

Home Search Collections Journals About Contact us My IOPscience

Two-photon spectroscopy of europium(III) elpasolites

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1999 J. Phys.: Condens. Matter 11 7851

(http://iopscience.iop.org/0953-8984/11/40/311)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 128.6.218.72 This content was downloaded on 24/08/2015 at 06:59

Please note that terms and conditions apply.

Two-photon spectroscopy of europium(III) elpasolites

J R G Thorne[†], M Jones[†], C S McCaw[†], K M Murdoch[†], R G Denning[†] and N M Khaidukov[‡]

† Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory,

South Parks Road, Oxford OX1 3QR, UK

‡ Russian Academy of Sciences, N S Kurnakov Institute of General and Inorganic Chemistry, 31 Leninskii Prospekt, 117907 Moscow, Russia

1 Lenniskii 110spekt, 117907 Wioseow, Russia

Received 24 June 1999, in final form 4 August 1999

Abstract. We present polarized two-photon excitation (TPE) spectra, including Zeeman data, for europium(III) in the elpasolites $Cs_2NaEuCl_6$ and $Cs_2NaYF_6:Eu^{3+}$. Approximately 80 and 60 levels of unambiguous symmetry have been assigned respectively in each compound up to 32 000 cm⁻¹ with the aid of a one-electron crystal field Hamiltonian. This represents the most complete and extensive data sets for Eu(III) f⁶ and Tb(III) f⁸. 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 (α , β , γ , T^i , i = 2, 3, 4, 6, 7, 8), spin–orbit coupling (ζ_{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:

$$H_{CF} = \sum_{i,q,k} B_q^{(k)} u_q^{(k)}(i)$$
(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 LaCl₃ (C_{3h} site) [4] and LaF₃ (C_2 site) [5], their analysis requires up to nine one-electron crystal field parameters.

0953-8984/99/407851+16\$30.00 © 1999 IOP Publishing Ltd



Figure 1. Energy level diagram for europium(III) and terbium(III) in zero field. The levels were calculated using the free ion parameters for $Cs_2NaEuCl_6$ in table 2 and those of [13] for $Cs_2NaTbCl_6$.

The ${}^{7}F_{J}$ and ${}^{5}D_{J}$ levels of europium(III) have been recently studied in Cs₂NaEuCl₆ [6] and Cs₂NaYF₆:Eu³⁺ [7] by single-photon spectroscopy, including parametrization using the same free ion and crystal field Hamiltonian as in this work, based on ~20 levels belonging to the ${}^{7}F_{J}$ and ${}^{5}D_{3,2,1,0}$ 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 Cs₂NaLnX₆ elpasolites with X = F, Cl and Br, we use two-photon excitation to identify the energies and symmetries for Ln = Eu, of a very much larger sequence of levels than has previously been compiled. Our analogous experimental results for Ln = Tb are to be found in [12] and [13], and for Ln = Sm in reference [14]. Other previous two-photon studies of rare-earth elpasolites have been limited to a small number of excited states in Cs₂NaGdCl₆ [15].



Figure 2. TPE spectra for (a) Cs₂NaEuCl₆ at 120 K and (b) Cs₂NaYF₆:Eu at 70 K for polarizations with $\alpha = 0^{\circ}$ and $\alpha = 45^{\circ}$.

2. Experiment

 $Cs_2NaY_{1-x}Eu_xF_6$ was synthesized by the reaction of aqueous solutions of CsF and NaF with mixtures of Eu_2O_3 and Y_2O_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 $Cs_2NaY_{0.8}Eu_{0.2}F_6$. Henceforth, we refer to this mixed Y/Eu material as Cs_2NaYF_6 : Eu^{3+} .



Figure 3. TPE spectra for (a) $Cs_2NaEuCl_6$ at 120 K and (b) Cs_2NaYF_6 :Eu at 70 K for polarizations with $\alpha = 0^{\circ}$ and $\alpha = 45^{\circ}$.

