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# Ce<sup>n+</sup> energy levels in alkaline-earth fluorides and cerium–electron, cerium–hole interactions

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**Abstract.** The energy levels of three cerium centres in CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> were calculated in the framework of the relativistic Dirac–Hartree–Fock formalism. In this study cerium was taken to be in various ionic states and lattice relaxation was included. The centres were the following: the charge-uncompensated cerium centre (Ce) and two charge-compensated cerium centres. The charge-compensating fluorine ion was situated at the (111) next-nearest-neighbour interstitial site (CeF<sub>nnn</sub>) or at the (100) nearest-neighbour interstitial site (CeF<sub>nn</sub>). We did not work with crystal field parameters, our method being *ab initio*. The results are compared with a variety of experimental data. Relaxation of the lattice around the cerium centres is crucial for the results. From the location of the energy levels, we conclude that only trivalent and tetravalent cerium centres are stable in the alkaline-earth fluorides. If free electrons are present, only the trivalent cerium centre is stable. The divalent centre without charge compensation is metastable. This is in agreement with experiment. Further, it is found that excitation of trivalent cerium centres by capture of an electron and a hole at the cerium ion is improbable. This agrees with earlier observations of the scintillation decay of Ce<sup>3+</sup>-doped BaF<sub>2</sub>.

## 1. Introduction

If in a pure crystal one excites electrons from the valence band into the conduction band, often de-excitation does not occur by direct recombination of free electrons in the conduction and holes in the valence band. Instead, the recombination involves intermediate states. One such intermediate state is the exciton, i.e. a state in which the electron and the hole are bound to each other due to their Coulomb attraction. The existence of such intermediate states is very important for the decay kinetics of the doped crystal. As an example BaF<sub>2</sub> doped with Ce<sup>3+</sup> may be mentioned, in which the x-ray excited Ce<sup>3+</sup> luminescence is for a large part due to energy transfer from the self-trapped exciton to Ce<sup>3+</sup> ions [1]. As a result, the effective decay time of the Ce<sup>3+</sup> luminescence in the ≤1 mol.% doped crystals is affected by the 630 ns decay time of the BaF<sub>2</sub> exciton [2, 3]. Therefore it is considerably slower than the 27 ns intrinsic decay time of the Ce<sup>3+</sup> centre in BaF<sub>2</sub> [1].

For scintillator materials applied in environments with high count rates or in time-of-flight detectors this lengthened decay time may be a serious drawback. Therefore, we are interested in luminescence processes where intermediate states do not seriously lengthen the Ce<sup>3+</sup> decay time. The simplest such process is the  $e + h \rightarrow \text{Ce}^{3+}$  energy transfer process. It involves capture of a free electron (or hole) into the Ce<sup>3+</sup> centre, forming a Ce<sup>2+</sup> (Ce<sup>4+</sup>) centre, followed by capture of a free hole (electron), which results in an excited Ce<sup>3+</sup> centre which subsequently decays radiatively. This process is not likely to occur if, for instance, the energy of the Ce<sup>3+</sup> centre together with that of the free electron (hole) is lower than the

energy of the  $Ce^{2+}$  ( $Ce^{4+}$ ) centre. For this reason, we performed the present study, in which we calculate the energy levels with lattice relaxation of several cerium centres in alkaline earth halides. The results give us some understanding of why the  $e + h \rightarrow Ce^{3+}$  process is so weak in  $BaF_2$ . Similar calculations are planned for the future in order to find materials in which this process is predominant, resulting in a fast decay of the  $Ce^{3+}$  luminescence and a high light yield.

## 2. Theoretical approach

For the calculation of cerium centre energies we used three computer programs. The first of these is MOLFDIR. The MOLFDIR (molecular Fock–Dirac) package was developed recently by Nieuwpoort's group at of the Chemistry Department of the University of Groningen [4]. The program calculates the energy levels of molecules by the Hartree–Fock method in the LCAO approach using Gaussian-type electronic orbitals. The new aspect of the approach is the use of completely *relativistic 4-component* wavefunctions. This is necessary for obtaining a reliable description of the 4f shell and fairly correct energy levels. The basis set for  $Ce^{n+}$  consisting of so called large component and small component parts was obtained as follows.

The uncontracted 18s/15p/12d/8f large-component part was taken from the work of van Piggelen [5], who has calculated non-relativistic basis sets for all triply ionized rare-earth ions. This set was extended with two d-type orbitals obtained by a fit to numerical results of the isolated  $Ce^{n+}$  ion. The small-component 15s/18p/15d/12f/8g basis was constructed from the large-component basis, using the extended kinetic-balance principle [6]. Similarly, we constructed the fluorine basis set from the contracted 43/31 basis for  $F^-$  given in [7]. All nuclei were approximated by point charges. The Breit interaction was neglected, because this interaction is only important for the inner shells. The calculations were done on a Cray Y-MP 4/64 supercomputer at SARA, Amsterdam.

The second package was GAUSSIAN 90™ [8]. This is a non-relativistic molecular program. It was used in those cases where relativistic effects play a minor role. The basis sets were taken from [7]: 43222/42211/422/1111 basis for cerium and 43/31 basis for fluorine.

The third package was HADES II. The HADES II (Harwell automatic defect examination system) program was developed at Harwell Laboratory, Oxfordshire, England. It calculates the minimum energy configuration of a defect in an infinite lattice. Interactions between the lattice constituents have to be supplied to the program in the form of parameters describing their polarizability and mutual repulsion. The polarizability is accounted for by representing the ions as point charges (cores), surrounded by charged spheres (shells) attached to the cores by harmonic springs. The repulsion is included as a potential acting between shells of different ions. More about the program can be found elsewhere, where both detailed [9] and brief [10] descriptions are given.

The MOLFDIR code is well suited for calculating detailed energy level structures. However, for a large number of atoms, calculations become lengthy and expensive. Therefore, MOLFDIR was used to calculate the energy levels of a relatively small cluster of ions containing cerium. The HADES II program, on the other hand, is well suited for calculating the relaxation of an infinite lattice, but is incapable of calculating energy level structures. Therefore, in order to obtain the energy levels for the infinite system, MOLFDIR and HADES II calculations were combined. The principle of the method of calculation is described below.

Using MOLFDIR we simulated the cerium centre by a  $CeF_8$  cluster, placed into a point-charge fluorite-type lattice. In this lattice, the cation-nearest fluorine distance  $r_{Ce-F_n}$  is

2.68 Å exactly. We will call this lattice the PC lattice. The CeF<sub>8</sub> cluster embedded in this lattice is shown in figure 1. In the MOLFDIR calculations, the PC lattice, which is virtually infinite, was represented by spherical shells around the CeF<sub>8</sub> cluster, containing 406 point charges. The value of the point charges in the two outer shells were adjusted such that the correct Madelung potential is obtained at the cerium and fluorine sites in the cluster: 17.602 eV and 9.470 eV respectively.

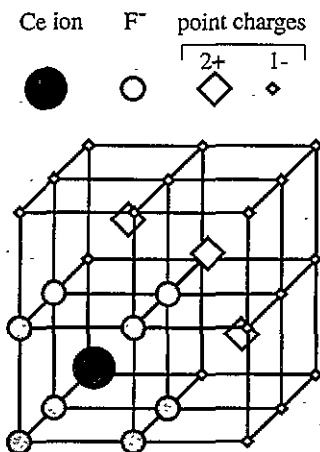


Figure 1. The CeF<sub>8</sub> cluster embedded in a unit cell of the PC lattice, as used in the MOLFDIR calculations. The nearest-neighbour cation-anion or point-charge distance is 2.68 Å exactly.

In the real alkaline-earth fluoride lattice, the distance  $r_{\text{Ce-F}_n}$  will generally differ from 2.68 Å. Therefore we also did MOLFDIR calculations for the configurations of figure 1, but with the eight nearest-neighbour fluorine ions radially displaced by a certain amount in order to get a curve of the total energy of the system as a function of  $r_{\text{Ce-F}_n}$ .

Each of the MOLFDIR-calculated energy against  $r_{\text{Ce-F}_n}$  curves were reproduced in a HADES II calculation. As in the MOLFDIR calculation, we simulated eight fluorine ions around a cerium ion, surrounded by the fixed point charges of the PC lattice, which have only Coulomb interaction with the ions. The HADES II input parameters for the cerium-fluorine repulsion were chosen such that, apart from a difference in zero-point energy, the HADES II energy curves were the same as the MOLFDIR results.

Using the repulsion parameters obtained in the HADES II program, the cerium centre was then simulated in a relaxing real alkaline-earth lattice instead of the fixed PC lattice. From this, the lattice relaxations and the energies associated with it were obtained.

For accurate results it is necessary that the MOLFDIR predictions are sufficiently close to reality. A check for this was provided by comparing MOLFDIR calculations of the free cerium ions to the energy levels known from experiment [11]. It turned out that MOLFDIR results for energy levels have to be corrected. Details are given in the next section.

### 3. Results

The calculations can be divided into three classes. First, energy levels of a small set of ions (Ce or CeF<sub>8</sub>) simulating the cerium centre are calculated using the MOLFDIR package. This was done for the Ce<sup>n+</sup> states, where  $n = 2, 3$  or 4 (section 3.1).

Second, for the interesting states the total energies were calculated for several values of the cerium-fluorine distance  $r_{\text{Ce-F}_n}$ . For reasons of economy, this was done with MOLFDIR

for a small number of distances. This was extended by additional calculations using the GAUSSIAN program. From the results obtained, for each of the states the cerium–fluorine repulsion input parameters for the HADES II code were determined (section 3.2).

Third, the HADES II program was used to obtain the energy levels of the cerium centres including lattice relaxation in the lattice of  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ . Also, the influence of a charge compensating interstitial fluorine ion was considered (section 3.3).

### 3.1. Energy levels of the $\text{Ce}(\text{F}_8)$ cluster calculated using MOLFDIR

Initially, the energy levels of the free  $\text{Ce}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ions were calculated. For each electronic configuration of an ion, the energy levels can be described by the mean energy of the configuration (weighted by the degeneracy of each level belonging to the configuration), and the position of the level relative to this average value. The average energy of, say, the  $4f5d$  configuration of  $\text{Ce}^{2+}$  was calculated by running the self-consistent field (SCF) part of the MOLFDIR package for 1/12 electron in each of the fourteen  $4f$  states and ten  $5d$  states. In the SCF run, the  $4f$  and  $5d$  wavefunctions were optimized for minimal average energy of the mixed  $4f^2$ ,  $4f5d$ ,  $5d^2$  configuration. Using these wavefunctions, a configuration-interaction (CI) calculation was performed, which yielded the splitting of the  $4f^2$ ,  $4f5d$  and  $5d^2$  configurations into terms. This calculation will be referred to as the  $4f$ ,  $5d$  run. We also did a similar calculation but with only 1/7 electron in each of the 14  $4f$  orbitals: the  $4f^2$  run. Of course, here only  $4f^2$  terms were calculated and the  $4f$  orbitals will be somewhat different from those obtained in the  $4f$ ,  $5d$  run.

For the  $\text{Ce}^{3+}$  ion, no CI calculation was necessary and the term energies relative to the average term energy are simply the  $4f$  and  $5d$  orbital energies relative to the average orbital energy, calculated by SCF if 1/14 electron was put into each of the fourteen  $4f$  orbitals ( $4f$  run) or 1/10 electron in each of the ten  $5d$  orbitals ( $5d$  run). An estimate of the accuracy of the above average-occupation calculations was obtained by also running  $\text{Ce}^{3+}$  for the  $5deF_g$  and  $5dt_2 (F_g + E_{2g})$  crystal field-split states separately. The resulting energies were  $0.10 \pm 0.02$  eV lower, which is due to the better optimization of the wavefunctions for each separate state. Finally, for the  $\text{Ce}^{4+}$  ion we only calculated the  $^1S_0$  ground-state energy.

