5d-level energies of Ce$^{3+}$ and the crystalline environment. II. Chloride, bromide, and iodide compounds

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Information on the energy of 5d levels of Ce$^{3+}$ in chloride, bromide, and iodide compounds has been collected. From this, values for the centroid shift and the crystal field splitting of the 5d configuration are obtained. The centroid shift will be related to the polarizability of the anions and further analyzed by means of the ligand polarization model. The crystal field splitting is to a large extent determined by the shape and size of the anion polyhedron coordinating Ce$^{3+}$. It will be analyzed in terms of the crystal field $B^6_2$ parameters. By combining centroid shift and crystal field splitting, the spectroscopic redshift of the first electric dipole-allowed $fd$ transition in Ce$^{3+}$-doped halide compounds will be interpreted. The observed trends provide insights into the relationship between the spectroscopic properties of Ce$^{3+}$ 5d levels and the crystalline environment.

I. INTRODUCTION

The first allowed $4f^{n}$ to $4f^{n-1} 5d$ transition of the free trivalent lanthanides is lowered in energy whenever it is put in a crystalline environment. This lowering is known as the spectroscopic redshift and in Ref. 1 and Ref. 2 it was shown that for all the trivalent lanthanides it is about the same if put in the same host crystal. It implies that once the first allowed $fd$ transition is known for just one of the trivalent lanthanides, then that of all others if in the same crystal can be predicted. This knowledge provides a powerful predictive tool. However, one likes to go beyond this and also understand the relationship between redshift and the type of crystalline environment one needs information on all 4f$^{n-1}$5d-level energies. This is only feasible for Ce$^{3+}$. It has the simplest spectroscopy, and, depending on the site symmetry, at most five energetically different 5d levels can be observed. New data and information gathered from literature provided the required information on 16 different compounds.

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II. EXPERIMENTAL DATA ON 5d-LEVEL POSITIONS

The available data on the spectroscopic redshift $D(A)$ of the halide compounds as tabulated in Ref. 2 can be seen in Fig. 1. The data are shown against a seven-digit identification number. Such number was assigned to each of the compounds and when treated as a running variable ($A$) it enables one to present and analyze the data in a systematic manner. The reader is referred to Ref. 2 for more information and motivation of the chosen classification scheme. On the scale in Fig. 1, the first two digits, which represent the types of anions in the host crystal, are of significance. A first inspection shows that the redshift tends to increase in going through the halide series from the fluorides to the iodides. The spread in redshift values is largest within the fluorides and tends to decrease in going to chlorides and bromides.

Of several Ce$^{3+}$-activated compounds, information is available on the energy of all five 5$d$ levels. The wavelengths of $fd$ transitions are compiled in Table I (see column 4). In cases when the $fd$ transition wavelengths are not yet fully certain like in Cs$_2$LiYBr$_6$, they are placed between brackets. In the case of octahedral or near octahedral (trigonal antiprism) symmetry, some of the $fd$ transition were assumed to be twofold or threefold degenerate 5$d$ levels. This is indicated by (2$\times$) or (3$\times$). From the wavelengths the centroid shift and crystal field splitting were calculated.

The second and third columns give information on the size and type of anion polyhedron coordinating Ce$^{3+}$. The size is expressed as the average distance $R_{av}$ to the $N$ coordinating anions; it was determined from crystallographic data. Occasionally $R_{av}$ was estimated by comparison with isostructural compounds and correcting for differences in cell volume or cation ionic radii.

The energy of the highest 5$d$ level, the centroid position, the energy of the lowest 5$d$ level, and the energy of emission from the relaxed lowest 5$d$ level to the $^2F_{5/2}$ ground state are shown in Fig. 2. All energies are relative to the centroid position of the free Ce$^{3+}$ ion located at 51 230 cm$^{-1}$. The differences between the relaxed and unrelaxed lowest transitions were as-

![Figure 1](image)

FIG. 1. Spectroscopic redshift of the trivalent lanthanides in the halogenide compounds (from Ref. 2). The hatched blocks represent the observed or predicted range of centroid shift values $\epsilon_c$.

TABLE I. Spectroscopic and crystallographic properties of Ce$^{3+}$-doped chloride and bromide compounds. $R_{av}$ is in pm. Type of polyhedron (poly) and point symmetry (sym) at the Ce site are given.