 $Cs_2NaEuCl_6$ 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 EuCl₃ was prepared from Eu₂O₃ using the ammonium chloride route [16] by vacuum decomposition of (NH₄)₂ [EuCl₅]. Any oxychloride present was converted to chloride



Figure 4. TPE spectra for (a) Cs₂NaEuCl₆ at 120 K and (b) Cs₂NaYF₆:Eu at 70 K for polarizations with $\alpha = 0^{\circ}$ and $\alpha = 45^{\circ}$.

by exposing the freshly made EuCl₃ to a stream of dry HCl gas at 450 °C for 36 hours. NaCl, CsCl and EuCl₃ powders in the appropriate ratio were mixed and transferred into an HF etched Bridgman tube. Cs₂NaEuCl₆ was prepared by growth at a temperature of 750–800 °C under a pressure of 7 atm Cl₂ which was employed to prevent the formation of divalent europium



Figure 5. TPE spectra for (a) Cs₂NaEuCl₆ at 120 K and (b) Cs₂NaYF₆:Eu at 70 K for polarizations with $\alpha = 0^{\circ}$ and $\alpha = 45^{\circ}$.

[17]. Transparent sections of the resulting boule were identified as $Cs_2NaEuCl_6$ 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 $Cs_2NaEuCl_6$ 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 Cs_2NaYF_6 lattice, the 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 cm⁻¹ (allowing non-resonant two-photon excitation (TPE) to states up to nearly $34\,000$ 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 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 ${}^{5}D_{1}$. The emission was corrected for variations in the laser intensity by referencing against the square of the laser energy, using a Molectron 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 ${}^{5}D_{0}$ and ${}^{5}D_{1}$ manifolds from which emission occurs to the ${}^{7}F_{J}$ crystal field levels. The observed ${}^{5}D_{1}$ emission decays with a lifetime of ~ 2 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 O_h. The ground state of Eu³⁺ in Cs₂NaLnX₆ has A₁ symmetry, from which single-colour two-photon transitions are allowed to A₁, E and T₂ excited states. Here we consider a beam propagating along [001], and define its polarization by the angle α of the electric vector with respect to [100]. When $\alpha = 0^{\circ}$, A₁ \rightarrow T₂ transitions are forbidden, while the intensity of A₁ \rightarrow E transitions is at a maximum. When $\alpha = 45^{\circ}$, the A₁ \rightarrow T₂ intensity is at a maximum, while the intensity of A₁ \rightarrow E transitions decreases by a factor of four. The intensity of A₁ \rightarrow A₁ transitions is independent of α .

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 7F_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. 7858

Table 1. Observed and calculated energy levels of Eu(III) in Cs_2NaLnX_6 (uncertain values are shown in parentheses: literature values [6, 7] are in italics).

