

## Absorption and emission spectra of Ce<sup>3+</sup> in elpasolite lattices

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### **Abstract**

The experimental determination of the electronic energy levels for Ce<sup>3+</sup> in some chloro-elpasolite hosts for both the ground 4f<sup>1</sup> and the excited 5d<sup>1</sup> configurations are described. High resolution f - f absorption and f - <sup>2</sup>T<sub>2g</sub> d absorption and emission spectra have been recorded at low temperatures for Ce<sup>3+</sup> diluted into various hexachloroelpasolite lattices. A fluorescence spectrum at ~ 50,000 cm<sup>-1</sup> is tentatively assigned to the emission from the highest 5d crystal field level, <sup>2</sup>E<sub>g</sub>, of a Ce<sup>3+</sup> impurity in Cs<sub>2</sub>NaErCl<sub>6</sub>, enabling the values of all the energy levels of both the 4f<sup>1</sup> and 5d<sup>1</sup> configurations to be given for

Ce<sup>3+</sup> in elpasolite hosts. Vibronic structure superimposed on the electronic transitions is analyzed in terms of a simple configurational coordinate model involving the ground and excited configurations. It is found that the difference in the Ce-Cl bondlength between the 4f<sup>1</sup> and 5d<sup>1</sup> configurations is ~0.04Å. Ab initio model potential calculations on the (CeCl<sub>6</sub>)<sup>3-</sup> cluster embedded in a reliable representation of the Cs<sub>2</sub>NaYCl<sub>6</sub> host support these conclusions.

## Introduction

At the beginning of the 4f and the 5f transition series, the f and d electronic configurations of the di-, tri-, and tetravalent free ions are very close in energy.<sup>1,2</sup> This is also true for these ions in compounds. For example, the lowest energy configuration for the Ce<sup>2+</sup> free ion is [Xe core]4f<sup>2</sup> with the beginning of the opposite parity 4f5d configuration at 3277 cm<sup>-1</sup>. However in a CaF<sub>2</sub> host the ground configuration is [Xe core]4f5d.<sup>3</sup> The Ce<sup>3+</sup> free ion has a 4f<sup>1</sup> ground configuration with the lowest 5d state at 49737 cm<sup>-1</sup>.<sup>1</sup> When this ion is placed in a crystal the lowest 4f to 5d electric dipole allowed transition has been reported to be in the range of 20,000 to 40,000 cm<sup>-1</sup> depending on the particular compound or matrix investigated.<sup>4</sup> Similarly, for the actinide or 5f series, the lowest 5f – 6d transition for the Pa<sup>4+</sup> ion diluted in Cs<sub>2</sub>ZrCl<sub>6</sub> is at 20,000 cm<sup>-1</sup>, but the free ion separation between ground 5f level and the first 6d level is ~ 50,000 cm<sup>-1</sup>.<sup>5</sup> In the few structurally characterized Th<sup>3+</sup> organometallic compounds the 6d<sup>1</sup> configuration has been found to be the ground configuration,<sup>6,7</sup> but the ground term is from the 5f configuration and the first 6d level is 10,000 cm<sup>-1</sup> higher in the Th<sup>3+</sup> free ion. The U<sup>3+</sup> ion in the LaCl<sub>3</sub> host has the first 5f<sup>3</sup> to 5f<sup>2</sup>6d<sup>1</sup> transition at approximately 22,000 cm<sup>-1</sup> although in the U<sup>3+</sup>/RbY<sub>2</sub>Cl<sub>7</sub> system this transition is found at ~ 14,000 cm<sup>-1</sup>.<sup>8</sup> Thus, as the degree of ionization increases and/or the atomic number is increased (for both the lanthanide and the actinide series) the f<sup>n</sup> configuration becomes increasingly stabilized so that the interconfigurational transitions are not observed in the visible or near ultraviolet region. Only at the beginning of both the lanthanide and actinide series is it possible to observe these two electronic configurations in this energy range.

For the lanthanide series the  $Ce^{3+}$  ion has been extensively studied and measured levels have been reported for both the ground  $4f^1$  configuration and the excited  $5d^1$  configuration. Figure 1 shows schematically the energy levels and nomenclature used for the  $4f^1$  and  $5d^1$  configurations of the  $Ce^{3+}$  ion diluted in choro-elpasolite hosts. The 6 K 4f-5d absorption and magnetic circular dichroism (MCD) spectra of  $Ce^{3+}$  diluted in  $Cs_2NaYCl_6$  were reported by Schwartz and Schatz.<sup>9</sup> They located the  $5d^1\ ^2T_{2g}\ \Gamma_8$  and  $\Gamma_7$  levels at  $28196\ cm^{-1}$  and  $29435\ cm^{-1}$  respectively. No further electronic absorption transitions were detected up to  $50000\ cm^{-1}$ . The  $5d^1\ ^2E_g\ \Gamma_8$  level was thus assumed to be  $>20000\ cm^{-1}$  above the  $^2T_{2g}$  baricenter. The EPR spectrum of the  $Ce^{3+}$  ion in  $Cs_2NaYCl_6$  has also been measured.<sup>10</sup> The 5d-4f luminescence from the  $^2T_{2g}$  state was recently reported under low resolution at 80 K, with about a 30  $\mu s$  lifetime.<sup>11</sup> The decay curves for X-ray- and vacuum ultraviolet- excited emission of  $Ce^{3+}/Cs_2LiYCl_6$  and  $Ce^{3+}/Cs_2LiLaCl_6$  have recently been reported.<sup>12,13</sup> Ionova *et al.* have cited the lowest  $\pi \rightarrow f$  charge transfer band in  $CeCl_6^{3-}$  near  $60000\ cm^{-1}$ .<sup>14</sup>

van't Spijker *et al.*,<sup>15</sup> reported the excitation spectra of the 425 nm ( $23530\ cm^{-1}$ ) emission of  $Ce^{3+}$  in  $Cs_2NaLaCl_6$ ,  $Cs_2NaCeCl_6$  and  $Cs_2NaLuCl_6$ . In each case, bands were observed near 210 nm and attributed to  $f - ^2E_g$  d transitions of  $Ce^{3+}$ . The wavelengths of these bands have been listed by Dorenbos,<sup>16</sup> with the addition of 210, 217 nm ( $47620, 46083\ cm^{-1}$ ) for  $Ce^{3+}/Cs_2NaYCl_6$ . The doublet structure (separation of the peak maxima  $\sim 1540\ cm^{-1}$ ) corresponded to absorption from both the  $^2F_{5/2}$  and  $^2F_{7/2}$  f-electron states to the d-electron  $^2E_g$  state at room temperature. Hence it is well-substantiated that the  $^2E_g$  state is near  $47000\ cm^{-1}$  in these cubic elpasolite hosts. This state also has been observed at  $42200\ cm^{-1}$  in the 300 K photoacoustic spectrum of  $Ce^{3+}/BaF_2$ .<sup>17</sup>

Rodnyi *et al.*<sup>13</sup> observed bands in the 300 K excitation spectrum of the 3.3 eV luminescence of  $Ce^{3+}$  in  $Cs_2LiLaCl_6$  at  $35730, 37908, 41134$  and  $45247\ cm^{-1}$ , which were assigned to  $f - d$  transitions of  $Ce^{3+}$ . The 19 eV-excited emission spectrum of  $Cs_2LiLaCl_6$  doped with 1%  $Ce^{3+}$  gave a broad band at  $26616\ cm^{-1}$ , assigned to  $d - f$  emission of  $Ce^{3+}$ , in addition to a broader feature ( $33069\ cm^{-1}$ ) assigned to core-valence luminescence. No emission was evident from the  $^2E_g$  state of  $Ce^{3+}$ .

In a more recent study of  $Ce^{3+}$  - doped  $Cs_2LiYX_6$ ,<sup>18</sup> even the neat  $Cs_2LiYCl_6$  showed extensive bands between  $48000-100000\ cm^{-1}$  in the excitation spectra of the 'host'

emission at  $29036\text{ cm}^{-1}$ . The 130 K excitation spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{LiYCl}_6$  (monitoring the  $\text{Ce}^{3+}$  emission at  $25003\text{ cm}^{-1}$ ) showed additional bands at roughly  $27000\text{-}32000$ ,  $36300$ ,  $42700$  and  $50000\text{ cm}^{-1}$ . The  $36300$  and  $42750\text{ cm}^{-1}$  bands were assigned to  $\text{Ce}^{3+}$  transitions: the lower energy band being due to a lower symmetry site, and the  $50000\text{ cm}^{-1}$  band to the  ${}^2\text{E}_g$  state. No emission was observed from the  ${}^2\text{E}_g$  level in  $\text{Ce}^{3+}$ -doped  $\text{Cs}_2\text{LiYX}_6$  under x-ray excitation, but emission from the  ${}^2\text{T}_{2g}$  level was observed.

In this paper we report the experimental determination of the electronic energy levels for  $\text{Ce}^{3+}$  in some chloro-elpasolite hosts for both the ground  $4f^1$  and the excited  $5d^1$  configurations. A preliminary account of the emission spectra from the lowest  $5d$  level of  $\text{Ce}^{3+}$  in  $\text{Cs}_2\text{NaYCl}_6$  to the  $4f^1$  energy levels has been given.<sup>19</sup> We have recorded an emission spectrum of  $\text{Cs}_2\text{NaErCl}_6$  at  $\sim 50,000\text{ cm}^{-1}$ , which we tentatively assign to the emission from the highest  $5d$  crystal field level of a  $\text{Ce}^{3+}$  impurity. Although the magnitude of the crystal field at the  $\text{Ce}^{3+}$  site in  $\text{Cs}_2\text{NaErCl}_6$  is not quite the same as for  $\text{Cs}_2\text{NaYCl}_6$  the differences should be relatively small since the ionic radii of  $\text{Er}^{3+}$  and  $\text{Y}^{3+}$  are similar. If the assumption is made that the differences in the crystal field strength are negligible, accurate data are available for both the  $4f^1$  and  $5d^1$  configurations in the elpasolite host. These data are analyzed and the parameters evaluated using the crystal field model.

We also report the results of supportive *ab initio* embedded cluster calculations<sup>20,21</sup> on  $(\text{CeCl}_6)^{3-}/\text{Cs}_2\text{NaYCl}_6$ .

