Calculation of the Band Gap Energy and Study of Cross Luminescence in Alkaline-Earth Dihalide Crystals.

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The band gap energy as well as the possibility of cross luminescence processes in alkaline-earth dihalide crystals have been calculated using the ab initio Perturbed-Ion (PI) model. The gap is calculated in several ways: as a difference between one-electron energy eigenvalues and as a difference between total energies of appropriate electronic states of the crystal, both at the HF level and with inclusion of Coulomb correlation effects. In order to study the possibility of occurrence of cross luminescence in these materials, the energy difference between the valence band and the outermost core band for some representative crystals has been calculated. Both calculated band gap energies and cross luminescence predictions compare very well with the available experimental and theoretical results.

KEYWORDS: band gap, cross luminescence, alkaline-earth dihalide scintillators.

I. INTRODUCTION

An important revival of the interest in luminescent materials is presently observed. This is mainly due to their practical applications in several fields, like nuclear spectroscopy, dosimetry, or two-dimensional detectors used for example in medical screens and crystallography to mention a few. Frequently these luminescent materials turn out to be single ionic crystals. Alkaline-earth dihalide crystals (pure or doped) are between the most important inorganic scintillators. Within this class of materials, fluoride crystals with the fluorite structure (CaF$_2$, SrF$_2$ and BaF$_2$) are the best known scintillators, and recent work has been devoted to their study when doping with lanthanum, Mn$^{2+}$, and Ce$^{3+}$ impurities. Chlorides are less used materials, though recent theoretical work on the scintillation properties of SrCl$_2$:Ce$^{3+}$ samples has been reported. Experimental studies of the luminescent emission from impurity centres in SrCl$_2$ and BaCl$_2$ single crystals have also been reported. Before formulating a model for the description of doped complexes like BaF$_2$:Ce$^{3+}$, fundamental information about the pure crystals should be compiled. Here, as a first step towards a more profound comprehension of optically active impurities, we have focused our interest on the description of the pure materials.

The calculation of the energy band gap ($E_{\text{gap}}$) of these materials is important for several reasons: when doping the crystals, it becomes necessary to locate the impurity levels in the band gap of the pure crystal. Furthermore, the gap is a very important quantity in the first step of the scintillation process, namely absorption of radiation leading to formation of electron-hole pairs. This step influences the global efficiency of the scintillator. Last but not the least, it is also important from the theoretical point of view, and it gives information on the goodness of the model.

The discovery of the fast luminescent component in the emission spectra of BaF$_2$ and the cross-luminescence (CL) mechanism has brought about a large activity in the field of scintillator research. BaF$_2$, with a 0.8 ns CL component is the inorganic scintillator with the fastest response. This makes BaF$_2$ a very attractive material for applications in positron emission tomography (PET), where a good time resolution is of paramount importance in order to suppress random coincidences and to use time-of-flight information. BaF$_2$ has also been proposed as a candidate material for detectors in high-energy physics, most recently at the new proton colliders SSC and LHC at CERN, where the important requirement is to differentiate events from different bunch crossings. In the CL mechanism, an electron is first promoted from the core band to the conduction band, leaving a hole in the core band, and next a valence band electron recombines with that hole giving rise to cross-luminescence and leaving a hole in the valence band (see Fig. 1). That hole can recombine then with the electron promoted to the conduction band, leading to selftrapped exciton (STE) emission. An important parameter in the study of cross luminescence is the energy separation between valence and core bands ($\Delta E_{\text{VC}}$), as it determines, for a given material, whether the occurrence of CL is possible or not. Specifically, this energy difference must be smaller than the band gap energy ($E_{\text{gap}}$) in order to observe CL. This is associated to the fact that, if the emission energy is smaller than the band gap, photon reabsorption inside the crystal or Auger emission of electrons are not possible.

