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Crystal-field analysis and calculation of two-photon absorption line strengths of dicesium sodium hexachlorogadolate(III)

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Abstract

The crystal-field energy level calculation of the $4f^7$ ion Gd^{3+} in the crystal $Cs_2NaGdCl_6$ has fitted 45 levels with standard deviation 12 cm^{-1} , with the energy parameters being consistent with those from other studies. The resulting eigenvectors have been employed in the calculation of two-photon absorption (TPA) intensities of transitions from the electronic ground state $^8S_{7/2}$ to the crystal-field levels of excited 6P , 6I and 6D multiplet terms. The TPA line strengths are highly polarization dependent and exhibit striking differences for linearly polarized incident radiation compared with circularly polarized radiation. The relative intensities are compared with those available from previous experimental studies and some reassignments have been made. Good agreement of calculated and experimental TPA spectra is found, except for the intensity ratio of the transitions to $^6P_{7/2}$ or $^6P_{5/2}$ compared with that to $^6P_{3/2}$, for linear and circular polarizations, where the calculation overestimates the ratio. Reasons for this disagreement are presented.

1. Introduction

The interpretation and analysis of the electronic spectra of Gd^{3+} in crystals have received rather less attention than those of other lanthanide ions. This is mainly because the excited state energy levels of the stable $4f^7$ configuration are at much higher energy than for other $4f^N$ systems and require the use of ultraviolet and vacuum ultraviolet absorption spectroscopy for their study. In the double group O the crystal-field (CF) levels of the $4f^7$ configuration are identified by the irreducible representations (IRs) Γ_i ($i = 6, 7, 8 \equiv E', E'', U$), and have ungerade parity. The previous CF energy level calculation for $Cs_2NaGdCl_6$ by Morrison *et al* [1] did not have available $4f^7$ experimental energy level data for CF levels for comparison, so that the validity of the parameter values

could not be assessed. For this system, with Gd^{3+} situated at a site of inversion symmetry, one-photon absorption (OPA) cannot uniquely manifest spectral features corresponding to direct transitions between CF levels since the transitions are strictly forbidden for the electric dipole (ED) mechanism, and are approximately magnetic dipole (MD) forbidden for most f–f transitions. Furthermore, the use of polarized light is not useful in identifying spectral transitions in this case. Fortunately, two-photon absorption (TPA) spectroscopy has been an important supplementary technique for the study of CF levels of lanthanide ions occupying a site with space inversion, because pure electronic transitions between certain CF levels are first order allowed and subject to large intensity variations when employing polarized radiation. However, there have previously been very few calculations of TPA intensities, and most of these have adopted various approximations of the intermediate states to avoid direct summation over a few ten thousands of intermediate states [2–4]. The TPA calculation for the $4f^7$ system $CaF_2:Eu^{2+}$ [5] represents a

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full calculation, but the drastically wide variation of the experimentally measured line widths of the TPA peaks makes the comparison with calculated TPA line strengths less definite.

The elpasolite host lattice $\text{Cs}_2\text{NaLnCl}_6$ has the attractive properties of providing Ln^{3+} ion sites of a high-symmetry O_h molecular point group. Since the conventional energy level parametrization involves only two CF parameters [6], such studies might be expected to be definitive for studying the trends of CF and atomic Hamiltonian parameters across the entire lanthanide series. However, both the quasi-free-ion parameters and CF parameters, reported in [7], were not consistent with the analogous parameters for other ions in the same host [6], which is beyond our expectation that quasi-free-ion parameters should change systematically across the entire series of Ln^{3+} .

