

POSITIONS OF 4f AND 5d ENERGY LEVELS OF Ce³⁺ IN THE BAND GAP OF CeF₃, YAO AND LSO

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Abstract—In this paper we take a different algorithm as approach, in an as simple way, the absorption bands of Ce 4f–5d transitions and the position of the Ce 4f and 5d levels in the gap for Ce-doped inorganic crystals. Calculations have been performed on CeF₃ and Ce-doped LaF₃, YAO and LSO. The calculated absorption bands are in good agreement with experimental data. The calculated position of the Ce levels in the gap is not good enough, but useful and in agreement with experimental data within a certain error.

INTRODUCTION

The excitation process can be divided into three stages (Andriessen *et al.*, 1994). In the first stage the radiative interaction with the crystal is eventually from a large number of electron–hole pairs. In the second stage these electron–hole pairs form excimer centres, which may diffuse through the crystal. In the third stage the excimer conditions on a scintillation centre and a photon is emitted.

Doping ionic crystals with radium can provide crystals with good scintillation properties or irradiation with X-rays or gamma rays. Crystal impurities in ionic crystals provide scintillation centres with an optimal wavelength of 300 to 350 nm. Detection of light of this wavelength is efficient and easy with modern day photomultiplier tubes.

CeF₃ and LaF₃:Ce are two crystals that have gained considerable interest in the last few years because they have a high density, are extremely radiation hard and their fast scintillation (10 ns) with a reasonable light yield (2000 photons/Mev).

YAO and LSO are two crystals which have been studied as possible candidates for scintillation crystals.

In this paper we will express ourselves with the third stage of the excitation process in CeF₃, LaF₃, YAO and LSO (the case of these crystals doped with Ce). For LaF₃:Ce reasonable accurate experimental values are known. In this system we function as a benchmark for our method.

THEORETICAL MODEL

Our theoretical model contains two separate approximations. Our approximation is contained with

the level of theory for the calculations, the other is concerned with the detailed representation of the crystal.

The properties we are interested in are mainly local properties of the Ce impurity. A band structure calculation cannot describe these local properties, so we use a cluster approximation. We represent the crystal with a cluster containing the Ce impurity and the first layers of the nearest neighbours of the crystal. The interaction with the rest of the crystal is represented by a formal number of point charges, which are chosen so as to guarantee the correct Madelung potential at the cluster size, due to the rest of the crystal. As can be seen from Fig. 1, it is essential to include the first layer of nearest neighbours of the host crystal to accurately describe the Ce 5d levels. The position of the band edge of the host crystal can only be a crude approximation, because of the very limited size of the cluster (Dieter, 1984). We use ab initio molecular quantum mechanical methods to compute all the energies we need. Ce is a rather heavy atom, so we expect relativistic effects to be important. In Fig. 2 we show the 4f and 5d levels of the Ce ion calculated with the fully relativistic Hartree–Fock–Dirac method (Acta. 1986; Vander, 1993) and with the non-relativistic Hartree–Fock method (Roothaan, 1956; Gauss *et al.*, 1992). It is clear from this figure that the distance between the Ce 4f and the Ce 5d levels can only be described correctly by a relativistic formulation. The same is the Ce 5d levels, however, is already correctly described by a non-relativistic formalism.

In Fig. 3 we show the fully relativistic energy difference between the average energy of the Ce 4f levels and the average of the energy of the Ce 5d levels for some crystals. It appears that the distance between the average of the Ce 4f and the

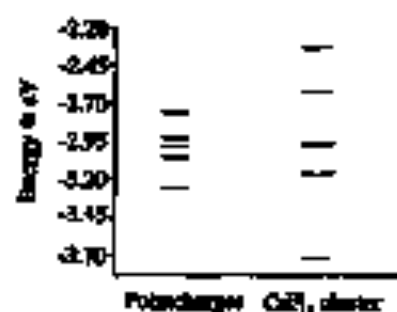


Fig. 1. Point charge model results for the 5d level splitting of the Ce^{3+} ion in LaF_3 , compared to that of a CeF_{11} cluster.

average of the Ce 5d levels is approximately the same. This was also found to hold for the distances from calculations and experiments on BaF_2 and LaF_3 .