**Table 1.** MOLFDIR-calculated average energies of the free cerium ion ( $\langle E_f^M \rangle$ ), cerium embedded in the PC lattice ( $\langle E_{\text{Ce,PC}}^M \rangle$ ) and the  $\text{CeF}_8$  cluster embedded in the PC lattice ( $\langle E_{\text{CeF}_8}^M \rangle$ ). Energies are given in atomic units (1 au = 27.211 396 eV = 219 474.63 cm<sup>-1</sup>). The valence electrons were forced to occupy each open shell orbital with equal probability.

Ion	Config.	Run	$\langle E_f^M \rangle$	$\langle E_{\text{Ce,PC}}^M \rangle$	$\langle E_{\text{CeF}_8}^M \rangle$
$\text{Ce}^{2+}$	$4f^2$	$4f^2$	-8860.60918	-8946.25900	-9741.25833
	$4f^2$	$4f, 5d$	-8860.57515	-8946.22480	-9741.22481
	$4f5d$	$4f, 5d$	-8860.65508	-8946.30660	-9741.29545
	$5d^2$	$4f, 5d$	-8860.44273	-8946.09484	-9741.08248
$\text{Ce}^{3+}$	$4f^1$	$4f^1$	-8859.99372	-8946.29039	-9741.31396
	$5d^1$	$5d^1$	-8859.79617	-8946.09363	-9741.11697
$\text{Ce}^{4+}$	$4f^0$	$4f^0$	-8858.71237		-9740.78169

Having calculated the free-ion energy levels, we subsequently placed the cerium ion into the PC lattice. After calculation of the energy levels in this case, where the only effect on the cerium energy levels is due to Coulomb interaction with the surrounding lattice, we replaced the eight nearest-neighbour point charges representing  $\text{F}^-$  ions by real  $\text{F}^-$  ions.

This is the situation shown in figure 1. The results obtained from calculations for these three cases, i.e. free cerium ion, cerium ion embedded in the PC lattice and  $CeF_8$  cluster embedded in the PC lattice, are shown in table 1 (average energies of the configurations) and figures 2 and 3 (term energies relative to the average).

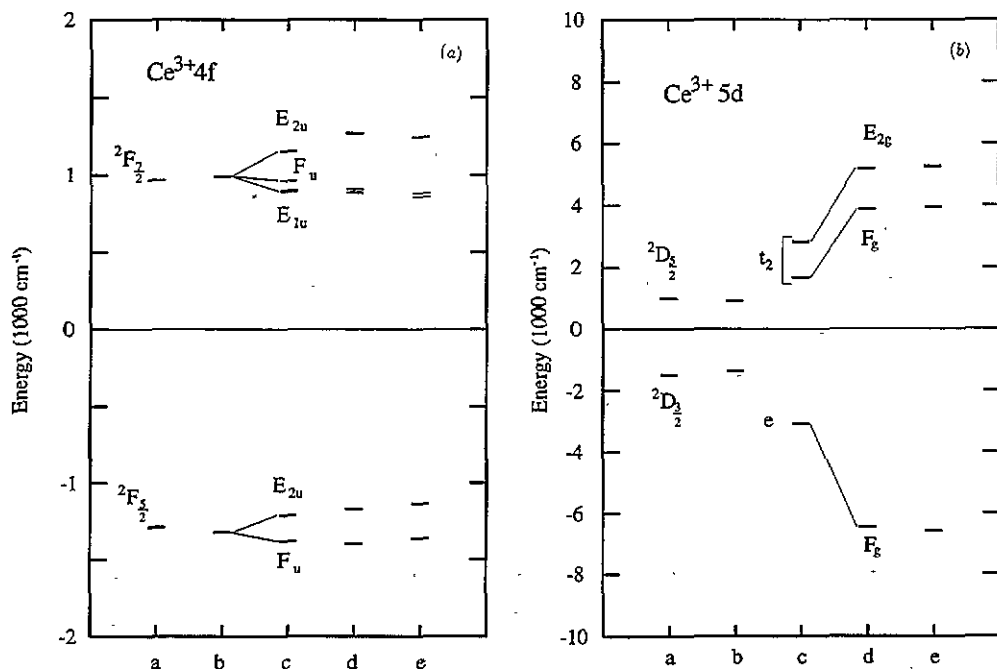
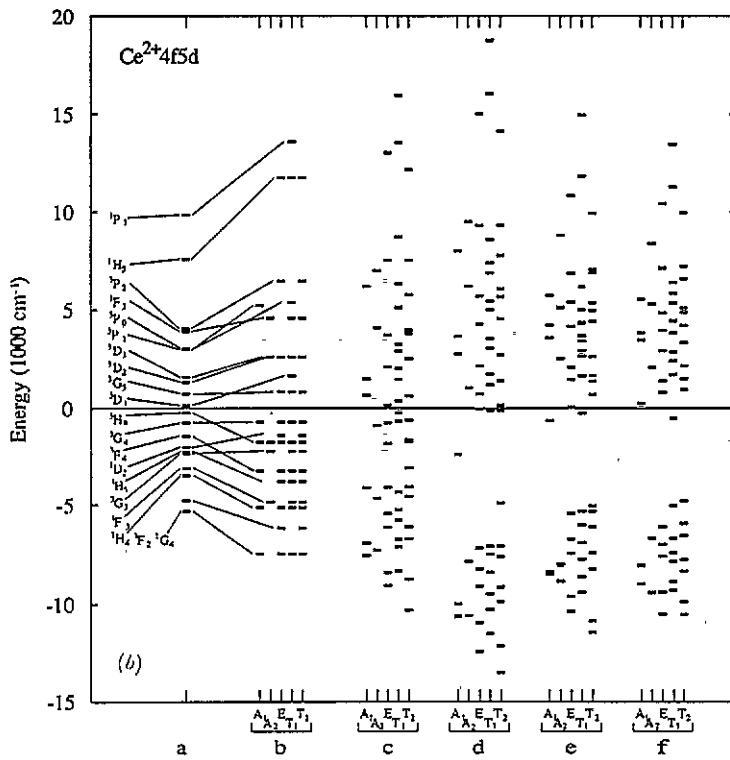
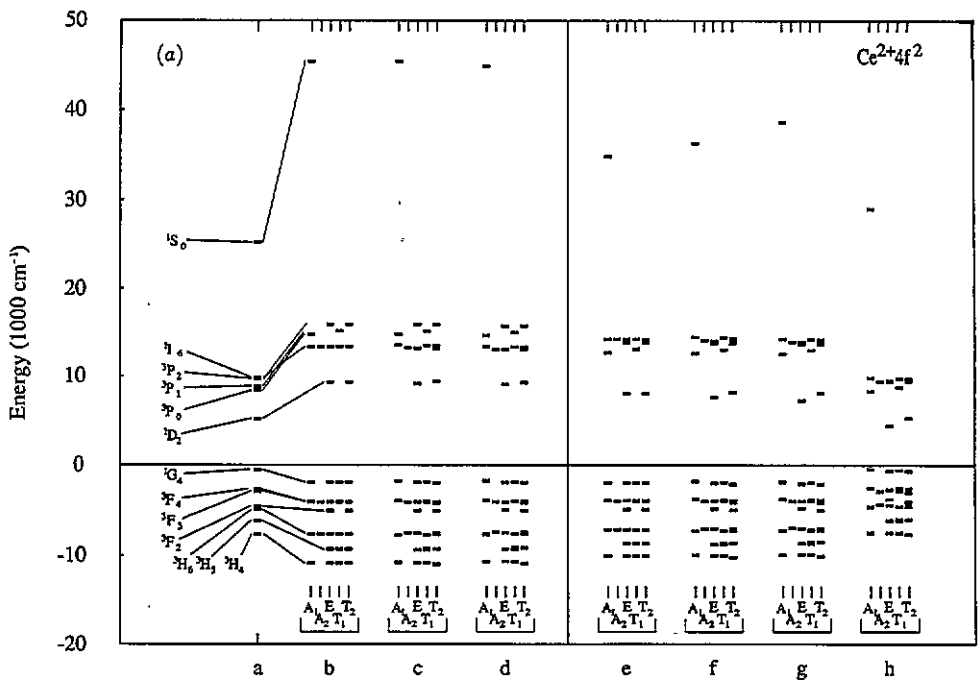
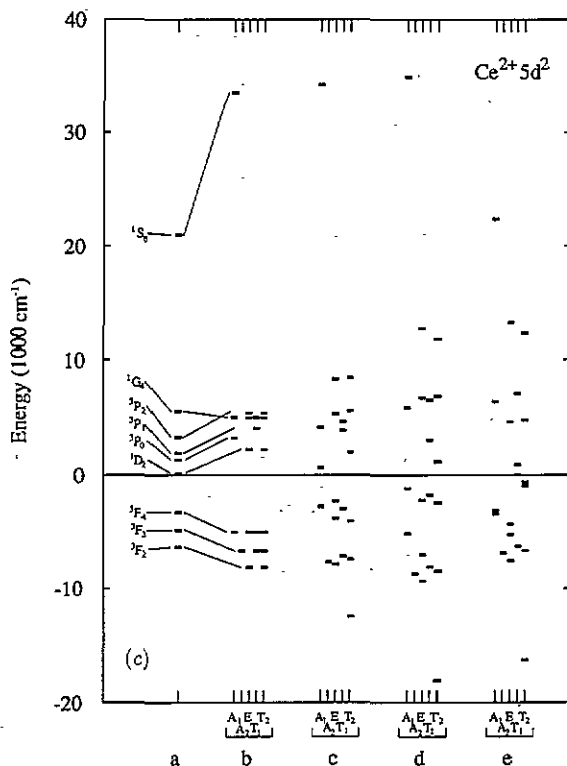


Figure 2. (a)  $Ce^{3+}$  4f energy levels. The weighted average is at zero. Shown are experimental free-ion levels [11] (a), MOLFDIR-calculated energy levels of the free ion (b), the  $Ce^{3+}$  ion embedded in the PC lattice (c) and the  $CeF_8$  cluster embedded in the PC lattice (d). Also shown are the levels of d corrected for the difference between a and b (e). (b). As (a), but for the  $Ce^{3+}$  5d levels.

It is interesting to calculate from table 1 the change in energy difference between the electronic configurations, on going from the free ion via a point-charge environment to the  $CeF_8$  cluster situation. If there is no electronic or lattice relaxation, for cerium incorporated in the lattice the energy difference  $\Delta E$  between a  $Ce^{2+}$  state and a  $Ce^{3+}$  state differs from the corresponding value in the free ion by the Madelung energy at the cerium site, which is 17.602 eV. The same holds for the energy difference  $\Delta E$  between  $Ce^{3+}$  and  $Ce^{4+}$  states. Table 2 shows that this is practically the case for the point-charge environment, but certainly not for the  $CeF_8$  configuration. Here, the energy difference  $\Delta E$  between a  $Ce^{n+}$  state and a  $Ce^{(n+1)+}$  state is enhanced. This is due to electron relaxations involving the fluorine electrons, which is strongest for the higher charged cerium ions. Table 2 shows that the effect is of the order of electron volts.