<table>
<thead>
<tr>
<th>compound</th>
<th>$(N):R_{av}$</th>
<th>(poly:sym)</th>
<th>5$d$-excitation bands (nm)</th>
<th>$\epsilon_c$(cm$^{-1}$)</th>
<th>$\epsilon_{cf}$(cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl$_3$</td>
<td>(6:275)</td>
<td>(tap:$C_{2v}$)</td>
<td>243, 250, 263, 274, 281</td>
<td>13000</td>
<td>5565</td>
<td>13</td>
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<tr>
<td>CaCl$_2$</td>
<td>(6:275)</td>
<td>(cub:$C_{2v}$)</td>
<td>242, 252, 266, 277, 292</td>
<td>13440</td>
<td>7075</td>
<td>4</td>
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<tr>
<td>cubic-BaCl$_2$</td>
<td>(8:329)</td>
<td>(cub:$C_{2v}$)</td>
<td>235, 245, 255, 316, 325</td>
<td>14390</td>
<td>12610</td>
<td>4</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>(9:307)</td>
<td>(1ccub:$C_{2v}$)</td>
<td>(224), 233, 240, 255, (2$\times$) 324</td>
<td>$\approx$ 13580</td>
<td>$\approx$ 12900</td>
<td>4</td>
</tr>
<tr>
<td>K$_2$LaCl$_3$</td>
<td>(7:285)</td>
<td>(1ccp:$C_{2v}$)</td>
<td>221, 239, 258, 316, 337</td>
<td>13710</td>
<td>15128</td>
<td>26</td>
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<td>CsSrCl$_3$</td>
<td>(6:280)</td>
<td>(tap:$O_h$)</td>
<td>219, ... , 332</td>
<td>15542</td>
<td>6</td>
<td></td>
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<tr>
<td>KCaCl$_3$</td>
<td>(6:261)</td>
<td>(tap:$O_h$)</td>
<td>210, ... , 338</td>
<td>18033</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>RbCaCl$_3$</td>
<td>(6:266)</td>
<td>(tap:$O_h$)</td>
<td>214, 220, (3$\times$) 334</td>
<td>15250</td>
<td>17489</td>
<td>6</td>
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<tr>
<td>Cs$_2$NaLaCl$_6$</td>
<td>(6:275)</td>
<td>(octa:$O_h$)</td>
<td>210, 217, 336, (2$\times$) 342</td>
<td>14742</td>
<td>18379</td>
<td>28</td>
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<tr>
<td>Cs$_2$NaGdCl$_6$</td>
<td>(6:265)</td>
<td>(octa:$O_h$)</td>
<td>(211, 216), (330), (2$\times$) 350</td>
<td>$\approx$ 15003</td>
<td>$\approx$ 18822</td>
<td>29</td>
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<tr>
<td>Cs$_2$NaYCl$_6$</td>
<td>(6:262)</td>
<td>(octa:$O_h$)</td>
<td>(210, 217), 331, (2$\times$) 345</td>
<td>$\approx$ 14854</td>
<td>$\approx$ 18634</td>
<td>29,30</td>
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<tr>
<td>Cs$_2$LiYCl$_6$</td>
<td>(6:263)</td>
<td>(octa:$O_h$)</td>
<td>207, 217, 327, (2$\times$) 349</td>
<td>14774</td>
<td>19656</td>
<td>29,31</td>
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<tr>
<td>LuCl$_3$</td>
<td>(6:258)</td>
<td>(tap:$C_2$)</td>
<td>196, 217, 325, (2$\times$) 340</td>
<td>13891</td>
<td>21609</td>
<td>33</td>
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<tr>
<td>Cs$_2$LiYBr$_6$</td>
<td>(6:277)</td>
<td>(tap:$C_2$)</td>
<td>(2$\times$) 235, (340), (2$\times$) 360</td>
<td>$\approx$ 17215</td>
<td>$\approx$ 14775</td>
<td>29</td>
</tr>
<tr>
<td>LuBr$_3$</td>
<td>(6:274)</td>
<td>(tap:$C_2$)</td>
<td>(2$\times$) 229, 342, 356, 370</td>
<td>16892</td>
<td>16641</td>
<td>33</td>
</tr>
</tbody>
</table>

*a*See Ref 27.

$b$Ref 28. $R_{av}$ was estimated from the lattice parameters from Ref. 7 and the ratio of cationic radii from Ref. 18.

*c*See Ref 32.

$d$See Ref 34.
5d-level energy is the Stokes shift $\Delta S$: their values can be found in Ref. 2. The chloride compounds in Fig. 2 and Table I are more or less arranged in order of increasing size of the crystal field splitting and decreasing coordination number around Ce$^{3+}$.

III. DISCUSSION

The crystal structure of the different compounds, particularly the type of anion polyhedron coordinating Ce$^{3+}$, and how it influences the crystal field splitting will be discussed first. From this, several trends will emerge. Next, the relationship between $\epsilon_{cfs}$ and polyhedral shape will be further analyzed employing the point charge electrostatic model. It will be followed by a discussion on the centroid shift analysis employing the ligand polarization model. Finally the centroid position, $(n)$ lowest 5$d$ level, and $(\bigcirc)$ relaxed lowest 5$d$ level of Ce$^{3+}$ in compounds.

A. Crystal field splitting

Figure 3 shows $\epsilon_{cfs}$ plotted against $R_{av} - \frac{1}{2} \Delta R$ for most of the compounds from Table I. Also data on the fluorides from Part I have been used. Like in Eq. (3), $\frac{1}{2} \Delta R$ accounts roughly for the lattice relaxation around Ce$^{3+}$. The straight dashed lines more or less connect the data of compounds with similar type of coordination polyhedron. From top to bottom these are the trigonal antiprism (tap), cube (cubal), dodecahedron (dhd), tricapped trigonal prism (3ctp), and cuboctahedron (6ctap). The straight solid lines with steeper slope more or less connect data of compounds with similar coordination polyhedron and with similar anions (F, Cl, or Br).

LaCl$_3$ shows the smallest crystal field splitting of all compounds. The La$^{3+}$ site is ninefold coordinated by chlorine in the form of a regular tricapped trigonal prism (3ctp: $C_{3h}$). Compared to NaYF$_4$, see Part I, with similar coordination but smaller $R_{av} - \frac{1}{2} \Delta R$, the splitting is almost two times less.

