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Optical-absorption spectra, crystal-field energy levels, and transition line strengths of holmium in trigonal $Na_3[Ho(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$

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Locations and assignments of 105 crystal-field levels are reported for Ho^{3+} in the trigonal $Na_3[Ho(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$ system. These levels were located and assigned from transitions observed in *axial* and σ- and π-polarized *orthoaxial* absorption spectra obtained on single-crystal samples at temperatures between 5 and 295 K. The absorption measurements spanned the 8000–37 000-cm^{-1} spectral region, and the assigned energy levels derive from 23 different $[SL]J$ multiplet manifolds of the $4f^{10}$ electronic configuration of Ho^{3+}, with principal SL parentages derived from nine different Russell-Saunders terms (^5I, ^5F, ^5S, ^3K, ^5G, ^3H, ^3L, ^3M, and ^5D). The empirical energy-level data are analyzed in terms of a parametrized model Hamiltonian for the $4f^{10}$ electronic configuration, assumed to be perturbed by a crystal field of trigonal dihedral (D_3) symmetry. Parametric fits of calculated-to-empirical energy-level data yield a rms deviation of ~ 9 cm^{-1} (between calculated and observed energies). The Hamiltonian parameter values obtained from these energy-level analyses are compared with results obtained from similar analyses of Ho^{3+} in other crystals *and* of other lanthanide (M^{3+}) ions in the $Na_3[M(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$ system. In addition to energy-level locations and assignments, quantitatively determined line strengths are reported for 42 transitions observed in the *axial* absorption spectra at 10 K, and for 19 transitions observed in the π-polarized *orthoaxial* absorption spectra at 10 K. Fifty of these transitions originate from the ground crystal-field level of the $^5I_8$ (ground) multiplet, and eleven originate from the second crystal-field level (located 14 cm^{-1} above ground) of $^5I_8$.

I. INTRODUCTION

The trigonal $Na_3[M(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ systems (where M^{3+} is a lanthanide ion and ODA denotes an oxydiacetate ligand, $^-OOCCH_2OCH_2COO^-$) are excellent models for examining lanthanide $4f^N$-electronic-state structure and $4f$-$4f$ radiative transition properties in a relatively complex but structurally well-defined ligand environment. At room temperature, single crystals of these systems have the space group $R32$ (D_3^7), the lanthanide ions M^{3+} are located at sites with D_3 symmetry, and the *tris*-terdentate $M(ODA)_3{}^{3-}$ complexes have D_3 point-group symmetry.[1–3] Each MO_9 coordination cluster forms a slightly distorted tricapped trigonal prism polyhedron (of D_3 symmetry), with top and bottom triangles defined by carboxylate oxygen atoms and the capping positions (on normals to the rectangular faces) occupied by ether oxygen atoms. The backbone of each bicyclic M(ODA) chelate system is nearly planar and stretches diagonally across a rectangular face of the MO_9 trigonal prism structure. The chelate rings contain highly anisotropic electronic charge distributions, and one may anticipate lanthanide–ligand-field interactions not present (or at least not readily apparent) in structurally simpler systems. Furthermore, single crystals of $Na_3[M(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ grow (spontaneously) in two enantiomorphic forms, which differ with respect to the absolute configuration of their constituent $M(ODA)_3{}^{3-}$ complexes *and* the chiral (left-handed or right-handed) arrangement of these complexes about the trigonal axis of the crystal.[4] Therefore, these systems exhibit *chiro-optical* properties that may be exploited in characterizing spectroscopic state structure and transition mechanisms.[5]

The optical and chiro-optical properties of $Na_3[M(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ systems have received considerable attention over the past 15 years,[4–45] but until recently their detailed analysis remained elusive except in a few transition regions of several systems. The most thorough and comprehensive spectroscopic studies have been reported for the neodymium,[40,44–46] samarium,[32–35] and europium[38,39] systems. The empirical data obtained for these systems were sufficient to support detailed analyses of $4f^N$ electronic state structure and energy levels, $4f$-$4f$ transition dipole strengths, and $4f$-$4f$ transition rotatory strengths. Intensity analyses proved to be particularly interesting with respect to implications regarding lanthanide–ligand–radiation field (M-L-$h\nu$) interaction mechanisms and the relationship of these mechanisms to ligand structure.[11,12,27,34,35,38,39,45]

In this paper we report results obtained from optical-absorption measurements on single crystals of trigonal $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ (referred to hereafter as HoODA). These measurements spanned the 8000–37 000-cm^{-1} spectral region, and they were carried out at sample temperatures between 5 and 295 K. Both unpolarized *axial* and polarized *orthoaxial* absorption spectra were measured, and more than 200 transitions between crystal-field (Stark) levels were located and assigned. Integrated intensities were quantitatively determined for 61 of the lines observed in the absorption spectra at 10 K. Energy levels and transitions were assigned according to optical selection rules based on D_3 site symmetry (at the Ho^{3+} ions), and the assigned energy levels were analyzed in terms of a model Hamiltonian that assumed D_3 crystal-field symmetry. The crystals retain uniaxial symmetry over the 5–295-K temperature range, and the polarized absorption intensity data conform closely to D_3 polarization selection rules over this temperature range. However, at temperatures below ~20 K several doubly degenerate levels (in D_3 symmetry) exhibit small splittings (≤ 4 cm^{-1}), indicating that trigonal site symmetry is lost at low temperature. This is compatible with previously reported evidence for low-temperature structural phase transitions in $Na_3[M(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ systems, which indicates that the crystal space group changes from $R32$ to $P321$ (D_3^2) and the lanthanide site symmetry is reduced from D_3 to C_2 (due to movement of the Na^+ ions off threefold axes).[16,19,40,47]

This is the first detailed report of optical spectra, energy-level assignments and analysis, and transition line strengths for holmium in $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ (a preliminary report was presented at the 18th Rare Earth Research Conference, Lake Geneva, WI, 1988).[43] Locations and assignments of 105 crystal-field levels are given and 61 transition line strengths are reported. The assigned crystal-field levels span 23 $[SL]J$ multiplet manifolds of the $4f^{10}$ electronic configuration, with principal SL parentages derived from nine different Russell-Saunders terms (^5I, ^5F, ^5S, ^3K, ^5G, ^3H, ^3L, ^3M, and ^5D). A parametric analysis of the empirical energy-level data, based on a model Hamiltonian of D_3 symmetry, yields calculated versus empirical energy-level fits with a rms deviation of 9 cm^{-1}. The crystal-field parameter values derived from this analysis are compared to those reported for other MODA systems, and the isotropic ("atomic") Hamiltonian parameters are compared to those reported for Ho^{3+} in other crystalline hosts. The eigenvectors of the model Hamiltonian characterized in this study are crucial to detailed analyses of the transition line-strength data. These analyses are reported in a separate paper.[48]

