	1	32 755	32 775	−20
	148	32 840	32 835	5	32 798	32 791	7
$^2D_{3/2}(2)$	149	32 980	32 966	14	33 014	33 008	6
	150	33 045	33 056	−11	33 091	33 091	0
$^2D_{5/2}(2)$	151	33 693	33 699	−6	33 750	33 765	−15
and	152		33 783			33 834	
$^2H_{11/2}(1)$	153	33 840	33 830	10	33 898	33 864	34
	154	34 050	34 071	−21	34 083	34 077	6
	155	34 110	34 123	−13		34 129	
	156	34 210	34 170	40	34 176	34 164	12
	157	34 260	34 256	4	34 246	34 246	0
	158	34 290	34 333	−43	34 341	34 346	−5
	159		34 475			34 432	
$^2F_{5/2}(2)$	160	37 789	37 799	−10	38 110	38 105	5
	161	37 900	37 920	−20	38 256	38 226	30
	162	38 065	38 043	22		38 376	

TABLE IV. (*Continued*).

		Nd:YAG			Nd:YSAG		
	Level	E (cm^{-1})			E (cm^{-1})		
$^{2S+1}L_J$ [a]	number	Expt.[b]	Calc.[c]	Δ (cm^{-1})	Expt.[d]	Calc.[c]	Δ (cm^{-1})
$^2F_{7/2}(2)$	163	39 202	39 232	−30	39 479	39 514	−35
	164		39 251			39 560	
	165	39 330	39 312	18		39 615	
	166		39 553			39 844	
$^2G_{9/2}(2)$	167		47 000			47 028	
	168		47 010			47 043	
	169	(47 200)	47 170			47 222	
	170		47 247			47 293	
	171		47 266			47 314	

[a]Identifies energy regions according to principal *SLJ* parentages.
[b]Levels 1–106, Ref. 14; levels 107–166, present study and Refs. 17 and 19.
[c]From calculations based on the Hamiltonian parameters listed in Table I (no SCCF).
[d]Levels 1–60, Ref. 21; levels 61–166, present study.

TABLE V. Energy levels of Nd^{3+} in LLGG and GSGG.

		Nd:LLGG			Nd:GSGG		
	Level	E (cm^{-1})			E (cm^{-1})		
$^{2S+1}L_J$ [a]	number	Expt.[b]	Calc.[c]	Δ (cm^{-1})	Expt.[d]	Calc.[c]	Δ (cm^{-1})
$^4I_{9/2}$	1	0	−1	1	0	−31	31
	2	102	105	−3	106	120	−14
	3	187	196	−9	168	190	−22
	4	287	305	−18	263	263	0
	5	710	724	−14	763	768	−5
$^4I_{11/2}$	6	1962	1956	6	1980	1964	16
	7	2003	1996	7	2004	1983	21
	8	2097	2093	4	2968	2064	4
	9	2129	2126	3	2103	2114	−11
	10	2347	2340	7	2391	2387	4
	11	2416	2427	−11	2432	2443	−11
$^4I_{13/2}$	12	3899	3891	8	3908	3893	15
	13	3920	3907	13	3917	3899	18
	14	4040	4033	7	4000	4000	0
	15	4059	4051	8	4012	4026	−14
	16	4315	4318	−3	4359	4345	14
	17	4338	4334	4	4372	4381	−9
	18	4407	4416	−9	4412	4429	−17
$^4I_{15/2}$	19	5783	5779	4	5778	5759	19
	20	5818	5818	0	5813	5816	−3
	21	5959	5965	−6	5913	5932	−19
	22	6009	6011	−2	5954	5956	−2
	23	6450	6451	−1	6497	6475	22
	24	6481	6486	−5	6510	6536	−26
	25	6526	6528	−2	6557	6559	−2
	26	6603	6609	−6	6643	6644	−1
$^4F_{3/2}$	27	11 417	11 413	4	11 432	11 431	1
	28	11 534	11 539	−5	11 494	11 476	18
$^4F_{5/2}$	29	12 402	12 3,75	27	12 354	12 350	4
and	30	12 477	12 458	19	12 390	12 397	−7
$^2H_{9/2}(2)$	31	12 567	12 496	71	12 405	12 432	−27
	32	12 598	12 602	−4	12 544	12 550	−6
	33	12 625	12 639	−14	12 586	12 617	−31
	34	12 659	12 695	−36	12 618	12 642	−24

TABLE V. (Continued).