The average energies in table 1 of each free-ion electronic configuration can be compared with experiment by making use of the data compiled in [11]. This comparison is made in table 3. The difference between the calculated and experimental average energies is of the order of a few eV. We mention two reasons for this deviation. First, the orbitals used are





**Figure 3.** (a)  $Ce^{2+} 4f^2$  energies. The weighted average is at zero. Shown are experimental free-ion levels (a) and MOLFDIR-calculated levels of the free ion (b),  $Ce^{2+}$  ion in the PC lattice (c) and  $CeF_8$  in the PC lattice (d). The levels b, c and d are calculated in the  $4f^2$  run. The levels e, f and g are the respective results from the  $4f, 5d$  run. The levels h are the g levels, corrected for differences between a and e. Along the abscissa the energy levels b–h are separated according to their Mulliken symmetry species ( $A_1, A_2, E, T_1$  and  $T_2$ ). (b)  $Ce^{2+} 4f5d$  energy levels. The weighted average is at zero. Shown are experimental free-ion levels (a) and MOLFDIR-calculated levels of the free ion (b), the  $Ce^{2+}$  ion in the PC lattice (c) and (d) the  $CeF_8$  cluster in the PC lattice. The levels b, c and d are obtained from the  $4f, 5d$  run. Levels e are as d but corrected for differences between a and b. Energy levels f are calculated by Alig and co-workers for  $Ce^{2+}$  in a cubic field corresponding to  $Dq = 1120 \text{ cm}^{-1}$  [12]. (c)  $Ce^{2+} 5d^2$  energy levels. The weighted average is at zero. Shown are experimental free-ion levels (a) and MOLFDIR-calculated levels for the free ion (b), the  $Ce^{2+}$  ion in the PC lattice (c) and the  $CeF_8$  cluster in the PC lattice (d). Levels b, c and d are obtained from the  $4f, 5d$  run. Levels e are as d but corrected for differences between a and b.

not really optimal. This is illustrated by the fact that the  $4f^2$  energy calculated in the  $4f^2$  run is lower than that calculated in the  $4f, 5d$  run. This is because the  $4f$  wavefunctions calculated in the  $4f^2$  run are better: they are optimized for minimum average  $4f^2$  energy, whereas in the  $4f, 5d$  run they are optimized for minimum energy of the average of all  $4f^2, 4f5d$  and  $5d^2$  terms. Second, CI interactions with states lying at higher energy than the  $4f$  and  $5d$  states are not included in the calculation. This correlation energy will be largest for those states where the electrons are nearest to one another. Hence, one expects that the  $Ce^{2+} 4f^2$  configuration will come out too high by a larger amount than the  $Ce^{2+} 4f5d$  configuration, which is indeed the case.

We may also compare the calculations of the free-ion term energies relative to the



**Table 2.** Relative configuration energy shifts  $\Delta\langle E_{\text{Ce,PC}}^M \rangle - \Delta\langle E_{\text{f}}^M \rangle$  and  $\Delta\langle E_{\text{CeF}_8}^M \rangle - \Delta\langle E_{\text{f}}^M \rangle$  (in eV).  $\Delta\langle E \rangle$  is the difference between the average energy of the cerium configuration and that of  $\text{Ce}^{3+} 4f$  in the same environment.  $\langle E_{\text{f}}^M \rangle$ ,  $\langle E_{\text{Ce,PC}}^M \rangle$  and  $\langle E_{\text{CeF}_8}^M \rangle$  are the MOLFDIR-calculated average energies of cerium as a free ion, embedded in the PC lattice and in the  $\text{CeF}_8$  cluster embedded in the PC lattice, respectively.

Ion	Config.	Run	$\Delta\langle E_{\text{Ce,PC}}^M \rangle - \Delta\langle E_{\text{f}}^M \rangle$	$\Delta\langle E_{\text{CeF}_8}^M \rangle - \Delta\langle E_{\text{f}}^M \rangle$
$\text{Ce}^{2+}$	$4f^2$	$4f^2$	17.602	18.261
	$4f^2$	4f, 5d	17.606	18.247
	4f5d	4f, 5d	17.555	18.500
	$5d^2$	4f, 5d	17.539	18.517
$\text{Ce}^{3+}$	$5d^1$	$5d^1$	-0.021	-0.015
$\text{Ce}^{4+}$	$4f^0$	$4f^0$		-20.383

**Table 3.** Free-ion average energies of each electronic configuration. Shown are calculated values ( $\langle E_{\text{f}}^M \rangle$ ) and values obtained from experimental data [11]. The energies are in eV and relative to the energy of the  $\text{Ce}^{4+}$  ion. Depending on the way the calculations were performed, the theoretical values varied within about 2 meV of the values shown.

Ion	Config.	Run	Calculated	Experimental
$\text{Ce}^{2+}$	$4f^2$	$4f^2$	-51.615	-56.009
	$4f^2$	4f, 5d	-50.689	-56.009
	4f5d	4f, 5d	-52.864	-55.889
	$5d^2$	4f, 5d	-47.086	-51.156
$\text{Ce}^{3+}$	$4f^1$	$4f^1$	-34.867	-36.598
	$5d^1$	$5d^1$	-29.492	-30.406
$\text{Ce}^{4+}$	$4f^0$	$4f^0$	0	0

average with experiment [11]. This is easily done by comparing the levels denoted a and b at the abscissa of figures 2 and 3. Theory and experiment coincide nicely for  $\text{Ce}^{3+}$  (within 10%: see figure 2), but somewhat less well for  $\text{Ce}^{2+}$  (within 30%: see figure 3).

The above comparison with experiment shows that to obtain the cerium energy levels accurately, a correction to the calculated values is necessary. We did this by adding the difference between each calculated free-ion level and its corresponding experimental equivalent, to all levels of  $\text{CeF}_8$  in the PC lattice corresponding to this level. For example, in figure 3(a) the first (lowest)  $A_1$  level from below in the  $4f^2$  configuration was associated with  ${}^3H_4$ , the second with  ${}^3H_6$ , the third with  ${}^3F_4$ , etc. By this correction procedure, all calculated energy levels of the free cerium ions were made to coincide with experiment. The term splittings of cerium in the PC lattice were not changed, which is only correct if no levels of the same symmetry are near the level to be corrected. For most levels of interest (especially the lower levels) this condition is satisfied.

The corrected energy levels are also shown in figures 2 and 3. The corrections of the  $\text{Ce}^{2+}$  levels were applied to the results of the 4f, 5d run. For the 4f5d configuration of  $\text{Ce}^{2+}$  we compared the corrected energy levels to crystal field calculations performed by Alig and co-workers [12]. The best fit to their calculations is found for  $Dq = 1120 \text{ cm}^{-1}$  in the cubic field. The corresponding energy levels are shown in figure 3(b). The difference between these levels (f) and our corrected calculated levels (e) is not larger than about  $1000 \text{ cm}^{-1}$ . We note that in the crystal field calculations of [12] empirical parameters were included such that the free  $\text{Ce}^{2+} 4f5d$  levels ( $Dq = 0$ ) coincide with the experimental ones within about  $200 \text{ cm}^{-1}$ . Then the crystal field strength (i.e.  $Dq$ ) was varied in order to

obtain coincidence with experimental observations. In our calculation, no fitting of the field strength is necessary, since this is directly calculated. In this connection it is interesting to note from the splittings that, especially for the Ce<sup>3+</sup> 5d and the Ce<sup>2+</sup> 4f5d and 5d<sup>2</sup> configurations, the effective crystal field introduced by point charges around the cerium ion is considerably less than that introduced by an environment with real nearest-neighbour fluorine ions.

We also compared the lower 4f<sup>2</sup> levels to results of Alig and co-workers [12]. For  $B_4 = -700 \text{ cm}^{-1}$  the splittings of the <sup>3</sup>H<sub>4</sub> and <sup>3</sup>H<sub>5</sub> terms agreed within 30 cm<sup>-1</sup>. For the <sup>3</sup>H<sub>6</sub> and <sup>3</sup>F<sub>2</sub> terms we found larger splittings than in [12]: agreement was within 70 cm<sup>-1</sup> for <sup>3</sup>H<sub>6</sub> and 130 cm<sup>-1</sup> for <sup>3</sup>F<sub>2</sub>.

### 3.2. HADES II input parameters

In the preceding section we were concerned with cerium ions surrounded by other ions and/or point charges at fixed positions, characterized by a cerium–nearest-fluorine distance  $r_{\text{Ce-F}_n} = 2.68 \text{ \AA}$  exactly. In general, cerium centres in alkaline-earth halides will not look like that. Therefore, we need to know what happens to the energy levels if  $r_{\text{Ce-F}_n}$  becomes different from 2.68 Å. This information can then be expressed in terms of HADES II input parameters, and so cerium centres can be simulated.

The HADES II parameters we wish to determine are the two repulsion parameters  $A$  and  $\rho$  which describe the repulsion interaction  $V(r) = A \exp(-r/\rho)$  between the cerium ion and a fluorine ion. For each of the cerium centre energy levels calculated in section 3.1, the dependence on  $r_{\text{Ce-F}_n}$  will be somewhat different, i.e.  $A$  and  $\rho$  differ for each level. In order to limit calculations, we have chosen to calculate  $A$  and  $\rho$  for only the most interesting energy levels. These are the lowest energy levels, which are (i) the Ce<sup>2+</sup> 4f<sup>2</sup> <sup>3</sup>H<sub>4</sub> T<sub>2</sub> level, (ii) the lowest Ce<sup>2+</sup> 4f5d T<sub>2</sub> level, (iii) the Ce<sup>3+</sup> 4f<sup>2</sup>F<sub>5/2</sub> F<sub>u</sub> level, (iv) the Ce<sup>3+</sup> 5d eF<sub>g</sub> level and (v) the Ce<sup>4+</sup> ground-state level.

For calculating the  $r_{\text{Ce-F}_n}$  dependence of the energy levels at many different  $r_{\text{Ce-F}_n}$  values, we used the GAUSSIAN package. Since the outside of the cerium ions is dominated by electrons occupying 5d, 6s, and 5p orbitals, which can be described reasonably in a non-relativistic way, the error made by this was considered to be small. We checked this with a limited number of MOLFDIR calculations of the average configuration energy. For  $r_{\text{Ce-F}_n} \in (2.55 \text{ \AA}, 2.81 \text{ \AA})$  we found agreement within 0.08 eV between the average Ce<sup>2+</sup> 4f<sup>2</sup> energy calculated using MOLFDIR and GAUSSIAN. Agreement was within 0.05 eV for the Ce<sup>2+</sup> 4f5d average energy. In the range  $r_{\text{Ce-F}_n} \in (2.41 \text{ \AA}, 2.68 \text{ \AA})$  we found agreement within 0.05 eV for the Ce<sup>3+</sup> 4f average energy. For Ce<sup>3+</sup> 5d we did more extensive MOLFDIR calculations; the results are shown in figure 4. The agreement between the MOLFDIR and GAUSSIAN calculated energies for the 5d eF<sub>g</sub> state is within 0.02 eV.

A remark should be made about the calculation of the  $r_{\text{Ce-F}_n}$  dependence of the lowest Ce<sup>2+</sup> 4f5d T<sub>2</sub> energy level. Avoiding lengthy calculations, we only calculated the average energy of the 4f5d levels. From this the  $r_{\text{Ce-F}_n}$  dependence of the energy of the lowest 4f5d T<sub>2</sub> level was obtained by adding the energy shift  $\Delta E_{\text{cf}}$  due to crystal field splitting. In cubic crystal fields,  $\Delta E_{\text{cf}}$  contains terms proportional to  $r_{\text{Ce-F}_n}^{-5}$  and to  $r_{\text{Ce-F}_n}^{-7}$  [12]. In our approximation, we assumed  $\Delta E_{\text{cf}} = C r_{\text{Ce-F}_n}^{-p}$ , with a  $p$  value equal to the one for the Ce<sup>3+</sup> 5d eF<sub>g</sub> state, which from figure 4 was found to be  $6.6 \pm 0.7$ . The constant  $C$  followed from the known crystal field splitting at  $r_{\text{Ce-F}_n} = 2.68 \text{ \AA}$  (cf a and e in figure 3(b)).