		Cs ₂ NaEuCl ₆					Cs ₂ NaYF ₆ :Eu			
			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE
1	$^{7}F_{0}$	A_{1g}	0	-7	7	$^{7}F_{0}$	A_{1g}	0	-7	7
2	$^{7}F_{1}$	T_{1g}	360	359	1	$^{7}F_{1}$	T_{1g}	337	347	-10
3	$^{7}F_{2}$	E_g	875	864	11	$^{7}F_{2}$	E_g	807	774	33
4	${}^{7}F_{2}$	T_{2g}	1091	1093	-2	$^{7}F_{2}$	T_{2g}	1065	1075	-10
5	$^{7}F_{3}$	A_{2g}	1804	1804	0	${}^{7}F_{3}$	A_{2g}	1789	1768	21
6	${}^{7}F_{3}$	T_{2g}	1904	1912	$^{-8}$	$^{7}F_{3}$	T_{2g}	1953	1976	-23
7	$^{7}F_{3}$	T_{1g}	1963	1966	-3	$^{7}F_{3}$	T_{1g}	2014	2027	-13
8	${}^{\prime}F_4$	T_{2g}	2665	2674	-9	${}^{\prime}F_4$	T_{2g}	2670	2642	28
9	${}^{\prime}F_4$	E_g	2975	2971	4	$^{\prime}F_{4}$	E_g	3041	3033	8
10	′F4	T_{1g}	3007	3016	-9	'F4	T_{1g}	3151	3170	-19
11	7F4	A_{1g}	3034	3054	-20	7F4	A_{1g}	3205	3238	-33
12	7 F5	T_{1g}	3811	3817	-6	7F5	T_{2g}	2021	3781	27
13	7 F5	E_g	3851	3850	1	7F5	T_{1g}	3821	3848	-27
14	7F5 7E	T_{2g}	38/0	3867	9	7F5 7F	E_g	(3911)	3872	39
15	7F5 7E	Γ_{1g}	4149	4119	30	7 F5 7 F	I_{1g}	4335	4296	39
10	7E	Eg T	4833	4855	-20	7E	Eg T	(4818)	4817	1
17	г ₆ 7г	1 2g	4009	4004	-15	7E	1 2g		4004	
10	г ₆ 7г.	A_{2g}	4945 5242	4940 5216	-5	г ₆ 7г.	A_{2g} T.		4943 5451	
20	7E	12g T.	5254	5250	20	7E	12g T.		5497	
20	г ₆ 7 _{Ес}	Δ_1	5283	5250	4	7 _E	Δ_1		5513	
21	10	Π1g	5205	5217	-	1.0	Alg		5515	
22	${}^{5}D_{0}$	A_{1g}	17 208	17 205	3	${}^{5}D_{0}$	A_{1g}	17 255	17 257	-2
23	${}^{5}D_{1}$	T_{1g}	18961	18972	-11	⁵ D ₁	T_{1g}	19 000	19004	-4
24	${}^{5}D_{2}$	T_{2g}	21 385	21 396	-11	${}^{5}D_{2}$	T_{2g}	21 389	21 406	-17
25	${}^{5}D_{2}$	E_g	21 495	21 469	26	${}^{5}D_{2}$	\mathbf{E}_{g}	21 568	21 540	28
26	⁵ D ₃	T_{1g}	24 261	24 282	-21	$^{5}D_{3}$	T_{1g}	24 274	24 283	-9
27	⁵ D ₃	T_{2g}	24 292	24 297	-5	⁵ D ₃	T_{2g}	(24 281)	24314	-33
28	°D3	A_{2g}	24 370	24 343	27	$^{2}D_{3}$	A_{2g}		24 392	
29	⁵ L ₆	A_{1g}	24 761	24 747	14	⁵ L ₆	A_{1g}	24 557	24 554	3
30	⁵ L ₆	T_{1g}	24 831	24 816	15	⁵ L ₆	T_{1g}		24 658	
31	⁵ L ₆	T_{2g}	24 905	24 899	6	⁵ L ₆	T_{2g}	24 802	24787	15
32	⁵ L ₆	A_{2g}	25 121	25 118	3	⁵ L ₆	A_{2g}		25 085	-
33	⁵ L ₆	T_{2g}	25 302	25 322	-20	⁵ L ₆	T_{2g}	25 453	25 446	10
34	⁵ L ₆	E_g	25 345	25377	-28	⁵ L ₆	E_g	25 500	25518	-18
35	³ L ₇	T_{1g}	25 893	25 886	7	³ L ₇	T_{1g}		25759	
36	°L7	E_g	25 926	25 914	12	°L7	E_g	25 855	25 862	-7
37	⁵ L ₇	T_{2g}	25 987	25 980	7	⁵ L ₇	T_{2g}	25 897	25 904	-7
38	⁵ L ₇	A_{2g}	26 099	26119	-20	${}^{5}G_{3}$	T_{1g}		26121	
39	$^{5}G_{2}$	E_g	26 162	26 1 52	10	$^{5}G_{2}$	E_g	26 190	26180	10
40	$^{5}G_{2}$	T_{2g}	26175	26183	$^{-8}$	⁵ L ₇	A_{2g}		26204	
41	⁵ G ₃	T_{1g}	26216	26 208	8	⁵ G ₃	T_{2g}	26 204	26206	-2
42	⁵ L ₇	T ₂₉	26 240	26231	9	${}^{5}G_{2}$	T _{2g}	26256	26273	-17
43	⁵ G ₃	-s T2,	26338	26352	-14	⁵ G₄	-s E.	26 295	26312	-17
44	⁵ G ₄	E _a	26339	26355	-16	⁵ G4	8 A1a	26344	26,338	6
45	5 ₁ -	g T.	26345	26344	1	5G.	т.		26344	5
46 16	5G	1 1 g	20 343	26 / 10	14	5G	1 1g T-	26256	20 344	26
40	U 4	A_{1g}	20424	20410	14	U ₆	1 2g	20 330	20 382	-20

