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## Two-photon spectroscopy of europium(III) elpasolites

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**Abstract.** We present polarized two-photon excitation (TPE) spectra, including Zeeman data, for europium(III) in the elpasolites Cs<sub>2</sub>NaEuCl<sub>6</sub> and Cs<sub>2</sub>NaYF<sub>6</sub>·Eu<sup>3+</sup>. Approximately 80 and 60 levels of unambiguous symmetry have been assigned respectively in each compound up to 32 000 cm<sup>-1</sup> with the aid of a one-electron crystal field Hamiltonian. This represents the most complete and extensive data set so far reported for Eu(III) at a cubic site. Comparisons are made between comparable data sets for Eu(III) f<sup>6</sup> and Tb(III) f<sup>8</sup>. Deviations from the predictions of the one-electron crystal field model are discussed in terms of the spin correlation crystal field.

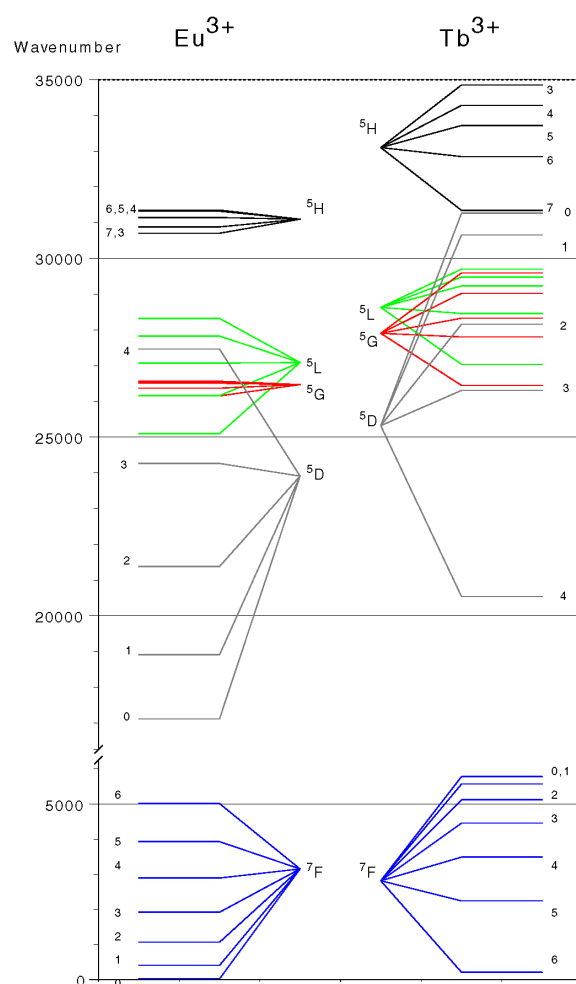
### 1. Introduction

A lanthanide ion in a crystal field can be described by a combination of a free ion Hamiltonian, and a crystal field potential which acts as a perturbation on the free ion states [1]. The former contains contributions from coulombic ( $F^k$ ,  $k = 2, 4, 6$ ), electrostatically correlated coulombic ( $\alpha, \beta, \gamma, T^i$ ,  $i = 2, 3, 4, 6, 7, 8$ ), spin-orbit coupling ( $\zeta_{so}$ ), two-electron spin-other-orbit ( $M^k$ ,  $k = 0, 2, 4$ ) and electrostatically correlated spin-orbit ( $P^k$ ,  $k = 2, 4, 6$ ) interactions. When parameterized in this way the Hamiltonian provides a satisfactory model of the free ion levels [2]. The crystal field is usually expressed as the sum of one-electron operators:

$$H_{CF} = \sum_{i,q,k} B_q^{(k)} u_q^{(k)}(i) \quad (1)$$

where  $u_q^{(k)}(i)$  is a unitary tensor operator for the  $i$ th f electron, of rank  $k$  where  $k = 2, 4, 6$ , with  $q$  restricted by symmetry. A rigorous test of the crystal field model requires a large energy level data set and a small number of crystal field parameters.

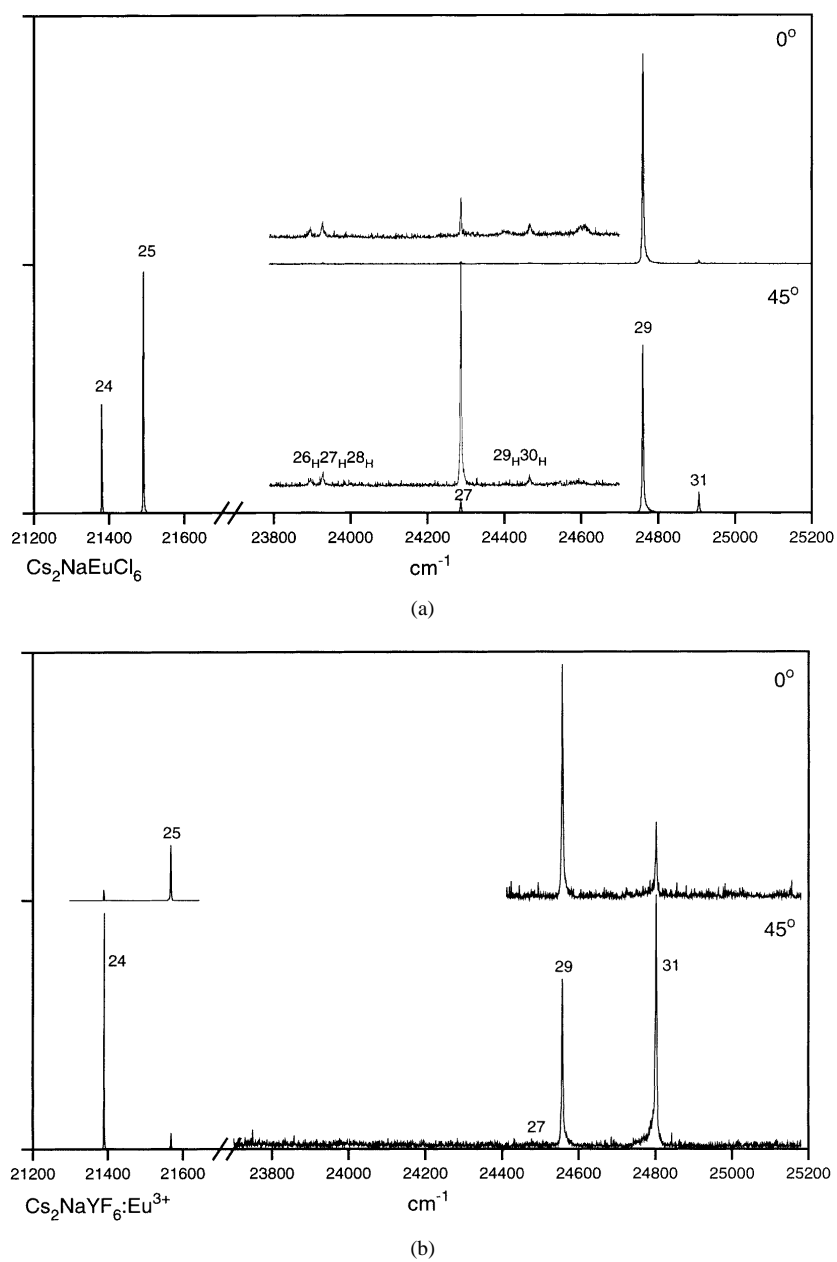
The cubic elpasolites provide an octahedral lanthanide(III) site, that requires only two one-electron crystal field parameters to model the f-electron–lattice interaction. However, one-photon f–f transitions are electric-dipole forbidden, magnetic-dipole transitions are not always observed and the absorption cross-section of vibronic transitions is low. Energy level determinations have relied mainly on emission data; these locate multiplet components near the ground state, but only a few upper levels. For this reason empirical Hamiltonians for lanthanide haloelpasolites have been based on an average of only 30 observed levels for each ion [1, 3]. Although large data sets comprising over 100 levels are available for many lanthanides in low symmetry hosts such as LaCl<sub>3</sub> (C<sub>3h</sub> site) [4] and LaF<sub>3</sub> (C<sub>2</sub> site) [5], their analysis requires up to nine one-electron crystal field parameters.



**Figure 1.** Energy level diagram for europium(III) and terbium(III) in zero field. The levels were calculated using the free ion parameters for  $\text{Cs}_2\text{NaEuCl}_6$  in table 2 and those of [13] for  $\text{Cs}_2\text{NaTbCl}_6$ .

The  ${}^7F_J$  and  ${}^5D_J$  levels of europium(III) have been recently studied in  $\text{Cs}_2\text{NaEuCl}_6$  [6] and  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  [7] by single-photon spectroscopy, including parametrization using the same free ion and crystal field Hamiltonian as in this work, based on  $\sim 20$  levels belonging to the  ${}^7F_J$  and  ${}^5D_{3,2,1,0}$  multiplets.

