Lattice relaxation study of the 4f-5d excitation of Ce$^{3+}$-doped LaCl$_3$, LaBr$_3$, and NaLaF$_4$: Stokes shift by pseudo Jahn-Teller effect

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The local geometry of La$^{3+}$ in the crystals LaCl$_3$, LaBr$_3$, and LaNaF$_4$ is that of a tricapped trigonal prism with $C_{3h}$ symmetry. If the crystals are doped with cerium, Ca$^{3+}$ replaces some of the La$^{3+}$ ions. The local geometry changes slightly when Ca$^{3+}$ is in the ground state (4f). However, in the 5d state, the relaxation of the lattice is quite different because the 5d levels experience a pseudo Jahn-Teller coupling with certain lattice displacements. This is because the lowest two 5d states (a singlet and a doublet, neglecting spin-orbit interaction) are very close in energy. We found that the Ca$^{3+}$ ion moves away from the centered position, accompanied by a strong deformation of the prism. One of the anions of the triangle of caps moves outward, also because of the pseudo Jahn-Teller distortion, and four anions of the prism move inward. The result is the occurrence of a 0.6–1.0 eV large Stokes shift in the 5d-4f emission. We analyzed the off-center movement of cerium in detail. For this study, we employed a widely used band structure code based on density functional theory. Ionic cluster calculations using the Hartree-Fock method confirm the results obtained and give additional information about the dynamics of the relaxation process.

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I. INTRODUCTION

There is a fast growing interest in ab initio calculations of properties of 4f-5d transitions of rare-earth ions in solids. This is partly a result of the pioneering work of Dorenbos, who in a series of papers made extensive compilations of experimental data of these transitions and succeeded to find simple semiempirical models for summarizing and predicting various properties of the 4f-5d transition. In the following, we give a short overview of this work and related ab initio studies by mentioning a number of important landmarks.

The compilations of experimental data on 4f-5d transitions started with work on the so-called crystal field depression of the 4f$^n$-5d levels of lanthanide ions due to the interaction with the lattice, which appears to be almost independent of the type of lanthanide. The semiempirical model formulated can predict 4f-5d energy differences rather accurately using two parameters. The parameters are the crystal field depression of the 5d state compared to the 4f state and the Stokes shift. The crystal field depression consists of a part arising from the crystal field splitting and another part, the so-called centroid shift, due to the lowering of all 5d levels by polarization of the lattice. The Judd-Morisson model was used to express the centroid or barycenter shift and was rather successfully applied to fluorides, chlorides, bromides, iodides, and oxides. Account has to be made for an additional part coming from covalency.

However, the crystal field component is not directly related to a simple property of the host crystal. Usually, it is expressed in terms of the well-known crystal field parameters. In addition, the Stokes shift of the emission lines is hard to put into a simple model. In Ref. 2, a picture shows the measured Stokes shift of Ce$^{3+}$ in more than 300 compounds. From this, it is obvious that this property has a complex character because the variation in values is so large that there must be several different mechanisms by which the 4f$^{n-1}$5d state relaxes after excitation. One of these mechanisms is the subject of this paper.

In subsequent years, the attention of our group was redirected to the positioning of the 4f$^{n-1}$5d levels compared to levels of the host crystal (valence and/or conduction band), also very important for the understanding of scintillation behavior and other luminescence properties. This led to the development of a rather successful three-parameter model for this position based on an additional experimental quantity: the charge transfer energy between the valence band and the impurity.

Now, considering these efforts both in gathering a vast amount of experimental data and in the formulation of simple models for ordering and predicting the 4f$^{n-1}$5d levels in any host crystal, one may wonder what the position is of present day theoretical approaches using ab initio quantum mechanical electronic structure theory.

Three methods of approach are in current use. First, we have the crystal field method based on a model Hamiltonian containing a large number of parameters related to physical effects. The values of the parameters are obtained by fitting to experimental data. Next, we have the ab initio methods, such as the ionic cluster model for calculations on the lanthanide ion in solids and the band structure approach very often based on density functional theory.

It appears that the first reaction on the interesting facts on the 4f$^n$-4f$^{n-1}$5d transitions sketched above came from Reid et al. The crystal field model used for many years in investigating 4f$^n$-4f$^m$ transitions was extended to include the 4f$^n$-4f$^{m-1}$5d spectra. These calculations shed light on the complicated interactions taking place on the excitation of a 4f electron to a 5d state and the coupling of the remaining 4f$^{n-1}$ core with the 5d electron. There is, however, not a direct relation with the compilation of experimental results mentioned above.