## Experimental

$\text{Cs}_2\text{NaCeCl}_6$  and other (Ce-doped) hexachloroelpasolites were prepared according to Morss method E.<sup>22</sup> The powders were passed through a Bridgman furnace at *ca.*  $850\text{ }^\circ\text{C}$  in vacuo in quartz tubes to give polycrystalline materials. The purity of the lanthanide oxides employed was 99.999% for  $\text{Pr}_6\text{O}_{11}$ , 99.9%  $\text{Tm}_2\text{O}_3$ , 99.999%  $\text{Er}_2\text{O}_3$  (all from Strem Chemicals), and 99.999%  $\text{Y}_2\text{O}_3$  (Berkshire Ores).  $\text{CeCl}_3$  (99.9%, Strem) was used to prepare neat  $\text{Cs}_2\text{NaCeCl}_6$  and Ce-doped  $\text{Cs}_2\text{LiYCl}_6$ . ICP-AES analyses showed that the  $\text{Y}_2\text{O}_3$  contained (relative to Y) 58 ppm Ce, 120 ppm Pr, and 17 ppm Nd. Similar

analyses, by direct calibration and by standard addition, were attempted for the  $\text{Er}_2\text{O}_3$  material but reliable data could not be obtained.

Infrared and absorption spectra were recorded using a Biorad FTS-60A spectrometer, equipped with DTGS and photomultiplier detectors, and using an Oxford Instruments closed-cycle cryostat with base temperature 10 K. Ultraviolet and emission spectra were also recorded using a  $\text{D}_2$  lamp, or 355 nm radiation from a Nd-YAG laser, together with a 0.5 m Acton monochromator equipped with a charge-coupled device. Raman spectra were recorded as described previously.<sup>23</sup> Some experiments were also performed at Hong Kong University, where the Stokes  $\text{H}_2$ -shifted harmonics of a Nd-YAG pulsed laser were used to excite polycrystalline  $\text{Ce}/\text{Cs}_2\text{NaYCl}_6$  and  $\text{Cs}_2\text{NaErCl}_6$  (assumed to contain traces of  $\text{Ce}^{3+}$ ) with the equipment described earlier.<sup>24</sup> The spectral resolution was between 2-4  $\text{cm}^{-1}$ . Spectral calibration was performed using various standard lamps and the wavelengths were corrected to vacuum.

Fluorescence spectra obtained at LBNL from the lowest 5d level to the 4f manifolds were obtained using a Xenon lamp as described previously.<sup>25</sup> The sample was cooled to  $\sim 10$  K using an Oxford Instruments model 1204 cryostat. The entrance and exit slits of the Spex 1403 double monochromator were set at 200  $\mu\text{m}$  for a resolution on the order of 1  $\text{cm}^{-1}$ . The spectra were calibrated with a mercury lamp and corrected to vacuum.

### Review of parametric theory

The Hamiltonian for the energy levels of an  $f$  electron in an octahedral crystal field may be written as<sup>26</sup>

$$H = H_{\text{SO}} + H_{\text{CF}}$$

$$H_{\text{SO}} = \zeta_{4f}(r) \mathbf{l} \cdot \mathbf{s}$$

$$H_{\text{CF}} = B_0^4 \left[ C_0^4 + \left(\frac{5}{14}\right)^{1/2} (C_{-4}^4 + C_4^4) \right] + B_0^6 \left[ C_0^6 - \left(\frac{7}{2}\right)^{1/2} (C_{-4}^6 + C_4^6) \right]. \quad (1)$$

The empirical parameters above include the crystal field parameters  $B_0^4$  and  $B_0^6$ , (utilizing the Wybourne notation) and the spin-orbit coupling constant  $\zeta_{4f}(r)$ . The matrix elements for the angular momentum operators  $\mathbf{s}$  and  $\mathbf{l}$  and the tensor operators  $C_q^k$  depend only on the angular coordinates and are evaluated by standard techniques.<sup>26,27</sup> For the  $4f^1$  configuration of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ , the spin-orbit interaction is larger than the crystal field interaction. The spin-orbit coupling interaction splits the  $f^1$  free ion state into two J levels,  $J=5/2$  and  $7/2$ , and the octahedral crystal field splits the ground  $J = 5/2$  term into a  $\Gamma_{7u}$  doublet and a  $\Gamma_{8u}$  quartet, using the double group notation for octahedral symmetry. Similarly the  $J = 7/2$  term splits into two doublets of  $\Gamma_{7u}$  and  $\Gamma_{6u}$  symmetry and one quartet of  $\Gamma_{8u}$  symmetry. Figure 1 shows the approximate energy level diagram and the nomenclature used.

The above Hamiltonian may also be utilized for the  $5d$  configuration. In this case the sixth order crystal field term  $B_0^6$  is equal to zero and the spin-orbit coupling constant is  $\zeta_{5d}(r)$ . However, unlike for the  $4f$  configuration, the  $5d$  configuration experiences a crystal field interaction that is considerably larger than the  $5d$  spin-orbit coupling. The octahedral ( $O_h$ ) crystal field splits the  $5d^1$  configuration into two levels, a triply orbitally degenerate  $T_{2g}$  lower state and a doubly orbitally degenerate  $E_g$  upper state. When the spin-orbit interaction is included, the  $T_{2g}$  level splits into a quartet  $\Gamma_{8g}$  lower level and a higher-lying doubly degenerate  $\Gamma_{7g}$  state. The  $E_g$  upper state transforms into a quartet  $\Gamma_{8g}$  state as shown in Figure 1. The solutions of the above Hamiltonian for a  $4f^1$  or a  $5d^1$  electron configuration are well known and will not be repeated.<sup>28</sup>

The emission and absorption transitions reported in this paper between the  $4f^1$  and  $5d^1$  configurations are allowed electric dipole transitions that originate or terminate either in crystal field states of  $\Gamma_{7u}$ ,  $\Gamma_{8u}$ , or  $\Gamma_{6u}$  symmetry for the  $4f^1$  configuration or  $\Gamma_{8g}$  or  $\Gamma_{7g}$  for the  $5d^1$  configuration. The electric dipole operator transforms as  $\Gamma_{4u}$ . Evaluating the direct products of the initial and final states with the electric dipole operator shows all purely electronic zero phonon transitions are allowed, with the exception of  $\Gamma_{7g} - \Gamma_{6u}$ . The  $f \leftrightarrow d$  transitions between  $\Gamma_7$  states may couple with totally-symmetric vibrational modes, whereas in addition the  $\tau_{2g}$  mode is potentially Jahn-Teller active between  $\Gamma_7$  and  $\Gamma_8$  states.

## f-f absorption spectra

The  $4f^1$  crystal field levels of  $\text{Cs}_2\text{NaCeCl}_6$  have been deduced from electronic Raman studies and are given in Table 1.<sup>23,29</sup> A crystal field fit gave  $\zeta_{4f} = 623 \text{ cm}^{-1}$ ,  $B_0^4 = 2119 \text{ cm}^{-1}$  and  $B_0^6 = 261 \text{ cm}^{-1}$ .<sup>30</sup> The f-f electronic absorption spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  and  $\text{Cs}_2\text{NaCeCl}_6$  have been reported and are dominated by magnetic dipole transitions.<sup>31</sup> Although the former is cubic at low temperatures, the latter undergoes a phase transition at 178 K.<sup>10,32-34</sup> The infrared absorption spectra were reinvestigated in this study and the derived energy levels are listed in Table 1. The magnetic dipole transitions ( ${}^2F_{5/2}$ ) $\Gamma_7 \rightarrow$  ( ${}^2F_{7/2}$ ) $\Gamma_7$ ,  $\Gamma_8$  are the most intense bands, with measured oscillator strengths  $4.8 \times 10^{-8}$  and  $5.1 \times 10^{-8}$  respectively in dilute  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ . The fact that values measured in neat  $\text{Cs}_2\text{NaCeCl}_6$  are smaller ( $6.3 \times 10^{-9}$  and  $1.7 \times 10^{-8}$ , respectively) is attributed to saturation effects.

## Vibrational spectra

The normal vibrations of the  $\text{Cs}_2\text{NaCeCl}_6$  crystal are described in the notation of Lentz, with the relationship to the  $\text{CeCl}_6^{3-}$  moiety mode vibrations being given in Table 2.<sup>35</sup> Assignments are included from the Raman and vibronic spectra. The energies of the stretching vibrations are somewhat higher in the  $\text{Cs}_2\text{NaYCl}_6$  lattice, with  $\nu_1$ , for example, being near  $300 \text{ cm}^{-1}$ . Also included in Table 2 are the results from normal coordinate calculations employing moiety mode and unit cell group models.<sup>36,37</sup>

## $4f^1 {}^2F_{5/2} - 5d^1 ({}^2T_{2g})$ absorption spectra

The 6 K ultraviolet electronic absorption spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  has previously been reported by Schwarz and Schatz.<sup>9</sup> It comprises electric-dipole allowed transitions from the  $4f^1 {}^2F_{5/2} \Gamma_{7u}$  ground state to the  $5d^1 {}^2T_{2g} \Gamma_{8g}$  and  $\Gamma_{7g}$  states. Prominent vibrational progressions in modes of  $300 \text{ cm}^{-1}$  and  $47 \text{ cm}^{-1}$  were built upon the zero

phonon lines. We have reinvestigated the spectra at 10 K, and our spectrum is very similar to that of Schwarz and Schatz, with fine structure in addition to the two prominent progressions. A further progression in a lattice mode of ca. 14-16 cm<sup>-1</sup> was reported by Schwarz and Schatz, although the first member is not evident in the present study or in their published spectrum. However, we do observe a shoulder at 32 cm<sup>-1</sup> above the zero phonon line, in agreement with Schwarz and Schatz.

The 10 K absorption spectra of *neat* Cs<sub>2</sub>LiPrCl<sub>6</sub> and Cs<sub>2</sub>LiTmCl<sub>6</sub> in the ultraviolet show f-d absorption bands due to Ce<sup>3+</sup> impurities (Fig. 2). The zero phonon line transition energies are listed in Table 3. The weak feature to low energy of  $\Gamma_{7u} \rightarrow \Gamma_{8g}$  in Ce<sup>3+</sup>/Cs<sub>2</sub>LiPrCl<sub>6</sub> is a hot band. The low energy part of Ce<sup>3+</sup>/Cs<sub>2</sub>LiTmCl<sub>6</sub> absorption spectrum overlaps the <sup>3</sup>H<sub>6</sub>-<sup>1</sup>D<sub>2</sub> f-f transition of Cs<sub>2</sub>LiTmCl<sub>6</sub>. Samples of elpasolite hosts doped with Ce<sup>3+</sup> concentrations of the order of 1% exhibit total absorption in this region. The vibrational progression frequencies, averaged over all the first members, are listed for the two strongest progression modes in Table 4.