II. EXPERIMENT

Single crystals of $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ were grown from aqueous solution following the methods of Albertsson.[1,2] Damp Whatman glass-microfiber filter paper was used to polish crystals to a thickness and shape suitable for optical measurements. Variable-temperature measurements between 10 and 295 K were carried out with the crystal sample mounted at the cold station in the sample compartment of a CTI-Cryogenics closed-cycle helium refrigerator and cryostat. The crystal was mounted on a one-piece copper mount using crycon grease and indium foil, and the copper mount was attached to the cold head of the refrigerator, with strips of indium providing a thermally conductive interface. Cold-head temperature was controlled using a Lake Shores Cryogenics, Inc. temperature controller (Model DRC-70), and it could be varied between approximately 10 K and room temperature. Variable-temperature measurements between 5 and 16 K were carried out with the crystal mounted in the sample compartment of an Air Products liquid-helium-transfer Heli-Tran refrigerator, with temperature control provided by an Air Products temperature controller.

Absorption spectra were recorded using either a Cary Model 17D or a Cary Model 2415 spectrophotometer. Unpolarized *axial* and σ- and π-polarized *orthoaxial* spectra were measured over the 270–1250-nm wavelength range, with a spectral resolution of ≤ 0.1 nm. In our measurements between 270 and 400 nm, the crystal thickness (optical pathlength) was 0.85 mm in the *axial* experiments and 1.0 mm in the *orthoaxial* experiments. In our measurements between 400 and 1250 nm, the crystal thickness was 0.33 mm in the *axial* experiments and 0.40 mm in the *orthoaxial* experiments. In all quantitative measurements of transition line strengths, the largest recorded absorbances were less than 70% of the spectrophotometer's full-scale absorbance limit. Wavelength accuracy in the recorded spectra was approximately $\Delta\lambda = 0.2$ nm, but the relative locations of assigned energy levels within any given multiplet-to-multiplet transition region were determined to within an uncertainty of ± 3 cm^{-1}.

III. OPTICAL SELECTION RULES AND LINE ASSIGNMENTS

All crystal-field levels split out of the $4f^{10}$ electronic configuration of Ho^{3+} in a trigonal dihedral (D_3) crystal-field potential may be classified as having A_1, A_2, or E symmetry in the D_3 point group. Therefore, all transitions between crystal-field levels may be classified (by symmetry) as $A_1 \leftrightarrow A_1$, $A_1 \leftrightarrow A_2$, $A_1 \leftrightarrow E$, $A_2 \leftrightarrow A_2$, $A_2 \leftrightarrow E$, or $E \leftrightarrow E$. Choosing a Cartesian coordinate system in which the z axis is coincident with the C_3 symmetry axis of our trigonal (D_3) system, the x and y components of both the electric- and magnetic-dipole moment operators (denoted here by $\boldsymbol{\mu}$ and $\mathbf{m}$, respectively) transform as the E irreducible representation of the D_3 point group, whereas the z component of each transforms as the A_2 irreducible representation. Given these symmetry properties of the electric- and magnetic-dipole moment operators, selection rules for each transition type in axial (α) and orthoaxial (σ- and π-polarized) absorption spectra of trigonal $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ may be summarized as in Table I.

The selection rules given in Table I are not sufficient for making unambiguous assignments of transitions without some *a priori* knowledge about the dominant transition mechanism (electric dipole *versus* magnetic dipole). In the present study, it was presumed that magnetic-dipole contributions to transition intensity could be calculated directly and reliably from eigenvectors of our model Hamiltonian (parametrized to achieve optimal calculated- versus experimental-energy-level fits). Magnetic-dipole strengths were calculated for *all* transitions occurring in the spectral regions of interest in this study, and the results of these calculations provided crucial assistance in making line assignments in several multiplet-to-multiplet transition manifolds. Among the

TABLE I. Electric (μ) and magnetic (m) dipole selection rules for transitions between crystal-field levels.

Transition	Axial spectra	Orthoaxial spectra σ-polarized	 π-polarized
$A_1 \leftrightarrow A_1$	forbidden	forbidden	forbidden
$A_1 \leftrightarrow A_2$	forbidden	m_z	μ_z
$A_1 \leftrightarrow E$	$(\mu_x,\mu_y);(m_x,m_y)$	(μ_x,μ_y)	(m_x,m_y)
$A_2 \leftrightarrow A_2$	forbidden	forbidden	forbidden
$A_2 \leftrightarrow E$	$(\mu_x,\mu_y);(m_x,m_y)$	(μ_x,μ_y)	(m_x,m_y)
$E \leftrightarrow E$	$(\mu_x,\mu_y);(m_x,m_y)$	$(\mu_x,\mu_y);m_z$	$\mu_z;(m_x,m_y)$

latter were the $^5I_8 \rightarrow {}^3K_8$, $^3K_7$, $^3L_9$, and $^3L_8$ transition regions, within which many transitions between crystal-field (Stark) levels are calculated to have substantial (*or* predominantly) magnetic-dipole character.[48] For each of the other transition regions examined in this study, magnetic-dipole contributions to line strengths were generally calculated to be very small and, in most cases, undetectable. Though small, magnetic-dipole transition moments make *essential* contributions to the *rotatory strengths* of transitions observed in circular dichroism spectra of $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$,[43] and analyses of these very complex spectra will be addressed in a future report.[49]

IV. CALCULATIONS AND DATA ANALYSIS

A. Energy levels

The $4f^{10}$ energy-level structure of Ho^{3+} in HoODA was analyzed in terms of a model Hamiltonian which 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.