$^{2S+1}L_J$ [a]	Level number	Nd:LLGG E (cm^{-1}) Expt. [b]	Calc. [c]	Δ (cm^{-1})	Nd:GSGG E (cm^{-1}) Expt. [d]	Calc. [c]	Δ (cm^{-1})
	35	12 817	12 788	29	12 745	12 734	11
	36	12 850	12 837	13	12 793	12 762	31
$^4F_{7/2}$	37	13 375	13 359	16	13 374	13 384	−10
and	38	13 462	13 456	6	13 430	13 426	4
$^4S_{3/2}$	39	13 582	13 571	11	13 555	13 549	6
	40	13 587	13 593	−6	13 566	13 567	−1
	41	13 602	13 612	−10	13 573	13 569	4
	42	13 648	13 664	−16	13 611	13 617	−6
$^4F_{9/2}$	43	14 645	14 656	−11	14 639	14 632	7
	44	14 717	14 733	−16	14 673	14 651	22
	45	14 775	14 751	24	14 791	14 758	33
	46	14 852	14 858	−6	14 810	14 832	−22
	47	14 964	14 973	−9	14 902	14 906	−4
$^2H_{11/2}(2)$	48	15 901	15 929	−28	15 860	15 851	9
	49	15 926	15 958	−32	15 865	15 860	5
	50		15 978		15 890	15 887	3
	51	15 991	15 990	1	15 900	15 895	5
	52	16 093	16 043	50	15 967	15 975	−8
	53	16 129	16 085	44	16 020	15 989	31
$^4G_{5/2}$	54	16 951	16 952	−1	16 910	16 913	−3
	55	17 042	17 042	0	17 008	16 997	11
	56	17 116	17 111	5	17 140	17 137	3
$^2G_{7/2}$	57		17 239		17 230	17 239	−9
	58		17 292		17 284	17 298	−14
	59	17 324	17 320	4	17 338	17 349	−11
	60	17 586	17 576	10	17 593	17 614	−21
$^4G_{7/2}$	61	18 825	18 806	19	18 773	18 755	18
	62	18 917	18 909	8	18 854	18 840	14
	63	18 935	18 934	1	18 884	18 892	−8
	64	19 032	19 027	5	19 004	19 016	−12
$^2K_{13/2}$	65		19 142			19 081	
and	66		19 318		19 207	19 180	27
$^4G_{9/2}$	67	19 361	19 368	−7	19 335	19 352	−17
	68	19 410	19 407	3	19 379	19 384	−5
	69	19 469	19 468	1	19 412	19 434	−22
	70		19 538		19 488	19 476	12
	71		19 555		19 521	19 521	0
	72	19 599	19 634	−35	19 592	19 590	2
	73	19 650	19 665	−15	19 652	19 642	10
	74	19 716	19 738	−22	19 735	19 734	1
	75	19 806	19 776	30	19 824	19 827	−3
	76		20 081		19 895	19 896	−1
$^2G_{9/2}(1)$,	77	20 833	20 813	20	20 730	20 725	5
$^2D_{3/2}(1)$,	78	20 859	20 879	−20	20 797	20 800	−3
$^4G_{11/2}$,	79	20 886	20 894	−8	20 846	20 841	5
and	80	20 912	20 915	−3	20 858	20 845	13
$^2K_{15/2}$	81	21 057	21 058	−1	20 980	20 985	−5
	82		21 065		21 043	21 040	3
	83	21 119	21 126	−7	21 096	21 095	1
	84	21 182	21 184	−2	21 146	21 136	10
	85	21 245	21 247	−2	21 207	21 202	5
	86	21 258	21 255	3	21 260	21 267	−7
	87		21 378		21 340	21 350	−10

TABLE V. (*Continued*).