Subsequently, a study was published directly related to the centroid shift of Ce$^{3+}$ in a number of compounds, showing that it is not easy to calculate the centroid shift using ab initio methods. Here, a cluster approach was taken using the Hartree-Fock method on a linear combination of atomic or-
bits of (HF-LCAO) extended with configuration interaction. A
simple embedding procedure was used for simulating the
host crystal around a cluster fragment containing the Ce$^{3+}$
ion. A similar but much more advanced study of the centroid
shift was published recently, containing a more detailed
analysis of the contributions and the influence of the basis
set. The Judd-Morisson effect does not show up clearly in
standard configuration interaction. It is likely that it is only
included if the basis set meets special requirements.

Next, we mention the work of Seijo and co-workers, who
at an early stage took interest in the matter and published
several papers directly related to the field. They per-
formed ab initio model potential (AIMP) embedded-cluster
calculations, applying the complete active space model with
second order perturbation theory on impurity ions in host
crystals, approximately taking into account all ions in the
lattice.

Particularly, their recent work on Ce$^{3+}$ in BaF$_2$ is of
interest here because in our earlier study on the centroid
shift of Ce$^{3+}$ in a number of crystals, we did calculations on
the same system. The quoted work makes the important ob-
servation that a calculation, like ours, with Madelung point
charge embedding can give strange results because of a se-
rious deformation of the 5d orbital due to the embedding
procedure. In our studies, we did not experience these prob-
lems, and our results for Ce$^{3+}$ agree well with their AIMP
results. A further study is required to find out the reason for
unwanted effects of Madelung point charge embedding on
the energy levels of ionic clusters. It very likely is a basis set
problem.

Finally, we mention the recent work of Watanabe et al.,
who, using the Dirac-DFT relativistic four-component for-
malism, conducted embedded-cluster calculations on Ce$^{3+}$
in several fluoride compounds.

The first band structure calculation on 4f-5d transitions of
a substantial number of triply ionized lanthanides was pub-
lished by Schmidt et al. The approach uses density func-
tional theory (DFT). The localized nature of the 4f shell
(self-interaction) prohibits the calculation of accurate energy
differences and, instead, a parameter model is proposed for
the calculation of 4f-5d energy differences. There have been
attempts to overcome this problem in order to conduct use-
ful band structure calculations for rare-earth impurities in
host crystals.

After this short overview of the background and the the-
oretical efforts taken, all related to the centroid shift, we now
turn to another important property of the 4f-5d transition, the
Stokes shift. As far as we know, the first ab initio study of
the Stokes shift of Ce$^{3+}$ in an ionic compound was done on
LiBaF$_3$ doped with cerium. The Stokes shift is as great as
0.8 eV and much greater than that in similar systems such as
BaF$_2$ (0.2 eV). A band structure approach was used for ana-
lyzing the large Stokes shift. It was found that only in the 5d
state does the Ce$^{3+}$ ion move from its centered position in the
direction of the assumed charge compensation. This results
in a strong deformation of the surroundings. In this way, the
large Stokes shift could be explained.

In Refs. 1 and 2, one can see that the Stokes shift can have
values ranging from almost zero to values as large as 1.3 eV. It is obvious from the former work on LiBaF$_3$ that
properties of the host crystal and the coupling of the (ex-
tended) 5d orbitals with lattice deformations or phonons are
responsible for this variation, and the standard textbook ex-
planation using the simple configurational coordinate model is often inadequate.

An even more complicated relaxation of the lattice on
excitation from 4f to 5d was found in LaCl$_3$ doped with
Ce$^{3+}$. This crystal has an excellent scintillation behavior,
and this behavior is partly due to the relatively large Stokes
shift of 0.72 eV avoiding any overlap between absorption
and emission. The origin of the large Stokes shift is due to a
complicated movement of the surrounding anions as a result
of the off-center movement of the Ce$^{3+}$ ion. The surrounding
anions form a tricapped trigonal prism, and this is strongly
deformed when Ce$^{3+}$ is in the lowest 5d state. This is appar-
tently an unexpected and somewhat suspicious result. It was
assumed that pseudo Jahn-Teller coupling is involved.

