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# Vacuum ultraviolet excitation spectra of lanthanide-doped hexafluoroelpasolites

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## Abstract

Vacuum ultraviolet excitation spectra at  $\sim 10$  K have been recorded for  $4f^N \rightarrow 4f^{N-1}5d$  transitions of  $\text{Cs}_2\text{NaYF}_6:\text{Ln}^{3+}$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Ho}, \text{Er}, \text{Tm}$ ). In these high bandgap hosts the lanthanide ions occupy octahedral symmetry sites. The spectra comprise broad, structured bands and in most cases the individual vibronic structure is not resolved. Simulations of the relative intensities and band positions in the spectra have been made by using parameter values from previous studies and/or by employing values from similar systems or estimating trends across the lanthanide series, without data fitting or parameter adjustments. The agreement with experimental results is reasonable except where the luminescent state being monitored is not efficiently populated nonradiatively from the  $4f^{N-1}5d$  state, or where additional bands are present. The latter are readily assigned to charge transfer transitions or the near-excitonic band. Comparison of the spectra has been made with those of other high symmetry lanthanide ion systems.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Most of the tri-positive lanthanide ions,  $\text{Ln}^{3+}$ , possess  $4f^N-4f^{N-1}5d$  electronic transitions in the ultraviolet and vacuum ultraviolet (VUV) spectral regions. Due to their applications for ultraviolet lasers [1–5], scintillators [6–8], quantum cutters [9–14] and vacuum ultraviolet [15, 16] or x-ray [17] phosphors, their  $4f^{N-1}5d-4f^N$  emission spectra have recently attracted much attention. The greater availability of synchrotron radiation has spurred renewed theoretical interest not only in the extension of the theoretical model developed for the  $4f^N$  configuration to the  $4f^{N-1}5d$  configuration [18–21], but also in more fundamental areas such as the first-principles analysis method [22, 23] and spin density functional procedure [24]. Fluoride hosts possess high bandgap energies ( $>10$  eV) and therefore permit the study of not only higher  $4f^N$  energy levels [25–30] but also the  $4f^{N-1}5d$  energy levels by absorption and excitation spectroscopy, although the former

technique has seldom been employed for technical reasons. Hence there have been many previous studies of the  $4f^{N-1}5d-4f^N$  emission and excitation spectra of  $\text{Ln}^{3+}$  doped into transparent fluoride hosts. Some of the early studies of rare earth ions doped into alkaline earth fluorides have been mentioned by Wegh *et al* [31]. Considering publications within mainly the last decade, the most popular host has been  $\text{LiYF}_4$ , which possesses  $S_4$  site symmetry for the guest  $\text{Ln}^{3+}$  at a single site and it has been doped with  $\text{Ln} = \text{Ce}$  [18, 32–38], Pr [18, 33, 35, 36, 38], Nd [3, 18, 33–36, 38–43], Sm [33], Eu [33], Gd [14, 44, 45], Tb [19, 46, 47], Dy [19, 34, 46], Ho [19, 46], Er [8, 18, 19, 31, 34, 35, 38, 42, 44, 46–50], Tm [8, 18, 19, 34, 35, 38, 46, 47, 51], Yb [19] and Lu [45, 51] for VUV investigations. Some other hosts employed with tri-positive lanthanide ions have been cubic  $\text{CaF}_2$  doped with Pr [33, 52–54], Nd [33], Sm [33], Gd [55, 56], Tb [47], Er [47], Tm [47, 53] and Lu [56] and  $\text{SrF}_2$  doped with Nd [57], Sm, Tb, Er and Tm [58–60], but for which different

rare earth sites may be present; YF<sub>3</sub> doped with Pr [61], Gd [45]; neat GdF<sub>3</sub> [44, 45, 62]; LaF<sub>3</sub> doped with Pr [61]; neat LuF<sub>3</sub> [45, 51, 62] and LuF<sub>3</sub> doped with Ce [32]; KMgF<sub>3</sub> doped with Ce [63], Pr [64]; NaYF<sub>4</sub>:Nd [43]; KYF<sub>4</sub> doped with Pr [65], Nd [66], Er [66, 67] and Tm [66, 67]; MGdF<sub>4</sub> (M = Na, K, NH<sub>4</sub>) doped with Nd [68], Eu [69] and Tm [68]; LiGdF<sub>4</sub> [44, 45, 62] doped with Ce [44] and Eu [13]; LiLuF<sub>4</sub> [45, 62] doped with Ce [32], Pr [61, 70, 71], Nd [3, 39] and Tb [72]; K<sub>2</sub>YF<sub>5</sub> doped with Pr [65]; KY<sub>3</sub>F<sub>10</sub> doped with Pr [53, 61], Nd [3] and Tm [53]; CsY<sub>2</sub>F<sub>7</sub> doped with Pr [65] and Er [67]; CsGd<sub>2</sub>F<sub>7</sub> doped with Pr [65], Tm [67] and Er [67]; LiKYF<sub>5</sub>:Pr [65]; LiKGdF<sub>5</sub> doped with Er [73] and Tm [73]; LiCaAlF<sub>6</sub> doped with Ce [37, 74], Nd [75], Eu [76] and Tm [44, 77]; LiSrAlF<sub>6</sub> doped with Eu [76] and Tm [78]; BaY<sub>2</sub>F<sub>8</sub> doped with Nd [3, 39] and Er [79]; BaSiF<sub>6</sub>:Pr [80]; K<sub>3</sub>YF<sub>6</sub>:Nd [81] and CaNaYF<sub>6</sub>:Ce [82]. Some of the important results from these experiments with fluoride hosts are briefly presented.

The interconfigurational spectra of Ln<sup>3+</sup> are electric-dipole-allowed transitions and comprise broad bands with some superimposed sharp lines at low, and also in some cases at higher, energy. The broad structure arises not only from the superposition of pure electronic transitions but also from the presence of vibrational progressions due to the contraction in bond distance in the 4f<sup>N-1</sup>5d configuration [83]. The real phonon spectrum of the host lattice, rather than displaced Gaussian curves [19, 36], has been employed in the simulations of low temperature absorption spectra of several systems [21, 45]. The reappearance of fine structure for high energy bands in the 4f<sup>N</sup>-4f<sup>N-1</sup>5d excitation spectra provided the realization that the 4f<sup>N-1</sup> core and the 5d electron are not strongly coupled [47]. Such high energy structure is associated with electronic transitions where the d electron is in the lower energy level and the 4f<sup>N-1</sup> core is highly excited. It was found that the barycenter of 4f<sup>N-1</sup>5d absorption shifts to higher energy when the initial 4f<sup>N</sup> energy level is at higher energy [40, 41]. This effect was attributed to a 'partial memory' of the initial 4f<sup>N</sup> state.