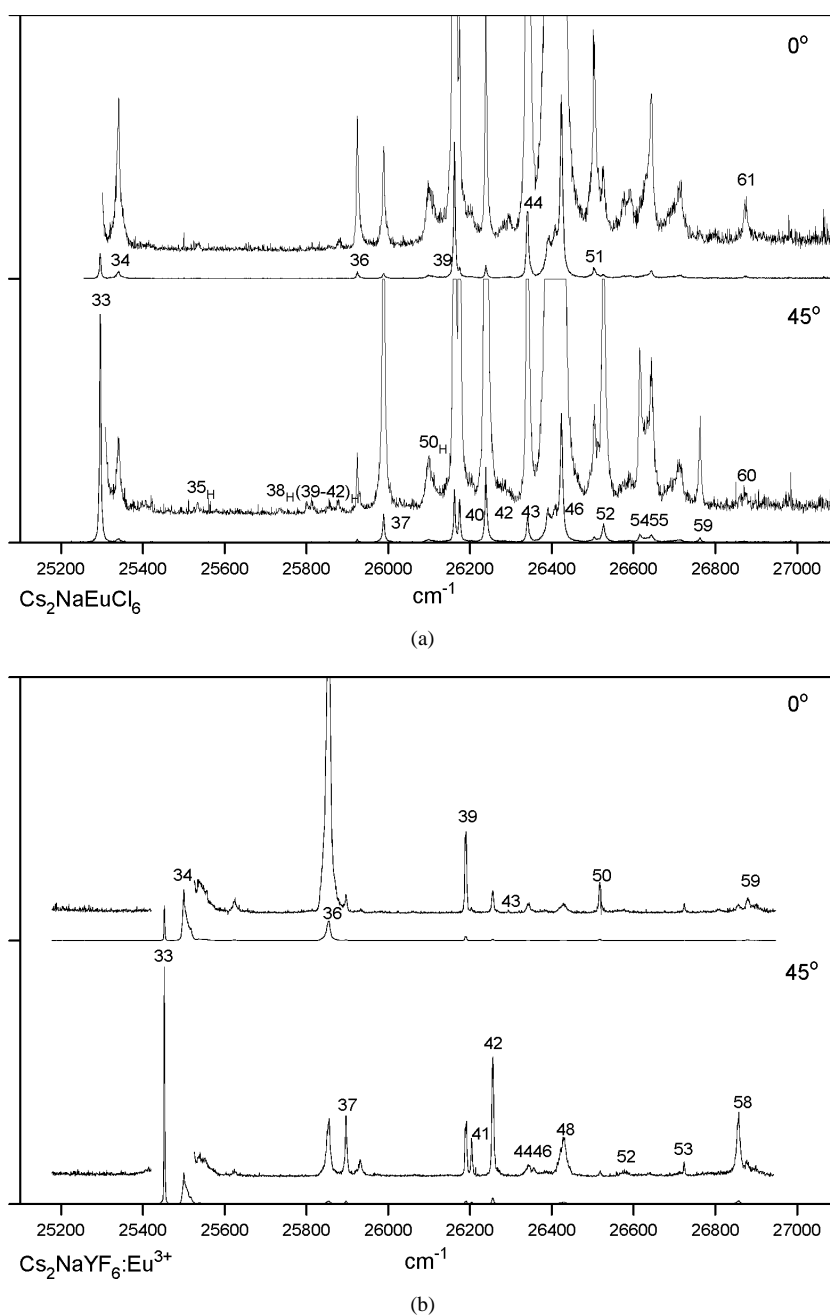
On the other hand, in two-photon spectroscopy, parity-conserving electronic transitions are allowed and the spectra contain little significant phonon structure [8]. As a result, this technique allows access to a large number of excited state energy levels in sites of octahedral symmetry. In this paper, which is part of a series [8–14] covering the  $\text{Cs}_2\text{NaLnX}_6$  elpasolites with  $X = \text{F}, \text{Cl}$  and  $\text{Br}$ , we use two-photon excitation to identify the energies and symmetries for  $\text{Ln} = \text{Eu}$ , of a very much larger sequence of levels than has previously been compiled. Our analogous experimental results for  $\text{Ln} = \text{Tb}$  are to be found in [12] and [13], and for  $\text{Ln} = \text{Sm}$  in reference [14]. Other previous two-photon studies of rare-earth elpasolites have been limited to a small number of excited states in  $\text{Cs}_2\text{NaGdCl}_6$  [15].



**Figure 2.** TPE spectra for (a)  $\text{Cs}_2\text{NaEuCl}_6$  at 120 K and (b)  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  at 70 K for polarizations with  $\alpha = 0^\circ$  and  $\alpha = 45^\circ$ .

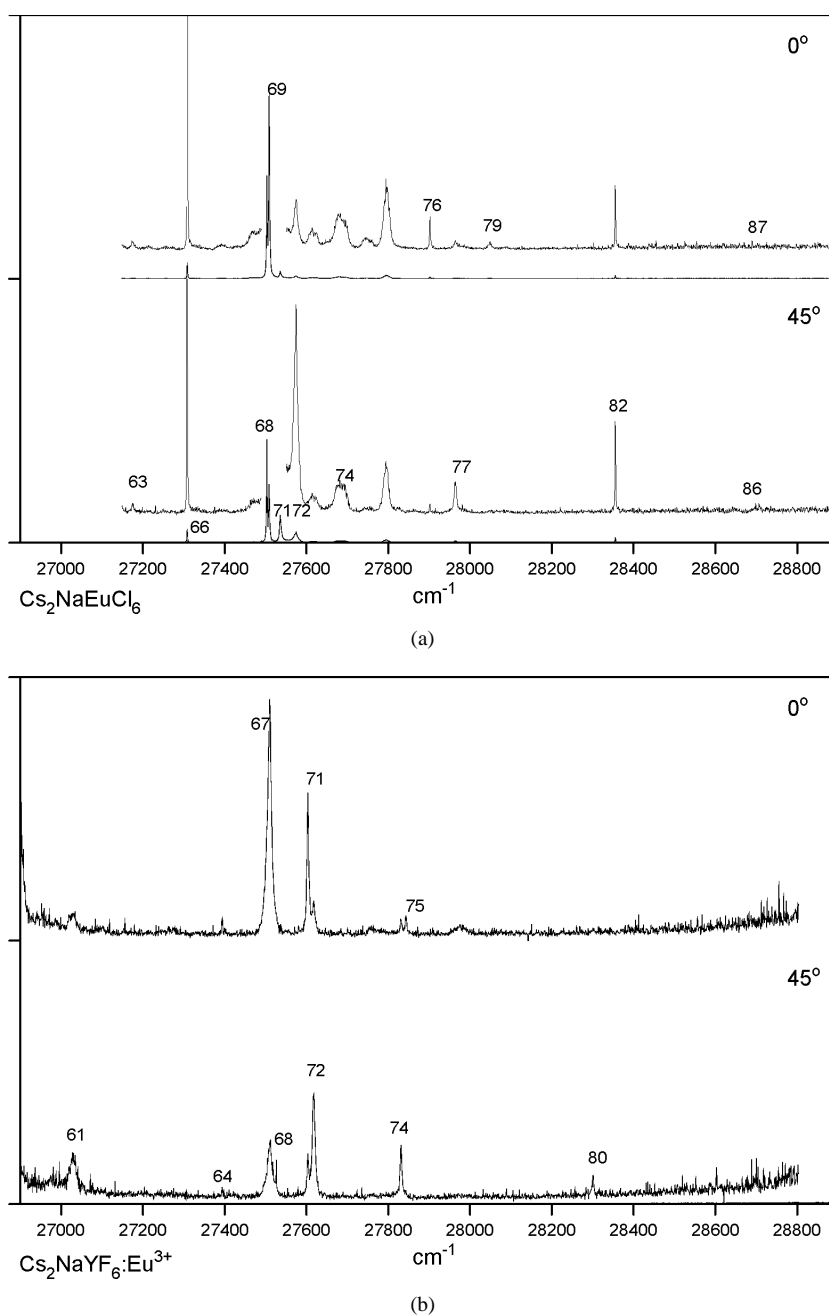
## 2. Experiment

$\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{F}_6$  was synthesized by the reaction of aqueous solutions of CsF and NaF with mixtures of  $\text{Eu}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  (99.995%) at a temperature of 750 K and pressures of 100–150 MPa [7]. The crystal used in this work had nominal composition  $\text{Cs}_2\text{NaY}_{0.8}\text{Eu}_{0.2}\text{F}_6$ . Henceforth, we refer to this mixed Y/Eu material as  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$ .