Cubic-BaCl$_2$ (8:329) and SrCl$_2$ (8:302) have the cubic fluorite crystal structure. The Ce ion is in a site with cubal eightfold coordination. In SrCl$_2$ the excess charge is compensated by means of a Cl$^{-}$ ion at the nearest interstitial site (349 pm) resulting in a monocapped cubal polyhedron (1ccubal) with $C_{4v}$ site symmetry. No information is available on the type of charge compensating defect in BaCl$_2$. The excitation spectra of Ce$^{3+}$ luminescence reported by Li and Leskelä can be interpreted as two low-energy levels arising from the doublet $e$ state plus three high-energy levels from the triplet $t$ states. It is not clear whether the 224-nm or the 255-nm band, see Table I, in SrCl$_2$: Ce belongs to this triplet. Possibly the 255-nm band is like other bands between 260 and 300 nm caused by aggregates of Ce$^{3+}$ ions, see Refs. 4 and 5.

Crystal field splitting of the cubic chlorides together with those of the cubic fluorites CaF$_2$, SrF$_2$, and BaF$_2$ are shown in Fig. 3. For these data, $R_{av} - \frac{1}{2} \Delta R$ represents the eight cubal halide ions, and the charge compensating anion was not included. Crystal field splitting in the chlorides is significantly smaller than in the fluorides.

In most of the compounds of Table I Ce$^{3+}$ is coordinated in the form of a (distorted) octahedron. In the chloride elpasolite Cs$_5$NaLuCl$_6$, $\epsilon_{cfs}$ is 18 400 cm$^{-1}$ and it increases with decreasing size of the rare-earth cation until 20 600 cm$^{-1}$ for Cs$_5$NaLuCl$_6$, see also Fig. 2. The largest crystal field splitting amongst the chlorides is observed for LuCl$_3$. The data on crystal field splitting in LuBr$_3$ and Cs$_5$LiYBr$_6$ can also be found in Fig. 3. It is about 5000 cm$^{-1}$ smaller than in the corresponding LuCl$_3$ and Cs$_5$LiYCl$_6$ compounds.

In Fig. 3, the octahedral (trigonal antiprism) crystal field splitting of the different compounds, including that of Rb$_2$NaScF$_6$ (see Part I), is shown. Octahedral splitting seems somewhat larger than that of cubal coordination. Compared to compounds with tricapped trigonal prism or cuboctahedral coordination, crystal field splitting appears about two times larger.
From fluorides to chlorides to bromides the ionic radius of the halide ion increases from 133 pm to 181 pm to 196 pm resulting in larger $R_i$. The dashed lines in Fig. 3 demonstrate that the rate of decrease of $\epsilon_{6s}$ with increase of halide ion size seems about the same for (tap), (cubal), and (3ctp) type of coordination.

The above characteristics can be exploited to interpret the excitation spectra of Ce$^{3+}$ luminescence in three distorted perovskite-type chloride crystals reported by Antonyak et al.$^6$ The excitation spectra of CsSrCl$_3$ and KCaCl$_3$ show more than five bands indicating that different Ce$^{3+}$ sites are present. It may be related with the manner of charge compensation. Antonyak et al. assume Ce$^{3+}$ to occupy the 12-fold coordinated monovalent cation site. However, based on the data in Fig. 3, the crystal field splitting of these large cubo-tetrahedral sites is expected to be less than 8000 cm$^{-1}$. The actual splitting is two times larger, which suggests that the distorted octahedral divalent cation site is occupied by Ce$^{3+}$. The excitation spectrum of RbCaCl$_3$ shows three bands. Assuming approximately octahedral coordination, the 342-nm excitation is assigned to the triplet $t_2$ 5d level and the bands at 214 and 220 nm to the split doublet $e$ 5d level.

All wavelengths are shown in Table I.

K$_2$LaCl$_3$ is isotypic with K$_2$PrCl$_3$ and has sevenfold coordination$^7$ in the form of a monocapped trigonal prism (1ctp). Crystal field splitting of K$_2$LaCl$_3$ is quite comparable with that of octahedral coordination.

The last chloride compound to be discussed is CaCl$_2$, which shows an unexpectedly small crystal field splitting of 7100 cm$^{-1}$. A value of around 17 000 cm$^{-1}$ for the sixfold coordinated Ca site in the rutile structure of CaCl$_2$ seems to be a more likely value, see Fig. 3. Possibly coordination is different from octahedral due to lattice relaxation or charge compensating defects. This will be discussed in more detail later.

### B. Angular part of the $B_0^1$ and $B_0^2$ crystal field parameters

The results in Fig. 3 show that the crystal field splitting depends on the type of anion polyhedron around Ce$^{3+}$. This dependence will be further analyzed by employing the PCEM of crystal field interaction. The interaction is simplified by assuming that only the nearest-neighbor anions, forming a polyhedron around Ce$^{3+}$, contribute to the crystal field potential at the Ce$^{3+}$ site. It is further assumed that all Ce to anion distances ($R_i$) are equal. In this work, the model will be applied to crystals with anion coordination polyhedra that can be seen as a combination of 2m prismatic, n equatorial and p axial ligands. The prismatic ligands form a prism or anti-prism with its $m$-fold rotation axis defined as the $z$ axis of our coordinate system. The equatorial or planar ligands are located in the x-y plane forming caps on the side faces of the (anti)prism. The $y$ axis is coincident with a two-fold symmetry axis of the polyhedron. The axial ligands located on the $z$ axis form caps on the top and/or bottom faces of the (anti)prism.