This study therefore had two aims. First, to fit the energy level dataset of Gd^{3+} in a manner that is consistent for this ion doped in other crystal lattices; and second, to rationalize the TPA intensities in the spectra of $\text{Cs}_2\text{NaGdCl}_6$. There have been some other previous experimental studies of this system. De Vries and Blasse [8] reported the luminescence spectrum at 4.2 K between 32 000 and 31 600 cm^{-1} , which comprises the transition from ${}^6P_{7/2}\Gamma_7$ to the electronic ground state ${}^8S_{7/2}$ and its associated vibronic sideband. These authors also reported the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}, {}^6P_{5/2}, {}^6I_{7/2}$ excitation spectra and, hence, located the CF energy levels of these multiplet terms. In addition to the work of Kundu *et al* [7], TPA studies of $\text{Cs}_2\text{NaGdCl}_6$ have been performed by Bouazaoui *et al* [9], and Dereń and Stręk [10]. The latter authors assigned some very weak bands in the TPA spectra to vibronic structure. Whereas the assignments to the gerade $\tau_{2g}\nu_5$ bending mode are reasonable, we consider that the assignments to ungerade lattice modes may have other origins. Dereń *et al* [11] also reported the visible anti-Stokes emission of Gd^{3+} in $\text{Cs}_2\text{NaGdCl}_6$. Although visible emission is indeed expected from 6G_J [12], these weak spectral features may also have another origin. In particular, the authors assigned intense bands above the luminescent level to $4f^7 \rightarrow 4f^65d$ absorption. In fact, we calculate the onset of the $4f^65d$ configuration to be much higher: above 74 000 cm^{-1} [13].

2. Theory

We have employed the same calculation method as that used in [5], except that we include only the usual one-body CF interaction here. Rather than repeating the rationale, the reader is therefore referred to [5] for a detailed explanation. Some further remarks are pertinent. The eigenvalues and eigenvectors of all the states in the $4f^7$ configuration were obtained using the conventional empirical Hamiltonian with adjustable quasi-free-ion and site-symmetry adapted one-body CF parameters [6]. The parameter values obtained are listed in table 1. The eigenvalues and eigenvectors of all the TPA virtual states in the $4f^65d$ configuration were obtained using the *extended* empirical Hamiltonian [14], which includes quasi-free-ion and one-body CF interactions in the $4f^6$ core, spin-orbit and CF interactions for the 5d electron, and Coulomb interaction between the 4f and 5d electrons. The same

Table 1. Optimized parameter values for the energy levels of the $4f^7$ configuration of Gd^{3+} in $\text{Cs}_2\text{NaGdCl}_6$. Restrictions adopted in the calculation are: $M^2 = 0.56M^0$, $M^4 = 0.38M^0$; $P^4 = 0.75P^2$, $P^6 = 0.38P^2$; $H_{cf}(4f) = B_4[C_0^{(4)}(4f) + \sqrt{5/14}(C_{-4}^{(4)}(4f) + C_4^{(4)}(4f))] + B_6[C_0^{(6)}(4f) + \sqrt{7/2}(C_{-4}^{(6)}(4f) + C_4^{(6)}(4f))]$; and $H_{cf}(5d) = B_4[C_0^{(4)}(5d) + \sqrt{5/14}(C_{-4}^{(4)}(5d) + C_4^{(4)}(5d))]$. The deviations of the optimization are given in terms $\sigma = [\sum_i (E_{\text{calc}}(i) - E_{\text{expt}}(i))^2 / (N_{\text{expt}} - N_{\text{param}})]^{1/2}$ and $\delta = [\sum_i (E_{\text{calc}}(i) - E_{\text{expt}}(i))^2 / N_{\text{expt}}]^{1/2}$, where $N_{\text{expt}} = 36$ is the number of measured levels and $N_{\text{param}} = 7$ is the number of variable parameters. The columns ‘Opt.’ and ‘Delta’ give the optimized values and their uncertainties obtained in the calculation (parameters stated without uncertainties were fixed in the optimization); column ‘Ref.[17]’ lists the average of the quasi-free-ion values for Gd^{3+} over many hosts, as in table 5 of [17]; and the final column lists the parameter values from [7]. The parameters employed to calculate the $4f^65d$ energy levels used for TPA calculations are also listed. All the parameters listed for $4f^7$ were also used for $4f^65d$, and those not listed are assigned with the same values as for the $4f^7$ configuration. The Hartree–Fock values for the 4f–5d Coulomb interaction parameters (in cm^{-1}): $F^2(\text{fd}) = 29\,905$, $F^4(\text{fd}) = 14\,477$; $G^1(\text{fd}) = 12\,348$, $G^3(\text{fd}) = 10\,614$, $G^5(\text{fd}) = 8235$, are scaled by factor η_{id} . The parameter E_{exc} is the separation between the barycenters of the $4f^65d$ and $4f^7$ configurations, which is chosen to give the onset of the $4f^65d$ levels, as predicted in [13]. The units of all energy parameters are cm^{-1} , and parameter ratios are dimensionless.