In the above way the  $r_{\text{Ce-F}_n}$  dependence of the lowest energy levels of each configuration were determined. From this we determined the  $A$  and  $\rho$  parameters for the cerium–fluorine interaction. This was done by performing HADES II calculations for the same system as

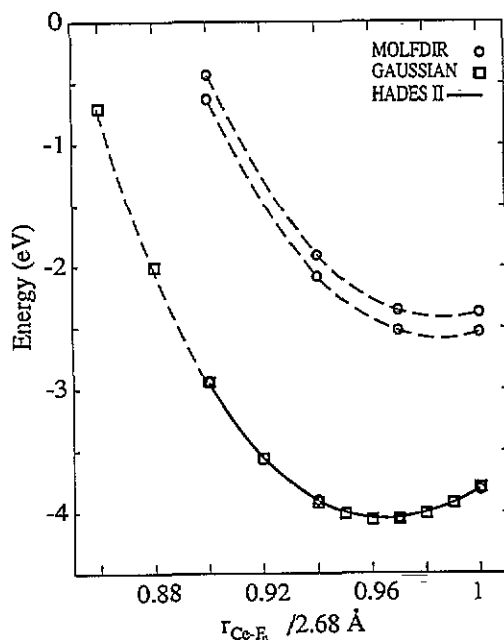


Figure 4.  $\text{Ce}^{3+}$  5d energy levels as a function of the distance  $r_{\text{Ce}-\text{F}_n}$ . Shown is the energy of the  $\text{CeF}_8$  cluster embedded in the PC lattice. The energy scale pertains to the MOLFDIR calculations. A constant was added to the 5d  $e\text{F}_g$  state GAUSSIAN results for coincidence with MOLFDIR values. This was also done for the HADES II curve, which was calculated using the cerium-fluorine parameters  $A = 16\,189\text{ eV}$  and  $\rho = 0.245\,8717\text{ \AA}$ . The nearest-neighbour fluorine ions were allowed to polarize. The broken curves merely serve as a guide to the eye.

was used for the MOLFDIR and GAUSSIAN calculations, i.e. a  $\text{CeF}_8$  cluster with varying distance  $r_{\text{Ce}-\text{F}_n}$ , embedded in the PC lattice. The fixation of the PC lattice point charges was realized by working with artificial repulsion and polarization parameters. The fluorine-fluorine interaction parameters and the fluorine polarization parameters were taken from Catlow and co-workers [13] and are reproduced in tables 4 and 5. The interaction of the  $\text{CeF}_8$  cluster with the point charges is purely Coulombic. The  $A$  and  $\rho$  parameters for the repulsion between cerium and fluorine were then adjusted such that the  $r_{\text{Ce}-\text{F}_n}$  dependence of the energy of the centre calculated by HADES II fitted the calculations using MOLFDIR and GAUSSIAN. The fits were accurate within 0.05 eV or less in the  $r_{\text{Ce}-\text{F}_n}$  ranges mentioned above. An example of such a HADES II fit is shown in figure 4.

Table 4. HADES II repulsion parameters for the interaction between two fluorine ions. The parameters are obtained from [13]. The fluorine-fluorine interaction is of spline form, defined as  $A \exp(-r/\rho)$  for  $r \in (0, r_b)$ , a fifth-order polynomial for  $r \in (r_b, r_m)$ , a third-order polynomial for  $r \in (r_m, r_a)$  and  $-C/r^6$  for  $r \in (r_a, \infty)$ . The polynomials are such that the fluorine-fluorine interaction is continuous in function and the first two derivatives for all fluorine-fluorine distances  $r$  and the minimum is at  $r_m$ . Parameters are the same for  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$ .

$A$ (eV)	1127.7
$\rho$ (Å)	0.2753
$C$ (eV Å <sup>6</sup> )	15.83
$r_a$ (Å)	3.031
$r_m$ (Å)	2.726
$r_b$ (Å)	2.0

The  $A$  and  $\rho$  parameters obtained from the fits are given in table 6. The values of the parameters depend on the host lattice assumed, because for each host lattice the fluorine polarization parameters differ, as table 5 shows. In the procedure used for obtaining the  $A$

**Table 5.** Shell-model polarization parameters for the host constituents [13]. The corresponding parameters for the cerium ion were taken to be the same as for Ba<sup>2+</sup>.

	CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>
Cation shell charge ( $ e $ )	5.24	7.53	-16.99
Cation spring constant (eV Å <sup>-2</sup> )	390.9	530.3	1709.1
Fluorine shell charge ( $ e $ )	-2.38	-3.70	-1.59
Fluorine spring constant (eV Å <sup>-2</sup> )	101.2	252.4	43.5

and  $\rho$  parameters we assumed that the amount of fluorine polarization allowed by MOLFDIR and HADES II were the same. The basis set used in the MOLFDIR calculations is large, meaning that little polarization will be missing because of limitations of the basis set. Nevertheless, the basis set is not infinite and some error remains. To obtain an estimate of this error, we also considered the worst case by assuming that MOLFDIR does not allow fluorine polarization at all. We will denote calculations under this assumption by 'no pol.'. The 'no pol.' HADES II parameters are obtained by fitting the MOLFDIR energy against  $r_{\text{Ce-F}_n}$  curves with the extra condition of no fluorine polarization. These parameters are also shown in table 6.

**Table 6.** Cerium-fluorine repulsion interactions  $V(r) = A \exp(-r/\rho)$ . Parameters are given for the lowest-energy states of cerium in each electronic configuration. The  $\rho$  values are the same for each crystal lattice, unless indicated otherwise. The parameters yield HADES II curves, coinciding with the MOLFDIR/GAUSSIAN calculations on the CeF<sub>8</sub> cluster embedded in the pc lattice. For Ce<sup>2+</sup>-F<sup>-</sup> distances between 2.6–2.8 Å and Ce<sup>3+</sup>-F<sup>-</sup> or Ce<sup>4+</sup>-F<sup>-</sup> distances between 2.4–2.7 Å coincidence is within 0.05 eV. Shown are the HADES II parameters to be used in combination with the fluorine polarization parameters of CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>, and also if no fluorine polarization is allowed ('no pol.').

Ce configuration	$\rho$ (Å)	A (eV)			
		CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>	No pol.
Ce <sup>2+</sup> 4f <sup>2</sup>	0.270 6526	8511	8010	9190	7717.297
Ce <sup>2+</sup> 4f5d	0.249 9535	14470	14070	15615	13477.533
Ce <sup>3+</sup> 4f	0.265 8732	8140	8140	8444	3809.444 <sup>(a)</sup>
Ce <sup>3+</sup> 5d	0.245 8717	11245 <sup>(b)</sup>	4519 <sup>(c)</sup>	16189	3625.830 <sup>(d)</sup>
Ce <sup>4+</sup>	0.296 1001	3570	3794	3356	4183.097

(a)  $\rho = 0.295\ 2519$  Å.

(b)  $\rho = 0.254\ 9954$  Å.

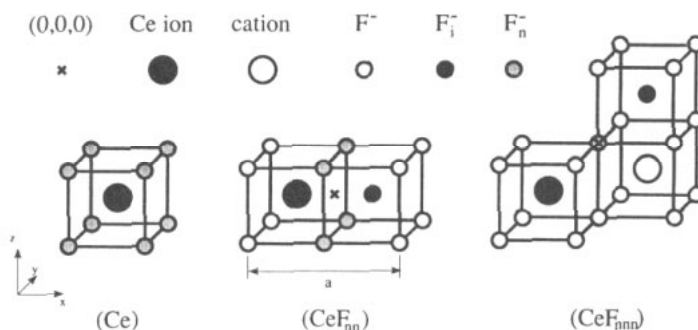
(c)  $\rho = 0.284\ 5617$  Å.

(d)  $\rho = 0.296\ 3948$  Å.

### 3.3. Cerium-centre simulations using HADES II

To calculate the energy levels of the cerium centres with lattice relaxation we used the HADES II parameters shown in tables 4–8. Apart from the cerium-fluorine repulsion parameters found in section 3.2, the parameters from [13, 14] were used. For the lattice constants we used the room temperature values obtained from [15, 16]. We considered three cerium centres: cerium charge-uncompensated (Ce) or accompanied by a charge-compensating interstitial fluorine ion at the (111) next-nearest-neighbour position (CeF<sub>nnn</sub>) or the (100) nearest-neighbour position (CeF<sub>nn</sub>). These cerium centres are shown in figure 5. Only the five lowest cerium states are considered: (i) Ce<sup>2+</sup>4f<sup>2</sup> <sup>3</sup>H<sub>4</sub> T<sub>2</sub>, (ii) Ce<sup>2+</sup>4f5d T<sub>2</sub> (the

lowest), (iii)  $Ce^{3+}4f^2F_{5/2}F_u$ , (iv)  $Ce^{3+}5d eF_g$  and (v)  $Ce^{4+}^1S_0$  (ground state). In the following we will sometimes denote these states simply by (i)  $Ce^{2+}4f^2$ , (ii)  $Ce^{2+}4f5d$ , (iii)  $Ce^{3+}4f$ , (iv)  $Ce^{3+}5d$  and (v)  $Ce^{4+}$ .



**Figure 5.** The three cerium centres considered: Ce,  $CeF_{nn}$  and  $CeF_{nnn}$ . The origin is denoted by a cross; in the Ce centre it is at the cerium ion. Due to lattice relaxations, the ion positions will differ from those shown here.

**Table 7.** HADES II repulsion parameters for the repulsive interactions  $A \exp(-r/\rho)$  between host cations and fluorine ions [13] or cerium ions. Interaction parameters of the host cations with cerium ions were assumed to be the same as those for interaction with  $La^{3+}$  [14].

	CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>
Cation-fluorine:			
A (eV)	1272.8	2298.5	5193.3
$\rho$ (Å)	0.2997	0.2917	0.2795
Cation-cerium:			
A (eV)	25549.6	14687.2	16050.9
$\rho$ (Å)	0.2152	0.2431	0.2575

**Table 8.** Room-temperature fluorine-fluorine nearest-neighbour distances (half the lattice constant  $a$ ) used in the HADES II calculations and the zero- and high-frequency relative dielectric permittivities calculated for the three host lattices.

	CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>
$a/2$ (Å)	2.731475	2.898	3.098
$\epsilon_{r,\infty}$	1.9995	2.0367	2.1845
$\epsilon_{r,0}$	6.7558	6.1480	6.7383

We now start to focus our attention on the centre with no charge compensation (Ce). To a first approximation, the energy of this centre is equal to the energy  $E_{CeF_8}^M$  of the  $CeF_8$  cluster surrounded by point charges, calculated using MOLFDIR. Two corrections to this value have to be made. First, as we have seen in section 3.1, a correction is necessary because the MOLFDIR value for the free cerium ion does not sufficiently coincide with the experimental

value. We will assume that this correction is independent of the surroundings of the cerium ion. Then in any surroundings the corrected energy  $E_{\text{CeF}_8}^{\text{M,E}}$  is found from

$$E_{\text{CeF}_8}^{\text{M,E}} = E_{\text{CeF}_8}^{\text{M}} - E_{\text{f}}^{\text{M}} + E_{\text{f}}^{\text{E}}. \quad (1)$$

Here  $E_{\text{f}}^{\text{M}}$  is the MOLFDIR-calculated free-ion energy and  $E_{\text{f}}^{\text{E}}$  is the experimentally observed one. The corrected energies  $E_{\text{CeF}_8}^{\text{M,E}}$  are listed in table 9.

**Table 9.** Correction of the MOLFDIR-calculated energy  $E_{\text{CeF}_8}^{\text{M}}$  of the CeF<sub>8</sub> cluster in the PC lattice for differences between calculated ( $E_{\text{f}}^{\text{M}}$ ) and experimental ( $E_{\text{f}}^{\text{E}}$ ) [11] free-ion energies. All energies pertain to the lowest state of each electronic cerium configuration indicated.

Ce configuration	$E_{\text{CeF}_8}^{\text{M}}$ (au)	$E_{\text{f}}^{\text{M}}$ (au)	$E_{\text{f}}^{\text{E}}$ (eV)	$E_{\text{CeF}_8}^{\text{M,E}} - 883 \text{ au}$ (eV)
Ce <sup>2+</sup> 4f <sup>2</sup>	-9741.30786	-8860.65871	0	9.546 985
Ce <sup>2+</sup> 4f5d	-9741.35709	-8860.68909	0.40625	9.440 323
Ce <sup>3+</sup> 4f	-9741.32032	-8859.99974	20.1974	11.473 90
Ce <sup>3+</sup> 5d	-9741.14639	-8859.80242	26.3640	17.003 99
Ce <sup>4+</sup>	-9740.78169	-8858.71237	56.9550	27.857 33

A second correction is required because of the replacement of the PC lattice surrounding the CeF<sub>8</sub> cluster by a relaxed alkaline-earth lattice. For this, the HADES II program was used. We calculated the following two defect formation energies.