For these polyhedral types, generalized expressions can be obtained for the so-called $B_0^2$ crystal field parameters.$^8$ In the case of 5d levels, the integer $k$ is restricted to 0, 2, and 4 and integer $q$ is a multiple of $m$ and $\leq k$. Of special interest are the $B_0^2$ and $B_0^4$ parameters. It is well known that the PCEM is too naive a model for a reliable calculation of crystal field parameters. Nevertheless, it will prove useful to relate qualitatively polyhedral shape with crystal field splitting. For that purpose only the so-called angular part of the crystal field parameters will be used. They will be denoted as $\Theta_k$ and can be written as a sum of an axial, equatorial, and prismatic contribution. The ones of interest are$^8$

$$\Theta_0^2 = p - \frac{n}{2} + m(3 \cos^2 \theta_{pr} - 1), \quad (4)$$

$$\Theta_0^4 = p + \frac{3n}{8} + \frac{m}{4}(35 \cos^4 \theta_{pr} - 30 \cos^2 \theta_{pr} + 3). \quad (5)$$

The prismatic angle $\theta_{pr}$ is the angle the 2m "prismatic" Ce$^{3+}$-halide bonds make with the $m$-fold axis. The expressions are the same for prismatic and antiprismatic coordination. The values for $\Theta_0^2$ reflect how the spatial arrangement of the anions, i.e., the shape of the polyhedron, influence the crystal field parameters.

Most of the coordination polyhedra in the compounds treated in this work can be seen as containing a trigonal (anti)prismatic part with (approximately) threefold rotation symmetry. The crystal field parameters of the cube, octahedron, and cubo-tetrahedron are usually described with the four-fold symmetry axis as quantization axis. However also a threefold rotation symmetry axis can be chosen. The cube is then seen as a (2ctap) biaxially capped trigonal antiprism ($p:n:m$ = $(2:0:3)$, the octahedron as trigonal antiprism (tap), and the cubo-tetrahedron as a sixequatorially capped trigonal antiprism (6ctap). This latter view is preferred here because it provides a direct comparison with many of the polyhedra lacking fourfold rotation symmetry.

In Table II information on several types of polyhedra with threefold symmetry axis ($m = 3$) is compiled. Typical values for the prismatic angle $\theta_{pr}$ can be obtained from real crystallographic structures or calculated using, for example, the hard sphere model (HSM).$^8,9$ The HSM value for the trigonal prism is 49°. Adding three equatorial ligands on the square faces of the cube yields the tricapped trigonal prism (3ctap) with $\theta_{pr} = 35.3^\circ$, a coordination type found in several hexa-aluminates like SrAl$_2$O$_9$. Axial ligands have an opposite effect, i.e., the prism is flattened and $\theta_{pr}$ increases. In LaF$_3$ with the thyrsonite structure, two axial and three equatorial ligands are present forming a five-capped trigonal prism (5ctap). The polyhedron is quite distorted and three $\theta_{pr}$ values of 60°, 62°, and 66° are obtained from the structure reported by Zalkin and Templeton.$^{10}$

The octahedron is a trigonal antiprism with $\theta_{pr}$ equal to the so-called cubic angle $\theta_c = \arccos(1/\sqrt{3}) = 54.7^\circ$. The effects of axial and equatorial ligands on the prismatic angle are quite similar as on the trigonal prism. Six equatorial ligands to form a cubo-tetrahedron reduces $\theta_{pr}$ to 35.3° (i.e., 90° $- \theta_c$). Two axial ligands yield the cube with larger $\theta_{pr}$ = 70.5° (i.e., 180° $- 2 \theta_c$).
The different contributions to the angular part of $B_2^4$ are shown in Fig. 4. The solid line represents the contribution from the prismatic ligands. Despite a strong variation in this contribution with $\theta_{pr}$, the total angular part of $B_0^2$ remains close to zero for the polyhedra of Table II. The six equatorial caps in the cuboctahedron and the two axial ones in the cube fully cancel the prismatic contribution resulting in zero value for $B_0^2$. A similar cancellation is observed for the pricapped and five-capped trigonal prism also resulting in relatively small value for the angular part of $B_0^2$ (see Table II).

Figure 5 shows the contributions to the angular part of the $B_0^4$ parameter. The prismatic contribution is large and negative for the trigonal prism and the octahedron. It is close to zero for the cube. Equatorial and axial ligands have positive contributions and may compensate (tricapped trigonal prism) or overcompensate (cuboctahedron) for the prismatic contribution. In the case of octahedral, cubal, and cuboctahedral coordination, one obtains the familiar result\(^{1,11}\) that $\Theta_0^4$ (cubal) $= -\frac{1}{2} \Theta_0^4$ (octa) and $\Theta_0^4$ (cubo) $= -\frac{1}{2} \Theta_0^4$ (octa). For (3ctp) and (5ctp) coordination the PCEM predicts $\Theta_0^4$ (3ctp) $\approx 0.6 \Theta_0^4$ (octa) and $\Theta_0^4$ (5ctp) $\approx -0.6 \Theta_0^4$ (octa).

Comparing the absolute values for the angular part of the $B_0^4$ parameter, see Table II, with observed crystal field splitting in Fig. 3 one observes similar ratios. Indeed experimentally, if $R_{av}^{-\frac{1}{3}} \Delta R$ remains constant, octahedral and cubal crystal field splitting are about the same and two times larger than cuboctahedral and (3ctp) crystal field splitting. Also the crystal field splitting of K$_2$LaCl$_5$ with (1ctp) coordination follows the size of the angular part of the $B_0^4$ parameter. It seems that for polyhedral types as in Table II this parameter is very important for the crystal field splitting; the $B_0^4$ parameter seems to be of less importance. It is noted that polyhedra containing a trigonal antiprism also have a nonzero $B_0^4$ parameter. It will mix different 5d states but it is not believed to effect $\epsilon_{5d}$ to a large extent, see also Sec. 2.7.2 in Ref. 8. For polyhedral coordination types as in Table II, it is now concluded that the magnitude of the angular part of the $B_0^4$ parameter as calculated from the PCEM is proportional to the total crystal field splitting.