The theoretical model for the 4f<sup>N</sup> configuration has been extended for 4f<sup>N-1</sup>5d to take into account atomic interactions: the direct and exchange Slater parameters for the Coulomb interaction between the 4f and 5d electrons, and the spin-orbit interaction and the crystal field interaction of the 5d electron [21, 33-36, 41]. The approximations made include the neglect of odd-parity crystal field parameters and, in the case of LiYF<sub>4</sub>, the assumption of higher (D<sub>2d</sub>) site symmetry of Ln<sup>3+</sup>. With the inclusion of the additional interactions into the usual 4f<sup>N-1</sup> model Hamiltonian, simulations of energies and intensities of 4f<sup>N-1</sup>5d-4f<sup>N</sup> emission and excitation spectra have been performed [18, 19, 33-36]. In these calculations, the fd Slater atomic parameters calculated from Cowan's code need to be considerably reduced due to the nephelauxetic effect. Also, the f-electron Slater and spin-orbit coupling parameters are slightly greater for the 4f<sup>N-1</sup>5d configuration than for 4f<sup>N</sup>. The electric dipole matrix element for the spin-allowed transition was found to decrease considerably from Ce<sup>3+</sup> to Tm<sup>3+</sup> [34], due to decreased overlap between the 4f<sup>N-1</sup> core and the delocalized 5d electron. The ions in the

second half of the lanthanide series show both spin-forbidden and spin-allowed transitions, with very different lifetimes [31] and with the energy splitting between the low-spin and high-spin 4f<sup>N-1</sup>5d-4f<sup>N</sup> bands decreasing from Tb<sup>3+</sup> to Tm<sup>3+</sup> due to decreasing exchange interaction with increasing nuclear charge [34]. The trends in energy parameters across the lanthanide series have been reviewed [84]. On collecting the relevant 4f<sup>N</sup> and 5d electron parameters for LiYF<sub>4</sub>:Ln<sup>3+</sup> from several publications [18, 19, 33, 35] it is interesting to observe their variation across the series. Although the magnitude of F<sup>2</sup>(fd) (or F<sup>4</sup>(fd)) was listed as similar for the ions Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup> and Tm<sup>3+</sup>, the value was rather different for the three ions Nd<sup>3+</sup>, Sm<sup>3+</sup> and Eu<sup>3+</sup>, as well as for Pr<sup>3+</sup>. The same comment applies to G<sup>1</sup>(fd), G<sup>3</sup>(fd) and G<sup>5</sup>(fd). In contrast, the spin-orbit coupling constant for the d electron showed a monotonic increase across the series from Ce<sup>3+</sup> to Tm<sup>3+</sup>. The fitted 5d crystal field parameters were found to have the same signs as the 4f parameters but were about 20 times larger because of the greater radial extension of 5d orbitals, as compared with 4f [36]. The second rank crystal field parameter B<sub>0</sub><sup>2</sup>(d) and the fourth rank parameter B<sub>0</sub><sup>4</sup>(d) did not show a smooth change across the lanthanide series, although overall the former decreased from Ce<sup>3+</sup> to Tm<sup>3+</sup> whereas the latter increased. The decreasing crystal field strength for the heavier rare earths was attributed to the lanthanide contraction [19]. Empirical rationalizations, generalizations and correlations of 5d level energies with respect to those of Ce<sup>3+</sup> and the host crystal conduction band have been made by Dorenbos and co-workers and are summarized elsewhere [85].

The present study aims to further test the computational model employed for the calculations of 4f<sup>N-1</sup>5d energy levels and 4f<sup>N</sup>-4f<sup>N-1</sup>5d transition intensities by studying the spectra of Ln<sup>3+</sup> with rather different coordination geometry in cubic hexafluoroelpasolite systems. Indeed the test is rigorous because, due to the O<sub>h</sub> site symmetry of Ln<sup>3+</sup> at the unique site [86], only two 4f<sup>N</sup> and one 5d crystal field parameters are employed in the calculations, compared with five and three, respectively, for the LiYF<sub>4</sub> host. Due to energy level degeneracies of up to fourfold, and restrictive O<sub>h</sub> point group selection rules, the interconfigurational spectra were expected to be simpler than for lower symmetry hosts such as LiYF<sub>4</sub>, although this was not found to be so in most cases. Furthermore, the high bandgap energy and the chemical inertness of the hexafluoroelpasolite systems make these systems attractive for the study of higher electronic configurations.

The magnetic properties [87], vibrational spectra [88] and intraconfigurational 4f<sup>N</sup>-4f<sup>N</sup> spectra of Nd<sup>3+</sup> [89], Eu<sup>3+</sup> [90, 91], Tb<sup>3+</sup> [92], Er<sup>3+</sup> [93], Tm<sup>3+</sup> [94] and Yb<sup>3+</sup> [95, 96] in lanthanide hexafluoroelpasolite systems have previously received attention. Some investigations of the 4f<sup>N-1</sup>5d-4f<sup>N</sup> spectra and/or VUV spectra of Cs<sub>2</sub>NaLnF<sub>6</sub> and Cs<sub>2</sub>NaYF<sub>6</sub>:Ln<sup>3+</sup> systems have previously been published. The results for hexafluoroelpasolite hosts doped with Ce<sup>3+</sup> and Pr<sup>3+</sup> are problematic because for these large cations there are several phases present in Ce<sup>3+</sup>-doped Rb<sub>2</sub>NaYF<sub>6</sub> [17, 97-99] and Ce<sup>3+</sup> occupies several sites in the crystal of Rb<sub>2</sub>KInF<sub>6</sub> [3, 99], as does Pr<sup>3+</sup> in Cs<sub>2</sub>KYF<sub>6</sub> [100].

The ion  $\text{Tb}^{3+}$  exhibits  $4f^8-4f^75d$  excitation bands above  $\sim 37\,000\text{ cm}^{-1}$  in the  $\text{Rb}_2\text{KInF}_6$  host (which undergoes a phase transition at low temperature so that the  $\text{Tb}^{3+}$  site symmetry is lowered to  $C_{2v}$  [3, 101]) although a spectral interpretation was not given [3, 99]. The  $4f^N-4f^{N-1}5d$  spectra of  $\text{Nd}^{3+}$  [89],  $\text{Er}^{3+}$  [102] and  $\text{Tm}^{3+}$  [102, 103] in the  $\text{Cs}_2\text{NaYF}_6$  host have been previously reported and are subsequently referred to with respect to the spectra obtained herein.

## 2. Experiment

### 2.1. Synthesis of the hexafluoroelpasolites

The  $\text{Cs}_2\text{NaYF}_6$  single crystals doped with  $\text{Nd}^{3+}$  (nominal concentration 1.0 at.%—hereafter abbreviated to 1.0%),  $\text{Sm}^{3+}$  (3%),  $\text{Eu}^{3+}$  (0.3%),  $\text{Gd}^{3+}$  (6.0, 30.0 and 50.0%),  $\text{Tb}^{3+}$  (1.0%),  $\text{Ho}^{3+}$  (10.0%),  $\text{Er}^{3+}$  (10%) and  $\text{Tm}^{3+}$  (1%) were synthesized under hydrothermal conditions [90]. The crystallographic details for the cubic host lattices are available [86].

### 2.2. Spectral measurements

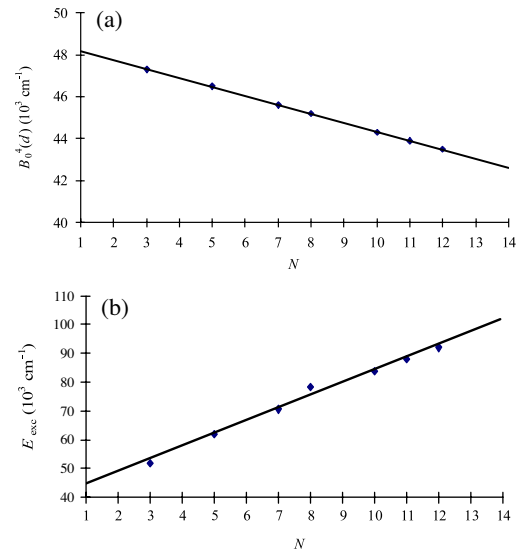
The measurements were performed at the SUPERLUMI station [104] of HASYLAB at DESY, using synchrotron radiation from the DORIS storage ring for excitation in the spectral range 70–280 nm. The excitation spectra were recorded with an instrumental resolution of  $\sim 0.3$  nm. The wavelength positions of all features in excitation spectra were determined with an accuracy better than 0.05 nm. A 0.3 m Czerny–Turner monochromator-spectrograph SpectraPro-308i (Acton Research Inc.) with an R6358P (Hamamatsu) photomultiplier tube was applied for selecting the monitored wavelength when measuring excitation spectra.