As for each type of crystal (i.e. oxides, fluorides, chlorides, etc.) we used our fully relativistic calculation to determine the distance between the energy of the average of the Ce 4f states and the energy of the average of the Ce 5d states, and then the distance between the average Ce 4f and 5d levels. After that we only need to perform a non-relativistic Hartree-Fock calculation on the rare earth cluster to determine the Ce 5d energy levels. This is done by doing one RHF calculation on the average of all Ce 5d states. From these levels we can then deduce the position of the average of the Ce 4f levels.

To determine the band gap and the positions of the valence and conduction band edges we perform a Hartree-Fock calculation on the ground state of a cluster of the host molecule and a General Valence Bond Open Shell Single calculation on the first excited state of the same cluster. The difference of the total energies of these calculations is taken as a reasonable estimate for the band gap.

From experiment it is known that the conduction band edge in the host crystal is formed by the metal fluorine. In our clusters we only have one neutral ion and consequently a delocalized metal d band cannot be formed. By adding a few very diffuse s functions to the basis set of the neutral atom we give

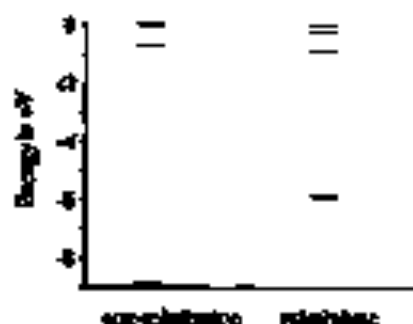


Fig. 2. The 4f and the 5d levels of a Ce^{3+} ion surrounded by six point charges on x, y and z axes (with symmetry C_{3v}).

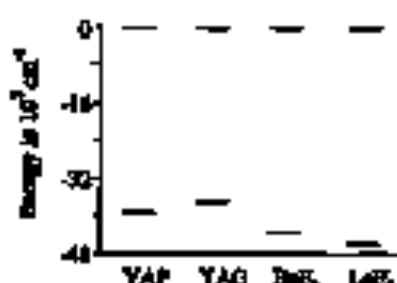


Fig. 3. Energy difference between the average of the Ce 4f and the average of the Ce 5d levels.

the system the possibility of forming a set of very diffuse (delocalized) s orbitals.

The position of the Ce 5d levels are an arbitrary scale, as given by their orbital energies. The Ce 4f levels are placed relative to the Ce 5d levels. To find the position of the Ce levels in the band gap we need to determine the positions of the valence and conduction band edges. There are two possibilities. We can assume that the orbital energy of the lowest unoccupied spherical orbital (diffuse metal s -type orbital) of the pure host crystal gives the edge of the conduction band and then place the valence band edge relative to this estimated conduction band edge, with this procedure shifting upward the highest occupied valence orbitals. We can also assume that the valence band edge is given by the orbital energy of the highest occupied $f(3d) 2p$ orbital and place the conduction band edge relative to this valence band edge.

Because the cluster we use is too small to give the oxygen or fluoride atoms a chance to form a bond with the $2p$ orbitals will be too low in energy. The diffuse metal s -type orbital of the host molecule cluster is expected to give a reasonable estimate for the conduction band edge. In our view we self-energy correction is needed and we have chosen the first alternative.

RESULTS

Figure 4 shows the results of the calculations on the fluorides and the corresponding experimental data. The numbers are also compiled in Tables 1 and 2.

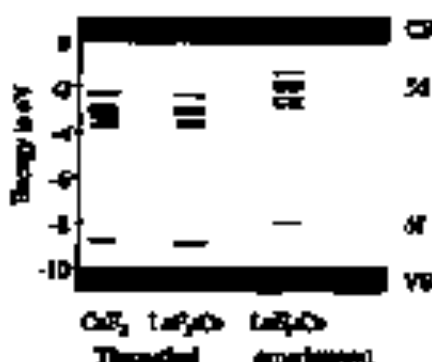


Fig. 4. The positions of the Ce levels in the band gap.

Table 1. The position in the gap for the Ce 4f and 5d levels. All energies are in eV.

	Theoretical values	
	CeF ₃	Experimental values CeF ₃ :Ce LaF ₃ :Ce
CB	0.06	0.00
5d	-2.33	-2.36
	-2.67	-2.67
	-3.06	-3.12
	-3.20	-3.04
	-3.70	-3.72
4f level	-8.90	-8.99
VB		-10.84

Table 2. The absorption bands for the Ce 4f-5d transitions. All energies are in 10³ cm⁻¹.