Equation (4) and Eq. (5) can also be used to predict the effects of polyhedral distortions and charge compensating defects on crystal field splitting. If the fourfold rotation axis is chosen as quantization axis, the angular part of $B_0^4$ equals $-3.11$ for cubal coordination with $(p:n:m:\theta_{pr}) = (0:0:4:54.7^\circ)$. The interstitial charge compensating halide ion in SrF$_2$, CaF$_2$, and SrCl$_2$ can now be seen as an axial ligand at $2/\sqrt{3} = 1.15$ times larger distance than the prismatic ones. It will reduce the magnitude of the angular part of the

![FIG. 4](image1.png) The angular part $\Theta_0^4$ of the $B_0^2$ crystal field parameter for several polyhedra with the threefold rotation axis defined as z axis. Solid curve, contribution from the prismatic anions. □, all contributions included.

![FIG. 5](image2.png) The angular part $\Theta_0^4$ of the $B_0^4$ crystal field parameter for several polyhedra with the threefold rotation axis defined as z axis. Solid curve, contribution from the prismatic anions. □, all contributions included.

<table>
<thead>
<tr>
<th>(poly:sym)</th>
<th>($p:n:\theta_{pr}$)</th>
<th>Example</th>
<th>$\Theta_0^4$</th>
<th>$\Theta_0^4$</th>
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</thead>
<tbody>
<tr>
<td>(2ctp:O$_h$)</td>
<td>(2:0:70.5°)</td>
<td>fluorites</td>
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<tr>
<td>(5ctp:D$_{3h}$)</td>
<td>(2:3:60°)</td>
<td>thysonites</td>
<td>$-0.25$</td>
<td>1.39</td>
</tr>
<tr>
<td>(tap:O$_h$)</td>
<td>(0:0:54.7°)</td>
<td>elpasolites</td>
<td>0</td>
<td>$-2.33$</td>
</tr>
<tr>
<td>(tp:D$_{3h}$)</td>
<td>(0:0:49°)</td>
<td>HSM-value</td>
<td>0.87</td>
<td>$-2.57$</td>
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<tr>
<td>(1ctp:C$_2v$)</td>
<td>(0:1:≈47°)</td>
<td>K$_2$PrCl$_4$</td>
<td>0.69</td>
<td>$-2.16$</td>
</tr>
<tr>
<td>(3ctp:D$_{3h}$)</td>
<td>(0:3:42°)</td>
<td>LaCl$_3$</td>
<td>0.34</td>
<td>$-1.15$</td>
</tr>
<tr>
<td>(6ctp:D$_{3h}$)</td>
<td>(0:6:35.3°)</td>
<td>hexa-aluminates</td>
<td>0</td>
<td>1.17</td>
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<tr>
<td>(6ctp:O$_h$)</td>
<td>(0:6:35.3°)</td>
<td>perovskites</td>
<td>0</td>
<td>1.17</td>
</tr>
</tbody>
</table>
$B_0^4$ parameter, see Eq. (5). Treating again $\Theta_0^4$ as an indicator for crystal field strength, it implies that the actual cubical crystal field splitting in CaF$_2$, SrF$_2$, and SrCl$_2$ is larger than that suggested by the data in Fig. 3. The difference may amount to several thousand cm$^{-1}$.

Polyhedral distortion may also explain the large Stokes shift that is observed whenever the coordination is cuboctahedral, tricapped trigonal prism, or five-capped trigonal prismlike, see also Part I and Ref. 12. With Ce$^{3+}$ in the ground state, the polyhedron is regular yielding small crystal field splitting. Upon excitation to the 5d configuration, the lattice will relax. Since crystal field splitting was already minimal, any distortion of the polyhedron will result in an enhancement of crystal field splitting. Effectively the lowest 5d level is further lowered in energy resulting in a large Stokes shift. Recent ab initio studies performed by Andriessen et al.$^{13}$ on LaCl$_3$:Ce$^{3+}$ and by Marsman et al.$^{14}$ on BaLaF$_3$:Ce$^{3+}$ indeed revealed these mechanisms.

Figure 3 shows data belonging to LiYF$_4$, LiLuF$_4$, BaY$_2$F$_8$, and BaLu$_2$F$_8$, each with dodecahedral type of coordination. All data fall close together and crystal field splitting is at least several thousand cm$^{-1}$ smaller than what one would expect in the case of cubical coordination. A dodecahedron does not possess an axis of threefold symmetry and its crystal field parameters therefore cannot be compared directly with those in Table II. Comparison with a cube is possible by approximating the actual polyhedron as two (interpenetrating) regular tetrahedra, i.e., two $m = 2$ antiprisms with twofold symmetry axis and $\theta_{pr} = \theta_r = 54.7^\circ$. 5 In the scheelite LiYF$_4$ (see Part I), one tetrahedron is elongated ($\theta_{pr} = \theta_r = 17^\circ$) and the other is squat ($\theta_{pr} = \theta_r + 12^\circ$). It yields a polyhedron with 12 triangular faces (dodecadeltahedron).