In our model, the $\hat{H}_a$ operator is defined by

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

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).[50,51] We define the crystal-field Hamiltonian as

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

where i labels the $4f$ electrons, $\hat{u}_{km}(i)$ is a one-electron unit-tensor operator, $\hat{\mathbf{S}}$ and $\hat{\mathbf{s}}_i$ denote total spin and one-electron spin operators, respectively, B_{km} denotes a standard (one-electron) crystal-field interaction parameter, and b_{km} denotes a *spin-correlated crystal-field* parameter.[52,53] In D_3 symmetry, $\hat{H}^{+}_{\mathrm{CF}}$ may be defined in terms of six B_{km} parameters and six b_{km} parameters: $(k,m)=(2,0)$, (4,0), (4,3), (6,0), (6,3), and (6,6). Each parameter may be chosen to be pure *real*, so our model crystal-field Hamiltonian (defined to have D_3 symmetry) contains a total of 12 independent parameters.

The atomic Hamiltonian, defined by expression (2), contains 20 parameters (including E_{av}), and the crystal-field Hamiltonian, defined by expression (3) and assuming D_3 symmetry, contains 12 parameters. The *complete* $\hat{H}_a$ operator was used in all of our energy-level calculations, although not all of the 20 parameters contained in this operator were used in performing parametric fits of calculated-to-experimental energy-level data *(vide infra)*. Calculations were carried out both *with* and *without* inclusion of the spin-correlated crystal-field (SCCF) terms in $\hat{H}^{+}_{\mathrm{CF}}$. The SCCF terms represent some (partial) consideration of electron-correlation effects in the $4f$-electron–crystal-field interactions, and recent work by Newman, Reid, and Richardson and co-workers[52–63] suggests that these effects may sometimes have a nonnegligible influence on the $4f^N$ energy-level structures of lanthanide systems. Energy-level calculations were performed in two steps. The atomic Hamiltonian was first diagonalized within the complete Russell-Saunders basis set of the $4f^{10}$ configuration, and the eigenvectors obtained from this calculation were then used to construct a suitable truncated intermediate-coupling $4f^{10}$ $[SL]JM_J$ basis within which the *total* (atomic+crystal-field) Hamiltonian was diagonalized. The latter basis set included all JM_J states (456) derived from $[SL]J$ multiplets with energies between 0 and 40 200 cm^{-1} (a total of 44 multiplets). The highest experimentally characterized energy level included in our parametric data fits was located at 36 082 cm^{-1}.

B. Transition line strengths

Intensities of transitions occurring between crystal-field levels are reported here in terms of transition line strengths. Separate line strengths were determined for transitions observed in unpolarized *axial* (α) absorption spectra and in σ- and π-polarized *orthoaxial* absorption spectra. For a transition between levels A (initial) and B (final), the respective line strengths were determined according to the following expressions:

TABLE II. Calculated and observed energy levels for Ho^{3+} in $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$.

				Energy (cm^{-1})		
Level No.	Multiplet[a]	$\|M_J\|$[a]	Γ[b]	Calculated[c]	Observed	Δ[d]
1	$^5I_8$	7	E	0	0	0
2		0	A_1	9	14	−5
3		5	E	71	63	8
4		6	A_2	109		
5		2	E	183		
6		3	A_1	189		
7		1	E	256		
8		0	A_1	273		
9		3	A_2	356		
10		4	E	359		
11		8	E	404		
12	$^5I_7$	6	A_2	5186		
13		6	A_1	5194		
14		5	E	5196		
15		4	E	5204		
16		3	A_2	5239		
17		2	E	5261		
18		1	E	5268		
19		3	A_1	5270		
20		0	A_2	5271		
21		7	E	5293		
22	$^5I_6$	4	E	8702	8705	−3
23		3	A_2	8705	8712	−7
24		3	A_1	8710		
25		5	E	8724	8719	5
26		2	E	8748	8747	1
27		6	A_1	8754		
28		6	A_2	8761	8752	9
29		1	E	8793	8787	6
30		0	A_1	8815	8806	9
31	$^5I_5$	3	A_2	11 265		
32		3	A_1	11 276		
33		4	E	11 279	11 281	−2
34		2	E	11 296		
35		5	E	11 304		
36		1	E	11 339		
37		0	A_2	11 361		
38	$^5I_4$	3	A_1	13 209		
39		4	E	13 303		
40		3	A_2	13 376		
41		0	A_1	13 379		
42		2	E	13 386		
43		4	E	13 524		
44	$^5F_5$	3	A_2	15 520	15 524	−4
45		4	E	15 527	15 532	−5
46		3	A_1	15 528	15 536	−8
47		2	E	15 558	15 555	3
48		1	E	15 630		
49		5	E	15 634		
50		0	A_2	15 651	15 636	15
51	$^5S_2$	0	A_1	18 504		
52		2	E	18 512	18 513	−1
53		1	E	18 524	18 525	−1

TABLE II. (*Continued*).

Level No.	Multiplet[a]	$\lvert M_J \rvert$[a]	Γ[b]	Energy (cm^{-1}) Calculated[c]	Energy (cm^{-1}) Observed	Δ[d]
54	$^5F_4$	0	A_1	18 574	18 573	1
55		4	E	18 627	18 624	3
56		1	E	18 642	18 636	6
57		0	A_1	18 659	18 651	8
58		3	A_2	18 682	18 673	9
59		2	E	18 716	18 705	11
60	$^5F_3$	0	A_2	20 638	20 650	−12
61		3	A_1	20 654	20 663	−9
62		1	E	20 679	20 688	−9
63		2	E	20 747	20 740	7
64		0	A_2	20 757	20 762	−5
65	$^5F_2$	0	A_1	21 124	21 124	0
66		2	E	21 147	21 141	6
67		1	E	21 195	21 185	10
68	$^3K_8(2)$	8	E	21 364	21 371	−7
69		3	A_2	21 388	21 388	0
70		4	E	21 390	21 394	−4
71		0	A_1	21 417		
72		1	E	21 419	21 419	0
73		3	A_1	21 423	21 426	−3
74		2	E	21 445	21 444	1
75		6	A_2	21 473	21 462	11
76		5	E	21 491	21 494	−3
77		0	A_1	21 520	21 518	2
78		7	E	21 523		
79	$^5G_6$	0	A_1	22 104	22 100	4
80		1	E	22 132	22 127	5
81		6	A_2	22 166	22 156	10
82		6	A_1	22 183	22 165	18
83		2	E	22 197	22 190	7
84		5	E	22 285	22 296	−11
85		3	A_2	22 308		
86		3	A_1	22 319		
87		4	E	22 330	22 335	−5
88	$^5F_1$	0	A_2	22 403	22 397	6
89		1	E	22 410	22 409	1
90	$^5G_5$	5	E	24 002	23 974	28
91		1	E	24 025	24 008	17
92		0	A_2	24 027	24 010	17
93		3	A_1	24 052		
94		2	E	24 076	24 083	−7
95		3	A_2	24 078	24 096	−16
96		4	E	24 090	24 114	−24
97	$^5G_4$	2	E	25 840	25 843	−3
98		3	A_2	25 879	25 898	−19
99		0	A_1	25 915		
100		2	E	25 944	25 941	3
101		4	E	25 967	25 968	−1
102		0	A_1	26 040	26 032	8

TABLE II. (*Continued*).