### **<sup>2</sup>T<sub>2g</sub> 5d<sup>1</sup> -4f<sup>1</sup> <sup>2</sup>F<sub>5/2</sub>, <sup>2</sup>F<sub>7/2</sub> emission spectra**

The Xe lamp-excited ~10 K emission spectrum of dilute Ce<sup>3+</sup>/Cs<sub>2</sub>NaYCl<sub>6</sub> is shown in Figure 3. Transitions are observed to the <sup>2</sup>F<sub>5/2</sub>, <sup>2</sup>F<sub>7/2</sub> terminal crystal field levels of Ce<sup>3+</sup>, as marked in Figure 3, and the derived energies are listed in Table 5. The lowest energy electronic origin is mostly self-absorbed, as is shown by the superposition of the absorption and 199.8 nm excited emission spectra from the 5d<sup>1</sup> level, both at 10 K (Figure 4). The mirror-image relationship of the absorption and emission spectra is not exact because, although the 0-0 transitions coincide, there are further electronic transitions which are unique to either absorption or emission. The energy difference between the maxima in the emission and absorption spectra, ca. 1920 cm<sup>-1</sup>, is therefore not solely related to vibrational energies, but also to the locations of the relevant 5d<sup>1</sup> and 4f<sup>1</sup> electronic states.

The D<sub>2</sub>-lamp and 355 nm excited luminescence spectra of Ce<sup>3+</sup>/Cs<sub>2</sub>NaYCl<sub>6</sub> at 10 K are similar to the 199.8 nm-excited spectrum, except that the highest energy bands are strongly self-absorbed. The 199.8 nm-excited emission spectrum of Ce<sup>3+</sup> doped into



$\text{Cs}_2\text{LiYCl}_6$  is generally similar to, but less well-resolved than, the spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  (Figure 5).

An additional, very weak, group of bands (not shown here) is observed in the 355 nm excited spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ , with the highest energy electronic origin at  $22210\text{ cm}^{-1}$ . Based upon this zero phonon line, progressions in vibrational modes of  $274$  and  $173\text{ cm}^{-1}$  are observed to low energy. Since the former energy is rather less than the Ce-Cl vibrational frequency of  $\text{CeCl}_6^{3-}$ , and these bands are located at *ca.*  $3300\text{ cm}^{-1}$  below the 5d - 4f electronic transition energy, a probable assignment is to the one quantum of the O-H vibration based upon the (unobserved) 5d - 4f zero phonon line of this trace impurity, partially hydrolysed  $\text{CeCl}_6^{3-}$  ion.

### **$^2\text{E}_g$ 5d<sup>1</sup>-4f<sup>1</sup> emission spectra**

Under 199.8 nm excitation at 10 K, a group of bands is observed in the emission spectrum of neat  $\text{Cs}_2\text{NaErCl}_6$  which cannot be associated with electronic transitions of  $\text{Er}^{3+}$  (Figure 6). We tentatively assign this emission to the  $\text{Ce}^{3+}$  5d<sup>1</sup>  $^2\text{E}_g$  state emitting to the 4f<sup>1</sup> electronic levels. The reasons for this assignment are because (i) the luminescence is clearly d - f and not f - f, and there are no f<sup>10</sup>d energy levels of  $\text{Er}^{3+}$  at such low energy; (ii) f - f luminescence from  $\text{Er}^{3+}$  would be quenched by the  $^4\text{D}_{1/2}$  state, just below  $47000\text{ cm}^{-1}$ ; (iii) the line intervals cannot be matched with energy level intervals of  $\text{ErCl}_6^{3-}$ . Furthermore, these bands are not evident in the emission spectrum of dilute  $\text{Er}^{3+}/\text{Cs}_2\text{NaYCl}_6$ , nor in the 218-nm excited spectra of  $\text{Cs}_2\text{NaErCl}_6$ . The electronic origin at highest energy is located at  $47080\text{ cm}^{-1}$  (Figure 6). The progressions in vibrational modes of  $49\text{ cm}^{-1}$  and  $297\text{ cm}^{-1}$  are characteristic of the 5d - 4f emission spectra described above. At the second member of the  $\nu_1$  progression there is an apparent doubling of bands, which can be explained by the presence of a further electronic state at  $594\text{ cm}^{-1}$  above the ground state. It is for these reasons that we believe these bands can be assigned to emission from the d<sup>1</sup>  $^2\text{E}_g$   $\Gamma_8$  state of a  $\text{Ce}^{3+}$  impurity in neat  $\text{Cs}_2\text{NaErCl}_6$ .

Only one further similar group of bands is observed to lower energy. For this weaker group of bands (Fig. 6), two further electronic origins can be assigned. The inferred

locations of the  $4f^1 \ ^2F_{7/2}$  states (Table 5) are however, rather lower (by about  $40 \text{ cm}^{-1}$ ) than expected from the energy levels of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ .

Since the 199.8 nm excitation energy is  $2954 \text{ cm}^{-1}$  to high energy of the highest energy zero phonon line of  $\text{Ce}^{3+}$ , it appears that either the absorption takes place into an  $\text{Er}^{3+}$  energy level, with subsequent energy transfer to  $\text{Ce}^{3+}$ ; or that cooperative ion effects occur. Strong emission from the 4f-energy levels of  $\text{Er}^{3+}$  is observed at lower energies, which masks the  $^2T_{2g} \text{ Ce}^{3+}$  transitions, if present.<sup>24</sup>

We have assigned the fluorescence spectra observed in  $\text{Cs}_2\text{NaErCl}_6$  beginning at  $47080 \text{ cm}^{-1}$  as the emission from the highest  $5d^1 E_g$  level to the 4f levels of the  $\text{Ce}^{3+}$  ion. This assignment is consistent with other observations for the  $\text{Ce}^{3+}$  ion in this energy range as discussed in the introduction. The observed vibronic spectra and the derived 4f energy levels given in Table 1 support this assignment. However no fluorescence from the  $E_g$  state was observed in the  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  system when this system was excited in the wavelength range of 192-210 nm at 10 K, although  $T_{2g}$  emission was observed. The calculated  $E_g$  emission intensities are in poor agreement with the experimental data (see below). One possibility for the quenching of the  $E_g$  emission in the  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  system is by energy transfer to killer sites. The most likely candidates are  $\text{Pr}^{3+}$  and/or  $\text{Nd}^{3+}$  since these ions have 5d levels in the 200 nm region. Analysis of the undoped  $\text{Cs}_2\text{NaYCl}_6$  crystal shows that these ions are present in relatively significant concentrations, so this is a possibility. Reliable analytical data could not be obtained for the  $\text{Er}_2\text{O}_3$  starting material used to prepare  $\text{Cs}_2\text{NaErCl}_6$ . If the amount of Pr/Nd in the  $\text{Cs}_2\text{NaErCl}_6$  crystal is significantly less than in the  $\text{Cs}_2\text{NaYCl}_6$  system, then this could be a possible explanation for the appearance of the  $5d^1 E_g$  emission. The fluorescence from the  $\text{Ce}^{3+} E_g$  state is unlikely to be quenched by  $\text{Er}^{3+}$  f-electron levels. Quenching by d-electron levels of  $\text{Nd}^{3+}/\text{Pr}^{3+}$  would not give rise to d - f emission from these lanthanide ions because  $\text{Nd}^{3+}$  does not exhibit d - f emission in elpasolites, and  $\text{Pr}^{3+}$  d - f emission is quenched by  $\text{Ce}^{3+}$ .

### **Vibrational progressions, linewidths and Condon parabolae**

Several vibrational progressions have been identified above in the  ${}^2T_{2g} 5d^1 - 4f^1 {}^2F_{5/2}$ ,  ${}^2F_{7/2}$  emission and absorption spectra of  $\text{CeCl}_6^{3-}$ . Selection rules for these spectra show that the vibrational mode must transform as the totally symmetric representation at the  $O_h$  crystal site of  $\text{Ce}^{3+}$ . Following the remarks of Schwartz and Schatz,<sup>9</sup> and by comparison of the progression intervals with Table 2, it is clear an alternative, the occurrence of Jahn-Teller effects, is not evident in the  ${}^2T_{2g}$  state. These authors assigned vibrational progression modes with energies of 16 and/or 32  $\text{cm}^{-1}$ . The first of these energies is comparable with the  $S_3$  rotatory mode, whereas the second energy could correspond to an acoustic mode. The occurrence of progressions in these modes would thus infer contributions to the intensity from points away from the zone center. Since these progressions are not well-resolved, and we do not observe corresponding features in the spectra of  $\text{Ce}^{3+}/\text{Cs}_2\text{LiLnCl}_6$ , we do not discuss these bands further. The strongest progressions in the spectra of  $\text{Ce}^{3+}/\text{Cs}_2\text{ALnCl}_6$  ( $A = \text{Na}, \text{Li}$ ) occur in the  $\nu_1 (\alpha_{1g}) \text{CeCl}_6^{3-}$  moiety (*i.e.* first shell) mode, with the energy rather greater than in neat  $\text{Cs}_2\text{ACeCl}_6$  because  $\text{CeCl}_6^{3-}$  is compressed in the crystalline hosts employed. The next prominent progression occurs in the mode near 44-49  $\text{cm}^{-1}$  in  $A = \text{Na}$  hosts, but in 51-54  $\text{cm}^{-1}$  in  $A = \text{Li}$  hosts. Clearly the energy of this mode is not very sensitive to the masses of  $\text{Ln}$  or  $A$ , but it is similar to that of the  $S_5 (\tau_{2g})$  mode. This progression mode can therefore be envisaged as a  $\mathbf{k} \neq 0$  totally symmetric mode (such as along the  $\Delta$  direction of reciprocal space), or more simply (but less accurately) as the totally symmetric stretch of the second shell,  $\text{CeCs}_8$ .