		Nd:LLGG			Nd:GSGG		
	Level	E (cm^{-1})			E (cm^{-1})		
$^{2S+1}L_J$ [a]	number	Expt. [b]	Calc. [c]	Δ (cm^{-1})	Expt. [d]	Calc. [c]	Δ (cm^{-1})
	88	21 468	21 484	−16	21 425	21 426	−1
	89	21 608	21 610	−2	21 518	21 532	−14
	90		21 650		21 586	21 589	−3
	91		21 668		21 660	21 654	6
	92	21 758	21 752	6	21 714	21 700	14
	93		21 775		21 774	21 776	−2
	94	21 791	21 800	−9	21 825	21 818	7
	95		21 854		21 885	21 899	−14
	96	21 882	21 861	21	21 914	21 912	2
	97	22 114	22 088	26	22 006	21 965	41
$^2P_{1/2}$	98	23 218	23 236	−18	23 163	23 141	22
$^2D_{5/2}(1)$	99	23 674	23 663	11	23 680	23 673	7
	100	23 804	23 814	−10	23 760	23 764	−4
	101	23 941	23 963	−22	23 810	23 799	11
$^2P_{3/2}$	102	26 178	26 161	17	26 140	26 173	−33
	103		26 333			26 231	
$^4D_{3/2}$	104		27 626		27 580	27 576	4
and	105	27 816	27 796	20	27 689	27 716	−27
$^4D_{5/2}$	106	27 980	27 970	10	27 836	27 826	10
	107	28 241	28 224	17	28 159	28 149	10
	108	28 377	28 396	−19	28 284	28 280	4
$^4D_{1/2}$	109	28 522	28 575	−53	28 335	28 331	4
$^2I_{11/2}$	110		28 611		28 500	28 501	−1
	111	28 910	28 907	3	28 677	28 677	0
	112	29 146	29 135	11	28 859	28 841	18
	113		29 175		29 018	29 036	−18
	114		29 391			29 153	
	115	29 455	29 419	36	29 250	29 240	10
$^2L_{15/2}$,	116		29 614		29 856	29 851	5
$^4D_{7/2}$,	117		29 804			29 878	
and	118	29 895	29 908	−13	29 900	29 893	7
$^2I_{13/2}$	119		29 971		29 932	29 927	5
	120	30 003	29 992	11	29 958	29 961	−3
	121		30 065		30 000	30 013	−13
	122		30 108		30 059	30 040	19
	123	30 175	30 195	−20	30 073	30 101	−28
	124		30 237		30 120	30 127	−7
	125		30 292			30 151	
	126	30 414	30 405	9	30 180	30 181	−1
	127		30 438		30 210	30 229	−19
	128		30 442		30 265	30 287	−22
	129		30 504		30 308	30 311	−3
	130		30 584		30 359	30 377	−18
	131		30 629			30 404	
	132		30 673		30 431	30 438	−7
	133	30 694	30 692	2	30 454	30 458	−4
	134	30 779	30 761	18	30 510	30 506	4
$^2L_{17/2}$	135		31 116		31 384	31 372	12
	136		31 257		31 450	31 469	−19
	137		31 474		31 470	31 487	−17
	138		31 535		31 522	31 541	−19
	139	31 585	31 613	−28	31 570	31 553	17
	140		31 697		31 662	31 631	31
	141		31 824		31 720	31 711	9

TABLE V. (Continued).

$^{2S+1}L_J$ [a]	Level number	Nd:LLGG E (cm^{-1}) Expt. [b]	Calc. [c]	Δ (cm^{-1})	Nd:GSGG E (cm^{-1}) Expt. [d]	Calc. [c]	Δ (cm^{-1})
	142		31 981		31 800	31 802	−2
	143		32 181			31 878	
$^2H_{9/2}(1)$	144		32 751		32 550	32 558	−8
	145		32 893		32 634	32 646	−12
	146		32 945		32 686	32 683	3
	147		33 004		32 713	32 716	−3
	148		33 053		32 797	32 777	20
$^2D_{3/2}(2)$	149	33 091	33 111	−20	33 300	33 311	−11
	150		33 252			33 373	
$^2D_{5/2}(2)$	151		33 874		33 860	33 861	−1
	152	33 979	33 991	−12		33 872	
	153		34 007			33 986	
$^2H_{11/2}(1)$	154	34 246	34 215	31		34 092	
	155		34 327			34 120	
	156		34 335			34 163	
	157	34 388	34 416	−28		34 348	
	158		34 503			34 400	
	159		34 606			34 417	

[a]Identifies energy regions according to principal SLJ parentages.
[b]Levels 1–73; Ref. 20; levels 74–157, present study.
[c]From calculations based on the Hamiltonian parameters listed in Table I (no SCCF).
[d]Levels 1–47; Ref. 22; levels 48–151, present study.