				Energy (cm^{-1})		
Level No.	Multiplet[a]	$\lvert M_J \rvert$[a]	Γ[b]	Calculated[c]	Observed	Δ[d]
103	$^3K_7(2)$	7	E	26 191	26 193	−2
104		3	A_2	26 207		
105		3	A_1	26 208		
106		2	E	26 210		
107		1	E	26 218	26 213	5
108		0	A_2	26 223		
109		5	E	26 241	26 231	10
110		6	A_1	26 246		
111		4	E	26 251	26 242	9
112		6	A_2	26 266	26 255	11
113	$^5G_5,{}^3H_6(4)$	5	E	27 623	27 625	−2
114		3	A_1	27 645	27 642	3
115		1	E	27 679	27 674	5
116		3	A_2	27 687		
117		1	E	27 690	27 684	6
118		4	E	27 732	27 734	−2
119		0	A_2	27 733	27 740	−7
120		3	A_1	27 775	27 787	−12
121		4	E	27 788		
122		2	E	27 797		
123		3	A_2	27 808	27 806	2
124		0	A_1	27 868		
125		1	E	27 900	27 867	33
126		6	A_2	27 911	27 907	4
127		0	A_1	27 918		
128		2	E	27 940	27 951	−11
129	$^5F_2$	0	A_1	28 296	28 287	9
130		2	E	28 314	28 307	7
131		1	E	28 371	28 364	7
132	$^5G_3,{}^3L_9$	2	E	28 838		
133		3	A_1	28 867		
134		0	A_2	28 890		
135		1	E	28 907	28 907	0
136		9	A_1	28 915		
137		9	A_2	28 916		
138		2	E	28 945	28 948	−3
139		1	E	28 966		
140		0	A_2	28 981		
141		3	A_1	28 994	28 987	7
142		0	A_2	29 000		
143		3	A_2	29 005	29 004	1
144		8	E	29 035	29 029	6
145		4	E	29 038	29 042	−4
146		5	E	29 156		
147		7	E	29 164		
148		6	A_1	29 168		
149		6	A_2	29 170		
150	$^3F_4(4)$	3	A_1	29 940		
151		2	E	29 940		
152		1	E	29 959		
153		3	A_2	29 985		
154		0	A_1	30 006		
155		1	E	30 024		

TABLE II. (*Continued*).

Level No.	Multiplet[a]	$\|M_J\|$[a]	Γ[b]	Energy (cm^{-1})		Δ[d]
				Calculated[c]	Observed	
156	$^3K_6(2)$	0	A_1	30 046		
157		2	E	30 072		
158		3	A_2	30 106		
159		1	E	30 137		
160		5	E	30 180		
161		3	A_1	30 181		
162		2	E	30 209		
163		3	A_2	30 216		
164		6	A_1	30 232		
165	$^5G_2$	2	E	30 850		
166		0	A_1	30 851		
167		1	E	30 905		
168	$^3D_3(1)$	0	A_2	33 161		
169		2	E	33 184		
170		1	E	33 240		
171		3	A_1	33 269		
172		0	A_2	33 272		
173	$^3P_1(2)$	1	E	33 415		
174		0	A_2	33 421		
175	$^3M_{10}, {}^3L_8$	5	E	33 978	33 969	9
176		6	A_1	33 986		
177		4	E	34 000	33 994	6
178		3	A_2	34 005		
179		10	E	34 036	34 034	2
180		6	A_2	34 078	34 071	7
181		0	A_1	34 112	34 114	−2
182		8	E	34 124		
183		1	E	34 155	34 154	1
184		3	A_1	34 179		
185		2	E	34 184		
186		9	A_1	34 213		
187		2	E	34 216		
188		8	E	34 238		
189		3	A_2	34 247		
190		1	E	34 251		
191		0	A_1	34 258		
192		8	E	34 272		
193		6	A_2	34 312		
194		7	E	34 317		
195		6	A_1	34 329		
196		6	A_2	34 379		
197		4	E	34 402	34 394	8
198		5	E	34 429	34 451	−22
199		0	A_1	34 433		
200	$^5G_4$	2	E	34 818	34 794	24
201		3	A_2	34 822	34 816	6
202		0	A_1	34 841	34 844	−3
203		4	E	34 852	34 858	−6
204		1	E	34 860	34 868	−8
205		0	A_1	34 873	34 875	−2
206	$^3G_3(2)$	3	A_2	35 152		
207		2	E	35 187		

TABLE II. (*Continued*).

Level No.	Multiplet[a]	$\lvert M_J\rvert$[a]	Γ[b]	Energy (cm^{-1}) Calculated[c]	Observed	Δ[d]
208		0	A_2	35 222		
209		3	A_1	35 307		
210		1	E	35 316		
211	$^5D_4$	3	A_1	35 950	35 942	8
212		2	E	35 965	35 967	−2
213		3	A_2	35 976	35 982	−6
214		1	E	36 024	36 021	3
215		4	E	36 086	36 082	4
216		0	A_1	36 131		
217	$^3P_0$	0	A_1	36 174		

[a] Identifies the *principal SLJM$_J$* components of the eigenvectors.
[b] Irreducible representation label in the D_3 point group.
[c] Calculated using the Hamiltonian parameter values listed in Table III.
[d] Difference between calculated and observed energies.