	Parameter	Opt.	Delta	Ref. [17]	Ref. [7]
$4f^7$	E_{AVG}	[87 278]		87 446	
	F^2	85 433	98	85 300	78 686
	F^4	59 484	72	60 517	70 120
	F^6	44 652	37	44 731	43 596
	ζ_{4f}	1503	4	1504	1505
$4f^7 + 4f^65d$	α	18		18.95	37
	β	−620		−620	−1905
	γ	1658		1658	1697
	T^2	308		308	
	T^3	43		43	
	T^4	51		51	
	T^6	−298		−298	
	T^7	338		338	
	T^8	335		335	
	M^0	3.2	0.1	2.99	1.59
	P^2	542		542	
	B_4	1839	99		1776
B_6	112	126		139	
σ	12.2			24.8	
δ	10.9				
$4f^65d$	$F^2(\text{f}^6\text{d})/F^2$	1.061			
	$F^4(\text{f}^6\text{d})/F^4$	1.066			
	$F^6(\text{f}^6\text{d})/F^6$	1.068			
	$\zeta_{4f}(\text{f}^6\text{d})/\zeta_{4f}$	1.077			
	$B_4(5d)$	36 809			
	E_{exc}	67 440			
	η_{id}	0.53			
ζ_{5d}	1132				

procedure as [13] was used to calculate the parameter values for the $4f^65d$ configuration and these are also listed in table 1. The summation over TPA virtual states was taken explicitly over all the obtained $4f^65d$ states by following [5]. This is in contrast to calculations based on perturbation expansion [2, 3, 15], and calculations based on neglecting f–d interactions [16].

3. Results and discussion

3.1. Energy level calculation

First, the results concerning our first aim are listed. Notably, consistent and well-defined quasi-free-ion parameters for Gd^{3+} in $\text{Cs}_2\text{NaGdCl}_6$ host have been obtained from our energy level calculation. The obtained ratios for the Coulomb parameters: $F^4/F^2 = 0.696$, $F^6/F^2 = 0.523$, are consistent with the ratios for Gd^{3+} in various other hosts [17] and the ratios for lanthanide ions across the lanthanide series [18]. The CF parameters B_4 and B_6 are also consistent with other lanthanide ions in the same host [18]. In table 2, the calculated energies of CF levels (E_{calc}) are compared with experimentally derived values (E_{expt}) from [7–9], and the energy difference (E_{diff}) is listed. The reduced residue of optimization ($\sigma = 12.2 \text{ cm}^{-1}$, table 1) obtained is compatible with results from other lanthanide ions (e.g. [19]).

3.2. Comparison of calculated and measured TPA line strengths

Concerning our second aim, table 2 gives the calculated TPA line strengths for transitions from the electronic ground state, using linearly polarized light with the electric vector in the (100), (110), and (111) directions, to excited CF levels between 31 940 and 40 730 cm^{-1} . The line strengths for circularly polarized light with the electric vector in the (100), (110) directions are also listed. The figures depicting TPA spectra in [7] and [9] show separate windows for transitions to different terms, so that a comparison of relative intensities for the entire experimental TPA spectra is not possible. Also, the actual polarization directions are not stated in [7, 9]. Therefore, we have compared the relative intensities within each spectral window by integrating individual bands, and the strongest spectral feature is denoted by A or B \dots for linearly polarized radiation, and by D' or E' for circularly polarized radiation. In some cases a spectral feature corresponds to several overlapping transitions, and this is indicated by horizontal lines in the E_{calc} , E_{expt} columns.