The crystals were cleaved prior to mounting onto the sample holder in a flow-type liquid helium cryostat. The crystallographic axes of the crystals when installed onto the sample holder were not oriented with respect to the polarization vector of exciting radiation. All measurements have been performed under ultra-high-vacuum conditions.

## 3. Theoretical

The standard phenomenological crystal field Hamiltonian and its extension given in [33] were used to calculate the  $4f^N$  and  $4f^{N-1}5d$  multi-electron energy levels. The parameter values (using the standard notations given in [33]) to describe the various interactions are listed in table 1.

Some remarks concerning the choice of parameter values for  $\text{LnF}_6^{3-}$  are pertinent because the spectra were not subjected to an optimized fitting, but were simulated by a reasonable choice of parameter values. First the  $4f^N$  parameters are mentioned. The parameters for the  $4f^8$  configuration of  $\text{Tb}^{3+}$  were obtained from a new fitting of the energy levels reported for  $\text{Cs}_2\text{NaTbF}_6$  by Berry *et al* [92]. The parameters for  $\text{Er}^{3+}$  [93] and  $\text{Tm}^{3+}$  [94] are available. The parameters given for  $\text{Cs}_2\text{NaYF}_6:\text{Nd}^{3+}$  [89] were used. There are no parameter values available for  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Ho}^{3+}$  so that the values from  $\text{LnCl}_6^{3-}$  were used for the host-insensitive free ion



**Figure 1.** Plots of  $E_{\text{exc}}$  and  $B_0^4(d)$  against  $N$ , number of  $4f^N$  electrons in  $\text{Ln}^{3+}$  for  $\text{Cs}_2\text{NaYF}_6:\text{Ln}^{3+}$ . The plot for (a) is  $B_0^4(d) = -426.56N + 48\,598$ . The fit for (b) is  $E_{\text{exc}} = 39\,121 + 4568N$ ;  $R^2 = 0.992$ .

parameters whereas for the crystal field parameters the values for  $\text{Sm}^{3+}$  were estimated from those for  $\text{SmCl}_6^{3-}$  using the ratios for  $\text{EuCl}_6^{3-}$  [105], i.e.,  $B_0^4(\text{SmF}_6^{3-}) = 1.5B_0^4(\text{SmCl}_6^{3-})$  and  $B_0^6(\text{SmF}_6^{3-}) = 1.7B_0^6(\text{SmCl}_6^{3-})$ ; the values for  $\text{Gd}^{3+}$  were estimated from those for  $\text{GdCl}_6^{3-}$  [105] using the average ratios for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , i.e.  $B_0^4(\text{GdF}_6^{3-}) = 1.77B_0^4(\text{GdCl}_6^{3-})$  and  $B_0^6(\text{GdF}_6^{3-}) = 1.42B_0^6(\text{GdCl}_6^{3-})$ ; the values for  $\text{Ho}^{3+}$  were estimated from those for  $\text{HoCl}_6^{3-}$  [105] using the ratios for  $\text{Er}^{3+}$ , i.e.  $B_0^4(\text{HoF}_6^{3-}) = 1.73B_0^4(\text{HoCl}_6^{3-})$  and  $B_0^6(\text{HoF}_6^{3-}) = 1.42B_0^6(\text{HoCl}_6^{3-})$ . It is noted that the  $4f^N \rightarrow 4f^{N-1}5d$  absorption spectra are not very sensitive to the values of those parameters.

Concerning the parameters for the  $4f^{N-1}5d$  configuration of  $\text{LnF}_6^{3-}$ ,  $B_0^4(d)$ , the cubic crystal field parameter for the 5d electron, was estimated by scaling the  $B_0^4(d)$  parameter for  $\text{CeCl}_6^{3-}$  [105] by the factor of 1.25 [106] and then decreasing it appropriately across the series using the same ratio as for  $\text{CaF}_2$  [19]. The ensuing linear relationship of  $B_0^4(d)$  with the number  $N$  in  $4f^N$  is shown in figure 1(a). This is the most important parameter for the structure of the f–d absorption spectra concerning the  $5d(t_{2g})-5d(e_g)$  splitting. The absorption spectra thus obtained are suitable for the indication of the absorption to 5d  $e_g$  orbitals, which are usually not so well resolved in the excitation spectra.

The  $F^2$ ,  $F^4$ ,  $F^6$  and  $\zeta_{4f}$  parameters for the  $4f^{N-1}$  core were scaled from the corresponding parameters for the  $4f^N$  configuration by the factor 1.06 to account for the contraction of 4f orbitals. The other core parameters, i.e.  $T^i$ ,  $M^0$ ,  $P^2$ ,  $B_0^4$  and  $B_0^6$ , are less important and were assigned the same values as those for  $4f^N$ . It is noted that there are no  $T^i$  parameters for the  $4f^2$  core of  $\text{Nd}^{3+}$  and the  $T^i$  parameters for the  $4f^{11}$  core of  $\text{Tm}^{3+}$  were assigned the values for the  $4f^{11}$  configuration of  $\text{Er}^{3+}$ .

Turning to the parameters for the 5d electron, the calculated Hartree–Fock (HF) values were used for  $\zeta_{5d}$ ,

**Table 1.** Energy parameters (in  $\text{cm}^{-1}$ ) used for the calculation of  $4f^N-4f^{N-1}5d$  absorption line strengths. Refer to section 3 for explanation.