It is evident that a further, weaker progression occurs in a vibrational mode of 180-193  $\text{cm}^{-1}$  for  $A = \text{Na}$ , and 237-252  $\text{cm}^{-1}$  for  $A = \text{Li}$ . This vibration can be envisaged as the contribution from the  $S_8 (\tau_{1u})$  mode away from the zone center, or alternatively, from the totally symmetric stretch of the third shell,  $\text{Ce-Na}_6$ . In all of these totally symmetric breathing modes, the  $\text{Ce}$  nucleus is stationary. Additional evidence for this latter “sodium” mode comes from the study of the linewidths and relative intensities of consecutive bands in the emission spectra. Considering the emission transition  ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$ , after subtraction of the continuous background, the first few bands can be better fitted by Gaussian rather than Lorentzian profiles (Fig. 7). This is presumably because some of the fitted bands comprise more than one component. The half-height

width shows an increase for the first few bands in the progression of the  $48 \text{ cm}^{-1}$  lattice mode, with a progressive decrease in intensity. A sharper feature is then apparent at  $190 \pm 3 \text{ cm}^{-1}$ , which must then correspond to the first member of a further progression. The lowest energy band in Figure 7 corresponds to the first member of the  $48 \text{ cm}^{-1}$  lattice mode progression upon the  $190 \text{ cm}^{-1}$  mode.

The wavefunctions obtained from Eq. (1) represent only the pure electronic wavefunctions. Considering also vibronic coupling, the intensity of an electronic transition from the initial state  $i$  to the final state  $f$  may be written (in the adiabatic approximation which assumes the electronic part is independent of the vibrational coordinates) as

$$I \propto |\langle i | er | f \rangle \langle l | m \rangle|^2 \quad (2)$$

where  $I$  is the intensity,  $er$ , the electric dipole operator, and  $l$  and  $m$  are the initial and final vibrational states, respectively.<sup>38,39</sup> If it is further assumed that the electronic-vibrational coupling is linear (i.e., the vibrational states in the ground and excited states are equal), and only the lowest vibrational level of the initial state is populated, then

$$I_n \approx e^{-S_{H-R}} \left( \frac{S_{H-R}^n}{n!} \right), \quad (3)$$

where  $S_{H-R}$  is the Huang-Rhys parameter and  $n$  is the vibrational quantum number of the terminal state.

The Huang-Rhys parameter can be evaluated from a harmonic progression in a vibrational mode. For the vibration corresponding to the normal coordinate  $Q_i$ ,

$$S_{H-R} = \frac{M\omega_i}{2\hbar} (\Delta Q_i)^2 \quad (4)$$

where  $M$  is the effective mass and  $\Delta Q_i$  is the difference between the equilibrium distances of the metal ion and the ligand in the ground and excited states for the vibrational mode  $\nu_i$  of angular frequency  $\omega_i$ .<sup>38,39</sup>

A similar method to relate the change in intensity along a vibrational progression to the change along the corresponding vibrational coordinate has been given by Yersin *et al.*<sup>40</sup> They have related the measured, relative vibronic intensities in emission  $I^{0,n}$  and absorption  $I^{m,0}$  (where  $m,n$  indicate the number of quanta) to the zero phonon line (ZPL) intensity,  $I^{0,0}$ . For the case of the  $\nu_1$  progressions:

$$\frac{I^{0,n}}{I^{0,0}} = \left[ \frac{E(\text{ZPL}) - n\nu_1}{E(\text{ZPL})} \right]^4 \left[ \frac{R_{0,n}}{R_{0,0}} \right]^2 \dots\dots\dots (5a)$$

$$\frac{I^{m,0}}{I^{0,0}} = \left[ \frac{E(\text{ZPL}) + m\nu_1}{E(\text{ZPL})} \right] \left[ \frac{R_{m,0}}{R_{0,0}} \right]^2 \dots\dots (5b)$$

where the overlap integrals  $R_{0,n}$  and  $R_{m,0}$  can be related to the displacement  $\Delta Q$  of the minimum of the potential surface of the excited electronic state along the  $\alpha_{1g}$  normal coordinate. Furthermore, the individual Ce-Cl bond length change,  $\Delta r = \Delta Q/\sqrt{6}$ . The Franck-Condon analyses were performed upon the emission and absorption spectra, after subtraction of the continuous background.<sup>41</sup>

The spectra shown in Figure 8 were fit by using the Huang-Rhys formulation for three oscillators,  $S_{\text{H-R1}}$  corresponding to the  $\sim 300 \text{ cm}^{-1}$   $\nu_1$  vibration,  $S_{\text{H-R2}}$  corresponding to the  $\sim 48 \text{ cm}^{-1}$  assigned to the totally symmetric stretch  $\nu_{\text{lattice}}$  vibration. The third frequency  $S_{\text{H-R3}}$  was used to fit the broad background. The line widths were treated as free parameters and the relative intensities of the two electronic transitions involved,  ${}^2T_{2g}$  (or  $E_g$ )  $\Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$  and  ${}^2T_{2g}$  (or  $E_g$ )  $\Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$ , were adjusted to give the best fit. Representative fits for the  $\sim 28000 \text{ cm}^{-1}$  emission of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYnCl}_6$  (from Fig. 3a) and for the  $\sim 48000 \text{ cm}^{-1}$  emission of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$  (from Fig. 6) are shown in Figure 8. Franck-Condon analyses using Eqs. 5a and 5b also were performed upon all the emission and absorption spectra, after subtraction of the continuous background<sup>41</sup> assuming that the vibrational frequencies are unchanged in the ground and excited states.

The derived parameters,  $\Delta r$  and  $\Delta Q$  are listed in Table 4. The displacement between the d- and f-electron potential energy hypersurfaces of 0.09-0.13 Å, represents a Ce-Cl bond length change of about 0.04 Å, which is <2% of the bond length. Similar changes have been obtained from the analysis of 5d  $\rightarrow$  4f emission transitions of Pr<sup>3+</sup> in elpasolite lattices.<sup>42</sup> The bond length change along the Cs<sup>+</sup> lattice mode coordinate from this analysis is 0.05-0.07 Å.

A similar fit was performed for the  $\sim 50,000$  cm<sup>-1</sup> emission assigned ( tentatively) as due to the  ${}^2E_g \Gamma_8 \rightarrow {}^2F_{5/2}$ . With this initial state the displacement between the d- and f-electron potential energy hypersurfaces is 0.08-0.09 Å, representing a Ce-Cl bond length change of about 0.035 Å, slightly smaller than found with the  ${}^2T_{2g} \Gamma_8$  as the initial state. The differences in bond distances found for transitions that are initiated from either the  $T_{2g}$  or the  $E_g$  orbitals can be rationalized by the differences in bonding in these two 5d orbitals (see below).

### **Electric dipole intensities and crystal field calculations**

The wavefunctions obtained from diagonalization of the matrices given by Eq. 1 can be used to evaluate Eq. 2. The radial part of Eq. 2 is the same for all transitions so we compare the calculated relative intensities with the measured relative intensities for the emission transitions in Table 6.

The measured electric dipole intensities from the  $T_{2g} \Gamma_8$  state to the 4f levels were obtained by subtracting an empirical background corresponding to the underlying broad background shown in Figure 3 from the spectra and then fitting the vibronic peaks with a Gaussian peak-fitting program. We estimate the accuracy of the experimental intensities obtained in this way to be about 50%. For transitions originating from the lowest level of the 5d<sup>1</sup> configuration, the agreement between the experimental and calculated relative intensities is reasonable.

With the assumption that Figure 6 corresponds to emission from the  ${}^2E_g$  state of Ce<sup>3+</sup>, then the relative intensities of transitions from this level are not in good agreement with calculation. This is not because the lower energy bands are absorbed by Er<sup>3+</sup> transitions

in  $\text{Cs}_2\text{NaErCl}_6$ , since there is a spectral window between  $44000\text{-}46000\text{ cm}^{-1}$  for the energy levels of  $\text{Er}^{3+}$ .

The calculated intensities show that the emission to the  $4f^1\ ^2F_{7/2}$  states should be considerably greater from the  $5d^1\ E_g$  levels than from the  $5d^1\ T_{2g}$  levels. The reason for this intensity change is because only transitions with  $\Delta J = 0, \pm 1$  are allowed. The  $5d^1\ E_g$  wavefunctions have  $\sim 65\%$   $L = 3, J = 5/2$  character and  $\sim 35\%$   $L = 3, J = 3/2$  character as compared to the  $\sim 35\%$   $L = 3, J = 5/2$  character and  $\sim 65\%$   $L = 3, J = 3/2$  character of the  $5d^1\ T_{2g}$  wavefunctions. Thus for the  $5d^1\ T_{2g}$  wavefunctions, the major component of the wavefunctions can not contribute any intensity (in the limit of zero crystal field mixing) to the  $4f^1\ J = 7/2$  levels. Nevertheless, the experimental intensities from the  $5d^1\ E_g$  levels are completely off from the calculated values. In fact the calculated values show the intensities to the  $4f^1\ J=7/2$  states should be larger than to the  $4f^1\ J=5/2$  states, completely in reverse to the observed values.

As expected the crystal field fits shown in Table 5 agree with the experimental energies quite well. In this case the number of observables and the number of parameters are comparable. A better test is the comparison of the calculated ground state  $4f^1\ \Gamma_{7u}\ g$  value  $g = -1.253$  with the experimental value,  $g = |1.266|$ .<sup>10</sup>

### ***Ab initio* calculations**

In order to complement the data with independent theoretical information, we performed wave function based *ab initio* calculations on the  $(\text{CeCl}_6)^{3-}$  cluster embedded in a reliable representation of the  $\text{Cs}_2\text{NaYCl}_6$  host. The results are summarized in Table 7. These calculations take into account the most important bonding interactions within the  $(\text{CeCl}_6)^{3-}$  unit, including electron correlation and scalar and spin-orbit coupling relativistic effects, and  $\text{Cs}_2\text{NaYCl}_6$  host embedding effects.