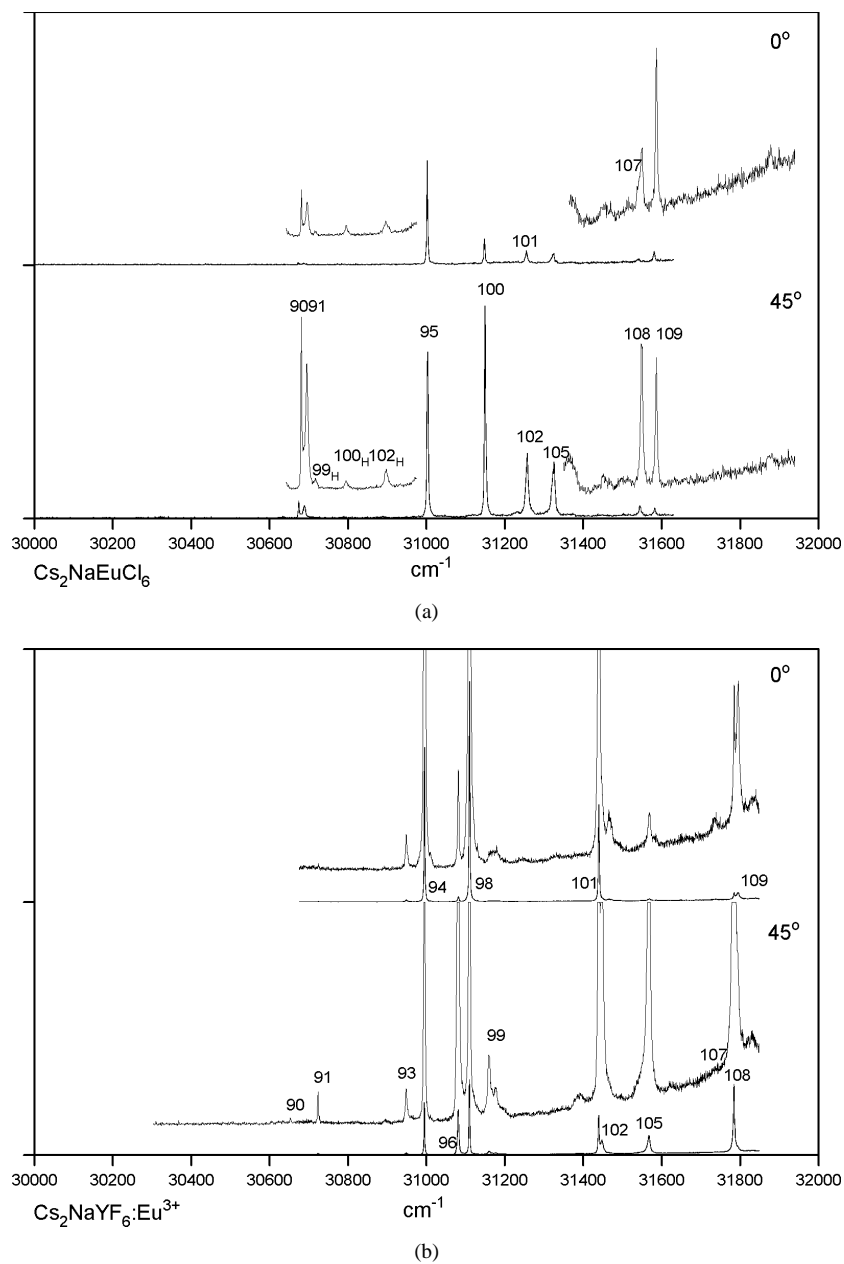
**Figure 3.** TPE spectra for (a)  $\text{Cs}_2\text{NaEuCl}_6$  at 120 K and (b)  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  at 70 K for polarizations with  $\alpha = 0^\circ$  and  $\alpha = 45^\circ$ .

$\text{Cs}_2\text{NaEuCl}_6$  crystals were grown from the fused component binary chlorides by the Bridgman method. NaCl (99.999%) and CsCl (99.9%) were purified by vacuum sublimation. Anhydrous  $\text{EuCl}_3$  was prepared from  $\text{Eu}_2\text{O}_3$  using the ammonium chloride route [16] by vacuum decomposition of  $(\text{NH}_4)_2[\text{EuCl}_5]$ . Any oxychloride present was converted to chloride



**Figure 4.** TPE spectra for (a)  $\text{Cs}_2\text{NaEuCl}_6$  at 120 K and (b)  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  at 70 K for polarizations with  $\alpha = 0^\circ$  and  $\alpha = 45^\circ$ .

by exposing the freshly made  $\text{EuCl}_3$  to a stream of dry  $\text{HCl}$  gas at  $450^\circ\text{C}$  for 36 hours.  $\text{NaCl}$ ,  $\text{CsCl}$  and  $\text{EuCl}_3$  powders in the appropriate ratio were mixed and transferred into an HF etched Bridgman tube.  $\text{Cs}_2\text{NaEuCl}_6$  was prepared by growth at a temperature of  $750\text{--}800^\circ\text{C}$  under a pressure of 7 atm  $\text{Cl}_2$  which was employed to prevent the formation of divalent europium



**Figure 5.** TPE spectra for (a)  $\text{Cs}_2\text{NaEuCl}_6$  at 120 K and (b)  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  at 70 K for polarizations with  $\alpha = 0^\circ$  and  $\alpha = 45^\circ$ .

[17]. Transparent sections of the resulting boule were identified as  $\text{Cs}_2\text{NaEuCl}_6$  by x-ray diffraction.

Crystals were oriented by Laue back reflection, and cut and polished with faces perpendicular to  $\{100\}$ . Low temperature emission spectra, for comparison with published work, were recorded excited at 355 nm.

It has been observed at 80 K that  $\text{Cs}_2\text{NaEuCl}_6$  adopts a lower symmetry phase [18] but we observed no depolarization of the excitation beam by the crystal at 100 K. Experiments were performed at temperatures of both 10 K and, to avoid deviations from cubic behaviour, at 120 K. Doped in the  $\text{Cs}_2\text{NaYF}_6$  lattice, the  $\text{EuF}_6^{3-}$  moiety is not subject to this distortion; spectra were recorded at 70 K.

The europium(III) ion is almost as good a candidate for a comprehensive two-photon study as terbium(III), because it has a window of linear absorption transparency between 5000 and 17 000  $\text{cm}^{-1}$  (allowing non-resonant two-photon excitation (TPE) to states up to nearly 34 000  $\text{cm}^{-1}$ ), and its high yield visible luminescence can be used to detect the excitation. TPE spectra were recorded by monitoring the emission intensity as a function of the excitation energy from an Nd:YAG pumped Spectra Physics PDL3 dye laser. The polarization integrity of the laser output was improved using a calcite polarizer, and the polarization angle varied using a double Fresnel rhomb. The beam was focused on to a {100} face of the sample mounted in an Oxford Instruments CF204 cryostat with wedged windows. The laser frequency was determined to  $<1 \text{ cm}^{-1}$  by simultaneously recording the opto-galvanic spectrum of an Ar discharge tube. Emission was detected directly through a series of bandpass and cutoff filters with a window centred near 550 nm corresponding to emission from  $^5\text{D}_1$ . The emission was corrected for variations in the laser intensity by referencing against the square of the laser energy, using a Molelectron LP141 photodiode. Zeeman spectra were recorded in a Thor Cryogenics magneto-optic cryostat at fields up to 5.0 T, as described elsewhere [11].

### 3. Results

An energy level diagram in the absence of the crystal field perturbation for europium(III), and terbium(III) for comparison, is shown in figure 1; it is intended to serve as a guide to the excited state manifold in the subsequent discussion. The levels indicate the energies of the free ion terms; groups of  $SLJ$  levels are labelled by their parent Russell–Saunders term which is shown as a hypothetical barycentre.

In europium(III), one-photon and two-photon absorption are followed by non-radiative decay to the  $^5\text{D}_0$  and  $^5\text{D}_1$  manifolds from which emission occurs to the  $^7\text{F}_J$  crystal field levels. The observed  $^5\text{D}_1$  emission decays with a lifetime of  $\sim 2 \text{ ms}$  at low temperature.

The mechanism, selection rules and polarization dependence of two-photon absorption have been previously described [8]. Since all the electronic states of interest have even parity, the *gerade* subscript is omitted from the irreducible representations of  $\text{O}_h$ . The ground state of  $\text{Eu}^{3+}$  in  $\text{Cs}_2\text{NaLnX}_6$  has  $A_1$  symmetry, from which single-colour two-photon transitions are allowed to  $A_1$ , E and  $T_2$  excited states. Here we consider a beam propagating along [001], and define its polarization by the angle  $\alpha$  of the electric vector with respect to [100]. When  $\alpha = 0^\circ$ ,  $A_1 \rightarrow T_2$  transitions are forbidden, while the intensity of  $A_1 \rightarrow E$  transitions is at a maximum. When  $\alpha = 45^\circ$ , the  $A_1 \rightarrow T_2$  intensity is at a maximum, while the intensity of  $A_1 \rightarrow E$  transitions decreases by a factor of four. The intensity of  $A_1 \rightarrow A_1$  transitions is independent of  $\alpha$ .