|                      | Parameter          | Nd <sup>3+</sup> | Sm <sup>3+</sup> | Eu <sup>3+</sup> | Gd <sup>3+</sup> | Tb <sup>3+</sup> | Ho <sup>3+</sup> | Er <sup>3+</sup> | Tm <sup>3+</sup> |
|----------------------|--------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 4f <sup>N</sup>      | $F^2$              | 72 188           | 78 165           | 83 897           | 78 686           | 86 758           | 94 584           | 97 398           | 101 576          |
|                      | $F^4$              | 52 625           | 56 612           | 59 986           | 70 120           | 62 610           | 67 847           | 68 093           | 71 602           |
|                      | $F^6$              | 35 372           | 40 172           | 41 361           | 43 596           | 49 470           | 47 274           | 55 532           | 50 563           |
|                      | $\zeta_{4f}$       | 871              | 1 166            | 1 327            | 1 505            | 1 694            | 2 130            | 2 327            | 2 639            |
|                      | $\alpha$           | 21               | 22               | 16.8             | 37               | 23               | 15               | 18               | 17               |
|                      | $\beta$            | -593             | -717             | -640             | -1 905           | -1 029           | -599             | -570             | -625             |
|                      | $\gamma$           | 1 445            | 1 564            | 1 750            | 1 679            | 1 608            | 1 884            | 1 631            | 1 820            |
|                      | $M^0$              | 2.11             | 2.13             | 2.4              | 1.59             | 2.84             | 3.00             | 3.60             | 1.15             |
|                      | $P^2$              | 192              | 2 600            | 245              | —                | 498              | 523              | 653              | 0                |
|                      | $T^2$              | 298              | 256              | 370              | —                | 523              | 287              | 451              | 451              |
|                      | $T^3$              | 35               | 26               | 40               | —                | 2                | 37               | 61               | 61               |
|                      | $T^4$              | 59               | 22               | 40               | —                | 38               | 98               | 100              | 100              |
|                      | $T^6$              | -285             | -141             | -330             | —                | -235             | -313             | -245             | -245             |
|                      | $T^7$              | 332              | 246              | 380              | —                | 367              | 421              | 305              | 305              |
|                      | $T^8$              | 305              | 382              | 370              | —                | 450              | 351              | 160              | 160              |
|                      | $B_0^4$            | 3 742            | 1 671            | 2 993            | 3 144            | 3 323            | 2 756            | 2 696            | 2 571            |
|                      | $B_0^6$            | 452              | 207              | 428              | 197              | 230              | 327              | 294              | 265              |
| 4f <sup>N-1</sup> 5d | $E_{\text{exc}}$   | 52 000           | 62 000           | 68 000           | 70 560           | 78 300           | 83 800           | 88 000           | 92 000           |
|                      | $B_0^4$ (d)        | 47 300           | 46 500           | 46 000           | 45 600           | 45 200           | 44 300           | 43 900           | 43 500           |
|                      | $\eta_{\text{fd}}$ | 0.55             | 0.55             | 0.55             | 0.55             | 0.55             | 0.55             | 0.55             | 0.55             |
|                      | $\zeta_{5d}$       | 1 216            | 1 351            | 1 419            | 1 488            | 1 557            | 1 697            | 1 768            | 1 839            |
|                      |                    |                  |                  |                  |                  |                  |                  |                  |                  |

following van Pieteron *et al* [19]. Values for the parameters describing the Coulomb interaction between the  $4f^{N-1}$  core and the 5d electron,  $F^k(\text{fd})$  ( $k = 2, 4$ ) and  $G^k(\text{fd})$  ( $k = 1, 3, 5$ ) were scaled from the HF values by the factor of  $\eta_{\text{fd}} = 0.55$ , optimized for the splitting between high-spin and low-spin states in  $\text{TbF}_6^{3-}$ . The parameter  $E_{\text{exc}}$ , which describes the position of the barycenter of  $4f^{N-1}5d$  relative to that of  $4f^N$ , was fine-tuned to give the measured onset of  $4f^N-4f^{N-1}5d$  absorption. The linear relationship of  $E_{\text{exc}}$  with  $N$  in  $4f^N$  is depicted in figure 1(b).

The transitions between  $4f^N$  and  $4f^{N-1}5d$  are electric-dipole-allowed and it is straightforward to calculate the matrix elements of the electric dipole moment operator between multi-electron wavefunctions of  $4f^N$  and  $4f^{N-1}5d$ . There is generally a displacement for the equilibrium positions of ligands in  $4f^N-4f^{N-1}5d$  transitions which results in the vibrational progression structure of the absorption and emission spectra, which is unresolved as broad bands with Stokes shifts. Since the detailed vibronic structures are not resolved, we adopted their crude simulation proposed by van Pieteron *et al* [33], i.e. by using Gaussian curves, displaced towards higher energy from the zero-phonon lines by  $E_{\text{shift}} = 600 \text{ cm}^{-1}$  and  $E_{\text{width}} = 1000 \text{ cm}^{-1}$ , as estimated from the experimental spectra.

## 4. Results and discussion

The  $\sim 10 \text{ K}$  excitation spectra of  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ho}^{3+}$  diluted into  $\text{Cs}_2\text{NaYF}_6$  are presented in this section, together with simulated spectra for  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  for which experimental results have previously been published. The boundary energy separating  $\text{Ln}^{3+}4f^N-4f^{N-1}5d$  transitions and  $\text{Cs}_2\text{NaYF}_6$  host absorption is located at  $\sim 88 500 \text{ cm}^{-1}$ . Characteristic bands are observed in all of the spectra, including a broad band at 120 nm, which corresponds to the near-excitonic band (direct optical creation of excitons),

and other features of host excitation at higher energies. A brief discussion of charge transfer (CT) transitions is given in section 4.1 and this is followed by discussions of the excitation spectra in sections 4.2–4.9.

### 4.1. Charge transfer (CT) transitions

Besides  $4f^N-4f^{N-1}5d$  absorption transitions in the VUV region, transitions due to  $F^--\text{Ln}^{3+}$  CT are also expected. The measured and estimated lowest  $4f^N-4f^{N-1}5d$  absorption energy,  $E_{4f-5d}$ , and charge transfer energy,  $E_{\text{CT}}$ , for lanthanide ions in  $\text{Cs}_2\text{NaYF}_6:\text{Ln}^{3+}$  are listed in table 2. Since the onset of  $4f \rightarrow 5d$  absorption of  $\text{Ce}^{3+}$  in  $\text{Cs}_2\text{NaYF}_6:\text{Ce}^{3+}$  is not available, the equation:

$$E_{4f-5d}(\text{Ln}^{3+}) = E_{4f-5d}(\text{Tb}^{3+}) + \Delta E_{4f-5d}(\text{Ln}^{3+}, \text{Ce}^{3+}) - \Delta E_{4f-5d}(\text{Tb}^{3+}, \text{Ce}^{3+}) \quad (1)$$

was used to calculate the lowest  $4f^N-4f^{N-1}5d$  absorption energy for all ions using the experimental  $\text{Tb}^{3+}E_{4f-5d}$  value from herein and the values  $\Delta E_{4f-5d}$  given by Dorenbos [107]. For  $\text{Tb}^{3+}$ , the onset of  $4f^8 \rightarrow 4f^75d$  absorption is given in table 2 under the column  $E_{4f-5d}$  (expt) and also in square brackets under the column  $E_{4f-5d}$  (calc). The equation:

$$E_{\text{CT}}(\text{Ln}^{3+}) = E_{\text{CT}}(\text{Eu}^{3+}) + \Delta E_{\text{CT}}(\text{Ln}^{3+}, \text{Eu}^{3+}) \quad (2)$$

was used to calculate the maximum of the  $F^--\text{Ln}^{3+}$  CT band for all ions using the  $\text{Eu}^{3+}E_{\text{CT}}$  (expt) value and  $\Delta E_{\text{CT}}$  given by Dorenbos [108]. The calculated  $E_{\text{CT}}(\text{Eu}^{3+})$  value is actually the measured value for  $\text{Cs}_2\text{NaYF}_6:\text{Eu}^{3+}$  herein and is given in table 2 in square brackets. The value is fairly close to that reported for  $\text{LiCaAlF}_6:\text{Eu}^{3+}$  [76]. The  $E_{\text{CT}}$  (expt) value for  $\text{Tm}^{3+}$  is the value for this ion in the host  $\text{LiCaAlF}_6$  [108] (given in [77]) and is expected to be a reasonable approximation (with errors up to a few thousand of  $\text{cm}^{-1}$ ) judging from the small variation of  $F^--\text{Eu}^{3+}$  CT band energies in various hosts [109].