(i)  $E_{\text{CeF}_8}^{\text{H}}$ . This is the formation energy of the CeF<sub>8</sub> cluster in the perfect PC lattice. More precisely, it is the energy needed for removing one 2+ point charge and its eight surrounding 1- point charges from the PC lattice, putting the Ce<sup>2+</sup> and eight F<sup>-</sup> ions in their place, and subsequently allowing the eight fluorine ions to polarize according to the F<sup>-</sup> parameters of the host material under consideration (CaF<sub>2</sub>, SrF<sub>2</sub> or BaF<sub>2</sub>, see table 5). In the 'no pol.' calculation fluorine polarization was not allowed. In neither calculation displacement was of any of the cores (nuclei) from the perfect PC lattice sites allowed. The results are shown in table 10. They depend on the fluorine parameters used (table 5), on whether or not the 'no pol.' assumption was used, and on the cerium parameters used (table 6).

**Table 10.** The formation energy  $E_{\text{CeF}_8}^{\text{H}}$  of the CeF<sub>8</sub> cluster in the PC lattice, calculated by HADES II. For cerium, the parameters given in table 6 were used. Polarization of the eight fluorine ions in the cluster was allowed in combination with the cerium fluorine repulsion parameters for CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub>. This polarization was not allowed in the 'no pol.' calculation. Energies are in eV.

Ce configuration	CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>	'No pol.'
Ce <sup>2+</sup> 4f <sup>2</sup>	3.090	2.936	3.249	2.846
Ce <sup>2+</sup> 4f5d	2.260	2.218	2.387	2.132
Ce <sup>3+</sup> 4f	-15.543	-15.646	-15.294	-14.367
Ce <sup>3+</sup> 5d	-15.840	-15.437	-15.769	-14.417
Ce <sup>4+</sup>	-34.418	-34.388	-34.354	-31.527

(ii)  $E_{\text{centre}}^{\text{H}}$ . This is the formation energy of a cerium centre in an alkaline-earth halide lattice. More precisely, it is the energy needed for removing one cation (Ca<sup>2+</sup>, Sr<sup>2+</sup> or Ba<sup>2+</sup>)

from the lattice, putting a cerium ion in its place, and subsequently allowing relaxation and polarization of all ions.

The total energy  $E_{\text{centre}}$  of the cerium centre can then be written as

$$E_{\text{centre}} = E_{\text{CeF}_8}^{\text{M.E}} - E_{\text{CeF}_8}^{\text{H}} + E_{\text{centre}}^{\text{H}}. \quad (2)$$

This expression was used for cerium in each of the five states considered in tables 9 and 10.

Subsequently we considered the two charge-compensated centres  $\text{CeF}_{\text{nnn}}$  and  $\text{CeF}_{\text{nn}}$  and calculated  $E_{\text{centre}}^{\text{H}}$  and from this  $E_{\text{centre}}$ , in the two cases  $\text{CaF}_2$  and  $\text{BaF}_2$ . For all cerium centres, the resulting energies are given in table 11. Table 11 shows the energies of the cerium centre, where cerium is in the lowest state of each electronic configuration and in several lattice configurations. The lattice configurations are defined by the positions of all cores (nuclei) in the case that the lattice is in equilibrium with the cerium ion in one of the five states. We denote the lattice configurations by the symbol for the corresponding cerium state. For example, the  $\text{Ce}^{3+}$  5d lattice configuration in combination with the  $\text{Ce}^{3+}$  5d electronic configuration is the minimum energy configuration, given the electronic state  $\text{Ce}^{3+}$  5d. But the  $\text{Ce}^{3+}$  5d lattice configuration in combination with the electronic  $\text{Ce}^{3+}$  4f configuration is a situation in which all lattice cores are fixed according to the  $\text{Ce}^{3+}$  5d electronic state, but the shells are relaxed in order to obtain minimum energy under this fixation.

Both situations in this example are of interest. Of course, one wishes to know the minimum energy lattice configuration given the  $\text{Ce}^{3+}$  5d electronic state; but the  $\text{Ce}^{3+}$  5d state can decay radiatively to the  $\text{Ce}^{3+}$  4f electronic state. This process is fast and the nuclei (cores) are not considered to be displaced during this process, whereas the electrons (shells) are. Thus, the situation immediately after the decay is described by the  $\text{Ce}^{3+}$  5d lattice configuration in combination with the  $\text{Ce}^{3+}$  4f electronic state.

In table 11, for the charge-uncompensated cerium centre in  $\text{CaF}_2$  and  $\text{BaF}_2$ , the 'no pol.' results are also shown. Comparing these to the corresponding results in table 11, for which it was assumed that MOLFDIR includes all of the fluorine polarization, shows that typically the results do not differ by more than 0.6 eV. An exception to this is the  $\text{Ce}^{4+}$  state, for which results differ by up to 1.1 eV. The 'no pol.' calculation is the worst case, since most probably the larger part of fluorine polarization is accounted for by the MOLFDIR calculations. This suggests that, due to incorrect incorporation of fluorine polarization, an error of several tenths of an electron volt may be introduced in the energy data in table 11.

This is supported by considering the ground-state energy differences between the (charge uncompensated)  $\text{Ce}^{3+}$  centre and the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  and  $\text{Ce}^{3+}\text{F}_{\text{nn}}$  centres. For this, the energy  $E_{\text{F}_i}^{\text{H}}$  of the isolated  $\text{F}_i^-$  centre was calculated using HADES II. From this and table 11 the ground-state energy  $E_{\text{Ce}^{3+}} + E_{\text{F}_i^-}$  of the infinitely separated  $\text{Ce}^{3+}$  and  $\text{F}_i^-$  centres is calculated. Comparing this energy to the  $E_{\text{Ce}^{3+}\text{F}_{\text{nnn}}}$  and  $E_{\text{Ce}^{3+}\text{F}_{\text{nn}}}$  ground-state energies in table 11 yields the energy needed for the reaction  $\text{Ce}^{3+} + \text{F}_i^- \rightarrow (\text{Ce}^{3+}\text{F}_{\text{nnn}} \text{ or } \text{Ce}^{3+}\text{F}_{\text{nn}})$ . The results are shown in table 12. We may compare these reaction energies to the energies needed for the  $\text{La}^{3+} + \text{F}_i^- \rightarrow (\text{La}^{3+}\text{F}_{\text{nnn}} \text{ or } \text{La}^{3+}\text{F}_{\text{nn}})$  reactions, as given by Corish and co-workers [14]. Corish and co-workers do not report cerium results, but table I in [14] suggests that  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  are very much alike. This comparison is also made in table 12. The difference between values found in [14] and by us is not more than 0.26 eV. In table 12, experimental data are shown, too. These show fair agreement with calculations.

Apart from the energy levels, we also obtained the positions of the ions. We only present the positions of the cerium ion, the interstitial fluorine ion  $\text{F}_i^-$ , and the lattice fluorine ions in

Table 11. Energies  $E_{\text{centre}}$  of three cerium centres in the alkaline-earth halides (centre = Ce,  $CeF_{\text{nm}}$  or  $CeF_{\text{nm}}$ ). For each electronic configuration  $E_{\text{centre}}$  is the energy in eV of the lowest state. The energies  $\Delta E_{\text{centre}}$  are relative to  $E_{\text{centre}}$  for the  $Ce^{3+}$  4f ground state. At the bottom row the absolute energies for this state are given. The 'no pol.' results were obtained assuming that MOLFRD does not include fluorine polarization; for the other data it was assumed that in the MOLFRD calculations all fluorine polarization was included.

Cerium configuration	Lattice configuration	$\Delta E_{\text{centre}}$			CaF <sub>2</sub>			SrF <sub>2</sub>			BaF <sub>2</sub>			No pol.		
		Ce	$CeF_{\text{nm}}$	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce	Ce
$Ce^{2+} 4f^2$	$Ce^{2+} 4f^2$	1.393	2.061	2.179	1.264	1.398	1.904	1.964	1.204	1.384						
$Ce^{2+} 4f^2$	$Ce^{3+} 4f$	3.466	4.029	4.212	3.363	3.598	4.064	4.193	2.865	3.036						
$Ce^{2+} 4f5d$	$Ce^{2+} 4f5d$	0.990	1.578	1.746	1.055	1.329	1.796	1.916	0.840	1.293						
$Ce^{2+} 4f5d$	$Ce^{3+} 4f$	2.622	3.133	3.362	2.756	3.027	3.466	3.660	2.226	2.640						
$Ce^{3+} 4f$	$Ce^{2+} 4f^2$	2.137	2.085	2.105	2.207	2.328	2.336	2.358	1.693	1.740						
$Ce^{3+} 4f$	$Ce^{2+} 4f5d$	1.686	1.660	1.674	1.786	1.815	1.831	1.865	1.407	1.415						
$Ce^{3+} 4f$	$Ce^{3+} 4f$	0	0	0	0	0	0	0	0	0						
$Ce^{3+} 4f$	$Ce^{3+} 5d$	0.003	0.051	0.009	0.011	0.0008	0.044	0.012	0.004	0.000						
$Ce^{3+} 4f$	$Ce^{4+}$	1.632	1.532	1.836	1.677	1.812	1.743	1.727	1.269	1.186						
$Ce^{3+} 5d$	$Ce^{2+} 4f^2$	7.600	7.530	7.554	7.638	7.895	7.891	7.929	7.183	7.264						
$Ce^{3+} 5d$	$Ce^{2+} 4f5d$	7.123	7.082	7.097	7.311	7.343	7.347	7.396	6.885	6.930						
$Ce^{3+} 5d$	$Ce^{3+} 4f$	5.360	5.402	5.345	5.424	5.390	5.431	5.380	5.433	5.468						
$Ce^{3+} 5d$	$Ce^{3+} 5d$	5.357	5.352	5.336	5.413	5.389	5.386	5.369	5.428	5.468						
$Ce^{3+} 5d$	$Ce^{4+}$	6.947	6.852	7.146	6.861	7.168	7.104	7.035	6.650	6.608						
$Ce^{4+}$	$Ce^{3+} 4f$	9.205	8.778	8.641	9.217	8.569	8.237	8.124	8.086	7.758						
$Ce^{4+}$	$Ce^{4+}$	7.443	6.950	6.902	7.413	6.580	6.148	6.209	6.726	6.475						
$E_{\text{centre}} - 883 \text{ au}$																
$Ce^{3+} 4f$	$Ce^{3+} 4f$	9.348	6.991	6.104	7.306	5.631	2.668	2.459	9.337	5.551						



**Table 12.** Energies  $E_{F_1}^H$  of the interstitial fluorine centre calculated by HADES II. Also given are the coordinates  $x$  describing the positions ( $\pm x, \pm x, \pm x$ ) of the eight nearest-neighbour fluorine ions, if the interstitial fluorine ion is located at (0, 0, 0). The energy  $E_{Ce^{3+}} + E_{F_1^-}$  of the isolated  $Ce^{3+}$  (from table 11) and  $F_1^-$  centres together, as well as the difference with the energies of the  $Ce^{3+}F_{nn}$  and  $Ce^{3+}F_{nn}$  centres, are derived. At the bottom of the table corresponding formation energies for the  $La^{3+}F_1^-$  centres are reproduced from [14]. Energies are in eV and apply to the ground state of the centres. Values between brackets are experimental data [17].

	CaF <sub>2</sub>	SrF <sub>2</sub>	BaF <sub>2</sub>
$E_{F_1}^H$	-2.177	-2.460	-2.560
$x$ (Å)	2.554	2.675	2.829
$E_{Ce^{3+}} - 883au + E_{F_1^-}$	7.171	4.846	3.071
$E_{Ce^{3+}F_{nn}} - E_{Ce^{3+}} - E_{F_1^-}$	-0.181		-0.403
$E_{Ce^{3+}F_{nn}} - E_{Ce^{3+}} - E_{F_1^-}$	-1.067	(-0.79)	-0.612
$E_{La^{3+}F_{nn}} - E_{La^{3+}} - E_{F_1^-}$	-0.384		-0.546
			(-0.44)
$E_{La^{3+}F_{nn}} - E_{La^{3+}} - E_{F_1^-}$	-0.799	(-0.79)	-0.423

the immediate vicinity of the middle of the centre  $Ce-F_1^-$  ((0, 0, 0) in figure 5). Generally, for these ions the displacements are largest. Their core positions are given in table 13. It is clear that lattice relaxation is substantial and so results based on a fixed host lattice are unreliable.