Table 1. (Continued)

	Cs ₂ NaEuCl ₆					Cs ₂ NaYF ₆ :Eu				
			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE
47	⁵ G ₆	T_{2g}		26410		⁵ L ₇	T_{1g}		26408	
48	⁵ G ₃	A_{2g}		26419		⁵ L ₇	T_{2g}	26429	26424	5
49	${}^{5}G_{5}$	T_{1g}		26420		${}^{5}G_{6}$	T_{1g}		26478	
50	${}^{5}G_{6}$	T_{1g}	26470	26470	0	${}^{5}G_{6}$	E_g	26518	26527	-9
51	${}^{5}G_{6}$	E_g	26 503	26 513	-10	${}^{5}G_{3}$	A_{2g}		26538	
52	${}^{5}G_{6}$	T_{2g}	26 527	26 532	-5	${}^{5}G_{6}$	T_{2g}	26579	26618	-38
53	${}^{5}G_{6}$	A_{2g}		26 573		${}^{5}G_{6}$	A_{1g}	26723	26688	35
54	${}^{5}G_{4}$	T_{2g}	26616	26616	0	⁵ L ₈	T_{2g}		26713	
55	${}^{5}G_{6}$	A_{1g}	26 645	26 629	16	${}^{5}G_{5}$	E_g		26745	
56	${}^{5}G_{5}$	E_g		26 665		${}^{5}G_{6}$	A_{2g}		26752	
57	${}^{5}G_{4}$	T_{1g}		26 689		${}^{5}G_{5}$	T_{1g}		26760	
58	${}^{5}G_{5}$	T_{1g}		26 701		${}^{5}G_{4}$	T_{2g}	26856	26823	33
59	${}^{5}G_{5}$	T_{2g}	26762	26719	42	⁵ L ₈	T_{1g}		26832	
60	⁵ L ₈	T_{2g}	26 854	26 861	-7	⁵ L ₈	\mathbf{E}_{g}	26879	26890	-11
61	⁵ L ₈	E_g	26 869	26 879	-10	${}^{5}G_{5}$	T_{2g}	27 031	26988	43
62	⁵ L ₈	T_{1g}		26 966		${}^{5}G_{5}$	T_{1g}		27 1 30	
63	⁵ L ₈	T_{2g}		27 175		⁵ L9	T_{2g}		27 366	
64	⁵ L ₈	E_g		27 294		⁵ L9	A_{1g}	27 393	27 394	-1
65	⁵ L ₈	T_{1g}	27 306	27 299	7	⁵ L9	A_{2g}		27 395	
66	⁵ L ₈	A_{1g}	27 312	27 306	6	⁵ L9	T_{1g}		27 416	
67	$^{5}D_{4}$	T_{1g}	27 501	27 507	-6	${}^{5}D_{4}$	E_g	27 510	27 518	-8
68	$^{5}D_{4}$	A_{1g}	27 502	27 508	-6	$^{5}D_{4}$	T_{2g}	27 526	27 525	1
69	$^{5}D_{4}$	E_g	27 509	27 513	-4	$^{5}D_{4}$	T_{1g}		27 586	
70	⁵ L ₉	A_{2g}		27 515		${}^{5}D_{4}$	A_{1g}		27 590	
71	⁵ L ₉	T_{2g}	27 535	27 525	10	⁵ L ₈	E_g	27 604	27 609	-5
72	${}^{5}D_{4}$	T_{2g}	27 574	27 568	6	⁵ L ₈	T_{2g}	27 618	27 605	13
73	⁵ L9	T_{1g}		27 614		⁵ L ₈	T_{1g}		27730	
74	⁵ L9	A_{1g}		27 692		${}^{5}L_{10}$	T_{2g}	27 832	27 824	8
75	⁵ L9	T_{1g}		27 894		${}^{5}L_{10}$	E_g	27 843	27 843	0
76	⁵ L9	E_g	27 900	27 897	3	⁵ L ₈	A_{1g}		27 889	
77	${}^{5}L_{10}$	T_{2g}	27 959	27 964	-5	${}^{5}L_{10}$	T_{1g}		27 896	
78	⁵ L9	T_{1g}		28 008		⁵ L9	T_{1g}		28 185	
79	${}^{5}L_{10}$	E_g	28 0 4 4	28 0 50	-6	⁵ L9	E_g		28 284	
80	⁵ L9	T_{2g}		28 062		⁵ L9	T_{2g}	28 301	28313	-12
81	⁵ L ₁₀	T_{1g}		28 146		⁵ L9	T_{1g}		28416	
82	⁵ L ₁₀	A_{1g}	28 356	28 3 38	18	⁵ L ₁₀	A_{1g}		28 5 4 1	
83	⁵ L ₁₀	T_{1g}		28 4 38		⁵ L ₁₀	T_{1g}		28731	
84	⁵ L ₁₀	T_{2g}		28 493		⁵ L ₁₀	T_{2g}		28811	
85	⁵ L ₁₀	A_{2g}		28 697		⁵ L ₁₀	A_{2g}		29 047	
86	${}^{5}L_{10}$	T_{2g}	28 706	28715	-9	⁵ L ₁₀	T_{2g}		29 082	
87	⁵ L ₁₀	Eg	28713	28 7 22	-9	⁵ L ₁₀	Eg		29 094	
88	⁵ H ₃	T_{1g}		30 556		⁵ H ₃	T_{1g}		30 5 17	
89	$^{5}\mathrm{H}_{7}$	T_{1g}		30 629		⁵ H ₇	T_{1g}		30 600	
90	$^{5}\mathrm{H}_{7}$	T_{2g}	30 676	30 664	12	$^{5}\mathrm{H}_{7}$	T_{2g}	30 654	30 641	13
91	$^{5}\mathrm{H}_{3}$	T_{2g}	30 690	30 692	-2	$^{5}\mathrm{H}_{3}$	T_{2g}	30724	30722	2
92	$^{5}H_{7}$	A29		30 804		$^{5}H_{7}$	A29		30 809	
93	$^{5}\mathrm{H}_{7}$	T_{2g}		30 970		$^{5}H_{4}$	A_{1g}	30 949	30962	-13
		-0					-0			