In the past, there has been a considerable deal of work devoted to calculate the band structure of some of these ionic crystals, mainly those with the fluorite structure. The purpose of the research carried out here is to study pure AX$_2$ crystals, where $A$ stands for Mg, Ca, Sr, Ba and $X$ for F, Cl, Br, I, by using instead a cluster approach. To this end we have used the Perturbed Ion (PI) model. The present work is an extension of our own previous research on ionic crystals, where first we calculated the band gap energies of alkali halide crystals and then studied several properties of the scintillators NaI:Tl$^+$ and CsI:Tl$^+$. Given the great technological significance of cross luminescence processes, we have also calculated the energy difference between the valence band and the upmost core band for some AX$_2$ materials, and compared it with the relevant gap energy. This allows to predict the occurrence of cross luminescence in these solids. Cluster approaches have been used...
in the past to study the CL mechanism in alkaline-earth fluorides by Andriessen et al.\textsuperscript{34} and also by Ikeda et al.\textsuperscript{35,36}

The paper is structured as follows: In the next section we show how to apply the PI model to the calculation of gap energies between valence and conduction bands and between valence and core bands. The results of the calculations are presented and discussed in section III. Section IV presents our conclusions.

II. CALCULATIONAL METHOD

A. Brief summary of the theoretical model

A detailed description of the PI method has been given in our previous work on band gap energies of alkali halide crystals\textsuperscript{27,28} and in the original work of Kunz and coworkers,\textsuperscript{37} so here we just give a brief resume. In order to calculate the electronic structure of ionic solids, and in particular the band gap energy, the traditional band theory approach could be directly applied. For doped crystals, however, the translational symmetry is lost, and the Bloch’s theorem does not apply. Cluster models, which have been successfully applied to the analysis of local crystal properties, provide an alternative, although any cluster approach has some inherent difficulties in dealing with delocalized conduction states (see, for example, ref.\textsuperscript{34}). The cluster approximation is based on a partition of the solid into a “cluster region” and “the rest of the crystal”. The main issues one has to address when using this approximation are the following: a) the election of the best partition of the crystal into “cluster” and “host” regions; b) a proper quantum mechanical description of the finite cluster; c) a precise description of the ions surrounding the cluster (this is necessary for a proper account of cluster-lattice interactions); and d) the consistency between the descriptions of the finite cluster and of the surroundings. As a matter of fact, issues c and d have received less attention than issues a and b. Issue d is frequently neglected, and the “rest of the crystal” is often simulated just by using point charges.\textsuperscript{27} More accurate lattice models have been considered, for example by Winter, Pitzer and Temple\textsuperscript{29} who introduced effective core potentials to describe the lattice cations nearest to the cluster. The significance of the cluster-lattice consistency was stressed by Kunz and coworkers\textsuperscript{27} who included the so-called localizing potentials in the description of the cluster. Besides, issue a is also a delicate point, as it is difficult to avoid surface effects at the cluster boundary when studying bulk properties with cluster models.

In the PI model, the “cluster” is reduced to its minimum size, a single ion, and cluster-lattice interactions are described in the framework of the Theory of Electronic Separability (TES) of Huzinaga et al.\textsuperscript{38} Being the “cluster” a single ion, boundary effects are avoided right from the start. Furthermore, the cluster approximation can be rigorously formulated within the TES, as cluster-lattice orthogonality is a fundamental requirement of that theory. Each ion in the lattice acts on the “cluster” density through an effective potential which includes nuclear, Hartree and exchange contributions. The electronic structure of each inequivalent ion in the crystal is self-consistently determined, thus avoiding the use of empirical parameters.\textsuperscript{27} Another feature of the PI model is that it does not invoke the Molecular Orbital LCAO approximation. The one-center character of the model leads to a large computational-time saving compared to any multi-center cluster approach.

The atomic-like orbitals used to describe each ion are expanded into a large set of Slater type (STO) basis functions\textsuperscript{40} because of their superior performance. The outputs of the PI model are a set of crystal-adapted wave functions for each ion, which are fully consistent, in the Self-Consistent-Field (SCF) sense, with the lattice potential, and the effective energies of the corresponding ions in the field of the crystal lattice. The effective energy is written as a sum of the net energies (or self-energies) of the ions in the crystal and the ion-lattice interaction energies. Once those quantities have been obtained, the total crystal energy is obtained as a sum of monocentric terms, involving net energies, and bicentric contributions coming from the interaction between ions.\textsuperscript{27} A correlation energy correction following the formula: $E_{\text{corr}} = E_{\text{CHF}} - E_{\text{CI}}$, is added to the net energies.\textsuperscript{38} The PI method is particularly well suited to model an impurity center in a crystal because we can describe the ions surrounding the impurity with lattice-consistent wave functions, rather than with Hartree-Fock free-ion wave functions. Applications of the PI model to these problems can be consulted in refs.\textsuperscript{29,41}.