#### 4. Discussion

In this section we compare some of the calculated energy levels of the  $Ce^{3+}$  and  $Ce^{2+}$  centre in  $CaF_2$  to experimental data (subsections 4.1 and 4.2). In subsection 4.3 we discuss the cerium centre energies of table 11. Subsection 4.4 is devoted to the implications of the energy levels found for emission of electrons or holes from the cerium centres. Connected to this, the stability of the cerium centres is discussed. In subsection 4.5 we consider energy transfer from electrons and holes to the  $Ce^{3+}$  centres.

##### 4.1. $Ce^{3+}$ results compared with experiment

The  $Ce^{3+}$  ion was studied optically by Loh and by Manthey [18,19]. We will compare our results for  $CaF_2$  to results from the measurements by Manthey. Our results hold at room temperature, whereas the results of Manthey were obtained at liquid nitrogen or liquid helium temperatures. However, the optical absorption spectra do not shift much on lowering the temperature [18], at least for the bands we are interested in. Table 14 summarizes our results. We observe that the calculated crystal field splittings of the 4f and 5d energy levels agree reasonably with experiment, considering the fact that the calculated values apply to the isolated Ce centre and the experimental values to the somewhat different  $CeF_{nn}$  centre. The difference between the weighted average  $4f^2F_{5/2}$  and  $4f^2F_{7/2}$  energies (levels e in figure 2(a)) is calculated correctly within  $150\text{ cm}^{-1}$ . However, the calculated difference between the lowest states of the 4f and the 5d configurations is too large by 1.4 eV and the calculated Stokes shift is too small. This is probably due to the limited cluster size in the MOLDIR calculation, which excluded the possibility of interaction between the cerium 5d and the  $Ca^{2+}$  4s and 3p states.

**Table 13.** Positions of the cerium ion (Ce), interstitial fluorine (F<sub>i</sub>) and lattice fluorine ion nearest to (0, 0, 0) (F<sub>n</sub>) in the three different cerium centres as shown in figure 5. In the (charge-uncompensated) Ce centre, the cerium ion is at (0, 0, 0) and the F<sub>n</sub><sup>-</sup> positions are (±x, ±x, ±x). In the CeF<sub>nnn</sub> centre the cerium, F<sub>i</sub><sup>-</sup> and F<sub>n</sub><sup>-</sup> positions are (x, x, x). In the CeF<sub>nn</sub> centre, cerium and F<sub>i</sub><sup>-</sup> positions are (x, 0, 0) and the F<sub>n</sub><sup>-</sup> positions are (x, ±y, ±y) (four equivalent positions).

Ce conf.	Coord.	CaF <sub>2</sub>			SrF <sub>2</sub>	BaF <sub>2</sub>			No pol.	
		Ce	CeF <sub>nnn</sub>	CeF <sub>nn</sub>	Ce	Ce	CeF <sub>nnn</sub>	CeF <sub>nn</sub>	CaF <sub>2</sub> Ce	BaF <sub>2</sub> Ce
Ce <sup>2+</sup> 4f <sup>2</sup>	Ce: x	0	-1.411	-1.272	0	0	-1.575	-1.405	0	0
	F <sub>i</sub> : x	—	1.436	1.370	—	—	1.552	1.526	—	—
	F <sub>n</sub> : x	1.506	0.017	0.062	1.533	1.586	-0.051	-0.041	1.493	1.563
	F <sub>n</sub> : y	1.506	0.017	1.596	1.533	1.586	-0.051	1.677	1.493	1.563
Ce <sup>2+</sup> 4f5d	Ce: x	0	-1.410	-1.266	0	0	-1.576	-1.400	0	0
	F <sub>i</sub> : x	—	1.425	1.352	—	—	1.531	1.490	—	—
	F <sub>n</sub> : x	1.484	-0.000	0.030	1.512	1.558	-0.077	-0.075	1.475	1.541
	F <sub>n</sub> : y	1.484	-0.000	1.578	1.512	1.558	-0.077	1.651	1.475	1.541
Ce <sup>3+</sup> 4f	Ce: x	0	-1.400	-1.223	0	0	-1.583	-1.378	0	0
	F <sub>i</sub> : x	—	1.373	1.266	—	—	1.407	1.248	—	—
	F <sub>n</sub> : x	1.406	-0.053	-0.086	1.422	1.446	-0.177	-0.222	1.412	1.450
	F <sub>n</sub> : y	1.406	-0.053	1.527	1.422	1.446	-0.177	1.570	1.412	1.450
Ce <sup>3+</sup> 5d	Ce: x	0	-1.401	-1.224	0	0	-1.584	-1.380	0	0
	F <sub>i</sub> : x	—	1.373	1.261	—	—	1.408	1.233	—	—
	F <sub>n</sub> : x	1.403	-0.053	-0.090	1.412	1.441	-0.178	-0.228	1.409	1.447
	F <sub>n</sub> : y	1.403	-0.053	1.524	1.412	1.441	-0.178	1.568	1.409	1.447
Ce <sup>4+</sup>	Ce: x	0	-1.386	-1.108	0	0	-1.588	-1.398	0	0
	F <sub>i</sub> : x	—	1.312	1.144	—	—	1.303	1.188	—	—
	F <sub>n</sub> : x	1.341	-0.105	-0.162	1.350	1.350	-0.270	-0.350	1.365	1.385
	F <sub>n</sub> : y	1.341	-0.105	1.465	1.350	1.350	-0.270	1.469	1.365	1.385

**Table 14.** Comparison between calculated energies for the Ce<sup>3+</sup> centre in CaF<sub>2</sub> and the corresponding experimental values (which are ascribed to the CeF<sub>nn</sub> centre) [19]. The MOLFDIR-calculated energies have been corrected for differences with free-ion experimental values. *E(S)* denotes the weighted average energy of all states *S*. 'Stokes shift' refers to the Stokes shift for the 4f<sup>2</sup>F<sub>5/2</sub>F<sub>u</sub> → 5d e F<sub>g</sub> transition. The crystal field splittings calculated with cation-anion separation *r* = 2.68 Å are converted to the CaF<sub>2</sub> case by assuming the splittings to be proportional to *r*<sup>-6.6</sup>. Energies are in cm<sup>-1</sup>.

	MOLFDIR <i>r</i> = 2.68 Å	MOLFDIR <i>r</i> = 2.435 Å	Experiment
<i>E</i> (4f <sup>2</sup> F <sub>5/2</sub> E <sub>2u</sub> ) - <i>E</i> (4f <sup>2</sup> F <sub>5/2</sub> F <sub>u</sub> )	224	421	579
<i>E</i> (4f <sup>2</sup> F <sub>7/2</sub> E <sub>2u</sub> ) - <i>E</i> (4f <sup>2</sup> F <sub>7/2</sub> E <sub>1u</sub> )	385	725	1370
<i>E</i> (4f <sup>2</sup> F <sub>7/2</sub> ) - <i>E</i> (4f <sup>2</sup> F <sub>5/2</sub> )	2253	2253	2396
<i>E</i> (5d t <sub>2</sub> E <sub>2g</sub> ) - <i>E</i> (5d e F <sub>g</sub> )	11842	22279	21438 <sup>(a)</sup>
<i>E</i> (5d e F <sub>g</sub> ) - <i>E</i> (4f <sup>2</sup> F <sub>5/2</sub> F <sub>u</sub> )		43204 <sup>(b)</sup>	31932
Stokes shift: Ce centre		57 <sup>(b)</sup>	
Stokes shift: CeF <sub>nnn</sub> centre		814 <sup>(b)</sup>	
Stokes shift: CeF <sub>nn</sub> centre		144 <sup>(b)</sup>	1280

(a) Energy difference between no-phonon peaks G ( $\lambda = 1873 \text{ \AA}$ ) and B ( $\lambda = 3131.7 \text{ \AA}$ ) [19].  
 (b) From table 11.

The Stokes shift was calculated as the sum of two contributions. The first is the energy

difference between the lowest  $\text{Ce}^{3+} 4f$  state in the 5d lattice configuration and the lowest  $\text{Ce}^{3+} 4f$  state in the 4f lattice configuration (see table 11), which corresponds to the energy difference between the  $4f^2 F_{5/2} F_u \rightarrow 5d e F_g$  zero phonon line and the maximum of the phonon wing in the emission spectrum. The second is the difference between the lowest  $\text{Ce}^{3+} 5d$  state in the 4f lattice configuration and the lowest  $\text{Ce}^{3+} 5d$  state in the 5d lattice configuration, which corresponds to the energy difference between the  $4f^2 F_{5/2} F_u \rightarrow 5d e F_g$  zero phonon line and the maximum of the phonon wing in the absorption spectrum. The two contributions are approximately equal in magnitude.

#### 4.2. $\text{Ce}^{2+}$ results compared with experiment

A comparison of the  $\text{Ce}^{2+}$  energy levels to calculations by Alig and co-workers [12] has been made in subsection 3.1. Reasonable-to-good agreement was found if, for the  $4f^2$  levels,  $B_4 = -700 \text{ cm}^{-1}$  was used and, for the  $4f5d$  levels,  $Dq = 1120 \text{ cm}^{-1}$  was used. Note that this holds if the cerium-fluorine distance is  $r = 2.68 \text{ \AA}$ . Alig and co-workers found good agreement between their calculations and optical absorption spectra in  $\text{CaF}_2$  if, for the  $4f^2$  levels,  $B_4 = -3000 \text{ cm}^{-1}$  was taken. Further, from the experimental fact that the lowest  $\text{Ce}^{2+} 4f5d$  level in  $\text{CaF}_2$  lies  $7080 \text{ cm}^{-1}$  below the lowest  $4f^2$  level they deduced that  $Dq = 1800 \text{ cm}^{-1}$  for the  $4f5d$  levels if there are no configuration shifts. From table 1 we observe that  $\langle E_{\text{CeF}_3}^M(\text{Ce}^{2+} 4f5d) \rangle - \langle E_{\text{CeF}_3}^M(\text{Ce}^{2+} 4f^2) \rangle$  is about  $2000 \text{ cm}^{-1}$  higher than  $\langle E_{\text{Ce}^{2+}}^M(\text{Ce}^{2+} 4f5d) \rangle - \langle E_{\text{Ce}^{2+}}^M(\text{Ce}^{2+} 4f^2) \rangle$ . In other words, some  $4f^2 - 4f5d$  configuration shift due to the cerium environment is present but it is not large. We may then compare our  $B_4$  and  $Dq$  values to those found by Alig and co-workers. For this, we need to convert our values, which apply to  $r = 2.68 \text{ \AA}$ , to the  $\text{CaF}_2$  case where  $r = 2.57 \text{ \AA}$  ( $= \sqrt{3} \times 1.484 \text{ \AA}$ , see table 13). If we assume the splittings to be proportional to  $r^{-6.6}$ , as was found for the  $\text{Ce}^{3+} 5d$  level splitting, then for the  $\text{CaF}_2$  case we calculate  $B_4 = -923 \text{ cm}^{-1}$  and  $Dq = 1477 \text{ cm}^{-1}$ . Here we used the fact that the splittings are roughly proportional to  $B_4$  and  $Dq$  [12]. The  $Dq$  value reasonably agrees with the one found by Alig and co-workers, meaning that the  $4f5d$  splittings are calculated correctly. Their  $B_4$  value on the other hand is larger than ours, meaning that our calculations underestimate  $4f^2$  splittings. This compares to the  $\text{Ce}^{3+}$  case, where the  $5d$  splittings were calculated correctly, but the  $4f$  splittings are too small (cf table 14).