First, the relative transition intensities within a given multiplet are considered, commencing with the lowest energy transitions. The experimental data for comparison are given in [7, 9] and the calculation results are given in table 2. For the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$ transition, three peaks (numbers 4–6 in table 2) are observed between 626.5 and 625.5 nm [9]. The middle one of the three peaks corresponds to the transition to ${}^6\text{P}_{7/2}\text{U}$, and is calculated to be the strongest peak. The other two peaks correspond to transitions to E'' and E' CF states and are each calculated to be about half the intensity of the middle one (to U), i.e. proportional to the terminal state degeneracies. The estimation from the printed spectra [9] shows that the middle peak is the strongest one (intensity denoted as A in table 2) and the other two peaks have intensities 0.45A and 0.61A. Thus the calculations agree with measurement reasonably well, considering the uncertainties in the estimation and the quadratic sensitivity of the TPA intensities to electric dipole moments. Similar agreement is obtained for the two peaks (numbers 7 and 8 in table 2) in the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{5/2}$ transition, between 614 and 615 nm [9], where the measured

intensities are B and 0.46B. Three peaks (numbers 36–38 in table 2) are observed for the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{D}_{9/2}$ transition [7], corresponding in increasing energy, to transitions terminating upon E', U(1) and U(2) CF levels. The calculated linear TPA line strengths are very anisotropic (table 2), with U(2) being strongest for (100)-polarized radiation, whereas U(1) is strongest for (110)- or (111)-polarized radiation. The relative average line strengths for linearly polarized incident light agree with measurements [7] reasonably well.

The experimental ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_{13/2,15/2}$ linear and circular polarization TPA spectra have been given in [7]. From the perturbation theory point of view, these transitions gain some strength only due to the mixing in intermediate states of bases of different total angular momentum quantum numbers. Contributions from those intermediate states comprising this mixing tend to cancel each other, but there are some small residues due to the difference in energy denominators. There are two points worth mentioning when comparing the calculated results for these transitions with measurements. First, the TPA intensities for circularly polarized radiation are measured to be slightly stronger than those for linearly polarized radiation, which is correctly predicted (table 2: in terms of D and D'). Second, the relative strengths and the separations for the seven peaks (numbered as shown in the experimental data columns in table 2: 26 and 27; 28; 29 and 30; 31; 32 and 33; 34; 35) in this spectral region are very well simulated, considering the strong mixing of multiplets. This mixing usually tends to result in poor agreement for calculated versus experimental energies, and the summation of many mutually canceling contributions to TPA usually tends to result in the poor agreement for calculated versus experimental line strengths.

Now we consider the inter-multiplet line strength ratios, at first focusing upon incident radiation of different polarizations: linear and circular. From table 2, the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_{13/2,15/2}$ TPA line strengths are predicted to be weaker than the linear TPA ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$, ${}^6\text{D}_{9/2}$ line strengths by two orders of magnitude, but no experimental comparison is available. However, the calculated very weak intensity of the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_{7/2}$ transitions can be verified by the high noise level of the spectrum presented in [9]. For the transitions to the ${}^6\text{D}$ multiplets, the intensity ratios of linear to circular polarization can be considered as well predicted (table 3). The intensity ratios for linear polarization for transitions to ${}^6\text{D}_{7/2}$, compared with ${}^6\text{D}_{5/2,3/2}$, are predicted to be too strong by a factor of 2–3 (i.e. from a ratio of ~ 1.25 for the dipole moments). As noted above, the intensities of all transitions from ${}^8\text{S}_{7/2}$ to the ${}^6\text{P}$ multiplet are well predicted. However the calculated intensity ratios for transitions to ${}^6\text{P}_{7/2}$, compared with those to ${}^6\text{P}_{5/2}$ and ${}^6\text{P}_{3/2}$, are considerably overestimated in the calculation, although the ${}^6\text{P}_{7/2}/{}^6\text{P}_{3/2}$ ratio is more consistent with the ratio for other systems [7]. For ${}^6\text{P}_{3/2}$, this is partly due to the sensitivity of the ratio due to the very small calculated intensity for ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{3/2}$ (table 2). In other words, this means some other mechanisms are operative for ${}^8\text{S}_{7/2}$ to ${}^6\text{P}_{3/2}$ TPA, which become important due to the very weak contributions from $4f^65d$ intermediate levels. The candidates for such contributions may be dynamical coupling mechanisms due to mixing of $4f^6$ with conduction band states transformed similar to a p orbital of the centered Gd^{3+} ion.