States of  $A_2$  and  $T_1$  symmetry are not accessible from the  $A_1$  ground state, but transitions to them become allowed at higher temperature due to thermal population of the  $T_1$  component of the  $^7\text{F}_1$  multiplet. Transitions from level 2 give rise to hot bands in the TPE spectrum, displaced to lower energy by  $\sim 350 \text{ cm}^{-1}$  relative to the cold transitions. Hot bands that have no counterpart in the cold spectrum indicate the position of  $T_1$  or  $A_2$  excited states.  $T_1 \rightarrow A_1$  transitions are forbidden, and the intensity of  $T_1 \rightarrow A_2$  and  $T_1 \rightarrow E$  transitions has the same angular dependence as an  $A_1 \rightarrow T_2$  transition. The angular dependence of the  $T_1 \rightarrow T_1$  and  $T_1 \rightarrow T_2$  intensities, however, is not constrained by symmetry.



**Table 1.** Observed and calculated energy levels of Eu(III) in Cs<sub>2</sub>NaLnX<sub>6</sub> (uncertain values are shown in parentheses: literature values [6, 7] are in italics).

Cs <sub>2</sub> NaEuCl <sub>6</sub>						Cs <sub>2</sub> NaYF <sub>6</sub> :Eu					
		Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$		Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$			
1	<sup>7</sup> F <sub>0</sub>	A <sub>1g</sub>	0	-7	7	<sup>7</sup> F <sub>0</sub>	A <sub>1g</sub>	0	-7	7	
2	<sup>7</sup> F <sub>1</sub>	T <sub>1g</sub>	360	359	1	<sup>7</sup> F <sub>1</sub>	T <sub>1g</sub>	337	347	-10	
3	<sup>7</sup> F <sub>2</sub>	E <sub>g</sub>	875	864	11	<sup>7</sup> F <sub>2</sub>	E <sub>g</sub>	807	774	33	
4	<sup>7</sup> F <sub>2</sub>	T <sub>2g</sub>	<i>1091</i>	1093	-2	<sup>7</sup> F <sub>2</sub>	T <sub>2g</sub>	<i>1065</i>	1075	-10	
5	<sup>7</sup> F <sub>3</sub>	A <sub>2g</sub>	<i>1804</i>	1804	0	<sup>7</sup> F <sub>3</sub>	A <sub>2g</sub>	<i>1789</i>	1768	21	
6	<sup>7</sup> F <sub>3</sub>	T <sub>2g</sub>	<i>1904</i>	1912	-8	<sup>7</sup> F <sub>3</sub>	T <sub>2g</sub>	<i>1953</i>	1976	-23	
7	<sup>7</sup> F <sub>3</sub>	T <sub>1g</sub>	<i>1963</i>	1966	-3	<sup>7</sup> F <sub>3</sub>	T <sub>1g</sub>	<i>2014</i>	2027	-13	
8	<sup>7</sup> F <sub>4</sub>	T <sub>2g</sub>	<i>2665</i>	2674	-9	<sup>7</sup> F <sub>4</sub>	T <sub>2g</sub>	<i>2670</i>	2642	28	
9	<sup>7</sup> F <sub>4</sub>	E <sub>g</sub>	<i>2975</i>	2971	4	<sup>7</sup> F <sub>4</sub>	E <sub>g</sub>	<i>3041</i>	3033	8	
10	<sup>7</sup> F <sub>4</sub>	T <sub>1g</sub>	<i>3007</i>	3016	-9	<sup>7</sup> F <sub>4</sub>	T <sub>1g</sub>	<i>3151</i>	3170	-19	
11	<sup>7</sup> F <sub>4</sub>	A <sub>1g</sub>	<i>3034</i>	3054	-20	<sup>7</sup> F <sub>4</sub>	A <sub>1g</sub>	<i>3205</i>	3238	-33	
12	<sup>7</sup> F <sub>5</sub>	T <sub>1g</sub>	<i>3811</i>	3817	-6	<sup>7</sup> F <sub>5</sub>	T <sub>2g</sub>		3781	3781	0
13	<sup>7</sup> F <sub>5</sub>	E <sub>g</sub>	<i>3851</i>	3850	1	<sup>7</sup> F <sub>5</sub>	T <sub>1g</sub>	<i>3821</i>	3848	-27	
14	<sup>7</sup> F <sub>5</sub>	T <sub>2g</sub>	<i>3876</i>	3867	9	<sup>7</sup> F <sub>5</sub>	E <sub>g</sub>	<i>(3911)</i>	3872	39	
15	<sup>7</sup> F <sub>5</sub>	T <sub>1g</sub>	<i>4149</i>	4119	30	<sup>7</sup> F <sub>5</sub>	T <sub>1g</sub>	<i>4335</i>	4296	39	
16	<sup>7</sup> F <sub>6</sub>	E <sub>g</sub>	<i>4835</i>	4855	-20	<sup>7</sup> F <sub>6</sub>	E <sub>g</sub>	<i>(4818)</i>	4817	1	
17	<sup>7</sup> F <sub>6</sub>	T <sub>2g</sub>	<i>4869</i>	4884	-15	<sup>7</sup> F <sub>6</sub>	T <sub>2g</sub>		4864	4864	0
18	<sup>7</sup> F <sub>6</sub>	A <sub>2g</sub>	<i>4945</i>	4948	-3	<sup>7</sup> F <sub>6</sub>	A <sub>2g</sub>		4945	4945	0
19	<sup>7</sup> F <sub>6</sub>	T <sub>2g</sub>	<i>5242</i>	5216	26	<sup>7</sup> F <sub>6</sub>	T <sub>2g</sub>		5451	5451	0
20	<sup>7</sup> F <sub>6</sub>	T <sub>1g</sub>	<i>5254</i>	5250	4	<sup>7</sup> F <sub>6</sub>	T <sub>1g</sub>		5482	5482	0
21	<sup>7</sup> F <sub>6</sub>	A <sub>1g</sub>	<i>5283</i>	5279	4	<sup>7</sup> F <sub>6</sub>	A <sub>1g</sub>		5513	5513	0
22	<sup>5</sup> D <sub>0</sub>	A <sub>1g</sub>	<i>17208</i>	17205	3	<sup>5</sup> D <sub>0</sub>	A <sub>1g</sub>	<i>17255</i>	17257	-2	
23	<sup>5</sup> D <sub>1</sub>	T <sub>1g</sub>	<i>18961</i>	18972	-11	<sup>5</sup> D <sub>1</sub>	T <sub>1g</sub>	<i>19000</i>	19004	-4	
24	<sup>5</sup> D <sub>2</sub>	T <sub>2g</sub>	21385	21396	-11	<sup>5</sup> D <sub>2</sub>	T <sub>2g</sub>	21389	21406	-17	
25	<sup>5</sup> D <sub>2</sub>	E <sub>g</sub>	21495	21469	26	<sup>5</sup> D <sub>2</sub>	E <sub>g</sub>	21568	21540	28	
26	<sup>5</sup> D <sub>3</sub>	T <sub>1g</sub>	24261	24282	-21	<sup>5</sup> D <sub>3</sub>	T <sub>1g</sub>	24274	24283	-9	
27	<sup>5</sup> D <sub>3</sub>	T <sub>2g</sub>	24292	24297	-5	<sup>5</sup> D <sub>3</sub>	T <sub>2g</sub>	<i>(24281)</i>	24314	-33	
28	<sup>5</sup> D <sub>3</sub>	A <sub>2g</sub>	24370	24343	27	<sup>5</sup> D <sub>3</sub>	A <sub>2g</sub>		24392	24392	0
29	<sup>5</sup> L <sub>6</sub>	A <sub>1g</sub>	24761	24747	14	<sup>5</sup> L <sub>6</sub>	A <sub>1g</sub>	24557	24554	3	
30	<sup>5</sup> L <sub>6</sub>	T <sub>1g</sub>	24831	24816	15	<sup>5</sup> L <sub>6</sub>	T <sub>1g</sub>		24658	24658	0
31	<sup>5</sup> L <sub>6</sub>	T <sub>2g</sub>	24905	24899	6	<sup>5</sup> L <sub>6</sub>	T <sub>2g</sub>	24802	24787	15	
32	<sup>5</sup> L <sub>6</sub>	A <sub>2g</sub>	25121	25118	3	<sup>5</sup> L <sub>6</sub>	A <sub>2g</sub>		25085	25085	0
33	<sup>5</sup> L <sub>6</sub>	T <sub>2g</sub>	25302	25322	-20	<sup>5</sup> L <sub>6</sub>	T <sub>2g</sub>	25453	25446	7	
34	<sup>5</sup> L <sub>6</sub>	E <sub>g</sub>	25345	25377	-28	<sup>5</sup> L <sub>6</sub>	E <sub>g</sub>	25500	25518	-18	
35	<sup>5</sup> L <sub>7</sub>	T <sub>1g</sub>	25893	25886	7	<sup>5</sup> L <sub>7</sub>	T <sub>1g</sub>		25759	25759	0
36	<sup>5</sup> L <sub>7</sub>	E <sub>g</sub>	25926	25914	12	<sup>5</sup> L <sub>7</sub>	E <sub>g</sub>	25855	25862	-7	
37	<sup>5</sup> L <sub>7</sub>	T <sub>2g</sub>	25987	25980	7	<sup>5</sup> L <sub>7</sub>	T <sub>2g</sub>	25897	25904	-7	
38	<sup>5</sup> L <sub>7</sub>	A <sub>2g</sub>	26099	26119	-20	<sup>5</sup> G <sub>3</sub>	T <sub>1g</sub>		26121	26121	0
39	<sup>5</sup> G <sub>2</sub>	E <sub>g</sub>	26162	26152	10	<sup>5</sup> G <sub>2</sub>	E <sub>g</sub>	26190	26180	10	
40	<sup>5</sup> G <sub>2</sub>	T <sub>2g</sub>	26175	26183	-8	<sup>5</sup> L <sub>7</sub>	A <sub>2g</sub>		26204	26204	0
41	<sup>5</sup> G <sub>3</sub>	T <sub>1g</sub>	26216	26208	8	<sup>5</sup> G <sub>3</sub>	T <sub>2g</sub>	26204	26206	-2	
42	<sup>5</sup> L <sub>7</sub>	T <sub>2g</sub>	26240	26231	9	<sup>5</sup> G <sub>2</sub>	T <sub>2g</sub>	26256	26273	-17	
43	<sup>5</sup> G <sub>3</sub>	T <sub>2g</sub>	26338	26352	-14	<sup>5</sup> G <sub>4</sub>	E <sub>g</sub>	26295	26312	-17	
44	<sup>5</sup> G <sub>4</sub>	E <sub>g</sub>	26339	26355	-16	<sup>5</sup> G <sub>4</sub>	A <sub>1g</sub>	26344	26338	6	
45	<sup>5</sup> L <sub>7</sub>	T <sub>1g</sub>	26345	26344	1	<sup>5</sup> G <sub>4</sub>	T <sub>1g</sub>		26344	26344	0
46	<sup>5</sup> G <sub>4</sub>	A <sub>1g</sub>	26424	26410	14	<sup>5</sup> G <sub>6</sub>	T <sub>2g</sub>	26356	26382	-26	