$$S_{AB}(\alpha)=3.06\times 10^{-39}[g_A/X_A(T)]\times\int_{A\to B}\varepsilon_\alpha(\bar{v},T)d\bar{v}/\bar{v}\ \text{esu}^2\,\text{cm}^2\ , \tag{4}$$

$$S_{AB}(p)=3.06\times 10^{-39}[g_A/X_A(T)]\times\int_{A\to B}\varepsilon_p(\bar{v},T)d\bar{v}/\bar{v}\ \text{esu}^2\,\text{cm}^2\ , \tag{5}$$

where p denotes σ- or π-polarization, g_A is the electronic degeneracy of level A, $X_A(T)$ is the fractional thermal (Boltzmann) population of level A at temperature T, ε_α and ε_p ($p=\sigma$ or π) are molar decadic absorption coefficients measured in the axial and orthoaxial absorption experiments, respectively, the integrations are over the $A\to B$ transition linewidth, and $\bar{v}$ denotes wave number (cm^{-1}) of the radiation. The molar decadic absorption coefficient (ε) is related to sample transmittance (T) and decadic absorbance (A) according to $\log_{10}(1/T)=A=\varepsilon c_m l$, where c_m denotes the molar concentration of absorbing species ($M\equiv$mol/liter), l denotes sample thickness (in cm), and ε has the units M^{-1} cm^{-1} (*or* equivalently cm^2/mmol). The Ho^{3+} concentration in Na$_3$[Ho(ODA)$_3$]·2NaClO$_4$·6H$_2$O is 2.174 mol/liter.

If we assume that only electric-dipole and magnetic-dipole transition processes contribute to the observed line intensities, then the line strengths (S_{AB}) may be expressed as follows:

$$S_{AB}(\alpha)=\chi_\alpha D^{(e)}_{AB,1}+\chi'_\alpha D^{(m)}_{AB,1}\ , \tag{6}$$

$$S_{AB}(\sigma)=\chi_\sigma D^{(e)}_{AB,1}+\chi'_\sigma D^{(m)}_{AB,0}\ , \tag{7}$$

$$S_{AB}(\pi)=\chi_\pi D^{(e)}_{AB,0}+\chi'_\pi D^{(m)}_{AB,1}\ , \tag{8}$$

where χ and χ' are correction factors for bulk (sample) refractivity effects on the electric-dipole and magnetic-dipole components of the radiation field, and

$$D^{(e)}_{AB,q}=\left|\sum_a\sum_b\langle Aa|\mu_q|Bb\rangle\right|^2\ , \tag{9}$$

TABLE III. Hamiltonian parameters of the $4f^{10}$ electronic configuration of Ho^{3+} in Na$_3$[Ho(ODA)$_3$]·2NaClO$_4$·6H$_2$O.

Parameter[a]	Value[b] (cm^{-1})
$E_{\rm av}$	48 492(22)
F^2	96 676(60)
F^4	68 601(60)
F^6	47 697(44)
$\zeta_{\rm s.o}$	2138(5)
α	18.3(1.8)
β	−618(11)
γ	1705(27)
T^2	378(22)
T^3	39.0(5.5)
T^4	65(12)
T^6	−260(19)
T^7	275(24)
T^8	359(18)
M^0	3.5(1.6)
M^2	$0.56M^0$
M^4	$0.38M^0$
P^2	688(21)
P^4	$0.75P^2$
P^6	$0.50P^2$
B_{20}	−88(18)
B_{40}	−836(21)
B_{43}	−578(18)
B_{60}	531(25)
B_{63}	777(20)
B_{66}	672(20)
N[c]	105
σ[e]	9.1

[a] See Eqs. (1)–(3) in the text. The SCCF terms were *not* included in $\hat{H}^{+}_{\rm cf}$.
[b] Determined by fitting the observed energy levels listed in Table II.
[c] Number of experimentally characterized energy levels included in the parametric data fits.
[d] rms deviation between calculated and observed energies (in units of cm^{-1}).

$$D^{(m)}_{AB,q} = \left| \sum_a \sum_b \langle Aa | m_q | Bb \rangle \right|^2 , \qquad (10)$$

where μ_q and m_q denote the qth components ($q = 0, \pm 1$) of the electric- and magnetic-dipole moment operators, respectively, and $q = 0$ is defined to be parallel to the threefold symmetry axis (the unique axis) of the crystal. The summations in expressions (9) and (10) are over the degenerate components of levels A and B.

All of the line strengths reported in this paper were determined from intensity measurements performed on samples at ~ 10 K. At this temperature, only the two lowest crystal-field levels of the ground multiplet manifold (${}^5I_8$) are populated: level 1 (ground), which is doubly degenerate (E); and level 2 (at 14 cm^{-1} above ground), which is nondegenerate (A_1). Many transitions originating or terminating on levels assigned as E (in D_3 symmetry) exhibit small splittings (≤ 4 cm^{-1}) in the 10 K spectra. Line strengths for these transitions were evaluated by summing over the intensities of the transition components.

TABLE IV. Major-component analysis of $4f^{10}$ state vectors.[a]