Table 2. Calculated energy levels (E_{calc}) for the $4f^7$ configuration and the TPA line strengths from $^8S_{7/2}$ to various $4f^7$ excited CF levels. The units are cm^{-1} for energies, and 10^{-50}cm^6 for TPA line strengths. The $4f^7$ and $4f^65d$ energy levels are calculated using the parameters given in table 1, and the TPA line strengths involve the radial integral $\langle 4f|r|5d \rangle = 0.0218 \text{ nm}$ (whose value only affects the overall rather than the relative TPA line strengths) taken from [20], calculated using a many-body perturbation theory [21].

The column headings: IR represents the irreducible representation of the CF level in the group O and m in brackets is a multiplicity number to distinguish levels of the same irrep belonging to the same multiplet; E_{diff} is the deviation of the calculated energy E_{calc} from the measured energy E_{expt} ; (100), (110) and (111) are the directions of electric field for linearly polarized light; C(100) and C(110) denote circularly polarized light propagated along the (100) and (110) direction, respectively. For measured TPA strengths, the directions of polarization/propagation of measurement were not specified in the figures of [7, 9, 10]. The measured relative intensities were obtained by integration for each section of the spectra in [9, 10] (as indicated) for $^6P_{7/2,5/2}$ and $^6I_{7/2}$ terminal multiplets, and from [7] for $^6I_{13/2,15/2}$ and $^6D_{9/2}$ multiplets. The strongest peak for each section is denoted as a symbol A, B, C, D (D' for circularly polarized light) or E.