In this paper, we analyze in detail why the Ce$^{3+}$ ion goes
off-center by studying the change in occupation of the lowest
5d orbitals. Also, the deformation of the prism and the influ-
ence of the theoretical model on the resulting Stokes shift are
explained.

Shortly after the experiments on Ce$^{3+}$-doped LaCl$_3$, van
Loef et al. found the crystal LaBr$_3$ doped with Ce$^{3+}$ to be
an even better scintillator. The crystal structure of this com-
pound is the same as that of LaCl$_3$, and it is obvious that it
should be included in our theoretical study.

Very recently, measurements were done on NaLaF$_4$
doped with cerium, a fluoride compound also containing the
tricapped trigonal prism as surroundings for the Ce$^{3+}$ ion.
The Stokes shift is substantially larger than that in the former
two compounds. It was chosen as the third system to study in
detail. Experimental details will be given below.

II. EXPERIMENTAL RESULTS ON Ce$^{3+}$ IN LaCl$_3$, LaBr$_3$, AND NaLaF$_4$

In Fig. 1, emission and excitation spectra are shown for the
three compounds LaBr$_3$, LaCl$_3$, and NaLaF$_4$ doped with
cerium. The data for LaBr$_3$ are taken from a recent publication in the field, those of LaCl$_3$ are from Ref. 21, and the NaLaF$_4$ data are yet to be published by us.

The spectra are drawn with the same energy scale to en-
able a direct comparison of properties such as linewidth,
splitting of the 5d level, and Stokes shift. All excitation spec-
tra belong to the emission line with the highest energy.

One can see that for NaLaF$_4$ the doublet structure of the
emission line arising from the $^2F_{5/2}$ and $^2F_{7/2}$ states is not
resolved. This is assumed to be due to the steep 4f energy
parabola in the configuration space belonging to the relaxed
5d state. Note the splitting of the 5d level into five compo-
ments with a small energy gap between the lowest and next
lowest excitation lines, particularly for LaCl$_3$ and LaBr$_3$. This may cause a pseudo-Jahn-Teller effect to distort the
environment.

The data in Table I give an overview of results from the
figures, which is important for our further study of the influ-
ence of lattice distortions on the Stokes shift. Finally, Fig. 2
shows the tricapped prism of anions around the Ce$^{3+}$ ion in
Our ab initio calculations showed that the crystal field caused by the six anions of the prism is more or less equal but opposite in sign compared to that of the three “caps” in the midplane. This results in a small crystal field splitting. It agrees with qualitative findings in Ref. 6 based on the crystal field in a simple point charge model. The arrows indicate ionic movements after the excitation of the cerium ion to the 5\textit{d} state. The ions without an arrow do not show sizable displacements. These results of our relaxation study will be discussed further on.

III. THEORETICAL MODELS AND DETAILS OF THE CALCULATIONS

We have used two approaches in studying the Stokes shift in the systems of interest. First, we used \textit{ab initio} relaxation of the lattice containing the Ce\textsuperscript{3+} ion using a band structure approach. Second, we conducted ionic cluster calculations using the geometries found and investigated additional properties of the mechanism that causes the Stokes shift. In the latter part, we present results of a simulation of the very start of the relaxation process by moving only the Ce\textsuperscript{3+} ion along the line found in the 5\textit{d} level relaxation study. Because of the fixed lattice, one can compare relaxation energies calculated with the band structure and the ionic cluster model.

<table>
<thead>
<tr>
<th>System</th>
<th>Emission (eV)</th>
<th>Excitation (eV)</th>
<th>Stokes shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>4.43</td>
<td>0.73</td>
</tr>
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<td></td>
<td>3.70</td>
<td>4.52</td>
<td></td>
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<td></td>
<td></td>
<td>4.71</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LaBr\textsubscript{3}</td>
<td>3.21</td>
<td>4.03</td>
<td>0.55</td>
</tr>
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<td></td>
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<td>4.37</td>
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<td></td>
<td></td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>NaLaF\textsubscript{4}</td>
<td>4.13</td>
<td>5.15</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.36</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>5.58</td>
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<td></td>
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<td>5.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.21</td>
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</tr>
</tbody>
</table>