Nd:YAG (levels 1–106) are taken from Kaminskii[14] since most of our results agree with his to within experimental error. Levels 107 to 166 come from the present study and are supported by the data of Gorban *et al.*[17] and Hua *et al.*[19] For Nd:YSAG experimental energy levels 1–60 (see Table IV) are taken from Ref. 21 and levels 61–165 come from the present study. In Table V the experimental energy levels 1–73 (Nd:LLGG) are taken from Ref. 20 and levels 74–157 derive from the present study. For Nd:GSGG experimental energy levels 1–47 come from Ref. 22 and levels 48–151 come from the present study.

III. ENERGY-LEVEL CALCULATIONS

The model Hamiltonian used in this study may be written as

$$\hat{H}=\hat{H}_a+\hat{H}_{\mathrm{CF}}^{+}\ , \tag{1}$$

where $\hat{H}_a$ is defined to incorporate the isotropic parts of $\hat{H}$ (including the spherically symmetric part of the $4f$-electron–crystal-field interactions), and $\hat{H}_{\mathrm{CF}}^{+}$ is defined to represent the nonspherically symmetric components of the *even-parity* crystal field. We refer to $\hat{H}_a$ as the *atomic* Hamiltonian and call $\hat{H}_{\mathrm{CF}}^{+}$ the *crystal-field* Hamiltonian. The $\hat{H}_a$ operator is defined as

$$\hat{H}_a=E_{\mathrm{av}}+\sum_k F^k\hat{f}_k+\alpha\hat{L}(\hat{L}+1)+\beta\hat{G}(G_2)+\gamma\hat{G}(R_7)+\sum_i T^i\hat{t}_i+\zeta_{\mathrm{s.o.}}\hat{A}_{\mathrm{s.o.}}+\sum_k P^k\hat{p}_k+\sum_j M^j\hat{m}_j\ , \tag{2}$$

where $k=2,4,6$; $i=2,3,4,6,7,8$; $j=0,2,4$; and the operators $(\hat{o})$ and their associated parameters are written according to conventional notation and meaning (with respect to the interactions they represent).[41–43]

The crystal-field Hamiltonian is defined as

$$\hat{H}_{\mathrm{CF}}^{+}=\sum_{k,m}\sum_i(B_{km}+b_{km}\hat{S}\cdot\hat{s}_i)\hat{u}_{km}(i)\ , \tag{3}$$

where i labels the $4f$ electrons; $\hat{u}_{km}(i)$ is a one-electron unit-tensor operator; $\hat{S}$ and $\hat{s}_i$ denote total spin and one-electron spin operators, respectively; B_{km} denotes a standard (one-electron) crystal-field parameter; and b_{km} denotes a SCCF parameter. In D_2 symmetry, all of the crystal-field parameters may be chosen real and both the $\{B_{km}\}$ and $\{b_{km}\}$ sets in Eq. (3) may be defined in terms of nine independent parameters: $(k,m)=(2,0)$, (2,2), (4,0), (4,2), (4,4), (6,0), (6,2), (6,4), and (6,6). The SCCF part of $\hat{H}_{\mathrm{CF}}^{+}$ provides a phenomenological representation of crystal-field correlation effects attributable to differences in the crystal field seen by $4f$ electrons with different spins (s_i) *relative* to the direction of the total $4f$-electron spin $(S=\sum_i s_i)$.[30] The phenomenological SCCF model has been used in a number of recently reported analyses of lanthanide $4f^N$ state structure in crystalline environments, although conclusions regarding its importance and utility remain speculative.[26–34]

All energy-level calculations were carried out by diagonalizing the total (atomic + crystal-field) Hamiltonian within the complete $SLJM_J$ basis set of the $4f^3$ electronic configuration. In our parametric fits of calculated to experimental data, 16 of the 20 parameters in $\hat{H}_a$ [see Eq. (2)] were used as independent fitting variables. Four of the atomic parameters, M^2, M^4, P^4, and P^6, were constrained according to $M^2=0.56M^0$, $M^4=0.38M^0$, $P^4=0.75P^2$, and $P^6=0.50P^2$. The crystal-field Hamiltonian $\hat{H}^+_{CF}$ was treated in three different ways in our fitting calculations: (1) no SCCF, all b_{km} parameters were set equal to zero, and only the nine B_{km} parameters were used in the calculations; (2) restricted SCCF, the b_{km} parameters were replaced by $c_k=b_{km}/B_{km}$ in Eq. (3), and data fits were performed using the nine B_{km} parameters and three c_k (k=2,4,6) parameters as fitting variables; (3) unrestricted SCCF, all nine B_{km} and b_{km} parameters were allowed to independently vary in performing fits. The restricted SCCF treatment (2) suppresses m-dependence in the b_{km}/B_{km} ratios.

