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Lattice relaxation study of the 4*f*-5*d* 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 (4*f*). However, in the 5*d* state, the relaxation of the lattice is quite different because the 5*d* levels experience a pseudo Jahn-Teller coupling with certain lattice displacements. This is because the lowest two 5*d* 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 5*d*-4*f* 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 4*f*-5*d* 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 this transitions and succeeded to find simple semiempirical models for summarizing and predicting various properties of the 4*f*-5*d* 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 4*f*-5*d* transitions started with work on the so-called crystal field depression[1,2] of the $4f^{n-1}5d$ 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 4*f*-5*d* energy differences rather accurately using two parameters. The parameters are the crystal field depression of the 5*d* state compared to the 4*f* 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 5*d* levels by polarization of the lattice. The Judd-Morisson model[3,4] was used to express the centroid or barycenter shift and was rather successfully applied to fluorides,[5] chlorides, bromides, iodides,[6] and oxides.[7] 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 be 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[8] 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.*[9] The crystal field model used for many years in investigating $4f^n$-$4f^n$ transitions was extended to include the $4f^n$-$4f^{n-1}5d$ spectra. These calculations shed light on the complicated interactions taking place on the excitation of a 4*f* electron to a 5*d* state and the coupling of the remaining $4f^{n-1}$ core with the 5*d* electron. There is, however, not a direct relation with the compilation of experimental results mentioned above.

Subsequently, a study[10] 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 orbitals (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[11] 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[11] that it is only included if the basis set meets special requirements.

Next, we mention the work of Seijo and co-workers,[12–15] who at an early stage took interest in the matter and published several papers directly related to the field. They performed *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[15] on Ce^{3+} in BaF_2 is of interest here because in our earlier study[11] 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 observation that a calculation, like ours, with Madelung point charge embedding can give strange results because of a serious deformation of the $5d$ orbital due to the embedding procedure. In our studies, we did not experience these problems, 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.*,[16] who, using the Dirac-DFT relativistic four-component formalism, 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 published by Schmidt *et al.*[17] The approach uses density functional 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[18] in order to conduct useful band structure calculations for rare-earth impurities in host crystals.

After this short overview of the background and the theoretical 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.[19] 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 analyzing 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 (extended) $5d$ orbitals with lattice deformations or phonons are responsible for this variation, and the standard textbook explanation using the simple configurational[20] coordinate model is often inadequate.

An even more complicated relaxation of the lattice on excitation from $4f$ to $5d$ was found[21] in $LaCl_3$ doped with Ce^{3+}. This crystal has an excellent scintillation behavior,[22] 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 apparently 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 influence 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.*[23] found the crystal $LaBr_3$ doped with Ce^{3+} to be an even better scintillator. The crystal structure of this compound is the same as that of $LaCl_3$, and it is obvious that it should be included in our theoretical study.

Very recently,[24] 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 $LaNaF_4$ doped with cerium. The data for $LaBr_3$ are taken from a recent publication[25] 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 enable a direct comparison of properties such as linewidth, splitting of the $5d$ level, and Stokes shift. All excitation spectra 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 components 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 influence of lattice distortions on the Stokes shift. Finally, Fig. 2 shows the tricapped prism of anions around the Ce^{3+} ion in