Tal	ble	1.	(Continued)	
-----	-----	----	-------------	--

	Cs2NaEuCl6				Cs ₂ NaYF ₆ :Eu					
			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE			Energy (cm ⁻¹)	Calc. E (cm ⁻¹)	ΔE
94	⁵ H ₃	A _{2g}		30977		${}^{5}H_{4}$	Eg	30 994	30 985	9
95	${}^{5}H_{4}$	A_{1g}	31 004	30996	8	${}^{5}H_{4}$	T _{1g}		31 0 39	
96	$^{5}\mathrm{H}_{7}$	E_g	(31 004)	31017	-13	$^{5}H_{6}$	T_{2g}	31 081	31 086	-5
97	$^{5}\mathrm{H}_{4}$	E_g		31 0 4 1		$^{5}\mathrm{H}_{5}$	T_{1g}		31 096	
98	$^{5}\mathrm{H}_{4}$	T_{1g}		31 0 45		$^{5}H_{6}$	E_g	31110	31 106	4
99	$^{5}\mathrm{H}_{7}$	T_{1g}	(31 066)	31 064	2	$^{5}\mathrm{H}_{5}$	T_{2g}	31160	31 184	-24
100	$^{5}\mathrm{H}_{6}$	T_{2g}	31 148	31 172	-24	$^{5}\mathrm{H}_{3}$	A_{2g}		31 260	
101	$^{5}\mathrm{H}_{6}$	E_g	31 215	31 232	-17	$^{5}\mathrm{H}_{7}$	E_g	31 4 39	31 4 56	-17
102	${}^{5}\mathrm{H}_{5}$	T_{2g}	31 257	31 259	$^{-2}$	$^{5}\mathrm{H}_{7}$	T_{2g}	31 447	31 44 1	6
103	${}^{5}\mathrm{H}_{5}$	T_{1g}		31 274		$^{5}H_{6}$	A_{2g}		31 499	
104	$^{5}\mathrm{H}_{6}$	A_{2g}		31 329		$^{5}\mathrm{H}_{7}$	T_{1g}		31 561	
105	$^{5}\mathrm{H}_{4}$	T_{2g}	31 327	31 338	-11	$^{5}\mathrm{H}_{4}$	T_{2g}	31 567	31 569	$^{-2}$
106	$^{5}H_{6}$	T_{1g}		31 514		$^{5}H_{5}$	T_{1g}		31724	
107	${}^{5}\mathrm{H}_{5}$	E_g	31 541	31 533	8	$^{5}H_{6}$	A_{1g}	(31748)	31758	-10
108	$^{5}\mathrm{H}_{6}$	T_{2g}	31 543	31 531	12	$^{5}H_{6}$	T_{2g}	31784	31774	10
109	$^{5}\mathrm{H}_{6}$	A_{1g}	31 581	31 541	40	$^{5}H_{5}$	E_g	31 795	31775	20
110	$^{5}\mathrm{H}_{5}$	T_{1g}		31 552		${}^{5}\mathrm{H}_{6}$	T_{1g}		31786	
111	$^{5}\mathrm{F}_{2}$	\mathbf{E}_{g}		33 520		$^{5}\mathrm{F}_{2}$	\mathbf{E}_{g}		32771	