FIG. 2. (Color online) Tricapped trigonal prism of fluorine anions around Ce\textsuperscript{3+} in NaLaF\textsubscript{4}. The arrows indicate the distortions of the local geometry after relaxation in the 5\textit{d} state of the cerium ion.
Similar to our study of LiBaF₃,¹⁹ we have used the Viena 
\textit{ab initio} simulation package (VASP).²⁶,²⁷ The program solves 
the Kohn-Sham equations for a periodic system using a plane 
wave basis set. We have used ultrasoft (US) Vanderbilt 
pseudopotentials,²⁸ as supplied by Kresse and Hafner.²⁹ The 
generalized gradient approximation was used for the 
handling of electron correlation and exchange. Where possible, 
we employed the projector augmented wave (PAW) method 
implemented by Kresse and Joubert ³⁰ in handling the 4f and 
5d states of the Ce⁴⁺ ion. We used the supercell approach, 
in order to minimize the interaction of Ce⁴⁺ with its periodic 
images. For economic reasons, the supercell was chosen to 
be a 2 × 2 × 2 unit cell fragment. Ce⁴⁺ replaces 1 in 16 La³⁺ 
ions.

Almost all calculations were done at the Γ point in reciprocal 
space. For some calculations (LaBr₃), we also used a 
3 × 3 × 3 Monkhorst-Pack sampling for checking the accuracy 
of this procedure. The relaxation accuracy was chosen to 
be higher than standard. The stopping criterion for ionic 
motion in energy change per step was set to 10⁻⁴. We kept 
other parameters of the relaxation studies at the standard 
values of the code.

The relaxations turned out to be rather difficult to perform, particularly for the 5d states. The reason is that the occupation of the 4f and 5d states is obtained by smearing over a range of orbital energies. This procedure speeds up convergence considerably. This means, however, that, for instance, for the 4f state, all seven 4f orbitals are occupied with a certain distribution. For the 4f state, this is not a problem because the separate 4f states have similar relaxation behaviors because they do not interact with the lattice. However, for the 5d states, the smearing causes a problem. When the Ce⁴⁺ ion is in the 5d(3z²−r²) state, in all of our systems the lowest state, the relaxation is quite different from that in, for instance, the 5d(x²−y²) state (next higher state).

Therefore, relaxation in the 4f state was done with standard Gaussian smearing, but for the 5d state, we only occupied the lowest orbital. This choice causes convergence to be slow, sometimes very slow, particularly if the lowest and next lowest 5d states are almost degenerate. The relaxation studies are very demanding but, using the real space projection scheme, can save much computer time. However, with this option the forces turned out to be too far off from those of the more demanding reciprocal space projection scheme, and it was therefore not used.

The pseudo Jahn-Teller coupling only comes into effect if there is already a certain displacement of the Ce⁴⁺ ion. Therefore, it seems necessary to start the 5d level relaxations with a certain displacement. However, because of numerical limitations, the symmetry is not strictly C₃ᵥ, and this displacement is not required but it speeds up the relaxation.

Further, it was found that relaxation studies, using PAW-type potentials, are particularly difficult to perform because the 4f states of the La³⁺ ion form the bottom of the conduction band and the 5d states of Ce⁴⁺ are high in the conduction band. Fortunately, there is a gap between the 4f and 5d states of La³⁺. At the bottom of the lanthanum 5d-type conduction band, we find the 5d levels of Ce⁴⁺, which can be used for the relaxation studies.

At this point, it is important to mention the fact that if one restricts the relaxation to retain the C₃ᵥ symmetry, the relaxation energy is much smaller than that for the unrestricted relaxation. The Stokes shift obtained is then around 0.15 eV, and so is in the normal regime.

B. Ionic cluster calculations and impact of spin-orbit interaction

The Stokes shift calculated with the band structure model is probably not very accurate because of a number of reasons. First, in most cases the 5d states are just below or in the conduction band, and this somewhat delocalizes the 5d orbitals with the result that the relaxation energy is too small. The positioning in the conduction band is an artifact and results from the small band gap, typical of DFT calculations.

A second cause of error is the spin-orbit coupling, which is absent in the band structure approach. This coupling will split and reposition the 5d levels and so influence the pseudo Jahn-Teller effect. This can be seen clearly from Fig. 1. In all excitation measurements, we see five lines, and from Table I, it is concluded that the spin-orbit interaction is of the same magnitude as the crystal field splitting. Therefore, it will modify the start of the relaxations in the 5d state because the lowest 5d state might be different from that of the DFT band structure model.