No.	State		Energy			Calc. TPA line strength					Measured TPA [7]	
	$^{2S+1}L_J$	IR (m)	E_{calc}	E_{expt}	E_{diff}	(100)	(110)	(111)	C(100)	C(110)	Linear	Circular
1	$^8S_{7/2}$	E''	0	0								
2	$^8S_{7/2}$	U	0									
3	$^8S_{7/2}$	E'	0									
4	$^6P_{7/2}$	E''	31 940	31 954	-14	166	184	191	22	27	0.61A [10]	
5	$^6P_{7/2}$	U	31 962	31 969	-7	362	360	360	51	50	A [10]	
6	$^6P_{7/2}$	E'	31 977	31 977	0	190	178	173	27	24	0.45A [10]	
7	$^6P_{5/2}$	E''	32 529	32 545	-16	9	8	7	12	12	0.46B [9]	
8	$^6P_{5/2}$	U	32 558	32 574	-16	13	16	17	23	24	B [9]	
9	$^6P_{3/2}$	U	33 138	33 143	-5	0	0	0	1	1		
10	$^6I_{7/2}$	E''	35 624	35 623	1	3	2	2	4	3	0.59C [9]	
11	$^6I_{7/2}$	U	35 679	35 682	-3	4	4	5	6	6	C [9]	
12	$^6I_{7/2}$	E'	35 713	35 711	2	1	0	0	1	1	0.23C [9]	
13	$^6I_{9/2}$	U(1)	35 978	35 984	-6	12	10	10	16	16		
14	$^6I_{9/2}$	U(2)	36 038	36 035	3	6	6	6	9	9		
15	$^6I_{9/2}$	E'	36 063	36 056	7	2	1	1	2	2		
16	$^6I_{17/2}$	U(1)	36 068	36 063	5	13	6	3	12	10		
17	$^6I_{17/2}$	E'(1)	36 070			1	4	5	5	5		
18	$^6I_{17/2}$	U(2)	36 074			11	8	6	13	12		
19	$^6I_{17/2}$	E''	36 077	36 069	9	3	2	1	3	3		
20	$^6I_{17/2}$	U(3)	36 077			3	5	6	7	7		
21	$^6I_{17/2}$	E'(2)	36 078			0.5	4	5	4	5		
22	$^6I_{11/2}$	E'	36 248	36 263	-15	10	7	6	12	11		
23	$^6I_{11/2}$	U(1)	36 270	36 278	-8	13	12	12	19	18		
24	$^6I_{11/2}$	E''	36 321	36 314	7	2	5	6	6	7		
25	$^6I_{11/2}$	U(2)	36 335	36 337	-2	9	6	5	10	9		
26	$^6I_{15/2}$	U(1)	36 384	36 392	-8	3	8	10	10	11		
27	$^6I_{13/2}$	E'	36 399			5	7	8	10	10	0.49D	0.50D'
28	$^6I_{15/2}$	U(2)	36 403	36 408	-5	20	8	4	18	15	0.64D	0.51D'
29	$^6I_{15/2}$	E''	36 423	36 430	-6	2	4	5	5	6	D	D'
30	$^6I_{13/2}$	U(2)	36 424			17	10	7	18	17		
31	$^6I_{13/2}$	E''	36 447	36 453	-6	1	5	7	6	7	0.30D	0.22D'
32	$^6I_{15/2}$	U(3)	36 457	36 472	-14	5	9	10	12	12	0.81D	0.74D'
33	$^6I_{15/2}$	E'	36 459			5	2	1	5	4		
34	$^6I_{13/2}$	E''(2)	36 492	36 499	-7	4	3	3	5	5	0.33D	0.14D'
35	$^6I_{13/2}$	U(2)	36 497	36 507	-10	5	6	6	8	8	0.60D	0.37D'
36	$^6D_{9/2}$	E'	39 233	39 219	14	8	93	121	97	118	0.60E	0.61E'
37	$^6D_{9/2}$	U(1)	39 294	39 294	0	88	166	192	210	229	E	0.73E'
38	$^6D_{9/2}$	U(2)	39 414	39 446	-32	234	124	87	240	213	0.72E	E'
39	$^6D_{1/2}$	E'	40 249	40 269	-20	12	6	4	10	9		
40	$^6D_{7/2}$	U	40 355	40 348	-4	200	141	122	203	189		
41	$^6D_{7/2}$	E''	40 361	40 359	13	37	98	118	94	109		
42	$^6D_{7/2}$	E'	40 409	40 393	16	122	68	50	108	95		
43	$^6D_{3/2}$	U	40 556	40 550	6	65	75	79	100	103		
44	$^6D_{5/2}$	E''	40 605	40 626	-21	49	56	58	79	81		
45	$^6D_{5/2}$	U	40 730	40 721	9	93	109	115	155	159		

3.3. Comparison with previous assignments of energy levels

When comparing the calculated energy levels obtained herein with those presented in [7], it can be noticed that, apart from differences in calculated energies, there are also

several differences in the assignments of CF level irreducible representations (IRs). Since the IRs were not determined experimentally, but rather assigned on the basis of calculated and observed energies, the following points concerning our revisions merit comment.

Table 3. Comparison of intensity ratios for TPA transitions to various final multiplets and/or under the incidence of linear (lin) and circular (cir) incident laser radiation.

Ratios		Expt. [7]	Calc.
${}^6D_{7/2}$	(lin:cir)	0.7	0.74–0.9
${}^6D_{7/2}$ versus ${}^6D_{5/2}$	(lin:lin)	0.8	1.6–2.5
${}^6D_{7/2}$ versus ${}^6D_{3/2}$	(lin:lin)	1.9	~4–6
${}^6P_{7/2}$	(lin:cir)	2.4	~7
${}^6P_{7/2}$ versus ${}^6P_{5/2}$	(lin:lin)	20	~28–35
	(cir:cir)	8	~3–4
${}^6P_{7/2}$ versus ${}^6P_{3/2}$	(lin:lin)	35	~1000–2000
	(cir:cir)	9	~200
${}^6P_{5/2}$ versus ${}^6P_{3/2}$	(lin:lin)	1.7	30–40
	(cir:cir)	1.1	40–50