Table 1. (Continued)

Cs <sub>2</sub> NaEuCl <sub>6</sub>					Cs <sub>2</sub> NaYF <sub>6</sub> :Eu				
		Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$			Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$
47	<sup>5</sup> G <sub>6</sub>	T <sub>2g</sub>	26 410		<sup>5</sup> L <sub>7</sub>	T <sub>1g</sub>		26 408	
48	<sup>5</sup> G <sub>3</sub>	A <sub>2g</sub>	26 419		<sup>5</sup> L <sub>7</sub>	T <sub>2g</sub>	26 429	26 424	5
49	<sup>5</sup> G <sub>5</sub>	T <sub>1g</sub>	26 420		<sup>5</sup> G <sub>6</sub>	T <sub>1g</sub>		26 478	
50	<sup>5</sup> G <sub>6</sub>	T <sub>1g</sub>	26 470	0	<sup>5</sup> G <sub>6</sub>	E <sub>g</sub>	26 518	26 527	-9
51	<sup>5</sup> G <sub>6</sub>	E <sub>g</sub>	26 503	-10	<sup>5</sup> G <sub>3</sub>	A <sub>2g</sub>		26 538	
52	<sup>5</sup> G <sub>6</sub>	T <sub>2g</sub>	26 527	-5	<sup>5</sup> G <sub>6</sub>	T <sub>2g</sub>	26 579	26 618	-38
53	<sup>5</sup> G <sub>6</sub>	A <sub>2g</sub>	26 573		<sup>5</sup> G <sub>6</sub>	A <sub>1g</sub>	26 723	26 688	35
54	<sup>5</sup> G <sub>4</sub>	T <sub>2g</sub>	26 616	0	<sup>5</sup> L <sub>8</sub>	T <sub>2g</sub>		26 713	
55	<sup>5</sup> G <sub>6</sub>	A <sub>1g</sub>	26 645	16	<sup>5</sup> G <sub>5</sub>	E <sub>g</sub>		26 745	
56	<sup>5</sup> G <sub>5</sub>	E <sub>g</sub>	26 665		<sup>5</sup> G <sub>6</sub>	A <sub>2g</sub>		26 752	
57	<sup>5</sup> G <sub>4</sub>	T <sub>1g</sub>	26 689		<sup>5</sup> G <sub>5</sub>	T <sub>1g</sub>		26 760	
58	<sup>5</sup> G <sub>5</sub>	T <sub>1g</sub>	26 701		<sup>5</sup> G <sub>4</sub>	T <sub>2g</sub>	26 856	26 823	33
59	<sup>5</sup> G <sub>5</sub>	T <sub>2g</sub>	26 762	42	<sup>5</sup> L <sub>8</sub>	T <sub>1g</sub>		26 832	
60	<sup>5</sup> L <sub>8</sub>	T <sub>2g</sub>	26 854	-7	<sup>5</sup> L <sub>8</sub>	E <sub>g</sub>	26 879	26 890	-11
61	<sup>5</sup> L <sub>8</sub>	E <sub>g</sub>	26 869	-10	<sup>5</sup> G <sub>5</sub>	T <sub>2g</sub>	27 031	26 988	43
62	<sup>5</sup> L <sub>8</sub>	T <sub>1g</sub>	26 966		<sup>5</sup> G <sub>5</sub>	T <sub>1g</sub>		27 130	
63	<sup>5</sup> L <sub>8</sub>	T <sub>2g</sub>	27 175		<sup>5</sup> L <sub>9</sub>	T <sub>2g</sub>		27 366	
64	<sup>5</sup> L <sub>8</sub>	E <sub>g</sub>	27 294		<sup>5</sup> L <sub>9</sub>	A <sub>1g</sub>	27 393	27 394	-1
65	<sup>5</sup> L <sub>8</sub>	T <sub>1g</sub>	27 306	7	<sup>5</sup> L <sub>9</sub>	A <sub>2g</sub>		27 395	
66	<sup>5</sup> L <sub>8</sub>	A <sub>1g</sub>	27 312	6	<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>		27 416	
67	<sup>5</sup> D <sub>4</sub>	T <sub>1g</sub>	27 501	-6	<sup>5</sup> D <sub>4</sub>	E <sub>g</sub>	27 510	27 518	-8
68	<sup>5</sup> D <sub>4</sub>	A <sub>1g</sub>	27 502	-6	<sup>5</sup> D <sub>4</sub>	T <sub>2g</sub>	27 526	27 525	1
69	<sup>5</sup> D <sub>4</sub>	E <sub>g</sub>	27 509	-4	<sup>5</sup> D <sub>4</sub>	T <sub>1g</sub>		27 586	
70	<sup>5</sup> L <sub>9</sub>	A <sub>2g</sub>	27 515		<sup>5</sup> D <sub>4</sub>	A <sub>1g</sub>		27 590	
71	<sup>5</sup> L <sub>9</sub>	T <sub>2g</sub>	27 535	10	<sup>5</sup> L <sub>8</sub>	E <sub>g</sub>	27 604	27 609	-5
72	<sup>5</sup> D <sub>4</sub>	T <sub>2g</sub>	27 574	6	<sup>5</sup> L <sub>8</sub>	T <sub>2g</sub>	27 618	27 605	13
73	<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>	27 614		<sup>5</sup> L <sub>8</sub>	T <sub>1g</sub>		27 730	
74	<sup>5</sup> L <sub>9</sub>	A <sub>1g</sub>	27 692		<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>	27 832	27 824	8
75	<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>	27 894		<sup>5</sup> L <sub>10</sub>	E <sub>g</sub>	27 843	27 843	0
76	<sup>5</sup> L <sub>9</sub>	E <sub>g</sub>	27 900	3	<sup>5</sup> L <sub>8</sub>	A <sub>1g</sub>		27 889	
77	<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>	27 959	-5	<sup>5</sup> L <sub>10</sub>	T <sub>1g</sub>		27 896	
78	<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>	28 008		<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>		28 185	
79	<sup>5</sup> L <sub>10</sub>	E <sub>g</sub>	28 044	-6	<sup>5</sup> L <sub>9</sub>	E <sub>g</sub>		28 284	
80	<sup>5</sup> L <sub>9</sub>	T <sub>2g</sub>	28 062		<sup>5</sup> L <sub>9</sub>	T <sub>2g</sub>	28 301	28 313	-12
81	<sup>5</sup> L <sub>10</sub>	T <sub>1g</sub>	28 146		<sup>5</sup> L <sub>9</sub>	T <sub>1g</sub>		28 416	
82	<sup>5</sup> L <sub>10</sub>	A <sub>1g</sub>	28 356	18	<sup>5</sup> L <sub>10</sub>	A <sub>1g</sub>		28 541	
83	<sup>5</sup> L <sub>10</sub>	T <sub>1g</sub>	28 438		<sup>5</sup> L <sub>10</sub>	T <sub>1g</sub>		28 731	
84	<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>	28 493		<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>		28 811	
85	<sup>5</sup> L <sub>10</sub>	A <sub>2g</sub>	28 697		<sup>5</sup> L <sub>10</sub>	A <sub>2g</sub>		29 047	
86	<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>	28 706	-9	<sup>5</sup> L <sub>10</sub>	T <sub>2g</sub>		29 082	
87	<sup>5</sup> L <sub>10</sub>	E <sub>g</sub>	28 713	-9	<sup>5</sup> L <sub>10</sub>	E <sub>g</sub>		29 094	
88	<sup>5</sup> H <sub>3</sub>	T <sub>1g</sub>	30 556		<sup>5</sup> H <sub>3</sub>	T <sub>1g</sub>		30 517	
89	<sup>5</sup> H <sub>7</sub>	T <sub>1g</sub>	30 629		<sup>5</sup> H <sub>7</sub>	T <sub>1g</sub>		30 600	
90	<sup>5</sup> H <sub>7</sub>	T <sub>2g</sub>	30 676	12	<sup>5</sup> H <sub>7</sub>	T <sub>2g</sub>	30 654	30 641	13
91	<sup>5</sup> H <sub>3</sub>	T <sub>2g</sub>	30 690	-2	<sup>5</sup> H <sub>3</sub>	T <sub>2g</sub>	30 724	30 722	2
92	<sup>5</sup> H <sub>7</sub>	A <sub>2g</sub>	30 804		<sup>5</sup> H <sub>7</sub>	A <sub>2g</sub>		30 809	
93	<sup>5</sup> H <sub>7</sub>	T <sub>2g</sub>	30 970		<sup>5</sup> H <sub>4</sub>	A <sub>1g</sub>	30 949	30 962	-13