These considerations motivated us to conduct ionic cluster calculations using the HF-LCAO approach using a non-relativistic as well as a relativistic four-component formalism. The codes were GAUSSIAN G98 (Ref. 31) for the former work and MOLFDIR (Ref. 32) for the latter. With these codes, we calculated the 5d level splitting in the G₁ geometry, to be compared with the data of Table I. Further, the Stokes shift was calculated, and a study was made on the influence of spin-orbit coupling on the start of the relaxation.

The latter study was done using the four-component code, where the spin-orbit coupling is included in the Dirac Hamiltonian. The basis sets used for the calculations with the G98 code were those defined in Ref. 11, Cbasf1 for cerium, Fbas for fluorine, and Clbas for chlorine. The basis set for bromine was similar to that of chlorine. For the MOLFDIR package, we used internal basis sets. These sets were all-electron bases. For cerium (5d), we used an uncontracted [18s,15p,12d] basis. For chlorine, the basis was a [7s,7p,1d] set, also not contracted. For the calculation of the 5d level splitting in a nonrelativistic formalism, we diagonalized the spin-orbit Hamiltonian in the space of the 5d levels.

These calculations were done on a cluster of nine anions surrounding the Ce⁴⁺ ion. The rest of the lattice was simulated by point charges, obtained by a least squares fit of the Madelung potential at a set of points in the cluster region. Configuration interaction was not used because it has only a minor influence on the results obtained.

IV. RESULTS AND DISCUSSIONS

In the following, we present results of the relaxation studies on the three systems of interest. In order to have a clear
The first one concerns the relaxation of the system when Ce$^{3+}$ is in the 4$f$ ground state. Interesting properties are the optimized distances from the Ce$^{3+}$ ion to the nearby anions compared with those of x-ray diffraction. Another important property is the 5$d$ level splitting obtained with the optimized geometry, corrected for spin-orbit interaction. The comparison with experiment shows the accuracy of the employed methods. The 5$d$ levels were also calculated with the HF-LCAO model using the $G_1$ geometry.

The second subsection presents results of the relaxation in the lowest 5$d$ state of Ce$^{3+}$ to geometry $G_2$. This is the most important part of the paper because of the peculiar lattice relaxation around the impurity. This relaxation is characteristic of the local geometry and the coupling of the 5$d$ states to the lattice vibrations. The Stokes shift was also calculated with the HF-LCAO model using the $G_1$ and $G_2$ geometries obtained, and the results are shown.

The third and last subsection is devoted to an investigation of the start of the pseudo Jahn-Teller relaxation and the influence of spin-orbit interaction. The impact of spin-orbit coupling on relaxation is investigated using the Dirac-Fock LCAO cluster formalism.

### A. Ground state relaxation

The three systems LaCl$_3$, LaBr$_3$, and NaLaF$_4$ belong to the same crystallographic space group $P6_3/m$. In the first two crystals, the anions are at the Wyckoff positions $6h$ and La is at position $2c$. For the chlorine compound, the lattice parameters were taken from Morosin, and for LaBr$_3$ from Kraemer et al. The compound NaLaF$_4$ is disordered. The sodium ions share the $2c$ site with lanthanum and partly occupy the octahedral site $2b$. It is not possible to treat this system with a band structure code. We did modify the structure by simply omitting the sodium ions and fully occupying the $2c$ site with lanthanum. The structure is now similar to that of the other two crystals. It is assumed that the relaxation behavior is not seriously affected because the local environment, the tricapped trigonal prism of Fig. 2, is similar.

In Table II, we present the results of relaxation calculations with Ce$^{3+}$ in the 4$f$ state. As mentioned above, we used a band structure code based on the DFT model. The unit cell

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**TABLE II.** Results of relaxation studies with Ce$^{3+}$ in the 4$f$ state. In all calculations, using US potentials, La$^{3+}$ is replaced by Ce$^{3+}$ with 4$f$ in the core. This is denoted by “semi.” $R_{\text{cap}}$ and $R_{\text{prism}}$ are the distances from the Ce$^{3+}$ ion to the three cap ions and the six prism ions, respectively, after relaxation. The numbers in parentheses refer to crystallographic data. The experimental values for the 5$d$ levels are from Table I. The spin-orbit correction was calculated with $\lambda=0.123$ eV.