TPE spectra from 21 000 to 32 000 cm⁻¹ are shown in figures 2–5. Two polarizations with $\alpha = 0^{\circ}$ and 45° 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°) 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 T₂ symmetry and level 25 E symmetry. There are, for example, unpolarized transitions to level 29 in both spectra, which must therefore have A₁ 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⁻¹ 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_1 and A_2 symmetry is possible in two ways. At elevated temperature, thermal population of the ${}^7F_1 T_1$ level allows transitions to levels of A_2 and T_1 symmetry. The larger 360 cm⁻¹ 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 Cs₂NaEuCl₆ 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



7861

Figure 6. Cs₂NaEuCl₆ 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 $Cs_2NaEuCl_6$ from [6] and $Cs_2NaEu_{0.2}Y_{0.8}F_6$ [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 7F_5 T₂ level at 3881 cm⁻¹, which deviates 100 cm⁻¹ from our final fit.

Parameter	Cs ₂ NaEuCl ₆	Cs ₂ NaYF ₆ :Eu ³⁺
$\overline{E_{av}}$	66 407	62 304
F^2	94 613	86460
F^4	87 348	62 286
F^6	51 081	29 844
α	62.5	16.5
β	-882	-3785
γ	-4368	4450
ζ_{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
σ	15.9	21.7
Ν	77	57

Table 2. Energy level parameters (cm⁻¹) for Eu³⁺ in Cs₂NaLnX₆. $M^2 = 0.560M^0$, $M^4 = 0.310M^0$; $P^4 = 0.750P^2$, $P^6 = 0.10P^2$.

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 σ . The free ion parameters, used to produce figure 1, indicate considerable configuration mixing, particularly for the 'twinned' levels of ⁵G and ⁵H, in europium(III) relative to terbium(III).

The low energy states $(1-34, {^7}F_{0-6}, {^5}D_{0-3}, {^5}L_6)$ 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 $(35-87, {^5}L_{7-10}, {^5}G_{2-6}, {^5}D_4)$ 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 ⁵H 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 ⁵H at 32 000 cm⁻¹) with a previous parametrization using the levels obtained from single-photon studies (up to ~25 000 cm⁻¹ including only ⁷F_J and ⁵D_{0,1,2,3}). We have also performed fits to the level subsets of quintet and septet (plus ⁵D_{0,1}, which are unperturbed by the crystal field), allowing *F*, *B* and ζ_{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 $B_a^{(k)}$ parameters are chosen to match the splitting of one sub-set of states,

	This work	This work	This work	[3]
No of levels N	77	56	23	27
Fitting range	$0-32000~{\rm cm}^{-1}$	Quintets	Septets+5D0,1	$0-25000~{\rm cm}^{-1}$
$B_0^{(4)}$	2206	2232	2282	2318
$B_0^{(6)}$	-305	-292	-346	-393

Table 3. Crystal field parameters for Eu³⁺ in Cs₂NaEuCl₆.

(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 Eu^{3+} in Cs_2NaYF_6 .