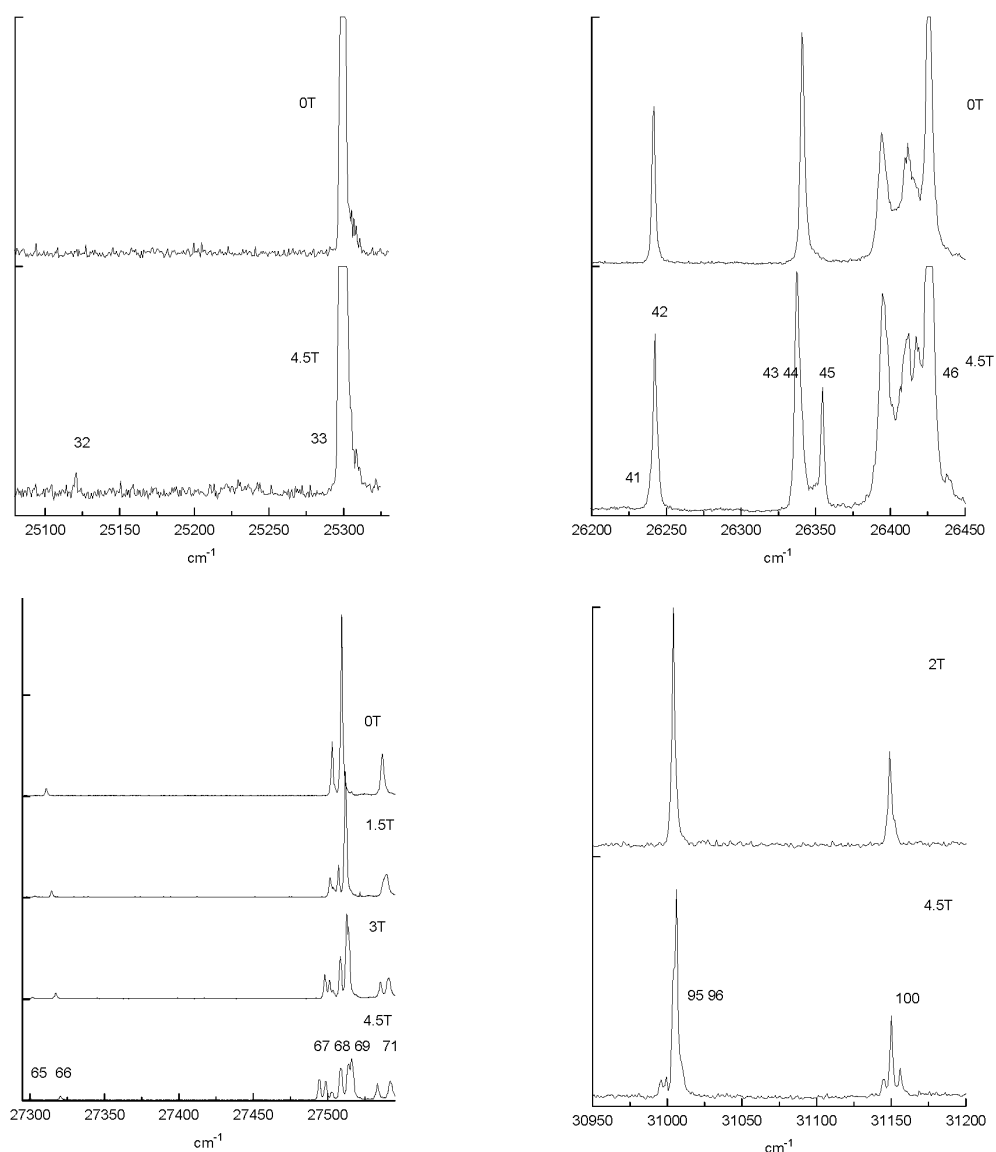
Table 1. (Continued)

		Cs <sub>2</sub> NaEuCl <sub>6</sub>			Cs <sub>2</sub> NaYF <sub>6</sub> :Eu			
		Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$		Energy (cm <sup>-1</sup> )	Calc. <i>E</i> (cm <sup>-1</sup> )	$\Delta E$
94	<sup>5</sup> H <sub>3</sub> A <sub>2g</sub>		30 977		<sup>5</sup> H <sub>4</sub> E <sub>g</sub>	30 994	30 985	9
95	<sup>5</sup> H <sub>4</sub> A <sub>1g</sub>	31 004	30 996	8	<sup>5</sup> H <sub>4</sub> T <sub>1g</sub>		31 039	
96	<sup>5</sup> H <sub>7</sub> E <sub>g</sub>	(31 004)	31 017	-13	<sup>5</sup> H <sub>6</sub> T <sub>2g</sub>	31 081	31 086	-5
97	<sup>5</sup> H <sub>4</sub> E <sub>g</sub>		31 041		<sup>5</sup> H <sub>5</sub> T <sub>1g</sub>		31 096	
98	<sup>5</sup> H <sub>4</sub> T <sub>1g</sub>		31 045		<sup>5</sup> H <sub>6</sub> E <sub>g</sub>	31 110	31 106	4
99	<sup>5</sup> H <sub>7</sub> T <sub>1g</sub>	(31 066)	31 064	2	<sup>5</sup> H <sub>5</sub> T <sub>2g</sub>	31 160	31 184	-24
100	<sup>5</sup> H <sub>6</sub> T <sub>2g</sub>	31 148	31 172	-24	<sup>5</sup> H <sub>3</sub> A <sub>2g</sub>		31 260	
101	<sup>5</sup> H <sub>6</sub> E <sub>g</sub>	31 215	31 232	-17	<sup>5</sup> H <sub>7</sub> E <sub>g</sub>	31 439	31 456	-17
102	<sup>5</sup> H <sub>5</sub> T <sub>2g</sub>	31 257	31 259	-2	<sup>5</sup> H <sub>7</sub> T <sub>2g</sub>	31 447	31 441	6
103	<sup>5</sup> H <sub>5</sub> T <sub>1g</sub>		31 274		<sup>5</sup> H <sub>6</sub> A <sub>2g</sub>		31 499	
104	<sup>5</sup> H <sub>6</sub> A <sub>2g</sub>		31 329		<sup>5</sup> H <sub>7</sub> T <sub>1g</sub>		31 561	
105	<sup>5</sup> H <sub>4</sub> T <sub>2g</sub>	31 327	31 338	-11	<sup>5</sup> H <sub>4</sub> T <sub>2g</sub>	31 567	31 569	-2
106	<sup>5</sup> H <sub>6</sub> T <sub>1g</sub>		31 514		<sup>5</sup> H <sub>5</sub> T <sub>1g</sub>		31 724	
107	<sup>5</sup> H <sub>5</sub> E <sub>g</sub>	31 541	31 533	8	<sup>5</sup> H <sub>6</sub> A <sub>1g</sub>	(31 748)	31 758	-10
108	<sup>5</sup> H <sub>6</sub> T <sub>2g</sub>	31 543	31 531	12	<sup>5</sup> H <sub>6</sub> T <sub>2g</sub>	31 784	31 774	10
109	<sup>5</sup> H <sub>6</sub> A <sub>1g</sub>	31 581	31 541	40	<sup>5</sup> H <sub>5</sub> E <sub>g</sub>	31 795	31 775	20
110	<sup>5</sup> H <sub>5</sub> T <sub>1g</sub>		31 552		<sup>5</sup> H <sub>6</sub> T <sub>1g</sub>		31 786	
111	<sup>5</sup> F <sub>2</sub> E <sub>g</sub>		33 520		<sup>5</sup> F <sub>2</sub> E <sub>g</sub>		32 771	