The difference between the lowest  $4f5d$  level in the  $4f5d$  lattice configuration and the lowest  $4f^2$  level in the  $4f^2$  lattice configuration corresponds to the zero phonon peak energy for the  $4f5d T_2(\text{lowest}) \rightarrow 4f^2 {}^3H_4 T_2$  transition. Depending on the cerium centre, for this difference table 11 gives a value between  $-3250$  and  $-3900 \text{ cm}^{-1}$ . This is smaller than the experimental value,  $-7080 \text{ cm}^{-1}$ . Probably, this is caused by the use of a  $4f^2, 4f5d, 5d^2$  average configuration in the MOLFDIR calculation.

#### 4.3. Energy levels of the cerium centres

We now summarize the main features of the energy levels given in table 11 for the three different cerium centres in the alkaline-earth fluorides. In figure 6 the energy levels of the  $\text{CeF}_{\text{nnn}}$  centre in  $\text{BaF}_2$  are visualized. The figure is related to a configuration coordinate diagram. Whereas often only one generalized coordinate is shown along the abscissa of a configuration coordinate diagram, the abscissa of figure 6 shows  $3N$  generalized coordinates ( $N$  is the total number of atoms in the lattice). This is because all vibrational modes of the lattice take part in the calculated core displacements. For practical purposes, only five points from the  $3N$ -dimensional configuration coordinate space are displayed in figure 6, which are the lattice configurations corresponding to the five lowest-energy states.

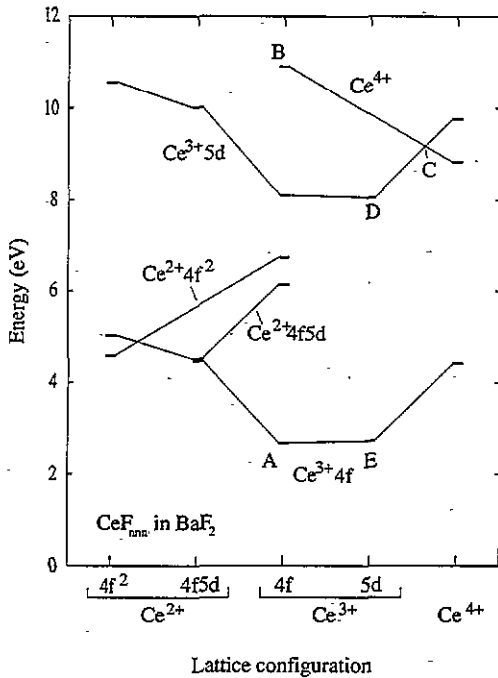


Figure 6. Schematic of the energy levels,  $E_{\text{centre}} - 883$  au, given in table 11 for the  $CeF_{\text{nnn}}$  centre in  $BaF_2$ . Data points for the same cerium electronic state are connected by straight lines.

The other centres shown in table 11 yield a more or less similar picture as figure 6. The main features are discussed below, starting with the cerium centres without charge compensation (Ce). The relative level energies (i.e. relative to the lowest  $Ce^{3+} 4f$  level) of the Ce centre are hardly different for  $CaF_2$  and  $SrF_2$ . But the energies of the Ce centre in  $BaF_2$  are different: the relative  $Ce^{2+}$  energies are 0.2–0.3 eV higher and the relative  $Ce^{4+}$  energy is 0.8 eV lower. This is related to the fact that in  $BaF_2$  the nearest-neighbour fluorine ions can relax inward by a greater amount than in  $CaF_2$  and  $SrF_2$  (cf table 13). Therefore, the  $Ce^{4+}$  centre in particular, and to a lesser extent the  $Ce^{3+}$  centre, have an extra low energy in  $BaF_2$ .

In the  $CeF_{\text{nnn}}$  and  $CeF_{\text{nn}}$  centres the electrons at cerium are less tightly bound than in the charge-uncompensated Ce centre. This is due to the extra negative charge near the cerium ion. Consequently, for the charge-compensated centres the  $Ce^{2+}$  level energies relative to the  $Ce^{3+}$  level energies will be higher than in the not charge compensated cerium centre, less energy being needed for removing the electron from the  $Ce^{2+}$  ion. Analogously, the  $Ce^{3+}$  level energies relative to the  $Ce^{4+}$  energy will be higher.

This is reproduced in the calculations. We find that the  $Ce^{2+}F_{\text{nnn}}$  levels are shifted upward relative to  $Ce^{3+}F_{\text{nnn}}$  states by 0.8 eV in  $CaF_2$  and 0.6 eV in  $BaF_2$ . The upward shift of the  $Ce^{3+}F_{\text{nnn}}$  levels relative to the  $Ce^{4+}F_{\text{nnn}}$  state is 0.5 eV in  $CaF_2$  and 0.4 eV in  $BaF_2$ . These shifts are about the same for each  $Ce^{2+}$  or  $Ce^{4+}$  level, irrespective the particular electronic configuration ( $4f^2$  or  $4f5d$  for  $Ce^{2+}$ ) or lattice configuration. The relative level energies of the  $CeF_{\text{nn}}$  centres differ from those of the corresponding  $CeF_{\text{nnn}}$  centres by no more than 0.2 eV. The small magnitude of this energy difference is caused by the tempering action of lattice relaxations.

#### 4.4. Electron or hole emission from cerium centres: centre stability

In the previous sections we have discussed the energy levels of the cerium centre and

transitions between those levels, where the cerium ion charge is preserved (optical absorption and emission). In this section we consider what happens if electrons or holes are captured or emitted from a cerium centre. The location of the energy levels (table 11) determines whether these processes are possible and what energies are involved.

We will consider interactions of free electrons and holes with the cerium centres. For this, the energy of the free electron and the free hole relative to the vacuum level have to be known. From reflectance measurements we know the band gap energy  $E_g$  of the host lattice:  $E_g = 12.1, 11.25$  and  $11.0$  eV for  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  respectively [20]. We expect the bottom of the conduction band to be located at approximately 0 eV, which would imply that the top of the valence band is located at  $-E_g$ . Photoemission studies confirm this [21, 22]. Most free electrons and holes created by some excitation of the crystal will interact with cerium centres only after thermalization. Therefore, we will only be concerned with cold electrons and holes: the electron has energy 0 eV and the hole has energy  $E_g$ .

We can now determine which cerium centres are unstable. A centre X, say, will be unstable in a lattice without free electrons and holes if either of the following processes are energetically favourable: (i)  $X \rightarrow X^- + h$ , i.e. emission of a free hole (h) from the X centre, or (ii)  $X \rightarrow X^+ + e$ , i.e. emission of a free electron (e). Below we investigate the possibility of hole or electron emission from the  $\text{CeF}_{\text{nnn}}$  centre in  $\text{BaF}_2$  (cf figure 6), where the cerium ion is in the divalent, trivalent or tetravalent state.

(a)  $\text{Ce}^{2+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{1+}\text{F}_{\text{nnn}} + h$ . This process requires 11.0 eV needed for creation of a free hole and a free electron, plus the energy needed for moving the free electron into the cerium ion. The latter energy is of the order of the 17.6 eV Madelung energy at a barium site minus the 10.9 eV (free ion)  $\text{Ce}^{1+}$  ionization energy [11]. Adding these contributions shows that the  $\text{Ce}^{2+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{1+}\text{F}_{\text{nnn}} + h$  hole emission process requires about 18 eV, so it will not occur.

(b)  $\text{Ce}^{2+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{3+}\text{F}_{\text{nnn}} + e$ . This requires 0 eV electron formation energy, minus the  $\text{Ce}^{2+}\text{F}_{\text{nnn}}$  ground-state energy, plus the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  ground-state energy. The total is  $-1.796$  eV, so this process can occur, meaning that the  $\text{Ce}^{2+}\text{F}_{\text{nnn}}$  centre is unstable against electron emission.

(c)  $\text{Ce}^{3+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{2+}\text{F}_{\text{nnn}} + h$ . This process is energetically unfavourable: the energy required is 1.796 eV + 11 eV. Hence the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  centre is stable against hole emission.

(d)  $\text{Ce}^{3+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{4+}\text{F}_{\text{nnn}} + e$ . The energy required for this is 0 eV electron formation energy plus the  $\text{Ce}^{4+}\text{F}_{\text{nnn}}$  ground-state energy minus the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  ground-state energy, which is 6.148 eV. Hence the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  centre is also stable against electron emission.

(e)  $\text{Ce}^{4+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{3+}\text{F}_{\text{nnn}} + h$ . This requires 11 eV hole formation energy minus 6.148 eV, so the  $\text{Ce}^{4+}\text{F}_{\text{nnn}}$  centre is stable against hole emission.

(f)  $\text{Ce}^{4+}\text{F}_{\text{nnn}} \rightarrow \text{Ce}^{5+}\text{F}_{\text{nnn}} + e$ . This is highly improbable, since it requires a great deal of energy because of the large 65.6 eV  $\text{Ce}^{4+}$  ionization energy [11]. Thus,  $\text{Ce}^{4+}\text{F}_{\text{nnn}}$  is also stable against electron emission.

We conclude that the  $\text{CeF}_{\text{nnn}}$  centre in  $\text{BaF}_2$  is only stable if the cerium ion is in its trivalent or tetravalent state. This holds if no free charge carriers are present that can be absorbed. On the other hand, if free electrons are present, the  $\text{Ce}^{2+}\text{F}_{\text{nnn}}$  centre is unstable: electron capture releases 6.148 eV.

The above analysis holds for all centres considered in table 11. Nevertheless, the energy levels of the charge-uncompensated cerium centres are slightly different from those of the  $\text{CeF}_{\text{nnn}}$  centre, since here the relative energies of the  $\text{Ce}^{2+}$  levels are lower and those of the  $\text{Ce}^{4+}$  levels are higher. This has an interesting implication for the stability of the  $\text{Ce}^{2+}$  centre. It remains unstable against electron emission, because the energy of the  $\text{Ce}^{3+}$  4f ground state with  $\text{Ce}^{3+}$  4f lattice configuration is lower than that of the  $\text{Ce}^{2+}$  4f5d ground

state with Ce<sup>2+</sup> 4f5d lattice configuration. But the energy of the Ce<sup>3+</sup> 4f ground state with Ce<sup>2+</sup> 4f5d lattice configuration is higher than the energy of the Ce<sup>2+</sup> 4f5d ground state with Ce<sup>2+</sup> 4f5d lattice configuration. The energy difference is  $E_b = 0.696, 0.731$  and  $0.487$  eV for CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> respectively. This means that for electron emission an energy barrier  $E_b$  has to be overcome: the charge-uncompensated Ce<sup>2+</sup> centre is metastable. This has been confirmed by experiment. After reducing Ce<sup>3+</sup> doped crystals chemically (additive colouration) the Ce<sup>2+</sup> absorption spectrum was not directly observed. Instead, a spectrum characterized by two absorption bands near 4000 and 7000 Å was observed. The Ce<sup>2+</sup> absorption spectrum arose on bleaching into the 4000 Å band [12, 23]. At room temperature this spectrum was slowly re-converted: Ce<sup>2+</sup> centres are replaced with the centres associated with the 4000 and 7000 Å absorption bands [12, 23]. These centres were shown to be (111) symmetry centres consisting of two electrons trapped at a Ce<sup>3+</sup>-nearest-neighbour fluorine vacancy complex [24–26].

The barrier energy  $E_b$  can be compared to photoconductivity experiments. Pedrini and co-workers found the onset of photoconductivity in Ce<sup>2+</sup>-containing CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> at 1.6, 1.3 and 1.1 eV respectively [23]. These values are up to 1 eV larger than our  $E_b$  values. However, it is not excluded that the photoconductivity thresholds are somewhat lower than according to Pedrini and co-workers, since they determined the threshold as the energy where the photocurrent fell below their instrumental resolution. Moreover, no clear structure in their photosensitivity curves can be observed near the energies reported.

#### 4.5. Electron or hole absorption by cerium centres: Ce<sup>3+</sup> excitation

We have been concerned above with centre stability and emission of a free electron or hole from a cerium centre. We will now consider electron or hole absorption at a cerium centre. Free electrons and holes may be created in the crystal if it is excited by high-energy radiation. After capture of an electron and a hole, the cerium centre may be left in an excited state, from which luminescence may result. We will only consider excitation of trivalent cerium centres, since these are most common (stable).