The 5d-excitation spectrum of Ce$^{3+}$ in LiYF$_4$ was recently analyzed in terms of the $B_0^4$ crystal field parameters by Reid et al.$^{15}$ Approximating the actual $S_4$ symmetry by $D_{2d}$, values of 10.519 cm$^{-1}$ and 24.549 cm$^{-1}$ were reported for $B_0^4$ and $B_0^6$, respectively, Employing Eq. (4) and Eq. (5), values of +0.64 and −1.45 are calculated for $\Theta_0^4$ and $\Theta_0^6$. Note that the proper signs for the crystal field parameters are predicted by the PCEM. Properties of LiYF$_4$ can best be compared with those of CaF$_2$ with only few pm larger $R_{av}$. A value of −36 600 cm$^{-1}$ was reported by Manthey$^{16}$ for the $B_0^6$ parameter of the Ce$^{3+}$ $C_{av}$ center in CaF$_2$. This much larger value as compared to that of LiYF$_4$ is also predicted from the PCEM where a value of −3.11 is obtained for $\Theta_0^4$.

C. Centroid shift

The average centroid shift in the fluoride compounds amounts to 13 500 cm$^{-1}$, which is more than twice larger than the average observed for fluoride compounds (see Part I). This large centroid shift and the slight but significant variations therein can be studied in more detail employing the ligand polarization model as expressed by Eq. (2).

In Fig. 6 the average centroid shift contribution by each of the coordinating anions is plotted against the effective distance defined in Eq. (3). Some curves demonstrating the $R_{eff}$ dependence are also shown. In Fig. 7 the same data together with those of the fluorides presented in Part I are shown.

The results reveal that despite the large effective metal to ligand distances in the chlorides, the contribution to the centroid shift per Cl$^-$ is several times larger than the contribution per F$^-$ ion. This is also reflected in the value for the parameter $\alpha_{sp}$, calculated from the observed centroid shift and compiled in Table III. For chlorides it appears to be about 6–8 times larger than for the corresponding fluoride compounds. Compared to this large increase, the further increase in going to the bromides is relatively modest. Within the chlorides one observes that the smallest values for $\alpha_{sp}$ are obtained when small cations like Lu$^{3+}$ are present in the structure. Presence of large cations like Ba$^{2+}$ or Sr$^{2+}$ yield large values for $\alpha_{sp}$. The same was observed for the fluorides in Part I. There it was explained by the attracting force on the anion charge cloud towards the cations. If it is large, as when small Lu$^{3+}$ ions are present, the anion electrons are more strongly bound resulting in larger oscillation force constants and smaller polarizability. The value for cubic-BaCl$_2$ ($\alpha_{sp} = 12.3$ Å$^3$) seems somewhat large. If one assumes the presence of a charge compensating chlorine ion at the nearest interstitial site a somewhat smaller value of

FIG. 6. The centroid shift $\epsilon_p$ per coordinating halide ion (N). The curves through some of the data show the dependence on $R_{eff}$. The average centroid shift in the chloride compounds amounts to 13 500 cm$^{-1}$, which is more than twice larger than the average observed for fluoride compounds (see Part I). This large centroid shift and the slight but significant variations therein can be studied in more detail employing the ligand polarization model as expressed by Eq. (2).

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FIG. 7. The centroid shift per coordinating halide ion. $\bigcirc$, the fluorides; $\bigtriangleup$, the chlorides; $\square$, the bromides; $\bigcirc$, predicted value for Cs$_3$GdI$_4$. The curves through the data show the dependence on $R_{eff}$. The average centroid shift in the chloride compounds amounts to 13 500 cm$^{-1}$, which is more than twice larger than the average observed for fluoride compounds (see Part I). This large centroid shift and the slight but significant variations therein can be studied in more detail employing the ligand polarization model as expressed by Eq. (2).

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11.7 Å³ would be obtained. The error can also be quite large because of the large value for $D_{R5}^2$ for Ce³⁺ on a B a₂ site.

A further test of the ligand polarization model is by comparing the value for the spectroscopic polarizability $\alpha_{sp}$ with actual in-crystal halide polarizabilities derived from macroscopic parameters like the refractive index or dielectric constant of the host crystals. Figure 8 shows the anion polarizability in the alkali halides and some alkaline-earth halides obtained from the work by Pearson et al. ¹⁷ $\alpha_{exp}$ is shown against the ionic radius of the cations obtained from Shannon. ¹⁸ $\alpha_{exp}$ and $\alpha_{sp}$ behave quite similarly. Within the fluorides and within the chlorides both increase with increasing size of the cations present in the structure. A large increase of $\alpha_{exp}$ is observed in going from fluorides to chlorides. The increase from chlorides to bromides is less pronounced. Similar features are observed for $\alpha_{sp}$, cf. the data for LuF₃ ($\alpha_{sp}=0.69$ Å³), LuCl₃ ($\alpha_{sp}=5.6$ Å³), and LuBr₃ ($\alpha_{sp}=9.6$ Å³) in Fig. 7.

D. Spectroscopic redshift

The results of the previous two sections on crystal field splitting and centroid shift will be combined here to discuss the redshift of the first $fd$ transition of Ce³⁺ in a wider collection of chloride, bromide, and iodide compounds.

FIG. 9. Spectroscopic redshift in the chloride compounds. The errors are typically ±250 cm⁻¹.