**Table 2.** The measured and estimated (using phenomenological models) lowest  $4f^N-4f^{N-1}5d$  absorption energy  $E_{4f-5d}$  and charge transfer (CT) energy  $E_{CT}$  for lanthanide ions in  $Cs_2NaYF_6:Ln^{3+}$ . (Refer to equations (1) and (2) for the definitions of symbols).

| $Ln^{3+}$        | $\Delta E_{4f-5d}$     | $E_{4f-5d}$ (calc)     |                | $E_{4f-5d}$ (expt)     |                 | $\Delta E_{CT}$        | $E_{CT}$ (calc)        |       | $E_{CT}$ (expt)        |      |
|------------------|------------------------|------------------------|----------------|------------------------|-----------------|------------------------|------------------------|-------|------------------------|------|
|                  | $10^3 \text{ cm}^{-1}$ | $10^3 \text{ cm}^{-1}$ | nm             | $10^3 \text{ cm}^{-1}$ | nm              | $10^3 \text{ cm}^{-1}$ | $10^3 \text{ cm}^{-1}$ | nm    | $10^3 \text{ cm}^{-1}$ | nm   |
| Ce <sup>3+</sup> | [0]                    | 32.1                   | 312            |                        |                 |                        |                        |       |                        |      |
| Pr <sup>3+</sup> | 12.2                   | 44.3                   | 226            |                        |                 | 19.7                   | 79.9                   | 125   |                        |      |
| Nd <sup>3+</sup> | 22.7                   | 54.8                   | 182            | 52.6                   | 190             | 18.5                   | 78.7                   | 127   | 82.6                   | 121  |
| Sm <sup>3+</sup> | 26.5                   | 58.6                   | 171            | 56.8                   | 176             | 9.4                    | 69.6                   | 144   |                        |      |
| Eu <sup>3+</sup> | 35.9                   | 68.0                   | 147            |                        |                 | [0]                    | [60.2]                 | [166] | 60.2                   | 166  |
| Gd <sup>3+</sup> | 45.8                   | 77.9                   | 128            | 75.8                   | 132             |                        |                        |       |                        |      |
| Tb <sup>3+</sup> | 13.2<br>(5.5)          | [45.3]<br>(37.6)       | [221]<br>(266) | 45.3<br>(37.4)         | 221<br>(267)    |                        |                        |       |                        |      |
| Dy <sup>3+</sup> | 25.1<br>(17.7)         | 57.2<br>(49.8)         | 175<br>(201)   |                        |                 | 16.4                   | 76.6                   | 131   |                        |      |
| Ho <sup>3+</sup> | 31.8<br>(29.1)         | 63.9<br>(61.2)         | 156<br>(163)   | 62.1<br>(58.5)         | 161<br>(171)    | 19.5                   | 79.7                   | 125   |                        |      |
| Er <sup>3+</sup> | 30.0<br>(27.0)         | 62.1<br>(59.1)         | 161<br>(169)   |                        | (58.8)<br>(170) | 18.2                   | 78.4                   | 128   |                        |      |
| Tm <sup>3+</sup> | 29.0<br>(27.0)         | 61.1<br>(59.1)         | 164<br>(169)   | 60.6<br>(58.4)         | 165<br>(171)    | 13.5                   | 73.7                   | 136   | ~80.6                  | ~124 |
| Yb <sup>3+</sup> | 38.0                   | 70.1                   | 143            |                        |                 | 3.5                    | 63.7                   | 157   |                        |      |

The data in round parentheses in table 2 for the ions from Tb<sup>3+</sup> to Yb<sup>3+</sup> represent the energies of the onset of spin-forbidden  $4f^N-4f^{N-1}5d$  absorption.

#### 4.2. Spectra of $Cs_2NaYF_6:Nd^{3+}$

The 9 K VUV excitation spectra of Nd<sup>3+</sup> in several hexafluoroelpasolite lattices have been previously reported [89]. The experimental spectrum (full line, figure 2(a)) comprises two groups of bands with their peaks separated by  $\sim 27\,000 \text{ cm}^{-1}$ . Saturation occurs for the lower energy group between 172 and 192 nm. The simulation shown in figure 2(a) (dashed line) utilizes similar parameters to those in [89] except that the 5d crystal field parameter has been increased by the factor 1.23. The poorer fit for the bands between 116 and 140 nm is attributed to the less efficient energy transfer to the emitting  $4f^{32}G(2)_{9/2}$  multiplet term when the initial  $4f^25d$  level is at a much higher energy.

#### 4.3. Spectra of $Cs_2NaYF_6:Sm^{3+}$

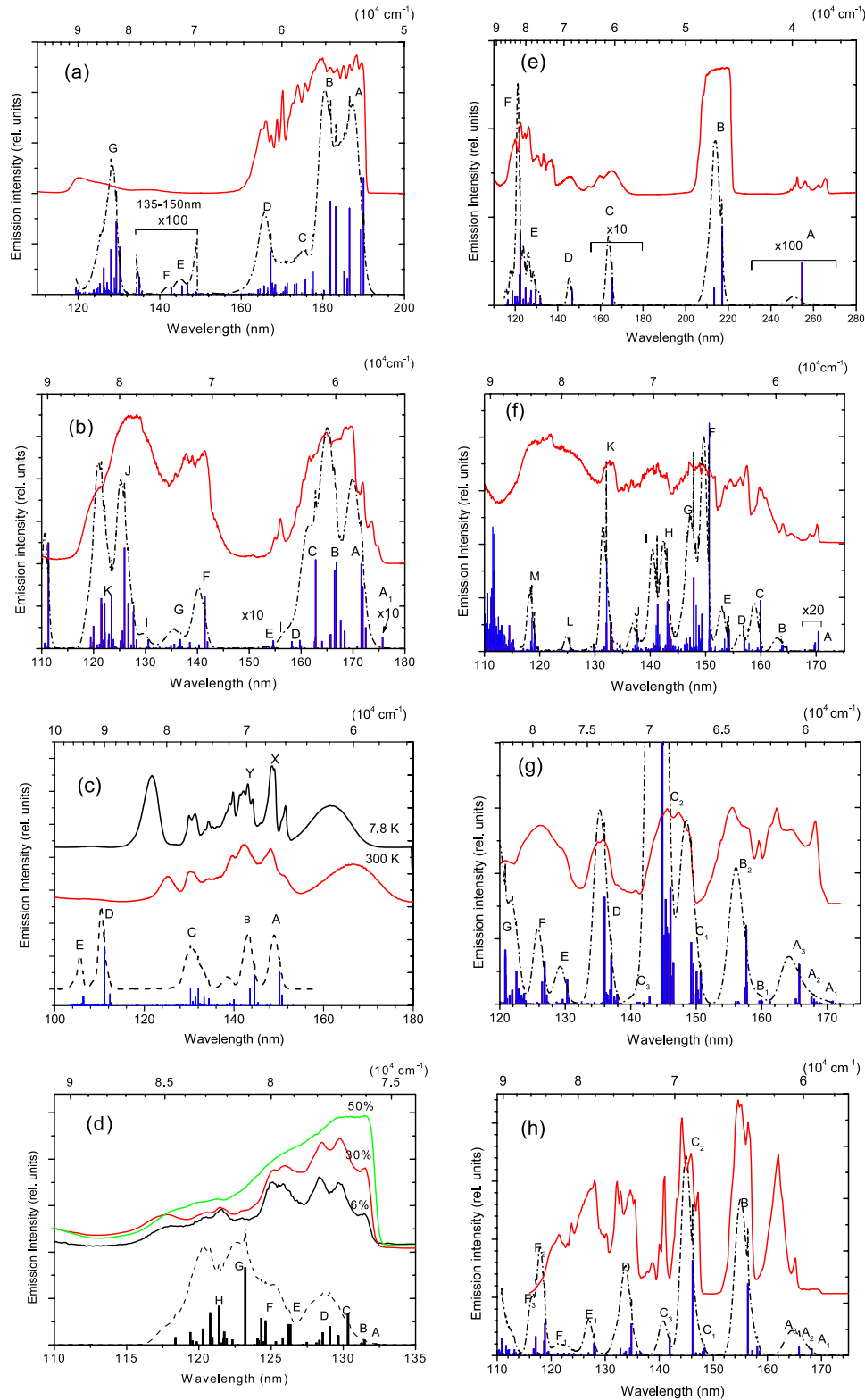
The excitation spectrum for  $Cs_2NaYF_6:Sm^{3+}$  (3%) at 12.4 K when monitoring the emission from the  $4f^5$  state ( ${}^4G_{5/2} + {}^4F_{5/2}$ ),  $\lambda_{em} = 598.6 \text{ nm}$ , is shown in figure 2(b). The initial ‘zero-phonon line’ is at 174.9 nm ( $57\,175 \text{ cm}^{-1}$ ). The term ‘zero-phonon line’ (subsequently ‘ZPL’) refers to the fact that vibrational structure is not resolved so that its location by taking the convoluted band maximum may not correspond to the real zero-phonon line (i.e. 0–0 transition). On closer inspection, the step-like appearance of a vibrational progression between 175 and 170 nm does not give progressive vibrational frequencies as expected for the totally symmetric Sm–F stretching vibration,  $\nu_s$  (Sm–F), so that other electronic transitions are present. Then to higher energy, further transitions produce unresolved structures between 162 and 170 nm. A vibrational progression is observed at the high energy side of this structure, starting with the ZPL at 161.5 nm