The details of the calculations follow. We use the *ab initio* model potential method, AIMP, as an embedding technique and as an effective core potential method.<sup>20,21</sup> The embedding potential we use for  $\text{Cs}_2\text{NaYCl}_6$  was obtained earlier.<sup>43</sup> The relativistic AIMP we use for Ce was obtained from Seijo<sup>44</sup> and represents its [Kr] core; the *ab initio* spin-orbit potential produced earlier<sup>45</sup> is used here with an empirical scaling factor 0.9;<sup>46</sup> the

basis set for the 4d5s5p4f5d valence is the (14s10p10d8f)/[6s5p6d4f] set.<sup>44</sup> For Cl, we use the [Ne] core AIMP and the (7s6p) basis set<sup>47</sup> extended with one diffuse *p*-function<sup>48</sup> and contracted as [3s4p]. Additional (7s4p)/[1s1p] basis set functions are located on the Na<sup>+</sup> ions along the 100, 010, and 001 directions that are next neighbors to the (CeCl<sub>6</sub>)<sup>3-</sup> cluster.<sup>43</sup> The electron correlation effects from the 36 3p electrons of the Cl ligands and the unpaired electron of Ce<sup>3+</sup> are included by means of Average Coupled Pair Functional Calculations, ACPF.<sup>49,50</sup> Finally, we use the spin-free-state-shifted spin-orbit Hamiltonian (sfss)<sup>51</sup> in an identical manner as described<sup>52</sup> for (PaCl<sub>6</sub>)<sup>2-</sup>, in order to put together the electron correlation effects and the spin-orbit coupling effects in a simplified way.

The calculated bond distances along the breathing mode shown in Table 7 are almost equal for all the states of the 4f<sup>1</sup> manifold; the slightly smaller values of the two  $\Gamma_{7u}$  states correspond to them being the only ones with 4f(a<sub>2u</sub>) orbital character, which is the f orbital most stabilized by the ligand field. All these states have essentially the same  $\nu_1$  vibrational frequency. The computed values compare well with the experimental data. The computed minimum-to-minimum energy differences are very reasonable when compared with experiment; in order to lower the mean average deviation from 260 cm<sup>-1</sup> it would probably be necessary to increase the methodological and computational demands to a very large extent. A more detailed analysis of these differences shows that its main contribution comes from a slight excess stabilization of the 4f(a<sub>2u</sub>) molecular orbital, (e.g. the mean average deviation from experiments is 80 cm<sup>-1</sup> for the  $\Gamma_{8u}$  and  $\Gamma_{6u}$  states, with no 4f(a<sub>2u</sub>) contribution) which indicates that these calculations may be slightly overestimating the effective ligand field.

The calculations on the 5d<sup>1</sup> manifold are perhaps more interesting. The bond distance of the two <sup>2</sup>T<sub>2g</sub> states,  $\Gamma_{8g}$  and  $\Gamma_{7g}$ , are the same and smaller than the bond distance of the 4f<sup>1</sup> states. The absolute value of the offset, 0.047 Å agrees well with the experimentally deduced value in Table 4. The fact that it is negative could not have been deduced from the analysis of the emission band shapes, which leads only to absolute values. The prediction of a cluster contraction in the transition from 4f to 5d(t<sub>2g</sub>) was also made in the corresponding case<sup>52</sup> of Pa<sup>4+</sup>; it has to be the result of a balance between opposite tendencies: to increase bond distance as a consequence of the larger size of the 5(6)d



orbital, on the one hand, and to reduce bond distance as a consequence of the larger bond covalency in the  $5(6)d^1$  states, on the other. An analysis of the detailed reasons leading to this contraction has been presented elsewhere.<sup>53</sup> The bond distance of the  $5d^1 \ ^2E_g \Gamma_{8g}$  is larger than that of the  $^2T_{2g}$  states, as usual for the  $O_h$  ligand field splitting of d states and corresponding to the  $5d(e_g)$  orbital being destabilized with respect to the  $5d(t_{2g})$ . The bond distance increases so as to make it larger than the  $4f^1$  bond distances by 0.017 Å. The calculated vibrational frequencies are very similar to the  $4f^1$  ones, only very slightly smaller, and they are again close to the approximate experimental value of  $300 \text{ cm}^{-1}$  deduced from absorption and MCD spectra of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ . The minimum-to-minimum energies from the ground state to the two  $^2T_{2g}$  states,  $\Gamma_{8g}$  and  $\Gamma_{7g}$ , are  $2700 \text{ cm}^{-1}$  too low, which is a reasonable result for a theoretically demanding  $4f \rightarrow 5d$  transition. Finally, the energy of the  $5d^1 \ ^2E_g \Gamma_{8g}$  state is calculated to be  $47260 \text{ cm}^{-1}$ . It agrees extremely well with the experimental observation in  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ , very probably as a consequence of compensation between an underestimation of the  $4f \rightarrow 5d$  baricenter and an overestimation of the ligand field, as already observed in the splitting of the  $4f^1$  manifold. In any case, the *ab initio* calculation strongly suggests the existence of the  $5d^1 \ ^2E_g \Gamma_{8g}$  state of the  $(\text{CeCl}_6)^{3-}$  unit  $46000\text{-}48000 \text{ cm}^{-1}$  above the ground state. This independent result supports the assignments of the emission spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$  in Fig. 6.

## Discussion and Conclusions

In this paper we have reported the results of detailed spectroscopic investigations of the  $\text{Ce}^{3+}$  ion in chloro-elpasolite hosts. The complete energy level schemes for the  $4f^1$  and  $5d^1$  configurations may be inferred from a combination of the fluorescence and absorption data from our work with earlier absorption data. Good fits were obtained for both the  $4f$  and  $5d$  levels using the crystal field model. However, although the calculated emission intensities from the  $5d \ T_{2g} \ \Gamma_8$  level were in reasonable agreement with the experimental intensities, the calculated intensities from the  $5d \ E_g \ \Gamma_8$  level were completely off. It is possible that admixtures of charge transfer states into the  $5d \ E_g$  state could be important.

Theoretical calculations are presented which give reasonable agreement with the experimental energy levels and support the assignment of the  $47080\text{ cm}^{-1}$  feature to the  $5d^1 E_g$  level. These calculations also show that the change in bond length between the  $4f^1$  and  $5d^1 T_{2g}$  configuration is contractive with a value of  $\sim 0.04\text{ \AA}$ , in excellent agreement with the experimental result (note that only the absolute value is obtained from the experimental results). This short bond for the  $5d T_{2g}$  state suggests that the covalency of this  $5d$  orbital with its consequent bond length shortening outweighs the lengthening of this bond due to the larger size of the  $5d$  orbital. A detailed analysis for this has been presented elsewhere.<sup>53</sup> By contrast, the experimental measurements from the  $E_g$  emission spectrum show a slightly smaller bond length change than for the  $T_{2g}$  state. The theoretical calculations predict an increase in this bond length relative to that in the ground  $4f$  configuration, which means a smaller bond length change than that obtained from the experimental analysis.

One factor that can account for some of these discrepancies hinges upon the subtraction of the broad background when integrating peaks in the emission or absorption spectra. Rather different results are obtained if the entire vibronic sideband is integrated (for example, in the Fig. 4 absorption spectrum, the maximum is at  $n = 1$  if individual bands are considered, but at  $n = 2$  quanta of  $\nu_1$  if the background is not subtracted). Although fits also were made assuming the background could be reproduced as a Gaussian function or by reproducing the background with a band coming from the Huang-Rhys equation with an empirical width, this may not necessarily account for the entire background. For example, (i) there are overlapping electronic transitions in some cases, and (ii) progressions in multiple quanta of odd vibrational modes may occur, partly giving rise to the broad underlying background. Furthermore, the relative intensities of the transitions involved with  $47080\text{ cm}^{-1}$  emission were in disagreement with the predicted relative intensities obtained for the allowed electric dipole calculations. Thus the relative measured intensities from which the bond length changes are obtained must be considered somewhat suspect.

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## Figure captions

Fig. 1. Schematic energy level diagram of the  $4f^1$  and  $5d^1$  configurations of the  $Ce^{3+}$  ion in a chloroelpasolite crystal field. Note the change in the energy scale between the  $4f^1$  and the  $5d^1$  configurations.

Fig. 2. 10 K absorption spectra of trace  $Ce^{3+}$  impurity in  $Cs_2LiPrCl_6$  and  $Cs_2LiTmCl_6$  between 28000 - 31000  $cm^{-1}$ . (The initial state is  $\Gamma_{7u}$  in all cases, and the terminal d-electronic states are labeled).

Fig. 3. 10 K UV xenon lamp excited emission spectrum of  $Ce^{3+}/Cs_2NaYCl_6$  between 28500 - 22500  $cm^{-1}$

Fig. 4. Comparison of 10 K absorption spectrum of  $Ce^{3+}/Cs_2NaYCl_6$  with the 199.8 nm excited emission spectrum at 10 K.

Fig. 5 Comparison of 199.8 nm excited 10 K emission spectra of (a)  $Ce^{3+}/Cs_2NaYCl_6$  and (b)  $Ce^{3+}/Cs_2LiYCl_6$ . The terminal f-electron states are labeled.

Fig. 6. 199.8-nm excited 10 K emission spectrum of  $Ce^{3+}/Cs_2NaErCl_6$  between 47000 - 43500  $cm^{-1}$ .

Fig. 7. Gaussian fits to the first few bands in the 10 K  ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$  emission spectrum of  $Ce^{3+}/Cs_2NaYCl_6$ . The numbers over the centers of the bands indicate the energy intervals (in  $cm^{-1}$ ) from the zero phonon line.

Fig. 8. Fits of the experimental emission spectra using the Huang –Rhys formulation as described in the text. Top)  $Ce^{3+}/Cs_2NaYCl_6$ :  $S_{H-R1}=1.275$ ,  $\omega_1=299 \text{ cm}^{-1}$ , line width= $14 \text{ cm}^{-1}$ ;  $S_{H-R2}=1.8$ ,  $\omega_1=47.5 \text{ cm}^{-1}$ , line width= $14 \text{ cm}^{-1}$ ;  $S_{H-R3}=4.39$ ,  $\omega_1=202 \text{ cm}^{-1}$ , line width= $145 \text{ cm}^{-1}$ ; intensity ratio of the transitions  ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$  to  ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u} = 2.0$ . Bottom)  $Ce^{3+}/Cs_2NaErCl_6$ :  $S_{H-R1}=1.13$ ,  $\omega_1=297 \text{ cm}^{-1}$ , line width= $9 \text{ cm}^{-1}$ ;  $S_{H-R2}=1.3$ ,  $\omega_1=48 \text{ cm}^{-1}$ , line width= $9 \text{ cm}^{-1}$ ;  $S_{H-R3}=1.55$ ,  $\omega_3=300 \text{ cm}^{-1}$ , line width= $105 \text{ cm}^{-1}$ ; intensity ratio of the transitions  $E_g \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$  to  $E_g \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u} = 0.13$ . The calculated spectra are shown as the dotted lines, the experimental data are shown as solid lines. Gaussian line shapes are assumed.