The smallest redshift values are found in the lower left corner of Fig. 9 and the largest ones in the top right corner. The smallest redshift is observed for the compounds with ninefold coordination like LaCl₃ ~not visible in Fig. 9!, CeCl₃, SrCl₂ (C₄v), and orthorhombic BaCl₂. Crystal field splitting in these compounds is relatively small because of the large site size. Furthermore, the relatively large coordination number yields polyhedra that produce small crystal field splitting. This is particularly so for the tricapped trigonal prism coordination in LaCl₃. More details on LaCl₃ and CeCl₃, which have the same crystal structure, can be found in Ref. 13.

RbGd₂Cl₇ and CsGd₂Cl₇ have sevenfold coordination in the form of a monocapped trigonal prism (1ctp). It is to be expected that crystal field splitting in these compounds, like in K₂LaCl₃, will be relatively large resulting in larger redshift than the compounds with ninefold coordination.

All other compounds in Fig. 9 have sixfold coordination. Apart from NaCl and CaCl₂, the redshift values fall within a relatively narrow range from 19000 to 21000 cm⁻¹. Like observed for the fluorides (see Part I), the cubic chloride elpasolites Cs₂NaRCl₄ ($R=$ La, Ce, Gd, Y, Lu) are the compounds with the largest redshift. The variations in centroid shift and crystal field splitting are quite subtle, see Fig. 2.

### Table III. Results from the ligand polarization model. Compounds are arranged according to increase of $\alpha_{sp}$. The entries for Cs₃Gd₂I₉ are predicted values.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_{eff}$ (pm)</th>
<th>$\epsilon_r/N$ (cm⁻¹)</th>
<th>$\alpha_{sp}$ (10⁻³⁰ m⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chlorides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LuCl₃</td>
<td>265</td>
<td>2315</td>
<td>5.61</td>
</tr>
<tr>
<td>Cs₂NaLuCl₆</td>
<td>267</td>
<td>2495</td>
<td>6.21</td>
</tr>
<tr>
<td>RbCaCl₃</td>
<td>267</td>
<td>2542</td>
<td>6.32</td>
</tr>
<tr>
<td>Cs₂LiYCl₆</td>
<td>268</td>
<td>2462</td>
<td>6.34</td>
</tr>
<tr>
<td>Cs₂NaYCl₆</td>
<td>268</td>
<td>2476</td>
<td>6.37</td>
</tr>
<tr>
<td>LaCl₃</td>
<td>294</td>
<td>1444</td>
<td>6.48</td>
</tr>
<tr>
<td>Cs₂NaGaCl₆</td>
<td>269</td>
<td>2501</td>
<td>6.51</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>275</td>
<td>2240</td>
<td>6.65</td>
</tr>
<tr>
<td>K₃LaCl₅</td>
<td>284</td>
<td>1959</td>
<td>7.08</td>
</tr>
<tr>
<td>Cs₂NaLaCl₆</td>
<td>274</td>
<td>2474</td>
<td>7.27</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>299</td>
<td>1509</td>
<td>7.5±0.5</td>
</tr>
<tr>
<td>cubic-BaCl₂</td>
<td>319</td>
<td>1800</td>
<td>12.3</td>
</tr>
<tr>
<td>bromides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LuBr₃</td>
<td>281</td>
<td>2815</td>
<td>9.62</td>
</tr>
<tr>
<td>Cs₂LiYBr₆</td>
<td>283</td>
<td>2869</td>
<td>10.2</td>
</tr>
<tr>
<td>iodides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs₃Gd₂I₉</td>
<td>(308)</td>
<td>(3300)</td>
<td>(19.6±1.1)</td>
</tr>
</tbody>
</table>

FIG. 8. Experimentally determined in-crystal anion polarizabilities $\alpha_{exp}$ in alkali- and alkaline-earth halides (data from Ref. 17) against the ionic radius of the cation.
The combined effect results in an increase of redshift by about 1000 cm\(^{-1}\) in going from Cs\(_3\)NaLaCl\(_6\) with the large La site to Cs\(_2\)NaLuCl\(_6\) with the small Lu site. The same holds for the values of spectroscopic crystal field splitting combined with relatively large Stokes shift of 5300 cm\(^{-1}\).

NaCl has a redshift of 14 400 cm\(^{-1}\), which is also very small for an octahedrally coordinated site. This together with the large Stokes shift of 6800 cm\(^{-1}\) also indicates that coordination is different from octahedral. Possibly charge compensation by means of replacement of a Na\(^+\) by a Cl\(^-\) ion may accomplish such coordination changes.

In CsCdBr\(_3\) (6:282) (octa: D\(_{3d}\)) two luminescing sites have been identified.\(^{19}\) The site with the smallest redshift has been attributed by van Uitert\(^{19}\) to Ce on a Cd site without charge compensation. The site with the largest redshift has been attributed to Ce–(Cd-vacancy)–Ce complexes. Note that a similar situation was encountered in KMgF\(_3\):Ce\(^{3+}\), see Part I. Also here charge compensation by means of K\(^+\) vacancies yields larger redshift than the uncompensated site. It is interpreted as follows: a cation vacancy does not provide any attractive force on the anion charge cloud. Enhanced anion polarizability and centroid shift is then to be expected.

IV. SUMMARIZING REMARKS AND CONCLUSIONS

At the outset of the study on the 5\(d\)-level positions of the trivalent lanthanides in inorganic crystals, one of the first aims was to collect and critically analyze the data available. It provided a database with predictive potential. The next aim was to understand the relationship between the value for the redshift and the type of crystalline environment. For that purpose knowledge on the centroid shift and the crystal field splitting of the 5\(d\) levels was needed.