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{\text{cap}}$ (Å)</th>
<th>$R_{\text{prism}}$ (Å)</th>
<th>DFT band structure</th>
<th>HF-LCAO cluster</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$R_{\text{cap}}$</td>
<td>$R_{\text{prism}}$</td>
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<td>Pure</td>
</tr>
<tr>
<td></td>
<td>(Å)</td>
<td>(Å)</td>
<td>Spin-orbit</td>
<td>Spin-orbit</td>
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<td></td>
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<td>2.95</td>
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<td>0.0</td>
</tr>
<tr>
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<td>(2.95)</td>
<td>(2.95)</td>
<td>0.15</td>
<td>0.0</td>
</tr>
<tr>
<td>(Semi)</td>
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<td>0.31</td>
<td>0.62</td>
<td>0.33</td>
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<td>0.53</td>
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<td>0.75</td>
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<td>0.0</td>
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<td>(3.10)</td>
<td>0.05</td>
<td>0.13</td>
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<tr>
<td>(Semi)</td>
<td>0.55</td>
<td>0.27</td>
<td>0.66</td>
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<td>CeBr$_3$</td>
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<td>0.73</td>
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<tr>
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<td>0.83</td>
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<td></td>
<td></td>
<td>0.66(0.94)</td>
<td>0.75</td>
<td>1.06</td>
</tr>
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</table>

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075124-5
was a $2 \times 2 \times 2$ supercell with 1 in 16 La$^{3+}$ ions replaced by Ce$^{3+}$. This guarantees a proper embedding in the host crystal. As noted earlier, we have used two different potentials for the system LaCl$_3$, denoted by US and PAW. For the US potential, it was necessary to replace the La$^{3+}$ ions by Ce$^{3+}$ with $4f$ in the core; otherwise, no stable solution could be found for the $5d$ states. So, actually, we have a CeCl$_3$ system with the LaCl$_3$ lattice. For the PAW potential, the actual system was LaCl$_3$. From a comparison of the results of the two calculations, we can measure the impact of the replacement of La$^{3+}$ by Ce$^{3+}$ with $4f$ in the core.

Using the geometry obtained ($G_1$), the $5d$ level splitting was calculated by exciting to the $5d$ state, and the results are shown in Table II, pure and with spin-orbit interaction. The spin-orbit parameter was taken to be 0.123 eV. As noted above, also the results of the HF-LCAO cluster calculations are shown.

It is obvious that the optimized geometry for LaCl$_3$ and LaBr$_3$ is equal to that of crystallographic data. We observe that all relaxations were done with constant volume. Also, one can see that for these two systems, the $5d$ level splitting very well agrees with experiment, both in DFT as in HF-LCAO. The latter values are slightly closer to experiment.

For NaLaF$_3$ (CeF$_3$), the relaxation results are quite different. First, we see that the distances to the six anions of the prism (see Fig. 2) become considerably smaller. The distance of 2.54 Å in the pure compound changes to 2.46 Å in our ordered structure. This might be understandable from a comparison with, for instance, the pure compound CeF$_3$. Apparently, the disordered distribution of sodium ions in NaLaF$_3$ increases the distances to the prism anions compared to those of the ordered crystal. Because there is a competition between the crystal field arising from the prism and that from the caps, this shortening of distances will change the $5d$ level splitting. In Table II, one can see the poor agreement of the $5d$ level splitting with experiment. The numbers in brackets show the level splitting if the distances from x-ray diffraction are used. The agreement with experiment is now much better and comparable with the other two systems.

For the pseudo Jahn-Teller effect to be effective, it is important that the distance of the lowest to the next lowest $5d$ level is small, and from Table II it is clear this condition is satisfied both for the theoretical as well as for the experimental results.

**B. Excited 5d state pseudo Jahn-Teller relaxations**

In the three systems under study, we let the system relax after exciting the Ce$^{3+}$ ion from $4f$ to the lowest $5d$ state. This means that for the US-type potentials, we had to change the Ce$^{3+}$ potential from the in-core $4f$ form to the one of the excited $5d$ state. For the PAW type, the potential for Ce$^{3+}$ remains the same but one has to find, in large amounts of excited states, the ones of the right type to occupy that state in starting the relaxations. As was mentioned earlier, the cerium ion had a small displacement from its centered position for speeding up convergence and getting the proper relaxation. The further procedure is straightforward and the prism of Fig. 2 will relax until the energy is lowest.

In Fig. 3, we show the final positions of the various ions for the system LaCl$_3$ in a unit cell viewed along the $z$ axis. We have placed an axis system at the prism of interest. The displacements of the ions in the $x$ and $y$ directions can be seen clearly. There are also displacements of four of the six anions of the prism in the $z$ direction, as shown in Fig. 2.