Table 1. f- and d electron energy levels (in  $\text{cm}^{-1}$ ) of  $\text{Ce}^{3+}$  in elpasolite lattices

Configuration	irrep	Electronic Raman, $\text{Cs}_2\text{NaCeCl}_6$ 20K	Electronic absorption, $\text{Cs}_2\text{NaCeCl}_6$ 90 K	Electronic absorption, $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ 10 K	Electronic absorption, $\text{Ce}^{3+}/\text{Cs}_2\text{NaTmCl}_6$ 90 K	Fluorescence $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ 10 K	Fluorescence $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ 10 K	Fluorescence $\text{Ce}^{3+}/\text{Cs}_2\text{LiYCl}_6$ 10 K
$4f^1\ ^2F_{5/2}$	$\Gamma_{7u}$	0	0	0	0	0	0	0
	$\Gamma_{8u}$	562, 580	563, 575	-	-	594	599	578
$4f^1\ ^2F_{7/2}$	$\Gamma_{7u}$	2161	2159	2159	2157	2125		
	$\Gamma_{8u}$	2663	2659	2674	(2676)	2628	2689	2674
	$\Gamma_{6u}$	3050	3048	-	-		3086	3061
$5d^1\ T_{2g}$	$\Gamma_{8g}$			28196			28193	28265
	$\Gamma_{7g}$			29435				
$5d^1\ E_g$	$\Gamma_{8g}$					47080		



Table 2. Vibrational assignments for Cs<sub>2</sub>NaCeCl<sub>6</sub>

Unit cell group mode and O <sub>h</sub> point group irrep.	Moiety mode and O <sub>h</sub> point group irrep.	20 K Raman spectrum	90 K f-f vibronic spectra	Calc. <sup>b</sup>	Calc. <sup>c</sup>
S <sub>1</sub> Ce-Cl sym. str.	$\nu_1 (\alpha_{1g})$	279	-	279	279
S <sub>2</sub> Ce-Cl str.	$\nu_2 (\epsilon_g)$	222	-	222	224
S <sub>3</sub> rotatory lattice ( $\tau_{1g}$ )	-	-	(~20) <sup>a</sup>	-	21
S <sub>4</sub> Cl-Ce-Cl bend	$\nu_5 (\tau_{2g})$	111	-	108	114
S <sub>5</sub> Cs transl. ( $\tau_{2g}$ )	-	46	-	-	48
S <sub>6</sub> Ce-Cl ant. str.	$\nu_3 (\tau_{1u})$	-	253(TO); 279(LO)	257	257
S <sub>7</sub> Cl-Ce-Cl bend	$\nu_4 (\tau_{1u})$	-	98(TO); 119(LO)	106	112
S <sub>8</sub> Na-Cl str. ( $\tau_{1u}$ )	-	-	(173) <sup>a</sup>	-	168
S <sub>9</sub> Cs transl. ( $\tau_{1u}$ )	-	-	56(TO); 69(LO)	-	53
S <sub>10</sub> Cl-Ce-Cl bend	$\nu_6 (\tau_{2u})$	-	74-84	77	76

<sup>a</sup>From the spectra of Cs<sub>2</sub>NaPrCl<sub>6</sub>; TO/LO transverse/longitudinal optic modes; str. stretch; sym. symmetric; ant. antisymmetric; trans. translatory.<sup>b</sup> Using 5-parameter General Valence Force-Field for moiety modes.<sup>36</sup> <sup>c</sup>Using 9-parameter unit cell group model.<sup>37</sup>

Table 3. f-d absorption spectra of Ce<sup>3+</sup> in elpasolite lattices

Lattice	Lattice parameter/Å <sup>a</sup>	Energy from <sup>2</sup> F <sub>5/2</sub> Γ <sub>7u</sub> (cm <sup>-1</sup> )		Energy difference (cm <sup>-1</sup> )
		<sup>2</sup> T <sub>2g</sub> Γ <sub>8g</sub>	<sup>2</sup> T <sub>2g</sub> Γ <sub>7g</sub>	
Cs <sub>2</sub> NaYCl <sub>6</sub>	10.733	28195±2	29435	1240
Cs <sub>2</sub> LiPrCl <sub>6</sub>	10.651	28363	29625	1262
Cs <sub>2</sub> LiTmCl <sub>6</sub>	10.439	28236	29489	1253
Cs <sub>2</sub> LiYCl <sub>6</sub>	10.479	28267	-	-

<sup>a</sup> From Meyer<sup>54</sup>

Table 4. Progression frequencies and bond length changes in  $f \rightarrow d$  transitions of  $Ce^{3+}$  in elpasolite lattices

Crystal Host	$Ce^{3+}$ concn. (mol %)	Transition	$\nu_1$ ( $cm^{-1}$ )	$\Delta Q(\nu_1)$ ( $\text{\AA}$ ) Ce-Cl	$\Delta r(\nu_1)$ ( $\text{\AA}$ ) <sup>a</sup>	$\nu(\text{lat})$ ( $cm^{-1}$ )	$\Delta Q(\text{lat})$ ( $\text{\AA}$ ) Cs-Cl	$\Delta r(\text{lat})$ ( $\text{\AA}$ ) <sup>a</sup>
Emission								
$Cs_2NaYCl_6$	0.5	${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$	$300 \pm 2$	0.12	0.050	$48 \pm 2$	0.14	0.050
		${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$	$298 \pm 3$	0.11	0.046	$48 \pm 2$	0.14	0.050
b		${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}, \Gamma_{7u}$	299	0.09	0.037	47.5	0.139	0.049
$Cs_2LiYCl_6$	1.0	${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$	$303 \pm 2$	0.11	0.043	$54 \pm 3$	0.18	0.062
		${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$	$301 \pm 1$	0.12	0.049	$52 \pm 3$	0.15	0.053
$Cs_2NaErCl_6$	-	$E_g \rightarrow {}^2F_{5/2} \Gamma_{7u}$	$297 \pm 5$	0.10	0.040	$49 \pm 3$	0.15	0.055
b		$E_g \rightarrow {}^2F_{5/2} \Gamma_{8u}, \Gamma_{7u}$	297	0.085	0.035	48	0.133	0.047
Absorption								
$Cs_2NaYCl_6$	0.01	${}^2F_{5/2} \Gamma_{7u} \rightarrow {}^2T_{2g} \Gamma_{8g}$	$299 \pm 2$	0.13	0.051	$44 \pm 3$	0.15	0.054
$Cs_2LiTmCl_6$	-	${}^2F_{5/2} \Gamma_{7u} \rightarrow {}^2T_{2g} \Gamma_{8g}$	$296 \pm 5$	-	-	$54 \pm 3$	-	-
$Cs_2LiPrCl_6$	-	${}^2F_{5/2} \Gamma_{7u} \rightarrow {}^2T_{2g} \Gamma_{8g}$	$285 \pm 5$	0.13	0.051	$51 \pm 2$	0.19	0.067

<sup>a</sup> Absolute values of bond length difference between the 4f and 5d states involved in the particular transition

<sup>b</sup> Results from the Huang-Rhys analysis (see text)

Table 5. Derived f- and d- electron energy levels from the 10K emission spectra of  $\text{CeCl}_6^{3-}$

State $nl^1 (2S+1)L_J$	irrep.	$\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ ( $\text{cm}^{-1}$ )	$\text{Ce}^{3+}/\text{Cs}_2\text{LiYCl}_6$ ( $\text{cm}^{-1}$ )	$\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ ( $\text{cm}^{-1}$ )	Calculated Levels ( $\text{cm}^{-1}$ ) <sup>a,b,c</sup>
$4f^1 \ ^2F_{5/2}$	$\Gamma_{7u}$	0	0	0	0
	$\Gamma_{8u}$	$599 \pm 3$	578	594	597
$4f^1 \ ^2F_{7/2}$	$\Gamma_{7u}$	-	-	2125	2167.
	$\Gamma_{8u}$	$2689 \pm 3$	2674	2628	2691
	$\Gamma_{6u}$	$3086 \pm 3$	3061	-	3085
$5d^1 \ T_{2g}$	$\Gamma_{8g}$	$28193 \pm 2$	$28265 \pm 3$	-	28196
	$\Gamma_{7g}$	29435	-	-	29435
$5d^1 \ E_g$	$\Gamma_{8g}$	-	-	47080	47125

<sup>a</sup>Data from  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ . For the  $5d^1$  configuration the  $\Gamma_{7g}$  level was taken from Schwartz and Schatz<sup>9</sup> and the  $\Gamma_{8g}$  level from the  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$  data.

<sup>b</sup>Parameters ( $\text{cm}^{-1}$ )  $4f^1$ :  $\zeta_{4f} = 624.1$ ,  $B_0^4 = 2208.$ ,  $B_0^6 = 249.6$ .

$5d^1$ :  $F^0 = 36015.4$ ,  $\zeta_{5d} = 792.7$ ,  $B_0^4 = 38709$ .

<sup>c</sup>  $g(\Gamma_{7u})$  (calc) = 1.253.

Table 6 Relative experimental and calculated electric dipole emission intensities for  $\text{CeCl}_6^{3-}$

	Relative Fluorescence Intensity from $5d^1 T_{2g} \Gamma_{8g}^a$ Experimental	Relative Fluorescence Intensity from $5d^1 T_{2g} \Gamma_{8g}$ Calculated	Relative Fluorescence Intensity from $5d^1 E_g \Gamma_{8g}^b$ Experimental	Relative Fluorescence Intensity from $5d^1 E_g \Gamma_{8g}$ Calculated
$4f^1 {}^2F_{5/2} \Gamma_{7u}$	.2	.76	1.0	1.0
$4f^1 {}^2F_{5/2} \Gamma_{8u}$	1.0	1.0	0.2	6.9
$4f^1 {}^2F_{7/2} \Gamma_{7u}$	-	.03	0.15	1.5
$4f^1 {}^2F_{7/2} \Gamma_{8'u}$	.05	.33	0.05	8.2
$4f^1 {}^2F_{7/2} \Gamma_{6u}$	.2	.30		5.3

<sup>a</sup> $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$

<sup>b</sup> $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$

Table 7 Ab initio embedded cluster calculations on  $\text{Cs}_2\text{NaYCl}_6:(\text{CeCl}_6)^{3-}$ .