TPE spectra from 21 000 to 32 000 cm<sup>-1</sup> are shown in figures 2–5. Two polarizations with  $\alpha = 0^\circ$  and  $45^\circ$  are shown for both the chloroelpasolite and fluoroelpasolite. Each peak is labelled with the sequence number of the final states in table 1. Hot bands are designated with the subscript H. Peaks having E symmetry are labelled on the upper ( $0^\circ$ ) spectrum where they are stronger. In most cases the symmetry of the final state is readily apparent. The intensity ratio between the two polarizations was usually large, approaching the theoretical limit. Thus in figure 2(b), we see immediately that level 24 has T<sub>2</sub> symmetry and level 25 E symmetry. There are, for example, unpolarized transitions to level 29 in both spectra, which must therefore have A<sub>1</sub> symmetry. Where necessary, ambiguities in the final state symmetry were resolved by monitoring the signal intensity as a function of polarization angle at the wavelength of each peak. The symmetry determined in this way is included in table 1.

The spectra have been corrected in the regions 25 000–27 000, 27 000–29 000 and 30 000–32 000 cm<sup>-1</sup> to indicate approximate relative TPE intensities that are consistent within each segment. We have not attempted to obtain accurate relative intensities across the whole spectrum.

Location of excited states with T<sub>1</sub> and A<sub>2</sub> symmetry is possible in two ways. At elevated temperature, thermal population of the <sup>7</sup>F<sub>1</sub> T<sub>1</sub> level allows transitions to levels of A<sub>2</sub> and T<sub>1</sub> symmetry. The larger 360 cm<sup>-1</sup> energy gap for Eu(III) renders this method less useful than in Tb(III), for appreciable excited state population is attained only at temperatures where the line broadening and fluorescence quenching obscure the spectra. More useful is to utilize a magnetic field to mix intensity into forbidden transitions [10, 11]. We have performed these experiments only for Cs<sub>2</sub>NaEuCl<sub>6</sub> and the larger data set for the chloro- compared to the fluoroelpasolite in table 1 reflects this fact, along with the more complete literature data available for the low energy states. Figure 6 shows selected parts of the chloroelpasolite two-photon spectrum in a magnetic field that we have utilized to locate particular ‘forbidden’ excited states, or to remove



**Figure 6.**  $\text{Cs}_2\text{NaEuCl}_6$  TPE spectra in a magnetic field at 4 K.

accidental degeneracy. Thus, peaks 32 ( $A_2$ ) and 41, 45, 65, 67 ( $T_2$ ) acquire intensity only in a magnetic field, whilst the degeneracy of peaks 95 and 96 ( $A_1, E$ ) is lifted by the presence of the field.

The energy level assignments (expressed in vacuum wavenumbers) are collected in table 1; those in parentheses are tentative. For consistency, we take published emission data, listed in italics in table 1, for pure  $\text{Cs}_2\text{NaEuCl}_6$  from [6] and  $\text{Cs}_2\text{NaEu}_{0.2}\text{Y}_{0.8}\text{F}_6$  [7], the sample used for the latter study coming from the same source, omitting the authors' 'uncertain' assignments from our fit. We reject only the uncertain assignment of the fluoride  ${}^7\text{F}_5$   $T_2$  level at  $3881\text{ cm}^{-1}$ , which deviates  $100\text{ cm}^{-1}$  from our final fit.

**Table 2.** Energy level parameters ( $\text{cm}^{-1}$ ) for  $\text{Eu}^{3+}$  in  $\text{Cs}_2\text{NaLnX}_6$ .  $M^2 = 0.560M^0$ ,  $M^4 = 0.310M^0$ ;  $P^4 = 0.750P^2$ ,  $P^6 = 0.10P^2$ .

Parameter	$\text{Cs}_2\text{NaEuCl}_6$	$\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$
$E_{av}$	66 407	62 304
$F^2$	94 613	86 460
$F^4$	87 348	62 286
$F^6$	51 081	29 844
$\alpha$	62.5	16.5
$\beta$	-882	-3785
$\gamma$	-4368	4450
$\zeta_{so}$	1342	1347
$T^2$	-256	-2987
$T^3$	-1388	-731
$T^4$	-725	52
$T^6$	-1064	1001
$T^7$	-1844	-3225
$T^8$	65	-2187
$M^0$	2.87	-1.35
$P^2$	333	-947
$B_0^{(4)}$	2206	3776
$B_0^{(6)}$	-305	-553
$\sigma$	15.9	21.7
$N$	77	57

The observed levels are listed in sequence, and can be compared with the energies calculated using a Hamiltonian in which the crystal field is represented as a sum over one-electron operators. The parameter values for this Hamiltonian are given in table 2 in wavenumber units; the number of levels fitted is  $N$ ; the standard deviation is  $\sigma$ . The free ion parameters, used to produce figure 1, indicate considerable configuration mixing, particularly for the ‘twinned’ levels of  $^5\text{G}$  and  $^5\text{H}$ , in europium(III) relative to terbium(III).

The low energy states (1–34,  $^7\text{F}_{0-6}$ ,  $^5\text{D}_{0-3}$ ,  $^5\text{L}_6$ ) are all isolated and the  $SLJ$  labels provide a good description. The identity of their components is unambiguous and their energies therefore stringently test the success of the parametrization. To higher energy, the states (35–87,  $^5\text{L}_{7-10}$ ,  $^5\text{G}_{2-6}$ ,  $^5\text{D}_4$ ) are heavily mixed, so that in some cases the  $SLJ$  labels are a serious over-simplification, and we avoid a discussion of systematic deviations between calculated and experimental splittings in those states where the underlying multiplet character is poorly defined. At still higher energy, the  $^5\text{H}$  manifold is well isolated, but the component states (88–110) are considerably mixed by the crystal field operator (particularly in the fluoroelpasolite) so that the  $J$  label alone is poorly defined.

Tables 3 and 4 compare the crystal field parameters obtained in this work (up to  $^5\text{H}$  at  $32\,000\text{ cm}^{-1}$ ) with a previous parametrization using the levels obtained from single-photon studies (up to  $\sim 25\,000\text{ cm}^{-1}$  including only  $^7\text{F}_J$  and  $^5\text{D}_{0,1,2,3}$ ). We have also performed fits to the level subsets of quintet and septet (plus  $^5\text{D}_{0,1}$ , which are unperturbed by the crystal field), allowing  $F$ ,  $B$  and  $\zeta_{SO}$  parameters alone to vary.

## 4. Discussion

### 4.1. The correlation crystal field

The inadequacies of a one-electron crystal field model have been realized for some time [19–22]. If the  $B_q^{(k)}$  parameters are chosen to match the splitting of one sub-set of states,

**Table 3.** Crystal field parameters for  $\text{Eu}^{3+}$  in  $\text{Cs}_2\text{NaEuCl}_6$ .

	This work	This work	This work	[3]
No of levels $N$	77	56	23	27
Fitting range	0–32 000 $\text{cm}^{-1}$	Quintets	Septets+ $^5\text{D}_{0,1}$	0–25 000 $\text{cm}^{-1}$
$B_0^{(4)}$	2206	2232	2282	2318
$B_0^{(6)}$	–305	–292	–346	–393

(Note  $B_0^{(4)} = 1.128B_0^4$  and  $B_0^{(6)} = -1.277B_0^6$ , for parameters  $B_0^k$  quoted in references [3] and [7].)