We will consider the Ce<sup>3+</sup>F<sub>nnn</sub> centre in BaF<sub>2</sub> as an example (cf figure 6). The free-electron capture process  $\text{Ce}^{3+}\text{F}_{\text{nnn}} + e \rightarrow \text{Ce}^{2+}\text{F}_{\text{nnn}}$  is energetically unfavourable because the Ce<sup>2+</sup>F<sub>nnn</sub> 4f5d states lie above the Ce<sup>3+</sup>F<sub>nnn</sub> 4f ground state, and the electron energy is 0 eV. On the other hand, in principle capture of a free hole is possible. In figure 6, capture of the hole,  $\text{Ce}^{3+}\text{F}_{\text{nnn}} + h \rightarrow \text{Ce}^{4+}\text{F}_{\text{nnn}}$ , corresponds to the transition from point A to point B. The energy needed for this hole capture process is  $E_{\text{Ce}^{4+}\text{F}_{\text{nnn}}} - E_{\text{Ce}^{3+}\text{F}_{\text{nnn}}} - E_h = 8.237 - 11.0 = -2.8$  eV (cf table 11). Thus, in the hole capture process, 2.8 eV has to be dissipated. After this the Ce<sup>4+</sup>F<sub>nnn</sub> centre relaxes to point C, where an electron with energy 0 eV may be captured. The resulting excited Ce<sup>3+</sup>F<sub>nnn</sub> centre relaxes from C to D. Upon radiative decay, it arrives at point E and subsequently relaxes to point A again.

The above excitation cycle is similar for all cerium centres:  $\text{Ce}^{3+}(\text{F}_{(n)nn}) + e \rightarrow \text{Ce}^{2+}(\text{F}_{(n)nn})$  electron capture will not occur and  $\text{Ce}^{3+}(\text{F}_{(n)nn}) + h \rightarrow \text{Ce}^{4+}(\text{F}_{(n)nn})$  hole capture is possible if an energy gap of 2–3 eV is bridged. However, these electron and hole capture processes are not the only conceivable ones. We will consider some other possibilities below.

*Electron capture.* That free-electron capture by a trivalent cerium centre is unlikely to occur does not mean that electrons cannot be captured at these centres. It is possible that the electron is captured not at the Ce<sup>3+</sup> ion but in its neighbourhood, due to the attractive positive effective charge of the Ce<sup>3+</sup> ion. The properties of the resulting centre, Ce<sup>3+</sup>(F<sub>(n)nn</sub>)–e would not change much if the cerium ion was replaced with another trivalent

rare-earth ion. Indications for the existence of such centres were found by Vakhidov and co-workers [27].

*Hole capture.* Whereas level energies do not forbid free-hole capture, it is unlikely that the free-hole capture rate will be very high because the effective positive charge of the  $\text{Ce}^{3+}$  ion repels holes. At small cerium concentrations the free-hole capture rate may therefore be considerably smaller than the hole self-trapping rate. The latter rate is rather large: the self-trapped hole ( $V_K$  centre) is generally formed within a few ps [28]. The self-trapping energy  $E_{V_K} - E_h$  is probably a few eV [29–31]. Hence, the energy needed for  $\text{Ce}^{3+}\text{F}_{\text{nnn}} + V_K \rightarrow \text{Ce}^{4+}\text{F}_{\text{nnn}}$  trapped hole capture in  $\text{BaF}_8$ , which is  $E_{\text{Ce}^{4+}\text{F}_{\text{nnn}}} - E_{\text{Ce}^{3+}\text{F}_{\text{nnn}}} - E_{V_K} = -2.8 \text{ eV} + E_h - E_{V_K}$ , is expected to be near zero or positive up to about 2 eV. Thus this  $V_K$  capture process need not be energetically favourable. In any case it is slow because of the 0.3 eV activation energy necessary for  $V_K$  hopping transport [32]. Summarizing, free-hole capture at the  $\text{Ce}^{3+}$  ion seems unimportant;  $V_K$  capture may be possible but is not a fast process. The argument, which is given here for the  $\text{Ce}^{3+}\text{F}_{\text{nnn}}$  centre in  $\text{BaF}_2$ , is similar for the other cerium centres.

The above suggests that cerium excitation by electrons and holes is not a fast process. An exception may be the  $\text{Ce}^{3+}(\text{F}_{(\text{n})\text{nn}}) + e \rightarrow (\text{Ce}^{3+}(\text{F}_{(\text{n})\text{nn}}) - e)$  electron capture process, within a few ps followed by  $(\text{Ce}^{3+}(\text{F}_{(\text{n})\text{nn}}) - e) + h \rightarrow (\text{Ce}^{3+})^*(\text{F}_{(\text{n})\text{nn}})$  free-hole capture (\* denotes excitation). However, at least at low cerium concentrations, this is apparently not a very important process, since most observed scintillation from cerium centres is slow [1].

## 5. Conclusions

We have calculated both formation energies and energy levels of the cerium centres  $\text{Ce}$ ,  $\text{CeF}_{\text{nnn}}$  and  $\text{CeF}_{\text{nn}}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$ . The calculational method is mainly *ab initio* and allows application in many other lattices. The combination of results of molecular cluster calculations with results of lattice relaxation studies provides a very detailed picture of the energy levels of the cerium ion in various configurations. The present study shows the importance of lattice relaxation. There is overall a satisfying agreement with experiment. In many cases, agreement is within a few tenths of an electron volt. A similar error was deduced from a comparison with the 'no pol.' data. However, the  $\text{Ce}^{3+} 4f \rightarrow 5d$  transition energy was found to be 1.4 eV too large. Moreover, the Stokes shift for this transition was too small. This is attributed to the small  $\text{CeF}_8$  cluster used in the MOLFDIR calculations.

The main conclusions drawn from the position of the energy levels are as follows.

First, due to lattice relaxations, the energy levels of the  $\text{CeF}_{\text{nn}}$  centre are, within about 0.2 eV, equal to those of the  $\text{CeF}_{\text{nnn}}$  centre. The electrons in both centres are less tightly bound than in the charge-uncompensated cerium centre. The relative energy levels of this cerium centre differ by up to 0.8 eV from those of the charge-compensated centres.

Second, the  $\text{Ce}$ ,  $\text{CeF}_{\text{nnn}}$  and  $\text{CeF}_{\text{nn}}$  centres are only stable if the cerium ion is in its trivalent or tetravalent state.

Third, if free electrons are present, the tetravalent cerium centres are unstable. They are turned into the trivalent state by electron capture.

Fourth, in its divalent state, the charge-uncompensated  $\text{Ce}$  centre is metastable, in agreement with experimental data.

Fifth, cold electrons cannot be captured at trivalent cerium ions. Possibly, electrons are captured near cerium ions.

Sixth, cold holes can be captured at trivalent cerium ions, provided a considerable lattice relaxation takes place. Because of the positive effective charge of the  $\text{Ce}^{3+}$  ion, the hole

capture rate is probably relatively small. This suggests that at low cerium concentrations, (fast) cerium ion excitation is unlikely, the holes being self-trapped in the host lattice before reaching cerium sites.

Finally, fast processes in which free electrons and holes are captured *near* the cerium ion instead of *at* the cerium ion were not considered in detail. Experimental results [1] suggest that these are of limited importance for the observed scintillation due to Ce<sup>3+</sup>.

It seems interesting to perform calculations similar to those reported in this paper for cerium-doped materials which exhibit fast cerium scintillation. It is anticipated that in this case efficient free-electron and free-hole capture is possible. Conversely, the present calculational method is thought to be helpful in searching for new materials in which fast excitation of the cerium centre is possible.

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### References

- [1] Visser R, Dorenbos P, van Eijk C W E, Meijerink A, Blasse G and den Hartog H W 1993 *J. Phys.: Condens. Matter* **5** 1659
- [2] Laval M, Moszynski M, Allemand R, Cormoreche E, Guinet P, Odru R and Vacher J 1983 *Nucl. Instrum. Methods* **206** 169
- [3] Visser R, Dorenbos P, van Eijk C W E and den Hartog H W 1992 *J. Phys.: Condens. Matter* **4** 8801
- [4] Aerts P J C 1986 *Thesis* University of Groningen
- [5] van Piggelen H U *Internal report, University of Groningen* (unpublished)
- [6] Visser O, Visscher L, Aerts P J C and Nieuwpoort W C 1992 *J. Chem. Phys.* **96** 2910
- [7] Huzinaga S (ed) 1984 *Physical Sciences Data* **16** (Amsterdam: Elsevier)
- [8] Frisch M J, Head-Gordon M, Trucks G W, Foresman J B, Schlegel H B, Raghavachari K, Robb M, Binkley J S, Gonzalez C, Defrees D J, Fox D J, Whiteside R A, Seeger R, Melius C F, Baker J, Martin R L, Kahn L R, Stewart J J P, Topiol S and Pople J A 1990 *GAUSSIAN 90<sup>TM</sup>, Revision J* (Pittsburgh, PA: Gaussian, Inc.)
- [9] Lidiard A B and Norgett M J 1972 *Computational Solid State Physics* ed F Herman, N W Dalton and T R Koeler (New York: Plenum) 385
- [10] Catlow C R A and Norgett M J 1973 *J. Phys. C: Solid State Phys.* **6** 1325
- [11] Martin W C, Zalubas R and Hogan L 1978 *Atomic Energy Levels: the Rare Earth Elements* (National Bureau of Standards)
- [12] Alig R C, Kiss Z J, Brown J P and McClure D S 1969 *Phys. Rev.* **186** 276
- [13] Catlow C R A, Norgett M J and Ross T A 1977 *J. Phys. C: Solid State Phys.* **10** 1627
- [14] Corish J, Catlow C R A, Jacobs P W M and Ong S H 1982 *Phys. Rev. B* **25** 6425
- [15] Wyckoff R W G 1963 *Crystal Structures* vol I (New York: Wiley-Interscience)
- [16] Hellwege K H and Hellwege A M (eds) 1973 *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, new series, group III, Vol. 7(a)-(h)* (Berlin: Springer)
- [17] Dorenbos P, Vrind S, Dolfing J and den Hartog H W 1987 *Phys. Rev. B* **35** 5766
- [18] Loh E 1967 *Phys. Rev.* **154** 270
- [19] Manthey W J 1973 *Phys. Rev.* **8** 4086
- [20] Rubloff G W 1972 *Phys. Rev. B* **5** 662
- [21] Poole R T, Szajman J, Leckey R C G, Jenkin J G and Liesegang J 1975 *Phys. Rev. B* **12** 5872



- [22] Pong W, Inouye C S and Okada S K 1978 *Phys. Rev. B* **18** 4422
- [23] Pedrini C, Pagost P O, Madej C and McClure D S 1981 *JP* **42** 323
- [24] Staebler D L and Schnatterly S E 1971 *Phys. Rev. B* **3** 516
- [25] Anderson C H and Sabisky E S 1971 *Phys. Rev. B* **3** 527
- [26] Alig R C 1971 *Phys. Rev. B* **3**(2) 536
- [27] Vakhidov Sh A, Kaipov B, Tavshunskii G A and Gapparov N 1976 *Opt. Spektrosk.* **40** 1099 (Engl. transl. 1976 *Opt. Spectrosc.* **40** 635)
- [28] Williams R T and Song K S 1990 *J. Phys. Chem. Solids* **51** 679
- [29] Norgett M J and Stoneham A M 1973 *J. Phys. C: Solid State Phys.* **6** 229 (1973)
- [30] Cade P E, Stoneham A M and Tasker P W 1984 *Phys. Rev. B* **30** 4621
- [31] Pandey R and Kunz A B 1988 *Phys. Rev. B* **38** 10150
- [32] Beaumont J H, Hayes W, Kirk D L and Summers G P 1970 *Proc. R. Soc. A* **315** 69
- [33] Harker A H 1989 *HADES III/PC: The Harwell Automatic Defect Evaluation System for Personal Computers* (Harwell: Publications Office)