Main character	State	$r(v_1)$ (Å)	$\Delta r(v_1)$ (Å)	$\nu_1$ ( $\text{cm}^{-1}$ )	$T_e$ ( $\text{cm}^{-1}$ ) <sup>a</sup>	Experimental zero-phonon levels ( $\text{cm}^{-1}$ )
$4f^1\ ^2F_{5/2}$	$\Gamma_{7u}$	2.723	0	305	0	0
	$\Gamma_{8u}$	2.727	0.004	307	831	596 <sup>b</sup>
$4f^1\ ^2F_{7/2}$	$\Gamma_{7u}$	2.724	0.001	307	2318	2125 <sup>c</sup>
	$\Gamma_{8u}$	2.727	0.004	307	3019	2686 <sup>b</sup>
	$\Gamma_{6u}$	2.727	0.004	307	3376	3083 <sup>b</sup>
$5d^1\ ^2T_{2g}$	$\Gamma_{8g}$	2.676	-0.047	293	25510	28195 <sup>b</sup>
	$\Gamma_{7g}$	2.676	-0.047	293	26716	29435 <sup>b,d</sup>
$5d^1\ ^2E_g$	$\Gamma_{8g}$	2.740	0.017	297	47263	47080 <sup>c</sup>

<sup>a</sup> Minimum-to-minimum energy differences.

<sup>b</sup> In  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ .

<sup>c</sup> In  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ .

<sup>d</sup> From Schwartz and Schatz<sup>9</sup>

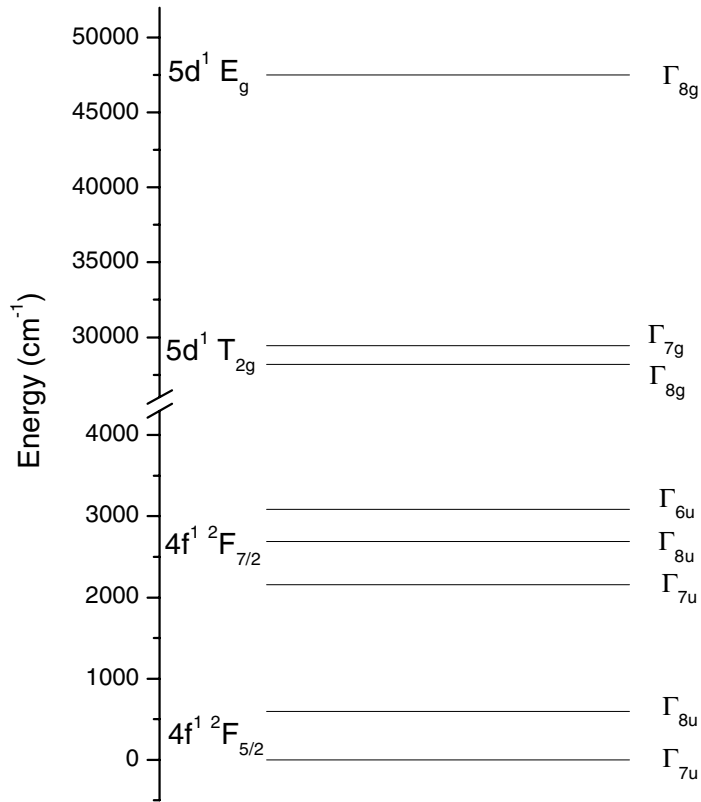


Figure 1 Schematic energy level diagram of the  $4f^1$  and  $5d^1$  configurations of the  $Ce^{3+}$  ion in a chloroelpasolite crystal field. Note the change in the energy scale between the  $4f^1$  and the  $5d^1$  configurations.

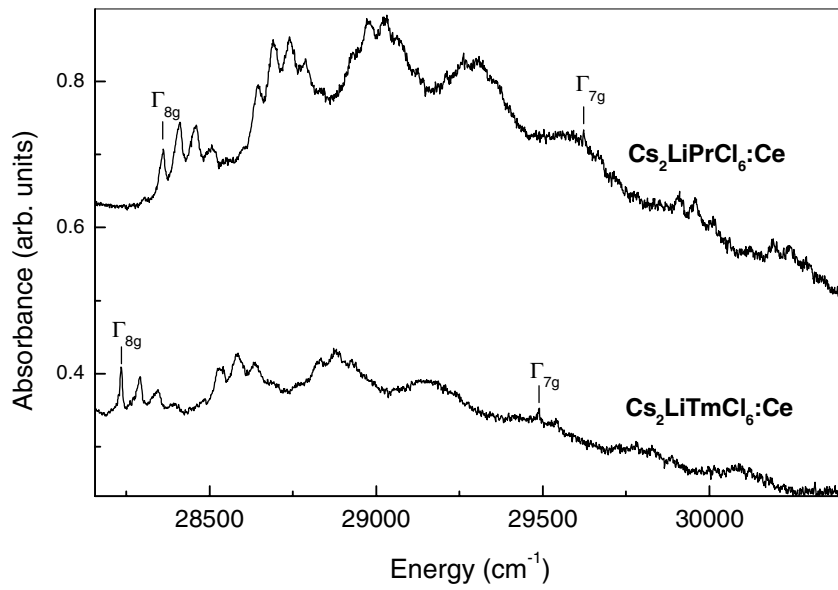


Fig. 2. 10 K absorption spectra of trace  $\text{Ce}^{3+}$  impurity in  $\text{Cs}_2\text{LiPrCl}_6$  and  $\text{Cs}_2\text{LiTmCl}_6$  between  $28000 - 31000 \text{ cm}^{-1}$ . (The initial state is  $\Gamma_{7u}$  in all cases, and the terminal d-electronic states are labeled).



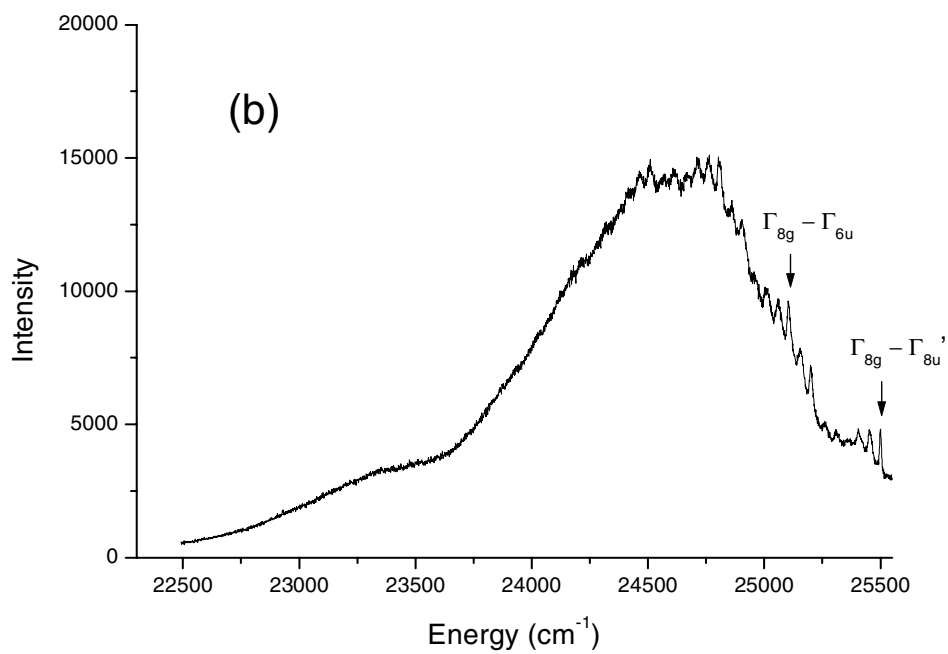
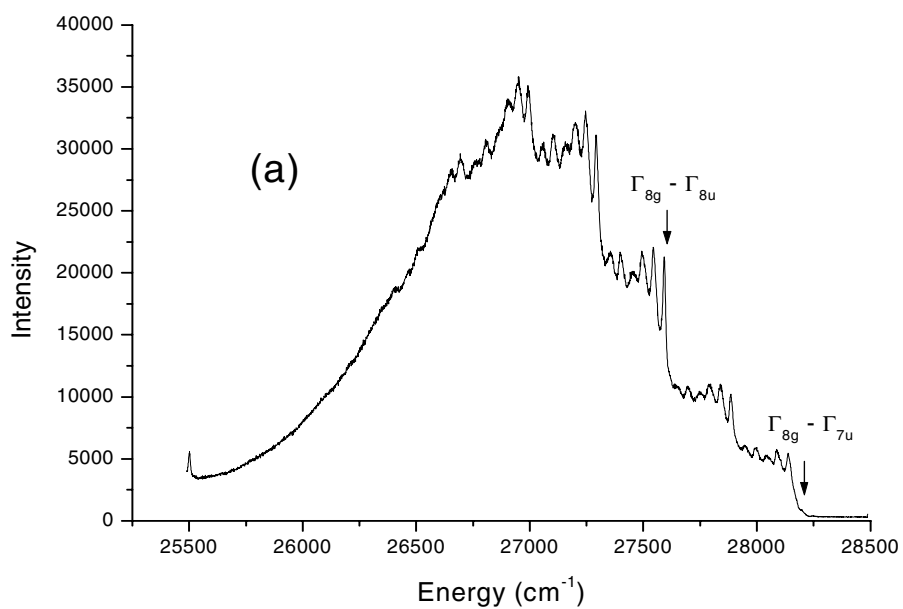


Fig. 3a,b. 10 K uv xenon lamp excited emission spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  between  $28500 - 22500 \text{ cm}^{-1}$