Multiplet label[b]	Energy (cm^{-1})		N[e]	Major SL (term) components[f]
	Calc.[c]	Expt.[d]		
${}^5I_8$	212	n.d.	3	$0.97\,{}^5I-0.22\,{}^3K(2)$
${}^5I_7$	5244	n.d.		$0.99\,{}^5I$
${}^5I_6$	8749	(8742)	7	$0.98\,{}^5I$
${}^5I_5$	11 309	n.d.	1	$-0.95\,{}^5I-0.20\,{}^3H(4)$
${}^5I_4$	13 369	n.d.		$0.95\,{}^5I+0.23\,{}^3H(4)$
${}^5F_5$	15 580	(15 582)	5	$-0.89\,{}^5F+0.32\,{}^3G(2)$
${}^5S_2$	18 520	n.d.	2	$-0.83\,{}^5S-0.37\,{}^3P(2)-0.24\,{}^5F-0.23\,{}^3D(1)$
${}^5F_4$	18 650	18 647	6	$-0.96\,{}^5F$
${}^5F_3$	20 700	20 704	5	$-0.95\,{}^5F-0.20\,{}^3D(1)$
${}^5F_2$	21 163	21 155	3	$-0.80\,{}^5F+0.40\,{}^5S-0.34\,{}^3D(1)$
${}^3K_8(2)$	21 455	(21 441)	9	$+0.75\,{}^3K(2)-0.41\,{}^3K(1)+0.32\,{}^3L-0.28\,{}^1L(2)+0.24\,{}^5I$
${}^5G_6$	22 230	(22 226)	7	$-0.90\,{}^5G+0.32\,{}^3H(4)-0.25\,{}^3H(1)$
${}^5F_1$	22 375	22 405	2	$-0.89\,{}^5F-0.39\,{}^3D(1)-0.20\,{}^3D(2)$
${}^5G_5$	24 049	(24 047)	6	$+0.65\,{}^5G+0.44\,{}^3G(2)+0.38\,{}^5F-0.35\,{}^3G(3)-0.20\,{}^3H(3)$
${}^5G_4$	25 925	(25 927)	5	$+0.76\,{}^5G+0.40\,{}^3G(2)-0.34\,{}^3G(3)+0.24\,{}^3F(3)$
${}^3K_7(2)$	26 242	n.d.	5	$0.81\,{}^3K(2)-0.44\,{}^3K(1)+0.31\,{}^3L$
${}^5G_5$	27 734	n.d.	5	$0.69\,{}^5G-0.39\,{}^3H(4)-0.32\,{}^3G(2)+0.26\,{}^3H(3)+0.23\,{}^3H(1)$
${}^3H_6(4)$	27 821	n.d.	6	$0.62\,{}^3H(4)-0.51\,{}^3H(3)+0.41\,{}^5G-0.32\,{}^3H(1)$
${}^5F_2$	28 336	28 326	3	$0.46\,{}^5F+0.41\,{}^5G-0.35\,{}^3D(1)+0.32\,{}^3F(4)-0.29\,{}^3P(2)$ $+0.26\,{}^3F(2)+0.25\,{}^1D(3)+0.24\,{}^5S-0.23\,{}^1D(2)$
${}^5G_3$	28 913	n.d.	1	$0.86\,{}^5G+0.28\,{}^3F(4)$
${}^3L_9$	29 021	n.d.	5	$0.95\,{}^3L+0.32\,{}^3M$
${}^3F_4(4)$	30 028	n.d.		$-0.44\,{}^3F(4)+0.36\,{}^3G(2)+0.34\,{}^3H(4)-0.29\,{}^5D+0.29\,{}^1G(4)$ $-0.28\,{}^3H(3)-0.27\,{}^5G-0.22\,{}^5I-0.22\,{}^3F(2)$
${}^3K_6(2)$	30 116	n.d.		$0.86\,{}^3K(2)-0.41\,{}^3K(1)$
${}^5G_2$	30 860	n.d.		$-0.73\,{}^5G-0.31\,{}^3D(1)-0.31\,{}^3F(4)+0.25\,{}^5F-0.24\,{}^3P(2)$ $-0.21\,{}^1D(3)$
${}^3D_3(1)$	33 224	n.d.		$0.78\,{}^3D(1)+0.41\,{}^3D(2)+0.23\,{}^5G-0.21\,{}^5F+0.20\,{}^5D$
${}^3P_1(2)$	33 411	n.d.		$0.73\,{}^3P(2)+0.48\,{}^3D(1)-0.36\,{}^5F+0.23\,{}^3P(3)+0.21\,{}^3D(2)$
${}^3M_{10}$	34 155	n.d.	4	$0.99\,{}^3M$
${}^3L_8$	34 275	n.d.	4	$0.82\,{}^3L+0.40\,{}^3M-0.36\,{}^3K(2)$
${}^5G_4$	34 840	34 842	6	$0.53\,{}^5G-0.48\,{}^5D-0.36\,{}^3G(2)-0.35\,{}^3F(4)+0.26\,{}^1G(4)$ $+0.24\,{}^3G(3)$
${}^3G_3(2)$	35 239	n.d.		$0.52\,{}^3G(2)-0.45\,{}^3F(4)-0.38\,{}^3F(2)-0.33\,{}^5D-0.33\,{}^3G(3)$ $+0.26\,{}^3F(3)+0.20\,{}^3G(1)$
${}^5D_4$	36 064	36 022	5	$0.51\,{}^5D+0.38\,{}^3H(4)+0.34\,{}^1G(4)-0.34\,{}^3H(3)-0.26\,{}^3G(2)$ $+0.21\,{}^3F(4)-0.21\,{}^1G(2)$
${}^3P_0(2)$	36 166	n.d.		$0.93\,{}^3P(2)+0.25\,{}^3P(3)$

[a] Calculated using the atomic Hamiltonian parameters listed in Table III.

[b] Conforms to labeling scheme used in Table II.

[c] Calculated eigenenergies of $[SL]J$ multiplets.

[d] Multiplet baricenter energies deduced from experimentally assigned crystal-field levels (listed in Table II). Approximate values for incompletely assigned multiplet manifolds are shown in parentheses. n.d. denotes not determined.

[e] Number of experimentally assigned crystal-field levels within a given multiplet manifold.

[f] Eigenvectors expressed in SL (term) basis.

TABLE V. Comparison of atomic Hamiltonian parameters reported for Ho^{3+} in several crystalline hosts.

	Values (cm^{-1})					
Parameter[a]	HoODA[b]	HoES[c]	Ho^{3+}:LaF_3[d]	Ho^{3+}:$LiYF_4$[e]	Ho^{3+}:$LaCl_3$[f]	$Cs_2NaHoCl_6$[g]
F^2	96 676	96 120	94 564	96 460	95 389	94 557
F^4	68 601	66 893	66 397	67 728	67 320	67 810
F^6	47 697	47 824	52 022	47 656	46 952	47 227
$\zeta_{s.o.}$	2138	2147	2145	2148	2138	2130
α	18.3	17.5	17.2	16.1	17.3	14.9
β	−618	−581	−607.9	−529	−629	−594
γ	1705	1922	[1800]	[1800]	2051	1890
T^2	378	207	[400]	[400]	281	[287]
T^3	39.0	50	37	[37]	37	[37]
T^4	65	47	107	[107]	99	[98]
T^6	−260	−203	−264	[−264]	−308	[−313]
T^7	275	290	316	[316]	418	[421]
T^8	359	270	336	[336]	342	[359]
M^0	3.5	3.63	2.54	2.91	3.02	[3.00]
P^2	688	771	605	507	529	[523]
F^2/F^4	1.41	1.44	1.42	1.42	1.42	1.39
F^2/F^6	2.03	2.01	1.82	2.02	2.03	2.00
F^4/F^6	1.44	1.40	1.28	1.42	1.43	1.44

[a] See Eq. (2) in text.
[b] Present work.
[c] C. K. Jayasankar and F. S. Richardson (unpublished results). HoES is an abbreviation for $Ho(C_2H_5SO_4)_3 \cdot 9H_2O$.
[d] See Ref. 64.
[e] See Ref. 63.
[f] See Ref. 62.
[g] See Ref. 58.