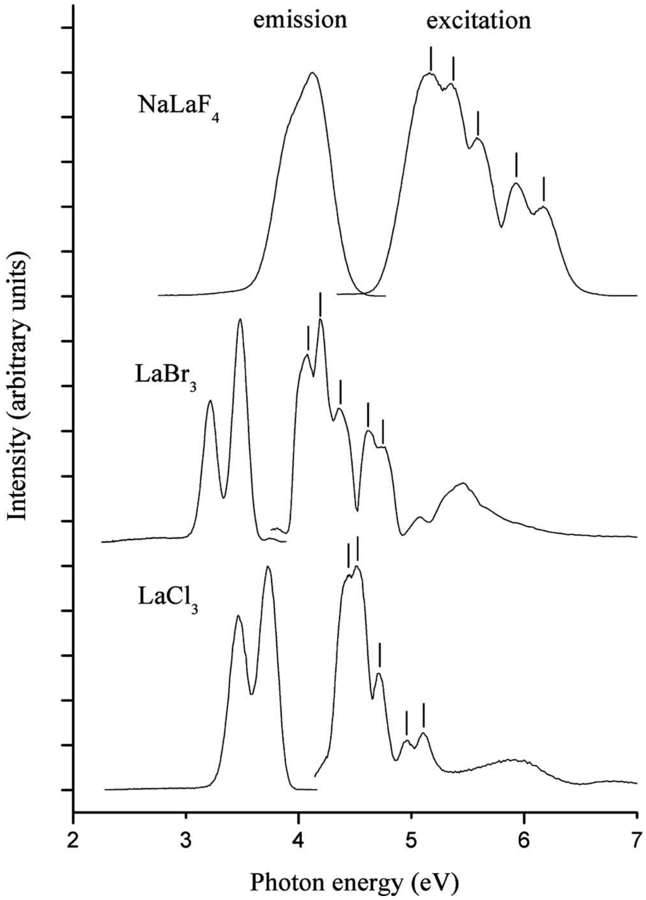

FIG. 1. Emission and excitation spectra of Ce^{3+} in $LaCl_3$, $LaBr_3$, and $NaLaF_4$.

$NaLaF_4$. 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*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 *ab initio* relaxation of the lattice containing the Ce^{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^{3+} ion along the line found in the 5*d* level relaxation study. Because of the fixed lattice, one can compare relaxation energies calculated with the band structure and the ionic cluster model.

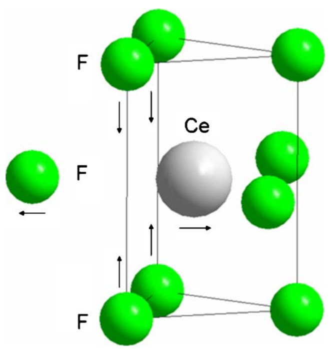

FIG. 2. (Color online) Tricapped trigonal prism of fluorine anions around Ce^{3+} in $NaLaF_4$. The arrows indicate the distortions of the local geometry after relaxation in the 5*d* state of the cerium ion.

A. Lattice relaxation studies

In calculating the Stokes shift, one has to optimize the geometry of the lattice around the Ce^{3+} ion. This has to be done for the (lowest) 4*f* state as well as for the lowest 5*d* state. In this paper, the optimized geometry of the 4*f* state will be referenced with G_1 and that of the 5*d* state with G_2. In obtaining the Stokes shift, the change in the energy of the system relaxing from G_1 to G_2 in the 5*d* state has to be added to the change in energy in the 4*f* state when the system moves back from G_2 to G_1.

The 5*d* state in the geometry G_1 splits into three levels, a singlet and two doublets of which the singlet (lowest) has type $3z^2\text{-}r^2$, the first doublet consists of the types $x^2\text{-}y^2$ and xy. The second (highest) doublet contains the types xz and yz. The z axis is along the prism sides in Fig. 2. The driving force for the relaxation in the 5*d* state is the pseudo Jahn-Teller coupling between the singlet and the next higher doublet.

TABLE I. Energy differences corresponding to the emission and excitation spectra of Ce^{3+} in $LaCl_3$, $LaBr_3$, and $NaLaF_4$.

System	Emission (eV)	Excitation (eV)	Stokes shift (eV)
$LaCl_3$	3.44	4.43	0.73
	3.70	4.52	
		4.71	
		4.96	
		5.10	
$LaBr_3$	3.21	4.03	0.55
	3.48	4.15	
		4.37	
		4.60	
		4.77	
$NaLaF_4$	4.13	5.15	1.02
		5.36	
		5.58	
		5.98	
		6.21	

Similar to our study of $LiBaF_3$,[19] we have used the Viena *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 Ce^{3+} ion. We used the supercell approach, in order to minimize the interaction of Ce^{3+} with its periodic images. For economic reasons, the supercell was chosen to be a $2\times2\times2$ unit cell fragment. Ce^{3+} replaces 1 in 16 La^{3+} ions.

Almost all calculations were done at the Γ point in reciprocal space. For some calculations ($LaBr_3$), we also used a $3\times3\times3$ 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 the occupation 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 Ce^{3+} ion is in the $5d(3z^2\text{-}r^2)$ state, in all of our systems the lowest state, the relaxation is quite different from that in, for instance, the $5d(x^2\text{-}y^2)$ 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 Ce^{3+} 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 C_{3h}, 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 La^{3+} ion form the bottom of the conduction band and the $5d$ states of Ce^{3+} are high in the conduction band. Fortunately, there is a gap between the $4f$ and $5d$ states of La^{3+}. At the bottom of the lanthanum $5d$-type conduction band, we find the $5d$ levels of Ce^{3+}, 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 C_{3h} 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 nonrelativistic 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 G_1 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, Cebasf1 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 Ce^{3+} 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

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_{caps} and R_{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.