Values of the Hamiltonian parameters derived from analyses in which *no* SCCF effects were included are listed in Table I for each of the neodymium garnet systems examined in this study. Also given in Table I are the numbers of energy levels included in our calculated-versus-experimental data fits and the rms deviations (σ) between calculated and experimental results. Calculated eigenenergies, based on the Hamiltonian parameters of Table I, are listed in Tables IV and V alongside the corresponding experimental values. The parameter values shown in Table I represent the distillate of a calculational scheme in which many different starting parameter sets (and subsets) were used in testing convergence of fits to the final values and in which differences between the results obtained for the four systems were thoroughly tested for reproducibility (when starting from a variety of points in the parameter space of the model). The latter tests were of particular importance because the results listed in Table I show quite significant differences between the systems (in several of the atomic and crystal-field parameters).

The results obtained from our *restricted* SCCF analyses are very similar to those obtained with no SCCF. The atomic parameters are essentially identical to those given in Table I, the B_{km} values (listed in Table II) are not significantly different, and the values obtained for the c_k parameters are small (see Table II). Inclusion of the restricted SCCF parameters, c_k, in our calculations reduces the σ values of the fits only slightly, and it has no special effects within any particular multiplet manifold.

Data analyses carried out within our *unrestricted* SCCF parametrization scheme produced atomic parameters essentially identical to those given in Table I, but many of the B_{km} crystal-field parameters were altered and the rms deviations (σ values) in the data fits were improved over those shown in Table I. The B_{km} and b_{km} parameter values obtained from these fits are listed in Table III along with $c_{km}=b_{km}/B_{km}$ ratios and σ values. No results are shown for the Nd:YAG system. In our analysis of this system, we encountered parameter stability and interaction (correlation) problems that could not be resolved satisfactorily. The parametric analyses carried out on experimental data sets of Nd:YSAG, Nd:GSGG, and Nd:LLGG were well behaved in a statistical sense, although several of the c_{km} ratios determined for these systems have magnitudes that are probably "unphysical" (too large). This is particularly apparent in the c_{22} and c_{44} values shown in Table III. Furthermore, the c_{km} ratios exhibit a strong m dependence, which is counter to predictions of the *superposition model* of lanthanide crystal fields.[30]

Complete sets of calculated eigenenergies based on the crystal-field parameters listed in Table III are not presented in this paper, but are available upon request. The most significant differences between these eigenenergies and the calculated energies shown in Tables IV and V are found in the following multiplet manifolds: $^4I_{9/2}$ (in GSGG and LLGG); $^4F_{5/2}$, $^2H_{9/2}$ (in YSAG and LLGG); $^2H_{11/2}$ (in YSAG and GSGG); $^2K_{15/2}$ (in YSAG and GSGG); and $^2L_{17/2}$ (in YSAG). A comparison of results for the $^2H_{11/2}(2)$ multiplet manifold of Nd:YSAG and Nd:LLGG is given in Table VI. The observed crystal-field splittings within this multiplet manifold have proved to be notoriously difficult to fit for a number of Nd^{3+} systems,[44–48] and we encountered similar difficulties in the present study. The results presented in Table VI show that inclusion of SCCF terms in our phenomenological Hamiltonian yields some modest improvement in calculated-versus-experimental data fits within the $^2H_{11/2}(2)$ multiplet manifold, but the fits still remain unsatisfactory. Similar results were obtained for the Nd:YAG and Nd:GSGG systems. With respect to *overall* quality of fits (for complete experimental data sets), the results obtained for Nd:YSAG show the most significant improvement with inclusion of SCCF terms.