V. RESULTS AND DISCUSSION

105 crystal-field levels were located and assigned from the absorption spectra measured in this study. These levels are identified in Table II along with all the calculated levels located between 0 and 36 200 cm^{-1}. The levels are characterized according to their principal *SLJ* (multiplet) parentage and M_J components, their crystal-field symmetry label (D_3 point-group irreducible representation), and their observed and/or calculated energies. The calculated energies given in Table II were obtained as eigenvalues of our model Hamiltonian, defined to *exclude* the SCCF terms in $\hat{H}^{+}_{CF}$ [see Eq. (3)], using the parameter values listed in Table III. These parameter values were obtained from a parametric fit of calculated to experimentally observed energy levels in which 22 of the Hamiltonian parameters were treated as fitting variables. Four of the atomic Hamiltonian parameters listed in Table III 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 rms deviation between the calculated and observed energies shown in Table II is 9.1 cm^{-1}.

Additional calculations were carried out in which the SCCF terms of $\hat{H}^{+}_{CF}$ were included. This added six more fitting parameters in our parametric data analysis [the b_{km} of Eq. (3)], but it did not have a significant influence on *either* the overall quality of fit *or* the fits within particular multiplet manifolds. The rms deviation between calculated and observed energies was 9.0 cm^{-1}, and the following values were obtained for the B_{km} and b_{km} parameters of $\hat{H}^{+}_{CF}$: $B_{20}=-68(18)$, $b_{20}=-57(18)$, $B_{40}=-818(24)$, $b_{40}=-16(21)$, $B_{43}=-584(18)$, $b_{43}=10(16)$, $B_{60}=490(26)$, $b_{60}=35(21)$, $B_{63}=792(19)$, $b_{63}=-2(16)$, $B_{66}=665(20)$, and $b_{66}=9(16)$ cm^{-1}. We note that the B_{km} parameter values are not significantly different from those given in Table III, and the ratios $|b_{km}/B_{km}|$ are ≤ 0.07 (except that for $k=2$). Our results suggest that the interactions represented by the SCCF terms in our model Hamiltonian have little influence on the Ho^{3+} energy-level structure character-

TABLE VI. Comparison of crystal-field energy parameters for $M^{3+}=Nd^{3+}$, Sm^{3+}, Eu^{3+}, and Ho^{3+} in *M*ODA, or $Na_3[M(ODA)_3] \cdot 2NaClO_4 \cdot 6H_2O$.

	Values (cm^{-1})			
Parameter	NdODA[a]	SmODA[b]	EuODA[c]	HoODA[d]
B_{20}	56	−19	−91	−88
B_{40}	−1111	−941	−947	−836
B_{43}	−943	−837	−781	−578
B_{60}	577	606	411	531
B_{63}	1358	1112	1035	777
B_{66}	886	794	755	672
N	116	144	61	105
σ (cm^{-1})	14.4	12.3	9.9	9.1

[a] From Ref. 44.
[b] From Ref. 33.
[c] From Ref. 38 and J. Quagliano (University of Virginia), unpublished results.
[d] From Table III of the present paper.

TABLE VII. Axial and π-polarized orthoaxial line strengths of absorptive transitions originating from the lowest crystal-field level (E) of the $^5I_8$ (ground) multiplet.

	Excited level[a]			Line strengths[c] (10^7 D^2)	
No.	Multiplet	Γ	$\bar{\nu}$(vac)[b] (cm^{-1})	$S(\alpha)$	$S(\pi)$
30	$^5I_6$	A_1	8806	548	n.d.
47	$^5F_5$	E	15 555	812	n.d.
50		A_2	15 636	128	n.d.
52	$^5S_2$	E	18 513	107	154
53		E	18 525	15.7	242
54	$^5F_4$	A_1	18 573	720	n.d.
57		A_1	18 651	152	n.d.
58		A_2	18 673	968	n.d.
59		E	18 705	466	724
60	$^5F_3$	A_2	20 650	572	n.d.
61		A_1	20 663	592	n.d.
62		E	20 688	150	570
66	$^5F_2$	E	21 141	74.0	302
67		E	21 185	15.4	136
68	$^3K_8(2)$	E	21 371	36.8	88.2
69		A_2	21 388	51.6	n.d.
70		E	21 394	33.2	n.d.
74		E	21 444	11.1	196
75		A_2	21 462	7.4	n.d.
76		E	21 494	22.2	n.d.
77		A_1	21 518	37.2	n.d.
79	$^5G_6$	A_1	22 100	1186	n.d.
80		E	22 127	n.d.	190
81		A_2	22 156	722	n.d.
83		E	22 190	n.d.	312
90	$^5G_5$	E	23 974	652	328
91		E	24 008	n.d.	758
98	$^5G_4$	A_2	25 898	83.6	n.d.
102		A_1	26 032	103	n.d.
107	$^3K_7(2)$	E	26 213	n.d.	12.2
111		E	26 242	n.d.	37.4
112		A_2	26 255	43.8	n.d.
113	$^3H_6(4)$	E	27 625	140	n.d.
114	$^5G_5$	A_1	27 642	160	n.d.
129	$^5F_2$	A_1	28 287	27.8	n.d.
201	$^5G_4$	A_2	34 816	76.4	n.d.
205		A_1	34 875	290	n.d.
211	$^5D_4$	A_1	35 942	141	n.d.
212		E	35 967	232	n.d.
214		E	36 021	131	n.d.
215		E	36 082	108	n.d.

[a] Numbering scheme, multiplet labels, and crystal-field symmetry labels (Γ) correspond to those used in Table II.

[b] Transition energy (in wave numbers).

[c] Line strengths were determined according to Eqs. (4) and (5) (see text), and they are expressed in units of 10^{-7} D^2 (D$\equiv$1 debye unit $=10^{-18}$ esu cm$=3.3356\times10^{-30}$ C m). n.d. denotes not determined.

TABLE VIII. Axial and π-polarized orthoaxial line strengths of absorptive transitions originating from the second crystal-field level (A_1) of the $^5I_8$ (ground) multiplet.