	This work	This work	This work	[7]
No of levels	57	44	15	19
Fitting range	$0-32000~{\rm cm}^{-1}$	Quintets	Septets+ ${}^{5}D_{0,1}$	$0-25000~{\rm cm}^{-1}$
$B_0^{(4)}$	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'):

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

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:

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

7864 J R G Thorne et al

 $c_{0}^{(4)}$

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

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

from which we estimate *positive* effective SCCF parameters for $Cs_2NaEuCl_6$:

$$c_0^{(6)} = +0.04$$
 $c_0^{(6)} = +0.3$

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^{3+} to become Eu^{2+} 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 oneelectron 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 σ is the standard deviation of the experimental or calculated levels about their respective barycentres.

In terbium(III) we have observed that ⁵D 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 ⁵D₂ and ⁵D₃ of the chloroelpasolite, the spread of the levels exceeds that predicted by 51% and 79% respectively; ⁵D₂ of the fluoroelpasolite is larger by 34%, ⁵D₃ 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].

Acknowledgments

We thank the EPSRC for financial support, and the Rutherford Appleton Laboratory for the use of a dye laser through the laser loan scheme. We also thank M F Reid for allowing us to use his F-Shell program.

References

- [1] Reid M F and Richardson F S 1985 J. Chem. Phys. 83 3831
- [2] Crosswhite H M and Crosswhite H 1984 J. Opt. Soc. Am. B 1 246
- [3] Tanner P A, Ravi Kanth Kumar V V, Jayasankar C K and Reid M F 1994 J. Alloys Compounds 215 349
- [4] Dieke G H 1968 Spectra and Energy Levels of Rare Earth Ions in Crystals (New York: Wiley)
- [5] Carnall W T, Goodman G L, Rajnak K and Rana R S 1989 J. Chem. Phys. 90 3443
- [6] Tanner P A and Liu Y 1994 J. Alloys Compounds 204 93
- [7] Tanner P A, Liu Y, Edelstein N M, Murdoch K M and Khaidukov N M 1997 J. Phys.: Condens. Matter 9 7817
- [8] Denning R G 1991 Eur. J. Solid State Inorg. Chem. 28 33
- [9] Berry A J, McCaw C S, Morrison I D and Denning R G 1996 J. Lumin. 66/67 272
- [10] Berry A J, Denning R G and Morrison I D 1997 Chem. Phys. Lett. 266 195
- [11] Berry A J, Denning R G and Morrison I D 1997 J. Chem. Phys. 106 8967
- [12] Berry A J, Morrison I D and Denning R G 1998 Mol. Phys. 93 1

7866 J R G Thorne et al

- [13] Morrison I D, Berry A J and Denning R G 1999 Mol. Phys. 96 43
- [14] Thorne J R G, Karunathilake A, Choi H, Denning R G and Luxbacher T 1999 J. Phys.: Condens. Matter 11 7867–79
- [15] Kundu L, Banerjee A K and Chowdhury M 1991 Chem. Phys. Lett. 181 569
- [16] Meyer G 1982 Mater. Res. Bull. 17 1447
- [17] Mroczkowski S 1970 J. Cryst. Growth 6 147
- [18] Haley L V and Koningstein J A 1976 J. Raman Spectrosc. 5 305
- [19] Judd B R 1977 Phys. Rev. Lett. 39 242
- [20] Newman D J, Siu G G and Fung W Y P 1982 J. Phys. C: Solid State Phys. 15 3113
- [21] Reid M F 1987 J. Chem. Phys. 87 2875
- [22] Judd B R 1980 J. Phys. C: Solid State Phys. 13 2695
- [23] Thomas K S, Singh S and Dieke G H 1963 J. Chem. Phys. 38 2180
- [24] Richardson F S, Reid M F, Dallara H F and Smith R D 1985 J. Chem. Phys. 83 3813
- [25] Faucher M, Garcia D, Caro P, Derouet J and Porcher P 1989 J. Physique 50 219
- [26] Crosswhite H M, Crosswhite H, Edelstein N and Rajnak K 1977 J. Chem. Phys. 67 3002
- [27] Denning R G, Berry A J and McCaw C S 1998 Phys. Rev. B 57 R2021
- [28] Leavitt R P 1982 J. Chem. Phys. 77 1661
- [29] Thorne J R G, McCaw C S and Denning R G in preparation