One of the most remarkable features, apart from the movement of the cerium ion, is the substantial displacement of one of the three cap anions (Cl$_1$) in a direction opposite to that of the cerium ion, and obviously the two displacements belong to the same vibration mode. Clearly, there is a similarity between the effect of the two movements because the displacement of one of the cap anions in the $C_{3h}$ symmetry also destroys the centering of the Ce$^{3+}$ ion.

There is a slight asymmetry in the displacements, but we can overlook these deviations and characterize the distortion of the prism by three parameters. The first one called $D_{C_{3v}}$ is the displacement of the cerium ion from its starting position. The second one is the displacement of the special anion and is denoted by $D_{cap}$. The third one is the displacement of the four prism anions and is referenced by $D_{prism}$. For positive displacements, the movement is outward, and for negative values, it is inward.

Table III shows the results of the $5d$ relaxation in the systems of interest. For the band structure method, the Stokes shift was calculated from the change $\Delta E_{5d}$ in total energy on relaxing from the geometry $G_1$ of the ground state to the final geometry $G_2$. $\Delta E_{5f}$ is the change in energy on relaxing back from $G_2$ to $G_1$. The cluster (HF-LCAO) results for the Stokes shift were obtained in a different way. Here, the excitation energy from $4f$ to the lowest $5d$ state is evaluated in both geometries. The difference between the two numbers gives the Stokes shift.

From Table III, it is clear that the calculated Stokes shifts are comparable with experiment, particularly for the cluster calculations in the systems LaCl$_3$ and LaBr$_3$. The PAW-type calculation, using real lanthanum ions, gives a substantially smaller relaxation than the US type. This is very likely a result of the much higher positioning of the $5d$ levels in the band gap. The orbital is more delocalized than that of the US.
The Stokes shift in LaCl₃ is around 0.1 eV. This shows that there is more space between the Ce³⁺ ion and the prism anions.

In our view, the reason is a reorientation of the occupied 5d orbital and used a different coloring (gray scale) for this orbital.

It is clear what happens. The occupied orbital at the start, being of type 3z²-r², turns after relaxation into one of type z²-x² by strongly mixing with the next higher orbital of type x²-y², where z is along the sides of the prism and the x axis is as shown in Fig. 3. The 5d charge distribution now points just between two of the cap anions, but on the opposite side also in the direction of the third cap anion (Cl₁). This anion feels a strong repulsive force because of the reoriented orbital and moves outward. Because of the increase in empty space between the cerium ion and the anions, the four neighboring prism anions get nearer, thus further lowering the energy. The strong mixing between the 5d orbital of types 3z²-r² and x²-y² occurs already for small values of the displacement.

This type of analysis (geometrical) is rather different from the standard approach of the Jahn-Teller effect, in which all

<table>
<thead>
<tr>
<th>System</th>
<th>DCe  (Å)</th>
<th>DCaps  (Å)</th>
<th>Dprism  (Å)</th>
<th>ΔE₅d (eV)</th>
<th>ΔE₄f (eV)</th>
<th>Stokes shift (eV)</th>
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</thead>
<tbody>
<tr>
<td>LaCl₃ US</td>
<td>0.32</td>
<td>0.21</td>
<td>-0.13</td>
<td>0.268</td>
<td>0.267</td>
<td>0.535</td>
</tr>
<tr>
<td>(Semi) CeCl₃</td>
<td>0.15</td>
<td>0.06</td>
<td>-0.11</td>
<td>0.169</td>
<td>0.204</td>
<td>0.373</td>
</tr>
<tr>
<td>LaCl₃ PAW</td>
<td>0.27</td>
<td>0.15</td>
<td>-0.13</td>
<td>0.182</td>
<td>0.225</td>
<td>0.406</td>
</tr>
<tr>
<td>LaBr₃ US</td>
<td>0.19</td>
<td>0.15</td>
<td>-0.03</td>
<td>0.199</td>
<td>0.313</td>
<td>0.512</td>
</tr>
<tr>
<td>(Semi) CeBr₃</td>
<td></td>
<td>-0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaLaF₄ US</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Semi) CeF₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

From the discussion in Sec. IV A, it is not a surprise that the results of NaLaF₄ do not compare very well with experiment. However, there is, even with the modified crystal, a relaxation in the Ce³⁺ ion. The question is why the cerium ion moves when it is excited to the 5d state. For clarity, we increased the density of the occupied 5d orbital and used a different coloring (gray scale) for this orbital.
local and global minima of the potential energy surface are found using a parametrized Hamiltonian. A detailed general analysis of the pseudo Jahn-Teller effect using this approach for a system like ours with a singlet and a doublet was found in a recent paper on the ozone molecule. The Hamiltonian is applicable for small displacements and shows that the effect is quadratic in the displacement of the Ce$^{3+}$ ion. The potential energy decreases in any direction in the plane of the caps and has three global minima, as is also obvious from our investigation.