- (i) The two CF levels of ${}^6P_{5/2}$ (numbers 7 and 8 in table 2) were measured at 32 545 and 32 574 cm^{-1} , with the former being assigned to U and the latter to E'' in [7] and references therein. The CF calculation herein predicts a CF splitting of 29 cm^{-1} between these levels, and reverses these IRs. The TPA intensity calculation predicts that the TPA line strength for the level U is twice that for the level E'' . Therefore, it is natural to assign the measured level at 32 574 cm^{-1} , with measured TPA intensity B , to the calculated higher CF level (32 558 cm^{-1}) of ${}^6P_{5/2}$ with IR U, and the measured level at 32 545 cm^{-1} , with measured TPA intensity $0.46B$, to the calculated lower CF level (32 529 cm^{-1}).
- (ii) The measured levels at 36 278 cm^{-1} (number 23 in table 2) and 36 507 cm^{-1} (number 35 in table 2) were previously assigned to IR E'' and E' , respectively. The CF calculation shows that the former belongs to ${}^6I_{11/2}$ and the latter belongs to ${}^6I_{13/2}$. Since ${}^6I_{11/2}$ splits into $E' + E'' + 2U$ (only one E''), the previous assignment of both measured levels 36 278 and 36 314 cm^{-1} to E'' is not possible and it is natural to assign 36 278 cm^{-1} to IR U instead. Similarly, ${}^6I_{13/2}$ splits into $E' + 2E'' + 2U$, and 36 507 cm^{-1} is naturally assigned to IR U.
- (iii) The measured level at 36 392 cm^{-1} was assigned to U in [7], but this band is likely to be the convolution of the ${}^6I_{15/2}$ level calculated at 36 399 cm^{-1} and the ${}^6I_{13/2}$ level at 36 384 cm^{-1} , judging from the calculated TPA line strengths.
- (iv) The measured level at 36 430 cm^{-1} was assigned to E'' in [7], but is now assigned to ${}^6I_{13/2}U$ (calculated at 36 424.4 cm^{-1} ; number 30 in table 2) with a lower energy shoulder ${}^6I_{15/2}E''$ (calculated to be at 1.9 cm^{-1} lower energy; number 29 in table 2). This assignment is supported by fact that the TPA line strength for ${}^6I_{13/2}U$ is about three times stronger (depending on the polarization of light) and in the measured TPA spectra there appears to be a shoulder for the peak at 36 430 cm^{-1} .
- (v) The CF calculations show that the three CF levels 40–42 for ${}^6D_{7/2}$ are of IRs U, E'' and E' in the order of increasing energy, which differs from the order of IRs: E'' , U and E' for ${}^6S_{7/2}$, ${}^6P_{7/2}$ and ${}^6I_{7/2}$. This difference is understandable, since for the $4f^7$ electronic configuration and under the one-body CF approximation,

the CF splitting is of second order in the sense that it is not due to the direct splitting of a single multiplet but only due to mixing of different multiplets. Herein the assignment of the three measured CF levels to calculation is different from that in [7] (which is E' , U, and E'' in the order of increasing energy). Unfortunately, the polarized TPA spectra for ${}^6D_{7/2}$ were not presented in the literature, otherwise a comparison of the calculated TPA line strengths with measured ones may serve to critically examine this assignment.

4. Conclusions

The small residue of optimization in the energy level calculation indicates that the correlation CF/configuration interaction effects play a less important role herein than for Eu^{2+} . This is partially due to the more spatially confined 4f orbitals in Gd^{3+} than for Eu^{2+} . Also, the much higher first ionization energy of the 4f electron in Gd^{3+} than in Eu^{2+} makes the mixing of relevant configurations (such as $4f^6$ with conduction band p electron states) to $4f^7$ much weaker in Gd^{3+} than for Eu^{2+} . Generally, for hexachloroelpasolites, a level is luminescent if the energy gap below it is spanned by more than four phonons. The highest energy phonon in this lattice is $\nu_1 \sim 290 \text{ cm}^{-1}$. Cross-relaxation processes which could depopulate the luminescent levels in $\text{Cs}_2\text{NaGdCl}_6$ do not occur because there are no low-lying multiplet terms. Notice that the gap between levels 35 and 36 is 2736 cm^{-1} , which is spanned by ~ 10 phonons in this host lattice, so that luminescence is expected to occur from ${}^6I_{13/2}U$ when it is suitably populated. A similar comment applies to levels 9 and 10 (energy gap 2480 cm^{-1}) so that luminescence is also expected from ${}^6P_{3/2}U$.