Theoretical values CeF ₃	Experimental values	
	LaF ₃ :Ce	LaF ₃ :Ce
40.3	40.7	40.3
42.9	42.9	42.7
43.3	43.4	43.9
46.9	46.7	46.3
51.3	51.3	51.3

There are only reasonably accurate experimental data available for LaF₃:Ce with less than 0.2% Ce (Mizuno *et al.*, 1994). We can see from Table 2 that the Ce levels in CeF₃ and LaF₃:Ce are virtually the same. This is hardly surprising, because CeF₃ and LaF₃ have the same crystal structure. There is only a small difference in the size of the unit cell and thus in the bond lengths.

From Fig. 4 we can see that there is good agreement between the calculated and the observed wavenumbers for the absorption due to the 4f-5d transition. In Fig. 4 we see a difference of 1 eV between the calculated and the observed (Mizuno *et al.*, 1994) positions of the levels in the gap. The uncertainty in the theoretical values which results from the two different methods is 1 eV for the functions and 2 eV for the orbitals.

In Tables 3 and 4 and Fig. 5 we list the results for the calculations on the oxides YAG and LSC. Experimental data for these systems are only available on the transition frequencies and not on the position of the levels in the gap (YAG: White, 1973; LSC: Suzuki *et al.*, 1993).

From Table 3 we see that the calculated transition frequencies for the oxides are in reasonable agree-

Table 3. The absorption bands for the Ce 4f-5d transitions. All energies are in 10³ cm⁻¹.

Theory	YAG		LSC	
	Experiment	Theory	Theory	Experiment
21.1	22.3	22.6	27.0	
25.4	26.8	26.4	30.6	
42.9	37.5	41.9		
44.1	43.3	43.8		
51.9		47.6		

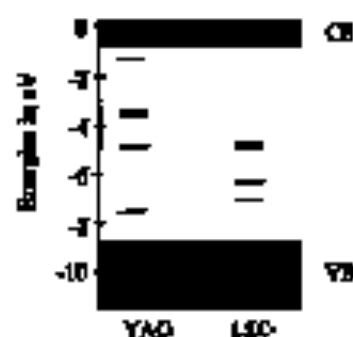


Fig. 5. The position of the Ce levels in the band gap.

ment with the experimental ones, although the agreement is not so good as with the fluorides.

In the case of YAG, the Ce ion partly replaces a Y atom. The radii of these two atoms is not the same. So in the real crystal we expect some relaxation of the atomic positions around a Ce impurity. In our calculations we did not take this relaxation into account. This may be the reason for the small discrepancies between the calculated and observed transition frequencies in YAG.

For LSC, the crystal structure is not precisely known. The crystal structure of a very similar compound with Yb instead of Lu has been determined. We used this crystal structure in our calculations. There are two sites equivalent to the Ce ion in the lattice to occupy. Because the ionic radii of Lu and Ce differ substantially, we expect some relaxation. Because of the very low site symmetry we do not expect a large orbital relaxation. We have used a radial relaxation of 5%, because otherwise a solution to the Hartree-Fock equations could not be found. In light of the above problems differences between the calculated and observed transition frequencies may be expected.

In Fig. 5 we list our predictions for the positions of the Ce levels in the band gap. The band gap is rather narrow, of the order of 6 eV. So our estimates of the band gap are likely to be 2 eV off. Our predictions for YAG look reasonable and are capable of explaining the observed phenomena. In our prediction for LSC the 5d levels are positioned very deep in the gap and the 4f levels are even in the valence band, which is very odd. We also find some shallow levels in the

Table 4. Predicted positions of the Ce levels in the band gap. All energies are in eV.

	YAG	LSC
VB	-0.77	-0.77
5d	-2.97	-4.93
	-1.20	-3.15
	-3.33	-4.39
	-5.52	-5.01
	-4.74	-7.70
4f	-7.51	-11.01
CB	-9.02	-9.02

gap above the SD levels. These levels could be the trapping levels observed by Viner *et al.* (1993). Unfortunately, there is not enough experimental data on LSC to discuss the validity of our predictions on LSC in more detail.

CONCLUSIONS

Our method is capable of accurately describing and predicting the Cu^{2+} $d-d$ transitions of Co-doped ZnO and ZnS. The prediction for the band gap and the position of the Cu levels in the band gap is rather inaccurate. To improve this situation we at least need a better description of the position of the non-polar and wurtzite bands. Further calculations on larger clusters will be performed.

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