			5*d* level splitting (eV)				
			DFT band structure		HF-LCAO cluster		
System	R_{caps} (Å)	R_{prism} (Å)	Pure	Spin-orbit	Pure	Spin-orbit	Expt.
$LaCl_3$	2.95	2.95	0.0	0.0	0.0	0.0	0.0
US	(2.95)	(2.95)	0.15	0.04	0.17	0.06	0.09
(Semi)			0.72	0.31	0.62	0.33	0.28
$CeCl_3$				0.72		0.64	0.53
				0.83		0.75	0.67
$LaCl_3$	2.95	2.95	0.0	0.0	0.0	0.0	
PAW	(2.95)	(2.95)	0.12	0.01	0.13	0.02	
			0.73	0.27	0.66	0.29	
				0.73		0.67	
				0.84		0.78	
$LaBr_3$	3.16	3.10	0.0	0.0	0	0.0	0.0
US	(3.16)	(3.10)	0.05	0.05	0.24	0.13	0.12
(Semi)			0.55	0.27	0.60	0.40	0.34
$CeBr_3$				0.62		0.62	0.57
				0.73		0.73	0.74
$NaLaF_4$	2.41	2.47	0.0	0.0(0.0)	0.0	0.0	0.0
(Semi)	(2.41)	(2.54)	0.025	0.07(0.29)	0.14	0.22	0.21
CeF_3			0.45	0.27(0.56)	0.52	0.27	0.43
				0.56(0.82)		0.66	0.83
				0.66(0.94)		0.75	1.06

overview of the results, the discussion is divided into three subsections.

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 (G_1), 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 6*h* and La is at position 2*c*. For the chlorine compound, the lattice parameters were taken from Morosin,[33] and for $LaBr_3$ from Kraemer *et al.*[34] The compound $NaLaF_4$ is disordered.[35] The sodium ions share the 2*c* site with lanthanum and partly occupy the octahedral site 2*b*. 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 2*c* 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 was a 2×2×2 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 $NaLaF_4$ (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 $NaLaF_4$ 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 5*d* 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.

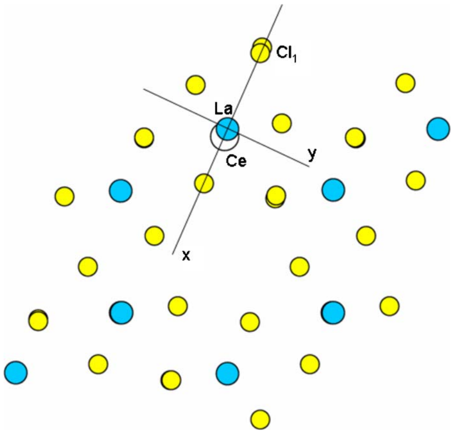

FIG. 3. (Color online) The ions in the unit cell of a 2×2×2 supercell of Ce^{3+} in $LaCl_3$ after relaxation in the lowest $5d$ state. The view is along the z axis.

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_{Ce}, 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 ΔE_{5d} in total energy on relaxing from the geometry G_1 of the ground state to the final geometry G_2. ΔE_{4f} 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

TABLE III. Results of pseudo Jahn-Teller relaxation of $LaCl_3$, $LaBr_3$, and $NaLaF_4$ doped with Ce^{3+}. D_{Ce}, D_{cap}, and D_{prism} are the distortion parameters of the tricapped prism. ΔE_{5d} is the relaxation energy in the $5d$ state and ΔE_{4f} is the relaxation energy in returning to the ground state.

						Stokes shift (eV)		
						Calc.		
System	D_{Ce} (Å)	D_{caps} (Å)	D_{prism} (Å)	ΔE_{5d} (eV)	ΔE_{4f} (eV)	Band structure	HF cluster	Expt.
$LaCl_3$ US (Semi) $CeCl_3$	0.32	0.21	−0.13	0.268	0.267	0.535	0.76	0.73
$LaCl_3$ PAW	0.15	0.06	−0.11	0.169	0.204	0.373	0.46	0.73
$LaBr_3$ US (Semi) $CeBr_3$	0.27	0.15	−0.13	0.182	0.225	0.406	0.60	0.55
$NaLaF_4$ US (Semi) CeF_3	0.19	0.15	−0.03 −0.08	0.199	0.313	0.512	0.76	1.02

potential, and therefore one can imagine that the relaxation is smaller. Apparently, the US potentials are more useful for calculating properties of the excited $5d$ states.