IV. DISCUSSION

Crystal-field energy-level analyses have been reported previously for each of the neodymium garnet systems examined in this study. However, those analyses were restricted to subsets of energy levels associated with J-multiplet manifolds lying below 18 000 cm^{-1}, and they were based on a calculated-to-experimental energy-level fitting procedure somewhat different from the one employed in the present study. Intermediate-coupling $f^3[SL]J$ wave functions were calculated using the free-ion Hamiltonian (and parameters) reported by Carnall *et al.*[49] for Nd^{3+} (aquo) ions, and these wave functions were then used as basis functions in the crystal-field energy-level calculations. Calculated-versus-experimental data fits were performed by treating the nine B_{km} parameters of the D_2 crystal-field Hamiltonian as free variables while also permitting the centroids of the $[SL]J$ multiplets to vary freely. This procedure is very effective in optimizing fits of calculated-to-observed crystal-field

TABLE VI. Calculated and observed crystal-field splittings within the $^2H_{11/2}(2)$ multiplet manifold of Nd:YSAG and Nd:LLGG.

Level number[a]	Expt. E (cm^{-1})	$\|M_J\|$[d]	Calc. (no SCCF)[b] E (cm^{-1})	ΔE (cm^{-1})[e]	$\|M_J\|$[d]	Calc. (with SCCF)[c] E (cm^{-1})	ΔE (cm^{-1})[e]
Nd:YSAG							
48	15 860	$\frac{1}{2}$	15 901	−41	$\frac{3}{2}$	15 888	−28
49	15 886	$\frac{9}{2}$	15 924	−38	$\frac{7}{2}$	15 910	−24
50		$\frac{7}{2}$	15 950		$\frac{1}{2}$	15 947	
51	15 960	$\frac{3}{2}$	15 957	3	$\frac{9}{2}$	15 967	−7
52	16 093	$\frac{5}{2}$	16 033	60	$\frac{5}{2}$	16 043	50
53	16 124	$\frac{11}{2}$	16 065	59	$\frac{11}{2}$	16 075	49
			($\sigma = 45$)[f]			($\sigma = 34$)[f]	
Nd:LLGG							
48	15 901	$\frac{1}{2}$	15 929	−28	$\frac{1}{2}$	15 925	−24
49	15 926	$\frac{3}{2}$	15 958	−32	$\frac{3}{2}$	15 949	−23
50		$\frac{7}{2}$	15 978		$\frac{9}{2}$	15 975	
51	15 991	$\frac{9}{2}$	15 990	1	$\frac{7}{2}$	15 992	−1
52	16 093	$\frac{5}{2}$	16 043	50	$\frac{5}{2}$	16 050	43
53	16 129	$\frac{11}{2}$	16 085	44	$\frac{11}{2}$	16 079	50
			($\sigma = 35$)[f]			($\sigma = 33$)[f]	

[a]Same numbering as in Tables IV and V.
[b]Calculations based on Hamiltonian parameters listed in Table I.
[c]Calculations based on Hamiltonian parameters listed in Table III.
[d]Identifies principal M_J component of eigenvectors.
[e]Difference between experimental and calculated energies (in cm^{-1}).
[f]rms deviation between calculated and experimental energies.

splittings within relatively isolated and distinct multiplet manifolds, and it yields quite favorable rms deviations for energy levels associated with most of the 13 multiplet manifolds lying below 18 000 cm^{-1} (a persistent exception is the $^2H_{11/2}(2)$ manifold). However, this procedure is not suitable for fitting energy levels in regions where multiplet manifolds are very close (or overlapping) and where $[SL]J$ parentages are indistinct. In these regions, adjustable atomic (free-ion) Hamiltonian parameters are crucial for achieving satisfactory data fits. In our analyses of energy levels up to 40 000 cm^{-1} (for Nd:YAG and Nd:YSAG) and 35 000 cm^{-1} (for Nd:LLGG and Nd:GSGG), we used 16 of the 20 parameters in our atomic Hamiltonian [see Eq. (2)] as fitting variables along with the crystal-field parameters.

Comparisons between crystal-field parameters derived from the present analyses (*without* inclusion of SCCF) versus those reported previously for the respective systems are given in Table VII. The only major discrepancies between the present versus previously reported parameter values are found in the Nd:GSGG parameter set, particularly among the rank-4 parameters. If we restrict our analysis only to the lowest 60 levels of Nd:GSGG, we obtain parameter values that closely match those report-

TABLE VII. Comparison of crystal-field parameters obtained from present vs previous analyses. All parameter values are given in cm^{-1}, and the parameters are defined according to Eq. (3) in the text. Parameter values taken from the literature were converted to the appropriate unit-tensor basis (see Table 4 of Ref. 15).