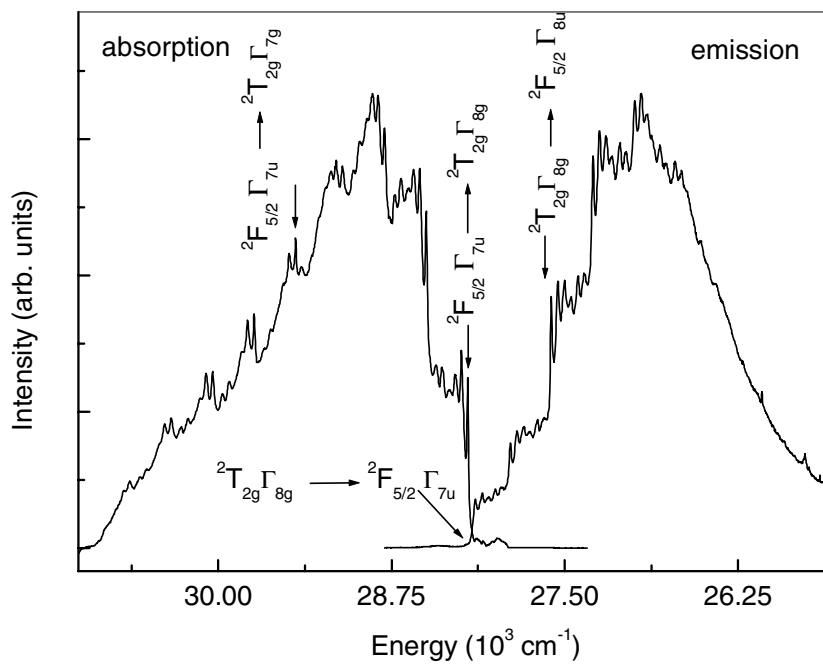


Fig. 4. Comparison of 10 K absorption spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  with the 199.8 nm excited emission spectrum at 10 K

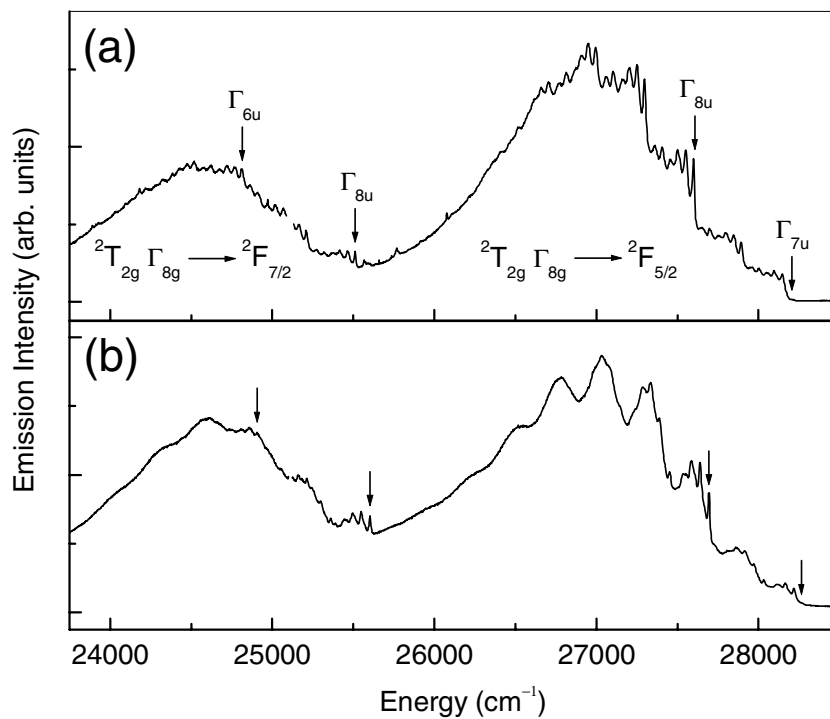


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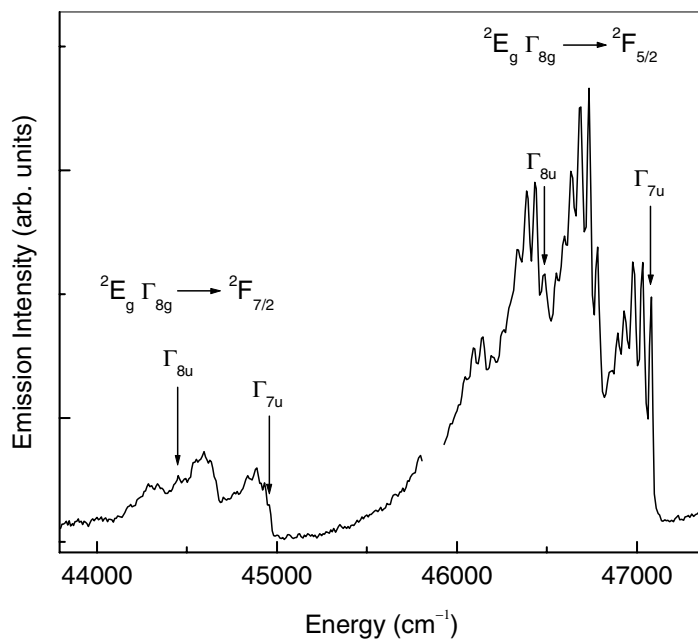


Fig. 6. 199.8-nm excited 10 K emission spectrum of  $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$  between 47000 - 43500  $\text{cm}^{-1}$ .

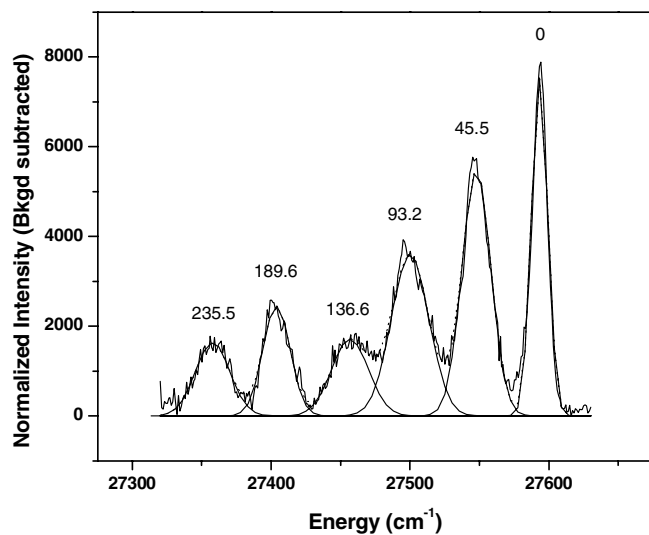


Fig. 7. Gaussian fits to the first few bands in the 10 K  ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$  emission spectrum of  $Ce^{3+}/Cs_2NaYCl_6$ . The numbers over the centers of the bands indicate the energy intervals (in  $cm^{-1}$ ) from the zero phonon line.

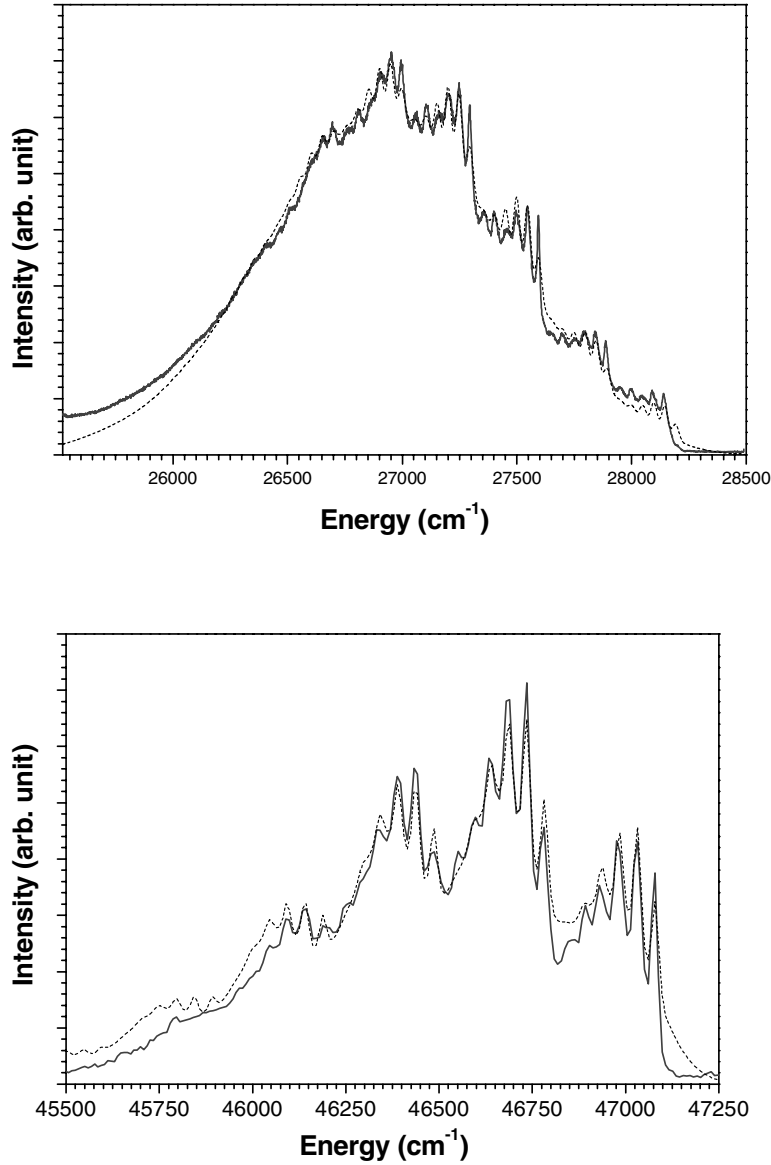
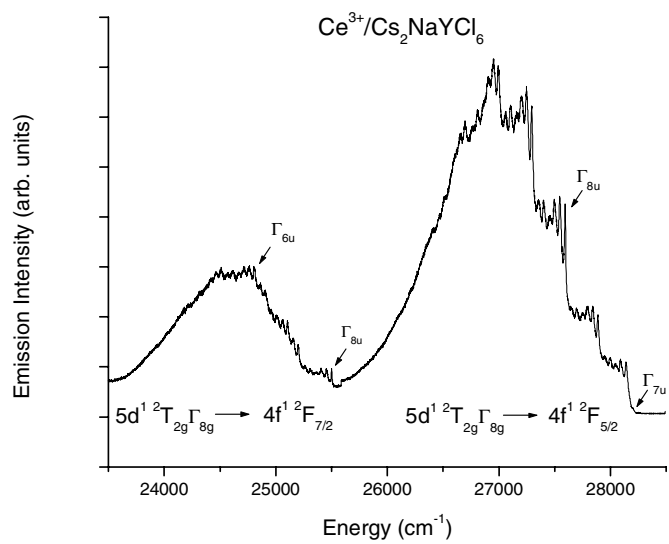


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