Crystal field splitting depends strongly on the shape and the size of the coordinating anion polyhedron. The point charge electrostatic model provides a convenient description for relating polyhedral shape and \(\varepsilon_{\text{cfs}}\). In particular the angular part of the crystal field parameter \(B_{\text{sp}}^6\) calculated from the PCEM seems often to be a good indicator for the largeness of \(\varepsilon_{\text{cfs}}\). The polyhedral size depends on the size of the substituted cation but more strongly on the size of the anions.

The ligand polarization model was employed to relate the centroid shift to one single parameter, the spectroscopic polarizability, which is independent on the coordination number and the metal to ligand distances in the structure. \(\alpha_{\text{sp}}\) behaves as function of the type of cations and anions in the host crystal in the same manner as that of the actual in-crystal halide ion polarizability \(\alpha_{\text{exp}}\) that can be derived from macroscopic properties. The spectroscopic polarizability \(\alpha_{\text{sp}}\) increases according to

\[
\text{anion vacancy}<\text{F}^<-\text{Cl}^-<\text{Br}^-<\text{I}^-. \tag{6}\]

This ordering is the same as that of the well-known nephelauxetic series. By means of the values for \(\alpha_{\text{sp}}\) now a quantitative interpretation is provided to this series.

The combined effect of centroid shift and crystal field splitting on the spectroscopic redshift in halogenide com-
pounds is summarized in Fig. 1. The vertical hatched blocks represent the (anticipated) range of centroid shift values. The range of contribution from the crystal field splitting to $D(A)$ is represented by the interval between the dashed lines. Its magnitude decreases by more than a factor of 2 in going from the fluorides to the iodides. The main reason for this is the increasingly larger ionic radius of the anions resulting in smaller crystal field splitting.

Within a halide group, the cations present in the crystal are important for variations in the redshift. Crystal field splitting for Ce$^{3+}$ on large cation sites that require large coordination number is usually small. Small cations require small coordination number and crystal field splitting is large for Ce$^{3+}$ on these sites. The cations are also important for the polarizability of the anions. The values for $\alpha_{sp}$ obtained by applying the ligand polarization model to the experimental data (see also Part I) appear to increase with the type of cation approximately as follows:

\[
\begin{align*}
&Mg^{2+} < Lu^{3+} < Th^{4+} < Y^{3+} < Li^{+} < La^{3+} < Ca^{2+} \\
&< Na^{+} < Sr^{2+} < Ba^{2+} < K^{+} < Rb^{+} < Cs^{+} < \text{cation vacancy},
\end{align*}
\]

(7)

where small high-valency cations are in the beginning of the series and large monovalency cations are at the end of the series. Note that the monovalent and divalent cations appear in sequence of increase of ionic radius, cf. Fig. 8.

It is not claimed in this work that the ligand polarization model is theoretically correct. Actually it is not. The assumptions made by Morrison to approximate the self-interaction will probably not hold for the extended $5d$ orbitals. Also the model as applied in this work ignores the contribution of the nephelauxetic effect and covalency to the centroid shift. Nevertheless, employing the model enables one to relate the centroid shift to one single parameter, i.e., the spectroscopic polarizability $\alpha_{sp}$. The complexity of the crystal structure is then rigorously removed. The fact that $\alpha_{sp}$ varies more strongly than the actual anion polarizability $\alpha_{exp}$ may signal the contribution of covalency effects to the centroid shift.

Finally, there appears to be an intimate relationship between spectroscopic polarizability and the concept of optical basicity. Over the past 30 years many papers by Duffy et al. have appeared on the oxidic chemistry of glasses,\textsuperscript{21} molten salts, and metallurgical slags.\textsuperscript{22} The acid-base reactions in the molten state, i.e., the chemical basicity of the melt, are quite important in the glass-making and steel-making industry.\textsuperscript{22} The basicity is directly related to the electron donating power of the anions, in this case oxygen. This donating power can be probed by measuring the spectroscopic redshift of the $3P_{1} \rightarrow 1S_{0}$ transition with Tl$^{3+}$, Pb$^{2+}$, or Bi$^{3+}$ dopants.\textsuperscript{23} Based on the observed redshift, a so-called optical basicity scale has been developed that is used in oxidic chemistry.\textsuperscript{24} The optical basicity $\Lambda$ depends on the cations present in the melt. Small high-valency cations yield small $\Lambda$ and large monovalent ones yield large $\Lambda$. Clearly the redshift of Tl$^{3+}$, Pb$^{2+}$ or Bi$^{3+}$ in oxides and the centroid shift of Ce$^{3+}$ in halides are caused by the same physical/chemical processes, and $\Lambda$ and $\alpha_{sp}$ are intimately related parameters.

Binks and Duffy\textsuperscript{25} also realized that optical basicity and in crystal oxygen polarizability are related. However, a model to relate both properties seems to be still lacking in the field of oxidic chemistry. The ligand polarization model applied in this work provides a direct link between (1) the centroid shift of the Ce$^{3+}$ $5d$ configuration, (2) the optical basicity concept in oxidic chemistry, and (3) the anion polarizability derived from macroscopic properties. In the planned following papers of this series, where oxides and sulfide systems are the subject of study, these relationships will be more firmly established.

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\begin{enumerate}
\end{enumerate}
32 \( R_{av} \) was estimated from D.H. Templeton and G.F. Carter, J. Phys. Chem. 58, 940 (1954) by comparing the cell volume with that of YCl3.