Parameter	Nd:YAG Present[a]	Nd:YAG Ref. 15[b]	Nd:YSAG Present[a]	Nd:YSAG Ref. 21	Nd:GSGG Present[a]	Nd:GSGG Ref. 22	Nd:LLGG Present[a]	Nd:LLGG Ref. 20
B_{20}	−690	−702	−819	−804	−467	−568	−1265	−1201
B_{22}	−158	−176	−224	−56	−117	−104	−361	−281
B_{40}	−343	−409	−206	−217	−907	−60	−114	−91
B_{42}	−2401	−2262	−2473	−2118	−2482	−2001	−2006	−1861
B_{44}	−1094	−1072	−988	−1347	−652	−1106	−819	−882
B_{60}	2315	2174	2040	2069	1734	1937	1729	1718
B_{62}	922	974	878	1028	567	857	792	777
B_{64}	−1124	−1069	−1087	−1018	−1035	−993	−811	−804
B_{66}	836	917	824	782	1030	819	830	783
N[c]	148	41	140	51	143	45	107	44

[a]From Table I of the present paper.
[b]From parameter set 1 in Table 6 of Ref. 15.
[c]Number of experimental levels fitted in parametric energy-level analyses.

ed in Ref. 22. However, calculations based on these parameter values give poor fits of the higher energy levels located for NG:GSGG.

The atomic parameter values listed in Table I for Nd:YAG and Nd:YSAG are generally quite similar to those reported previously for $Nd:LaCl_3$,[34] $NdAlO_3$,[50] $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$,[50] and Na_3[Nd(oxydiacetate)$_3 \cdot NaClO_4 \cdot 6H_2O$.[47] However, there are some significant differences between these parameter values and those listed in Table I for Nd:GSGG and Nd:LLGG. The most notable differences are seen in the F^4, F^6, T^2, and T^8 parameters. This differentiation between the aluminum versus gallium garnet systems might be attributable to the relative substitutional site volumes (for Nd^{3+} ions) in the respective lattice structures. The substitutional sites in the gallium garnet lattice are larger than those in the aluminum garnet lattice.[23,36,37] It is interesting to note, however, that the crystal-field parameter values listed in Table I do not show a clear-cut differentiation between the aluminum and gallium garnet systems. In fact, the largest differences between crystal-field parameters are found for the Nd:GSGG versus Nd:LLGG systems.

Rationalization of the differences between the Hamiltonian parameters derived for the respective systems (in terms of detailed structural and mechanistic considerations) was beyond the scope of this study. Calculations based on the semiempirically derived parameter sets yield reasonably good agreement between calculated and observed energy levels up to 34 000 cm^{-1}. This suggests that the phenomenologically determined parameter values might be suitable for detailed analysis in terms of crystal-field structure and interaction mechanisms. However, more stringent tests of the parametric Hamiltonians are needed, particularly with respect to the quality of their eigenvalues. Quantitative line-strength analyses for optical transitions between Stark levels would be of considerable help in this regard.[47,51–56] Quantitative intensity analyses of multiplet-to-multiplet transition manifolds have been reported for a number of neodymium garnet systems. However, line-strength data for transitions between individual Stark levels remain sparse. We have measured line strengths for 86 crystal-field transitions in Nd:YAG and are analyzing these data in terms of a parametric intensity model applied previously to other lanthanide systems.[47,51,56] Successful application of this model is critically dependent on having accurate crystal-field state vectors. Preliminary results from our analyses of the Nd:YAG intensity data indicate that the state vectors generated by the Hamiltonian parameters listed in Table I for Nd:YAG provide a quite satisfactory basis for transition line-strength analysis and interpretation.[57]

Comparative energy-level analyses were the principal focus of the study reported here. These analyses were based on a parametric Hamiltonian for the $4f^3$ electronic configuration of Nd^{3+} ions in crystal sites of D_2 symmetry, and they permitted a phenomenological characterization of both atomic and crystal-field Hamiltonian parameters. This characterization is a necessary precursor to more detailed studies and analysis of optical properties and processes associated with transitions between Stark levels in neodymium garnet systems. Inclusion of spin-correlated crystal-field (SCCF) effects in our energy-level analyses must be viewed primarily as an exploratory excursion that produced interesting, but inconclusive, results. The possible importance of these effects remains unclear, and our results suggest that they merit further investigations.

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