Some important points emerge from the intensity calculations. Although the lowest energy level of Gd^{3+} , ${}^8S_{7/2}$, can be considered as 8-fold degenerate for the study of optical properties, the TPA line strengths are highly polarization dependent. For instance, the TPA intensity for linearly polarized incident radiation is very different from that for circularly polarized radiation, and it also depends on the direction of polarization direction: sometimes very strongly. Theoretically, without J -mixing, the summation of multiplet–multiplet TPA line strengths (i.e., summation of line strengths for transitions from ${}^8S_{7/2}$ to all final CF levels of the same multiplet ${}^{2S+1}L_J$) are polarization independent. The calculated results herein are substantially different from this approximation, which indicates the importance of J -mixing, caused by CF interactions.

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References

- [1] Morrison C A, Leavitt R P and Wortman D E 1980 *J. Chem. Phys.* **73** 2580
- [2] Judd B R and Pooler D R 1982 *J. Phys. C: Solid State Phys.* **15** 591

- [3] Downer M C, Cordero-Montalvo C D and Crosswhite H 1983 *Phys. Rev. B* **28** 4931
- [4] Bouazaoui M, Jacquier B, Linarès C, Stręk W and Cone R L 1991 *J. Lumin.* **48/49** 318
- [5] Burdick G W, Burdick A, Deev V, Duan C K and Reid M F 2006 *J. Lumin.* **118** 205
- [6] Tanner P A, Kumar V V R K, Jayasankar C K and Reid M F 1994 *J. Alloys Compounds* **215** 349
- [7] Kundu L, Banerjee A K and Chowdhury M 1991 *Chem. Phys. Lett.* **181** 569
- [8] de Vries A J and Blasse G 1988 *J. Chem. Phys.* **88** 7312
- [9] Bouazaoui M, Jacquier B, Linares C and Stręk W 1991 *J. Phys.: Condens. Matter* **3** 921
- [10] Dereń P J and Stręk W 1996 *J. Lumin.* **69** 295
- [11] Dereń P J, Stręk W and Krupa J-C 1998 *Chem. Phys. Lett.* **298** 217
- [12] Tian Z, Liang H, Han B, Su Q, Tao Y, Zhang G and Fu Y 2008 *J. Phys. Chem. C* **112** 12524
- [13] Duan C-K, Tanner P A, Meijerink A and Babin A 2009 *J. Phys.: Condens. Matter* **21** 395501
- [14] Reid M F, van Pieterse L, Wegh R T and Meijerink A 2000 *Phys. Rev. B* **62** 14744
- [15] Burdick G W and Reid M F 1993 *Phys. Rev. Lett.* **70** 2491
Burdick G W and Reid M F 1993 *Phys. Rev. Lett.* **71** 3892
- [16] Ning L X, Wang D Y, Xia S D, Thorne J R G and Tanner P A 2002 *J. Phys.: Condens. Matter* **14** 3833
- [17] Görrler-Walrand C and Binnemans K 1996 *Handbook on the Physics and Chemistry of Rare Earths* ed K A Gschneidner Jr and L Eyring (Amsterdam: Elsevier) chapter 23, pp 121–283
- [18] Duan C K and Tanner P A 2010 submitted
- [19] Faucher M D and Tanner P A 2006 *J. Phys.: Condens. Matter* **18** 8503
- [20] Chen T, Duan C K and Xia S D 2007 *J. Alloys Compounds* **439** 363
- [21] Duan C K and Reid M F 2005 *J. Chem. Phys.* **122** 094714