Further progress of the relaxation as we described above cannot be easily casted into equations. Therefore, we did not study the theory in more detail and just conducted numerical relaxations.

C. Further analysis of the relaxation process

In order to investigate numerically the start of the relaxation, we made a special relaxation study of the system LaCl$_3$ in which the Ce$^{3+}$ ion moves along the x axis shown in Fig. 3. All other ions are fixed. The view is along the z axis. Note the two triangles of anions around the origin. The larger one is that of the caps and the smaller one is that of the prism (see also Fig. 2). Because of the fixed lattice, we also performed a relaxation calculation using the cluster approach, and a direct comparison is possible between relaxation results from the two models. The relaxation using the cluster approach is not very accurate because the embedding point charges have an effect on the repulsive forces in the prism, but the results are useful enough for the current study.

Figure 5 shows the results of this relaxation. As expected, one can see that after exciting the system from 4f to 5d, the energy of the system arrives on the top of a potential hill. In any direction, the system can lower the energy. The lowering is largest in the positive x direction, the direction of the ultimate relaxation discussed above. We note that the “relaxation energy” calculated with the HF-LCAO formalism is substantially larger then that of the DFT band structure calculation. This supports the view that the values of the Stokes shift calculated with the Hartree-Fock model are more accurate. However, the minima in the two curves are not at the same displacements. This is very likely a result of the point charge embedding of the HF-LCAO calculations.

At the deepest point (global minimum), there is a large mixing of the lowest 5d orbital of type 3z$^2$-r$^2$ with the next higher orbital of type x$^2$-y$^2$ in such a way that the resulting orbital approximately has a z$^2$-x$^2$ character. In the opposite direction, there seems to be a second (local) minimum, where the mixing is such that the final orbital has a z$^2$-y$^2$ character. This minimum is not a minimum at all. It occurs only in the radial direction. However, in the angular direction, the minimum is at $\pm$60° from the two nearest global minima and so it is actually a saddle point. The spin-orbit interaction will modify the relaxation picture because the lowest 5d state may not be of type 3z$^2$-r$^2$ and the doublet x$^2$-y$^2$, $xy$ will split. From Fig. 1, it is clear that this splitting is so large that the pseudo Jahn-Teller effect is seriously affected, at least when it starts. For larger displacements, the crystal field will probably dominate the spin-orbit effect.

In order to support this view, we conducted Dirac-Fock LCAO cluster calculations on the LaCl$_3$ system. The four-component formalism elegantly includes the spin-orbit interaction. In this way, we can study the start and the end of relaxation with and without this interaction. In Table IV, we show the results of these calculations. It is not a surprise to see that at the end of relaxation, the influence of the spin-orbit interaction is small, but the start of relaxation is indeed drastically changed by the spin-orbit interaction.

V. CONCLUDING REMARKS

The theoretical analysis of the Stokes shift in the crystals LaCl$_3$, LaBr$_3$, and NaLaF$_4$ doped with cerium has provided strong evidence for an unexpectedly large deformation of the direct environment the Ce$^{3+}$ ion in the excited 5d state. It explains some of the larger Stokes shifts of rare-earth ions in ionic hosts. This study has also shown that a relatively small effect, the pseudo Jahn-Teller effect, leads to a kind of snowball effect in the surrounding lattice (the prism), thereby increasing the Stokes shift drastically.

<table>
<thead>
<tr>
<th>Displacement (Å)</th>
<th>Relaxation energy (eV)</th>
<th>HF-LCAO</th>
<th>Dirac-LCAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.01</td>
<td>0.003</td>
<td>0.12</td>
</tr>
<tr>
<td>0.15</td>
<td>0.11</td>
<td>0.12</td>
<td>0.12</td>
</tr>
</tbody>
</table>