(presumably corresponding to the simulated band D) with the initial vibrational quantum of  $470 \pm 10 \text{ cm}^{-1}$ , which apparently decreases with successive members. The vibrational frequency is similar to the value expected from the ground state (Raman spectrum [88]) but the measurement performed herein with moderate resolution does not permit an exact comparison. A new transition is clearly observed at 156.0 nm (presumably corresponding to E) with the initial progression frequency  $\sim 460 \text{ cm}^{-1}$ . Two other groups of bands are at higher energy. The first group is partially resolved between 134 and 145 nm, whereas the second group is stronger and broader between 116 and 134 nm. The final states marked in figure 2(b) belong to A<sub>1</sub>–E:  ${}^6[({}^5I)t_{2g}]$ ; F–G:  ${}^6[({}^5F)t_{2g}]$ ; I–J:  ${}^6[({}^5G)t_{2g}]$  and K:  ${}^6[({}^5K)e_g]$ .

#### 4.4. Spectra of $Cs_2NaYF_6:Eu^{3+}$

Figure 2(c) compares the excitation spectra of the  ${}^5D_0 \rightarrow {}^7F_1$  emission of Eu<sup>3+</sup> in  $Cs_2NaYF_6:Eu^{3+}$  (0.3%) at 7.8 and 300 K. The simulated  $4f^6 \rightarrow 4f^55d^1$  transitions are shown underneath and show the absence of two broad bands above. Unlike the interconfigurational transitions, which do not exhibit marked wavelength shifts with decreasing temperature, these two broad bands are distinguished by their shifts to shorter wavelengths: from 167 to 162 nm, and from 125 to 122 nm. Of the two bands, the longer wavelength one corresponds to the Eu<sup>3+</sup>–F<sup>–</sup> CT transition whilst the shorter wavelength one is the near-excitonic transition.

The final states marked in the simulation of figure 2(c) correspond to A, B:  ${}^7[{}^6H, t_{2g}]$ ; C:  ${}^7[{}^6F, t_{2g}]$  and D, E:  ${}^7[{}^6H, e_g]$ . The transitions to the latter states, D, E, lie above the bandgap so that they are not observed. The simulation predicts four major bands in the spectrum but it does not agree well with the fine structure in the low temperature spectrum partly because of our simplified treatment of phonon sidebands. Furthermore, the 7.8 K spectrum does not resolve individual vibronic progression structure with a distinct interval, but



**Figure 2.** Experimental excitation spectra (full lines) and simulated  $4f^N-4f^{N-1}5d$  absorption spectra (dashed lines) for  $\text{Cs}_2\text{NaYF}_6:\text{Ln}^{3+}$ . The vertical bars show the calculated locations and relative intensities of pure electronic transitions. The simulated convolutions follow [19] and employ  $E_{\text{shift}} = 600 \text{ cm}^{-1}$  and  $E_{\text{width}} = 1000 \text{ cm}^{-1}$ . Refer to the text for the explanations of labels. (a)  $\text{Ln} = \text{Nd}$ ,  $\lambda_{\text{em}} = 289 \text{ nm}$ ,  $T = 9 \text{ K}$ . Notice the ordinate scale expansion in the simulated spectrum between 135 and 150 nm; (b)  $\text{Ln} = \text{Sm}$ ,  $\lambda_{\text{em}} = 598.6 \text{ nm}$ ,  $T = 12.4 \text{ K}$ . The zero-phonon lines are enlarged by 10 times for clearer display in the ranges 175–180 nm and 145–156 nm; (c)  $\text{Ln} = \text{Eu}$ ,  $\lambda_{\text{em}} = 591 \text{ nm}$ ,  $T = 7.8$  and  $300 \text{ K}$ . (d)  $\text{Ln} = \text{Gd}$ ,  $\lambda_{\text{em}} = 313 \text{ nm}$ ,  $T = 8.9 \text{ K}$  (6%),  $T = 8.2 \text{ K}$  (30%),  $T = 8.2 \text{ K}$  (50%). The ordinate scales are arbitrary for the three concentrations. (e)  $\text{Ln} = \text{Tb}$ ,  $\lambda_{\text{em}} = 541 \text{ nm}$ ,  $T = 12.6 \text{ K}$ . The simulated intensities in the regions between 155 and 180 nm and 230 and 270 nm are enlarged by factors of 10 and 100, respectively. (f)  $\text{Ln} = \text{Ho}$ ,  $\lambda_{\text{em}} = 559 \text{ nm}$ ,  $T = 12.3 \text{ K}$ . In the region between 167 and 175 nm the intensities are enlarged by 20 times in the simulation. (g)  $\text{Ln} = \text{Er}$ ,  $\lambda_{\text{em}} = 175 \text{ nm}$ ,  $T = 10 \text{ K}$ . (h)  $\text{Ln} = \text{Tm}$ ,  $\lambda_{\text{em}} = 177 \text{ nm}$ ,  $T = 10.5 \text{ K}$ .

shows convoluted bands of different electronic transitions. The simulated transitions to A and B each comprise two intense zero-phonon lines, which are separated by  $221\text{ cm}^{-1}$  (for A) and  $482\text{ cm}^{-1}$  (for B). The observed splittings of the bands marked X and Y are  $243\text{ cm}^{-1}$  and  $504\text{ cm}^{-1}$ , respectively, which could correspond to the separations of the convoluted structure of A and B.