**Table 4.** Crystal field parameters for  $\text{Eu}^{3+}$  in  $\text{Cs}_2\text{NaYF}_6$ .

	This work	This work	This work	[7]
No of levels	57	44	15	19
Fitting range	0–32 000 $\text{cm}^{-1}$	Quintets	Septets+ $^5\text{D}_{0,1}$	0–25 000 $\text{cm}^{-1}$
$B_0^{(4)}$	3776	3896	3471	3540
$B_0^{(6)}$	–553	–515	–613	–488

they often give a poor description of other multiplets. For terbium(III) the maximum spin multiplicity components of the ground state are well modelled in isolation, but the quality of the fit deteriorates with the inclusion of states associated with higher energy terms [3, 23–26]. Each multiplet then experiences a different effective crystal field strength and the combined fit of all energy levels yields a weighted average value, about which systematic variations may be anticipated.

It is clear from tables 3 and 4 that crystal field parameter differences between our full data set parametrizations and those performed with smaller data sets are reasonably small. In the chloroelpasolite, however, the average crystal field experienced by the septet manifold is larger than that experienced by the quintet manifolds. Preliminary investigation shows that there is a small *decrease* in the crystal field parameters for the chloroelpasolite, both fourth and sixth order, in the quintet compared to the septet manifold.

This result is in contrast to those we obtain for Tb(III) [9] and Sm(III) [14] in chloroelpasolites, which show an average *increase* in effective crystal field parameters with lower spin multiplicity; that is, the one-electron crystal field *under-estimates* the average splitting in the states of next-to-maximum multiplicity in these two ions.

Early suggestions [19, 20] for a suitable physical origin for a correlated crystal field included a spin dependent effect ('the SCCF'):

$$H_{SCCF} = \sum_{i,q,k} b_q^{(k)} \mathbf{S} \cdot \mathbf{s}_i u_q^{(k)}(i) \quad (2)$$

SCCF parameters  $b_q^{(k)}$  take into account changes in the radial wavefunction of the  $i$ th 4f electron, according to its spin orientation  $s_i$  and the total spin  $S$ , in response to the difference in exchange energy. The importance of SCCF is measured by the parameters  $c_q^{(k)} = b_q^{(k)} / B_q^{(k)}$  such that:

$$H_{TOTAL} = H_{CF} + H_{SCCF} = \sum_{i,q,k} B_q^{(k)} u_q^{(k)}(i) (1 + \mathbf{S} \cdot \mathbf{s}_i c_q^{(k)}). \quad (3)$$

These parameters have been observed experimentally [1] to take values  $c_q^{(k)} \cong \pm 0.1$ , yet the expectation that the radial extent of the highest multiplicity wavefunction is the smallest should clearly lead to *negative* values of  $c_q^{(k)}$  [19, 22]. Experimentally, we observe (table 3) that the fractional changes in effective  $B_0^{(4)}$  and  $B_0^{(6)}$  on going from the septet ( $S = S_{MAX}$ ) to the quintet ( $S = S_{MAX} - 1$ ) manifold in the europium chloroelpasolite are –2% and –16% respectively.

In terms of effective crystal field parameters, we obtain from equation (3):

$$B_0^{(k)} \text{ effective}(S = S_{MAX} - 1) / B_0^{(k)} \text{ effective}(S = S_{MAX}) \simeq (1 - 0.5c_0^{(k)}) \quad (4)$$

from which we estimate *positive* effective SCCF parameters for Cs<sub>2</sub>NaEuCl<sub>6</sub>:

$$c_0^{(4)} = +0.04 \quad c_0^{(6)} = +0.3.$$

An alternative spin dependent ‘covalency’ effect has been suggested [22], whereby certain spin states of some lanthanides would be particularly susceptible to mixing of charge transfer transitions. Charge transfer mixing (ligand-to-metal) would be particularly favourable in the ground septet state of europium, reflecting the tendency of Eu<sup>3+</sup> to become Eu<sup>2+</sup> in its octet state. Intuitively, the radial extent of the f orbitals should be much larger in Eu(II) where the effective nuclear charge seen by an f electron is considerably reduced. Greater mixing of CT states in the septet compared to the quintet manifold would lead to the crystal field shrinking at higher energy. A contraction of the crystal field at lower spin multiplicity is evidenced by positive values of  $c_0^{(4)}$  and  $c_0^{(6)}$  for europium(III). The charge transfer (CT) or covalency mechanism has been shown [22] to act in a sense opposite to that of the SCCF mechanism. It has been shown [20] that this mechanism can be treated within the same parametrization scheme as the SCCF, and that all the effective parameters  $c_q^{(k)}$  indeed have opposite sign. The possibilities of ligand-to-metal CT effects in *excited* states of the lanthanides in the second half of the series, and of metal-to-ligand CT in Tb(III) have also been suggested [20, 22]; all these in principle contribute to the sign of effective SCCF parameters.

Our results from the fluoroelpasolite are ambiguous and reflect the uncertainty in the fit of the septet manifold alone for which only 13 states have been located. The apparent 12% *increase* in the fourth order CF parameter and 16% *decrease* in the sixth order parameter in the quintet state in table 4: ( $c_0^{(4)} = -0.2$ ,  $c_0^{(6)} = +0.3$ ) may reflect a balance in the opposing SCCF and CT contributions. The latter would be expected to be less dominant for the case of the fluoride where ligand-to-metal charge transfer is less extensive than in the chloroelpasolite.

Because of its dependence upon the total spin, the SCCF Hamiltonian contains both one-electron and two-electron contributions [21]. In principle, an apparent discontinuity [1] in the magnitude of the sixth-rank one-electron crystal field parameters at the half-filled shell can be reconciled on the basis of an interference between the one-electron operators, whose matrix elements change sign on going from  $f^N$  to  $f^{14-N}$ , and two-electron operators whose sign remains unchanged [21]. In practice, a spin-dependent correlation crystal field (SCCF) which merely increases with lower spin multiplicity would not physically explain the discontinuity in the crystal field parameters at the halfway point of the lanthanide series. An anomalously increased (CT mixed) crystal field in the septet state of europium would, however, account for large differences in the effective one-electron parameters between Eu(III) and Tb(III), particularly when applied to limited data sets [1].

#### 4.2. Rogue multiplets

In a number of lanthanides ‘rogue multiplets’ are found, for which the crystal field splitting is either far too large or small relative to that predicted by calculations that use one-electron operators. Some of these effects may be explicable in terms of spin dependent theories, but others far exceed the  $\pm 20\%$  changes that are typical for SCCF parametrization [27]. The anomalous spread (percentage deviation) of a multiplet is commonly quantified [28] by  $100(\sigma_{exp} - \sigma_{calc})/\sigma_{calc}$ , where  $\sigma$  is the standard deviation of the experimental or calculated levels about their respective barycentres.

In terbium(III) we have observed that <sup>5</sup>D is one such deviant manifold, showing greatly reduced CF splitting compared to a one-body model [9]. It is apparent, however, that in

europium(III) the  $^5D$  splittings exceed those predicted by the averaged CF parameters. In  $^5D_2$  and  $^5D_3$  of the chloroelpasolite, the spread of the levels exceeds that predicted by 51% and 79% respectively;  $^5D_2$  of the fluoroelpasolite is larger by 34%,  $^5D_3$  is incompletely defined. Interestingly, the expansion of  $^5D$  in Eu(III) and contraction in Tb(III) are multiplet specific effects that oppose the general trend occurring in the quintet states for these two ions.

The data together may thus be taken as evidence that the deviations in these multiplets have opposing directions in terbium(III) and europium(III). Such would be the predicted effect when two electron crystal field operators (the matrix elements of which remain the same sign in Tb and Eu) should have been included with the one-electron crystal field Hamiltonian (the matrix elements of which have opposite sign in Tb and Eu). The data indicate the importance of large correlation effects in the crystal field that are certainly not explicable by a simple spin dependent effect. This observation may also account in part for the apparent discontinuity in the magnitude of the sixth-rank one-electron crystal field parameters. The much reduced value in Tb(III) compared to Eu(III), would be the result of the observed  $^5D$  deviancy in the limited data sets previously used in the analysis of these two ions.

## 5. Conclusions

We have obtained extensive data for Eu(III) in cubic crystal fields in both chloro- and fluoroelpasolite lattices. The effect of the ligand on the crystal field splitting of a large number of multiplets, in an isostructural series, can now be directly compared with complementary data for Tb(III). Our data provide an opportunity to understand the influence of ligand properties and f electron number on correlation effects, and to determine the physical origin of various CCF operators. Charge transfer in the septet ground state of europium appears to be the dominant mechanism for the effective spin-dependent crystal field. Multiplet specific two-body effects of unidentified physical origin are also observed to occur in higher lying states.

Experimental data over a similar energy range in samarium(III)  $d^5$  are presented in this journal [14], and a full discussion of the spin (SCCF) and orbital (LCCF) dependence of the effective crystal field in the Sm, Eu and Tb (III) ions will be presented shortly [29].

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