No.	Excited level[a] Multiplet	Γ	$\bar{\nu}$(vac)[b] (cm^{-1})	Line strengths[c] (10^{-7} D^2) $S(\alpha)$	$S(\pi)$
44	$^5F_5$	A_2	15 510	n.a.	1310
47		E	15 541	889	n.d.
52	$^5S_2$	E	18 499	127	n.d.
55	$^5F_4$	E	18 610	1140	n.d.
58		A_2	18 659	n.a.	1180
60	$^5F_3$	A_2	20 636	n.a.	852
67	$^5F_2$	E	21 171	165	n.d.
68	$^3K_8(2)$	E	21 357	118	n.d.
69		A_2	21 374	n.a.	266
98	$^5G_4$	A_2	25 884	n.a.	195
113	$^3H_6(4)$	E	27 611	182	n.d.

[a] Numbering scheme, multiplet labels, and crystal-field symmetry labels (Γ) correspond to those used in Table II.

[b] Transition energy (in wave numbers).

[c] Line strengths were determined according to Eqs. (4) and (5) (see text), and they are expressed in units of 10^{-7} D^2 (D$\equiv$1 debye unit $=10^{-18}$ esu cm$=3.3356\times10^{-30}$ C m). n.a. denotes not allowed (see selection rules in Table I). n.d. denotes not determined.

ized in this study. However, locations, assignments, and analyses of more energy levels derived from spin-triplet multiplets are needed to support a definitive assessment of SCCF effects in the HoODA system.

Table IV shows a major-component analysis of $4f^{10}$ $[SL]J$ state vectors calculated using the atomic Hamiltonian parameters listed in Table III. Results are shown for the first 31 (lowest-energy) multiplet levels, and they include eigenenergies and the major SL (term) components of the eigenvectors. Multiplet baricenter energies deduced from experimentally assigned crystal-field levels (listed in Table II) are also given in Table IV. The atomic Hamiltonian parameters obtained in this study are compared in Table V to those reported for Ho^{3+} in other crystalline hosts. A comparison of crystal-field parameters (B_{km}) for several $Na_3[M(ODA)_3]\cdot2NaClO_4\cdot6H_2O$ systems is presented in Table VI.

Among the multiplet manifolds shown in Table II, the $^5G_5$ multiplet centered at $\sim$24 047 cm^{-1} exhibits the poorest agreement between calculated and observed crystal-field splittings. The energy difference between the highest and lowest crystal-field levels split out of this multiplet is calculated to be 88 cm^{-1}, but is observed to be 140 cm^{-1}. This multiplet has significant spin-triplet character (see Table IV), but the SCCF operators in our model Hamiltonian have a negligible effect on the crystal-field splittings calculated within this multiplet. It is interesting to note that this multiplet poses similar problems in parametric energy-level analyses of Ho^{3+} in other systems, such as Ho^{3+}:LaF_3,[51] $Cs_2NaHoCl_6$,[58] and $Ho(C_2H_5SO_4)_3\cdot9H_2O$.[65]

Line strengths were determined for 42 transitions observed in the *axial* absorption spectra measured at 10 K, and for 19 transitions observed in the π-polarized *orthoaxial* absorption spectra at 10 K. Fifty of the empirically determined line strengths are for transitions originating from the doubly degenerate (E) ground crystal-field level of the $^5I_8$ (ground) multiplet, and these line strengths are given in Table VII. Eleven of the empirically determined line strengths are for transitions originating from the second crystal-field level (A_1, located 14 cm^{-1} above ground) of $^5I_8$, and these line strengths are given in Table VIII. Among the transition regions examined in this study, the most intense absorption lines were observed within the $^5I_8\rightarrow{}^5G_6$, $^5F_4$, and $^5F_5$ multiplet-to-multiplet transition manifolds. A detailed analysis of the intensity data is presented in Ref. 48.

VI. CONCLUSION

The energy-level data and analyses reported in this paper provide a reasonably good description of the $4f^{10}$ energy-level structure of Ho^{3+} in $Na_3[Ho(ODA)_3]\cdot2NaClO_3\cdot6H_2O$ (between 8000 and 37 000 cm^{-1}). The parametric model Hamiltonian used in the energy-level analyses proved to be generally satisfactory in fitting calculated-to-observed energy levels, although observed crystal-field splittings within the $^5G_5$ multiplet manifold (centered at $\sim$24 047 cm^{-1}) remain problematical. Inclusion of spin-correlated crystal-field (SCCF) interaction terms in the model Hamiltonian led to some modest improvement in calculated- versus experimental-energy-level fits, but our results suggest that SCCF interactions (as represented in our model) have little influence on the Ho^{3+} state structure characterized in this study.

Only the three lowest crystal-field levels of the $^5I_8$ (ground) multiplet could be located and assigned with certainty, but the locations and assignments *calculated* for the remaining eight levels (split out of $^5I_8$) are qualitatively compatible with spectroscopic observations made on samples at $T > 80$ K. Generally, absorption spectra obtained above 80 K were too congested to permit detailed transition assignments. Attempts to excite and detect photoluminescence from the HoODA system were unsuccessful. Among the *M*ODA systems examined in our laboratory ($M =$Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er), strong luminescence has been observed for the Sm,[32] Eu,[19] Gd,[66] Tb,[20] and Dy (Ref. 42) systems, but none has been observed for the Nd, Ho, and Er systems.

Single crystals of $Na_3[Ho(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ retain uniaxial symmetry from room temperature down to 5 K. However, at temperatures below ~ 20 K, we found evidence that axial site symmetry is lost at the Ho^{3+} ions. This evidence is based on small splittings ($\leq 4\ cm^{-1}$) observed in transitions originating from (or terminating on) crystal-field levels predicted to be doubly degenerate (E) in the D_3 symmetry group. These splittings are most apparent in transitions originating from the ground crystal-field level of $^5I_8$. Our spectroscopic measurements are not adequate for characterizing the local structural modifications (or crystallographic phase transition) responsible for the energy-level splittings observed at low temperature. However, given the small magnitude of these splittings *and* the retention of D_3 selection rules in the axial and polarized orthoaxial line intensity distributions, it is reasonable to assume that the effective crystal field sensed by the $4f$ electrons of Ho^{3+} deviates only slightly from D_3 symmetry. Both the energy-level analysis presented in this paper and the transition intensity analysis presented in Ref. 48 are based on this assumption. The intensity analysis focuses on the empirical line-strength data given in Tables VII and VIII, and it makes use of spectroscopic state vectors that are defined as eigenvectors of the model Hamiltonian characterized in this study [according to Eqs. (1)–(3) and the parameter values listed in Table III].

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