From the discussion in Sec. IV A, it is not a surprise that the results of $NaLaF_4$ do not compare very well with experiment. However, there is, even with the modified crystal, a large off-center movement, comparable to the other two. The distortion is more irregular, and this is the reason that in the D_{prism} column there are two numbers. The movements of the four prism ions are not as shown in Fig. 2. Two of the set have a different relaxation than the other two, a result of the C_{3h} symmetry: The triangle of the cap anions does not line up with the triangles of the prism as they would in a D_{3h} symmetry. The difference is largest for $NaLaF_4$, and therefore two values are given. It is very likely that the relaxation would be larger if the prism anions were shifted away to the positions in the real crystal because then there would be more space between the Ce^{3+} ion and the prism anions.

The large value of the Stokes shift results from the strong deformation of the prism. In Sec. IV C, it will be shown that for a displacement of the Ce^{3+} ion alone, with fixed lattice, the Stokes shift in $LaCl_3$ is around 0.1 eV. This shows that the other two displacements add substantially to the effect. In the relaxations, they result from the movement of the cerium ion. The question is why the cerium ion moves when it is excited to the $5d$ state.

In our view, the reason is a reorientation of the occupied $5d$ orbital by (pseudo Jahn-Teller) mixing with the next higher $5d$ states, thereby lowering the energy because of a smaller repulsion with the anions. In order to illustrate this, we calculated an isosurface of the electronic density of the ions of the tricapped trigonal prism. For the cerium ion, only the occupied $5d$ orbital was included. The isosurface was calculated before and after relaxation. Figure 4 shows the rendering of these surfaces. For clarity, we increased the density 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 $3z^2$-r^2, turns after relaxation into one of type z^2-x^2 by strongly mixing with the next higher orbital of type x^2-y^2, 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 (Cl_1). 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 $3z^2$-r^2 and x^2-y^2 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,[36] in which all

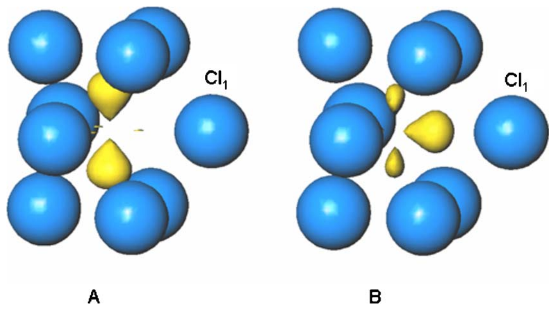

FIG. 4. (Color online) Isosurfaces of electronic density of the nine ions of the tricapped prism in $LaCl_3$ (A) before and (B) after relaxation in the $5d$ state. For the Ce^{3+} ion in the center, only the density of the occupied $5d$ orbital is rendered. In picture (A) the $5d$ orbital points in the z direction, and in picture (B) it points just toward the special anion Cl_1 in the xy plane of the caps.

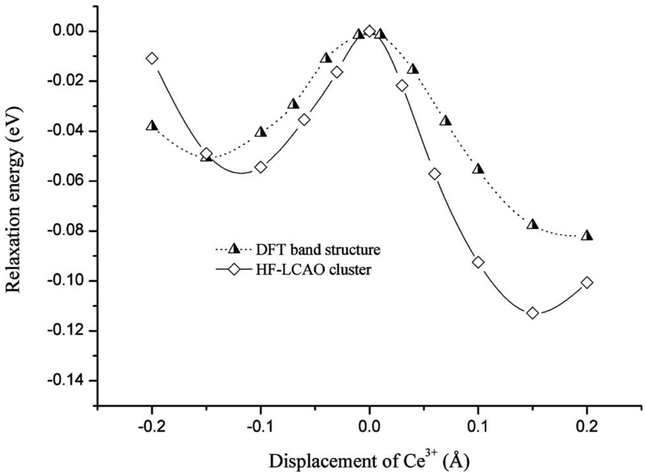

FIG. 5. Energy curves of the relaxation where only the Ce^{3+} ion moves along the x axis of Fig. 3. The curves were calculated both with the band structure model and with the cluster model.

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[37] 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.

TABLE IV. Influence of spin-orbit interaction on relaxation energy.

Displacement (Å)	Relaxation energy (eV) HF-LCAO	Dirac-LCAO
0.02	0.01	0.003
0.15	0.11	0.12

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 ±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.

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