#### 4.5. Spectra of $\text{Cs}_2\text{NaYF}_6:\text{Gd}^{3+}$

Figure 2(d) shows the excitation spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Gd}^{3+}$  between 8.2 and 8.9 K for three different dopant ion concentrations whilst monitoring the  $4f^7\ ^6P_{7/2} \rightarrow ^8S_{7/2}$  emission at 313 nm. The features are more clearly resolved for the 6% doping and consist of structured bands between 114 and 132 nm. Calculations show that there are many bands in this region and these are labeled as A–H in figure 2(d). All these bands are due to the splitting of the high-spin  $^8[(^7F)t_{2g}]$  states mainly under 4f and 5d spin–orbit interactions. The simulated absorption spectrum shows poor agreement with the experimental excitation spectrum. This is attributed to the closeness of the  $4f^7 \rightarrow 4f^65d$  transitions to the host bandgap where photoionization occurs and where other competing processes, such as excitonic and defect absorption, can compete with 4f–5d absorption. In fact, the transition intensities become more under-estimated on progressing from the lowest energy transition up to higher energy. The simulation predicts a second group of bands between 93 and 105 nm with comparable integrated intensity to that of the first group but these features lie above the edge of the host absorption, preventing their experimental observation under one-photon excitation.

#### 4.6. Spectra of $\text{Cs}_2\text{NaYF}_6:\text{Tb}^{3+}$

The lanthanide ions of the second half of the series possess the possibilities of both spin-forbidden and spin-allowed 4f–5d transitions (or transitions to both high-spin and low-spin 5d states). For  $\text{Tb}^{3+}$ , the  $4f^7\ ^8S$  core can couple with the 5d  $t_{2g}$  electron to give  $^9D$  and  $^7D$  multiplets, and by Hund's rule the former is lower in energy. Since the electronic ground state of the  $4f^8$  configuration is  $^7F_6$ , the lower energy transitions to  $^9D$  are expected to be much weaker than the higher energy ones to  $^7D$ . Figure 2(e) (upward shifted solid curve) shows the 12.6 K excitation spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Tb}^{3+}$  (1%) by monitoring the  $^5D_4 \rightarrow ^7F_5$  emission at 541 nm. The mainly spin-forbidden group of bands is observed as a structured group between 245 and 267 nm. Only three electronic transitions are expected in this region [110] and these can be assigned to the three groups of bands. Three features were observed in the same region in the 7 K absorption spectrum of  $\text{Rb}_2\text{KInF}_6:\text{Tb}^{3+}$  (1%) but in that case the  $\text{Tb}^{3+}$  ion is situated at a distorted octahedral site [101]. In figure 2(e), the highest energy group of spin-forbidden bands (246.5–252.6 nm) is the most clearly resolved and the initial  $\nu_8$  (Tb–F) vibrational quantum based upon the ZPL is  $\sim 475\text{ cm}^{-1}$ , compared with the ground state value of  $468\text{ cm}^{-1}$  [92]. Additional structure is observed with the derived vibrational energy of  $225\text{ cm}^{-1}$ . The assignment of structure in the  $4f^8\text{--}4f^75d$  absorption spectrum

of  $\text{Cs}_2\text{NaTbCl}_6$  was to breathing modes of the second and third coordination shells of  $\text{Tb}^{3+}$ . It is not clear whether the band at  $225\text{ cm}^{-1}$  in the present case corresponds to the maximum of unresolved bands, or to a single feature. The frequency is higher than the ground state  $t_{2g}$  moiety mode in  $\text{Cs}_2\text{NaTbF}_6$  ( $194\text{ cm}^{-1}$  [92]). The lowest energy group of spin-forbidden bands (between 260 and 268 nm) is broader with a separation of  $\sim 472\text{ cm}^{-1}$ . A major difference with the corresponding spectra of  $\text{Cs}_2\text{NaTbCl}_6$  is that the maximum intensity of the totally symmetric mode vibrational progression upon the electronic origin is at the  $\nu = 0$  member in the present case, compared with  $\nu = 1$  for the chloride. This indicates a smaller change in the configuration coordinate diagram between the ground and excited state equilibrium nuclear configurations in the present case.

The total intensity saturation of the bands between 224 and 201 nm is indicative of transitions to the terminal low-spin states. There is then a spectral window until the next group of bands at higher energy commences at 174 nm.

The calculated f–d absorption line strengths are shown below the experimental spectrum, figure 2(e), with sticks being zero-phonon lines and the dashed–dotted curve being the convolution as described above. The calculation is enlarged for better display in the ranges from 155 to 180 nm and 230 to 270 nm by 10 and 100 times, respectively. The final states belong to A:  $^9[(^8S)t_{2g}]$ , B:  $^7[(^8S)t_{2g}]$ , C:  $^9[(^8S)e_g]$ , D:  $^7[(^8S)e_g]$ , E:  $^7[(^6P)e_g]$  and F:  $^7[(^6I)e_g]$ . The calculations show that A contains three groups, with the second and third groups being calculated to be weaker and, at  $830\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$ , lower in energy than the first group, respectively.

#### 4.7. Spectra of $\text{Cs}_2\text{NaYF}_6:\text{Ho}^{3+}$

Figure 2(f) shows the 12.3 K excitation spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Ho}^{3+}$  (10%) by monitoring the  $^5S_2 \rightarrow ^5I_8$  emission at 559 nm. The onset of absorption is at 170.6 nm and the first band (at 170.2 nm;  $58\,760\text{ cm}^{-1}$ ) has a repeating interval of  $455\text{ cm}^{-1}$ . A broad feature is observed between these two bands, at  $\sim 290\text{ cm}^{-1}$  above the lowest energy band. Clearly, these weak features correspond to spin-forbidden transitions. The remaining spectrum, between 113 and 167 nm, comprises several groups of bands with some structure and consists of many overlapping transitions. The lower sticks and dashed–dotted convolution show the theoretical simulation of this structure and the calculation is enlarged for better display in the range 167–175 nm by 20 times. The calculated  $4f^95d$  levels start at  $57\,600\text{ cm}^{-1}$ . The regions A–D are dominated by transitions to high-spin  $^7[(^6H)t_{2g}]$  terminal states, whereas E–G correspond to low-spin  $^5[(^6H)t_{2g}]$  terminal states. Region H corresponds to  $^5[(^6F)t_{2g}]$ , whereas I ( $^7[(^6H)e_g]$ ) may not be efficient for excitation due to delocalization of the  $e_g$  orbitals. Region J is a mixture of  $^5[(^4F(3))t_{2g}]$  and  $^7[(^6H)e_g]$ . Region M presumably corresponds to the ‘hump’ at 121.9 nm on the observed broad band between 130 and 113 nm. This broad band, with a maximum at 119 nm, is assigned to the excitonic transition, but it is at a similar energy to the F– $\text{Ho}^{3+}$  CT transition, which is estimated from section 4.1 to center at  $\sim 118\text{ nm}$ .



#### 4.8. Spectra of $\text{Cs}_2\text{NaYF}_6:\text{Er}^{3+}$

The 10 K excitation spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Er}^{3+}$  (10%) when monitoring 5d–4f emission at 175 nm [102] is shown in figure 2(g) and it is more clearly resolved and consists of structured bands between 120 and 170 nm. The calculated  $4f^{10}5d$  levels start at  $58\,400\text{ cm}^{-1}$  (171 nm). The regions marked in figure 2(g) have the following terminal state correspondences: A<sub>1</sub>–A<sub>3</sub>: dominated by  $^6[(^3\text{I})t_{2g}]$ ; B<sub>1</sub>, B<sub>2</sub> and C<sub>3</sub>:  $^6[(^3\text{I})t_{2g}]$  with a considerable mixture of  $^4[(^5\text{I})t_{2g}]$ ; C<sub>1</sub>, C<sub>2</sub>, D:  $^4[(^3\text{I})t_{2g}]$ ; E and F:  $^5[(^5\text{F})t_{2g}]$ ; where the 5d electron is in the lower  $t_{2g}$  orbital throughout. By contrast, the terminal state of G is  $^6[(^3\text{I})e_g]$ , which may not be efficient due to delocalization of the  $e_g$  orbital. The CT band is predicted to be near 120 nm.

#### 4.9. Spectra of $\text{Cs}_2\text{NaYF}_6:\text{Tm}^{3+}$

The spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Tm}^{3+}$  has previously been simulated [103] and is included herein for completeness, using different parameter values. The 10.5 K excitation spectrum of  $\text{Cs}_2\text{NaYF}_6:\text{Tm}^{3+}$  (1%) by monitoring the  $4f^{11}5d \rightarrow 4f^{12}$  emission is shown in the upper part of figure 2(h), together with the simulation underneath. The  $4f^{12}$  ground multiplet term of  $\text{Tm}^{3+}$  is  $^3\text{H}_6$ . The calculated  $4f^{11}5d$  levels start at  $58\,300\text{ cm}^{-1}$  (171.5 nm), with mainly high-spin states A<sub>1</sub>–A<sub>3</sub>, C<sub>1</sub> and C<sub>3</sub>, which are dominated by  $^5[(^4\text{I})t_{2g}]$ . Regions B, C<sub>2</sub> and D are dominated by low-spin final states  $^3[(^4\text{I})t_{2g}]$ . To higher energy, the bands E<sub>1</sub> (terminal state  $^3[(^4\text{F})t_{2g}]$ ), F<sub>1</sub> and F<sub>3</sub> ( $^3[(^2\text{H}(2))t_{2g}]$ ) all represent excited  $4f^{11}$  core states with the d electron in the lower  $t_{2g}$  orbital. The simulation shows good agreement between 130 and 160 nm but the expected strong excitation transition (F<sub>2</sub>) to the  $^3[(^4\text{I})e_g]$  terminal state may not be efficient due to delocalization of the  $e_g$  orbitals. The feature in the region 115–135 nm is assigned to the CT band, which is estimated to peak around 124 nm. The differences with the previous simulation in [103] are mainly to short wavelengths of 138 nm. The parameters employed are rather different from those in [103], particularly for the 5d crystal field parameter, which is reduced by 13%.

## 5. Conclusions

The  $\sim 10$  K VUV excitation spectra of tri-positive lanthanide ions in the  $\text{LnF}_6^{3-}$  moiety situated at octahedral sites of the hexafluoroelpasolite host have been presented and analyzed herein. The host lattices employed are particularly suitable for probing the  $4f^{N-1}5d$  configurations due to their chemical inertness and high energy bandgap. Most of the observed structure represents electric-dipole-allowed  $4f^N \rightarrow 4f^{N-1}5d$  transitions, together with vibrational structure based upon them. In nearly all cases, the ensuing spectral congestion from many overlapping transitions does not permit a detailed analysis to be made of individual electronic transitions. The theoretical calculations have provided reasonable interpretations of the experimental results, with some additional bands not present in the simulations corresponding to CT and excitonic transitions. The calculations were not performed by data fitting but rather

by selection of parameters from previous studies or by extrapolation of a trend throughout the lanthanide series.

It is instructive to compare the present results with those from other fluoride systems doped with lanthanide ions. However, nearly all of the systems mentioned in section 1 correspond to low symmetry environments of  $\text{Ln}^{3+}$  and the comparison is not meaningful. There are two exceptions. First, the VUV excitation spectra of  $\text{Tm}^{3+}$  in the  $\text{LiMAlF}_6$  ( $M = \text{Ca}, \text{Sr}$ ) hosts [77, 78], and the VUV absorption spectrum of  $\text{Nd}^{3+}$  in  $\text{LiCaAlF}_6$  [75], have been reported. In this host, the  $\text{Ln}^{3+}$  ions are situated at the  $\text{Ca}^{2+}$  D<sub>3d</sub> site in a trigonally elongated octahedral coordination. There is a clear one-to-one correspondence of the first four groups of  $4f^{12} \rightarrow 4f^{11}5d$  bands for  $\text{Tm}^{3+}$  in these hosts and in the  $\text{Cs}_2\text{NaYF}_6$  host. However, as also for the  $4f^3 \rightarrow 4f^25d$  spectrum of  $\text{Nd}^{3+}$ , all of the bands are situated at higher energies in the  $\text{LiCaAlF}_6$  host than in the elpasolite. True *et al* [77] have remarked that the peak energy of the first fd band depends on the crystal field splitting, increasing with increasing Ln–F bond distance. In fact, the Ca–F distance (229 pm) [111] in the  $\text{LiCaAlF}_6$  host is a little longer than the Y–F distance (227 pm) in  $\text{Cs}_2\text{NaYF}_6$ . It is interesting that, by adjusting the Ln–F distance in similar host lattices, the absorption band positions could therefore be tuned.

The second comparison is made with the  $\text{CaF}_2$  host, where at low dopant ion concentrations ( $\sim 0.001$  at.%),  $\text{Ln}^{3+}$  is situated at the center of a cube of  $\text{F}^-$  ions [33], although other sites and clusters dominate at higher concentrations [54–56]. The eight-coordination  $\text{O}_h$  symmetry environment again provides the splitting of the d-electron orbitals into  $e_g$  and  $t_{2g}$  representations, but the ordering of these two is the opposite of the present study. Without considering fine structure, the features in the lower region of the VUV excitation spectra of  $\text{MF}_2$  ( $M = \text{Ca}, \text{Sr}$ ) doped with  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  [33, 58] are generally similar, and at similar wavelengths, to the present spectra. This is because the structure corresponds to the coupling of the  $4f^{N-1}$  core with a given 5d orbital for the lowest crystal field level and is mainly due to the interactions in the  $4f^{N-1}$  core and the exchange interaction between  $4f^{N-1}$  and the given 5d orbital [112–114] which do not change appreciably for the fluoride hosts. In the case of  $\text{Tb}^{3+}$ , the first spin-allowed and spin-forbidden transitions are at similar wavelengths in the  $\text{Cs}_2\text{NaYF}_6$  and  $\text{MF}_2$  [18, 58, 59] hosts. The detailed structure of the spin-forbidden transition is different, however. For  $\text{CaF}_2:\text{Tb}^{3+}$  [18] there are two groups of bands whereas there are three groups in figure 2(e). The difference lies in the selection rules for the  $\text{O}_h$  molecular point group since only transitions to terminal states with  $\text{T}_{1u}$  irreps are electric-dipole-allowed. Coupling the  $^8\text{S}$  core with  $t_{2g}$  or  $e_g$  orbitals gives three or two  $\text{T}_{1u}$  states, respectively.

As in the present study, the parameter values for modeling the spectra of  $\text{CaF}_2:\text{Ln}^{3+}$  were not fitted. The 5d crystal field parameter was taken from the fit to the corresponding spectra of  $\text{Ce}^{3+}$  and then scaled across the lanthanide series. Its magnitude is slightly greater in the present simulations. Compared with the  $4f^N$  parameters for  $\text{CaF}_2:\text{Ln}^{3+}$ , the magnitude of the fourth-order crystal field parameter is greater herein (with opposite sign), whereas the (smaller) sixth-order parameter is smaller for the elpasolites.

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