B. Band gaps

The band gap energy can be defined as the difference between the two following energies: a) the energy necessary to ionize the crystal by removing an electron from the top of the valence band (the threshold energy $E_t$); b) the energy gained by putting an electron at the bottom of the empty conduction band of the perfect crystal (the electronic affinity $\chi$):

$$E_{\text{gap}} = E_t - \chi. \quad (1)$$

To calculate $\chi$ we have to model an electron in the conduction band, that is in a delocalized state. The strong ion-lattice orthogonality required by the TES would force that electron to be localized on a given ion. We can, however, obtain a reasonable description of a delocalized conduction state by relaxing some of the orthogonality requirements imposed by the TES (see below). The electronic affinity $\chi$ is always a small quantity, close to zero for all these ionic materials.\textsuperscript{38,42} and our description gives values of the correct order of magnitude (a few tenths of eV). As typical errors in measured gaps are $\sim 0.5$ eV, the quantitative determination of the band gap energy is not critically affected by our approximations. All the calculations are performed at the experimental crystal structures.\textsuperscript{27,28} We proceed now to calculate the band gap energy in several ways. In a first calculation we approximate the
threshold energy $E_t$ by the energy eigenvalue (with opposite sign) of the highest occupied anionic orbital obtained in a PI calculation for the pure crystal at the HF level. This corresponds to the Koopmans’ approximation to the ionization potential. To obtain $\chi$, we simulate a singly charged alkaline-earth cation $A^+$ as an impurity in the field created by the pure crystal ($A^+: A^{2+}X^-_2$), and equate $\chi$ to the eigenvalue (with opposite sign) of the outermost s-orbital of that cation. To allow for the delocalization of the orbital over a substantial region of the crystal, we enlarge the basis set taken from Clementi and Roetti for $A^+$ with some diffuse functions and relax the orthogonality requirement between that s orbital and the surrounding lattice. This eigenvalue is close to zero (in no case is $-\epsilon$ greater than 0.2 eV). According to the definition (eq. 1), our first calculation of the gap reads:

$$E_{gap} = \epsilon_{ns}(A^+: A^{2+}X^-_2) - \epsilon_{mp}(X^-: A^{2+}X^-_2)$$

(2)

where $n=3,4,5,6$ (m=2,3,4,5) for $A^+$, $Ca$, $Sr$ and $Ba$ ($F$, $Cl$, $Br$ and $I$, respectively. In recent studies, de Boer and de Groote have shown that the conduction band of those ionic crystals formed with alkali or alkaline-earth cations is associated mainly to anionic levels. Thus, we have checked the effect of centering the conduction electron on an anionic site. As long as we enlarge the anion basis set with enough diffuse functions, the value of $\chi$ is almost insensitive to the election of specific center for the conduction electron.

In a second calculation, the band gap energy is obtained as a difference of total energies, as in a typical ΔSCF calculation. This approach includes orbital relaxation effects, improving thus over Koopmans’ approximation. The independent processes of removing an electron from a halogen anion and of placing that electron on the conduction band read now:

$$E_t = E_{\text{crystal}}(X^0: A^{2+}X^-_2) - E_{\text{crystal}}(A^+: A^{2+}X^-_2),$$

(3)

and

$$\chi = E_{\text{crystal}}(A^{2+}X^-_2) - E_{\text{crystal}}(A^+: A^{2+}X^-_2),$$

(4)

respectively. $E_{\text{crystal}}(X^0: A^{2+}X^-_2)$ represents the energy of the crystal with a single neutral halogen impurity and $E_{\text{crystal}}(A^+: A^{2+}X^-_2)$ the energy of a crystal with a delocalized electron although centered on an alkaline-earth ion (see above). In the process of calculating the energies of the systems $X^0: A^{2+}X^-_2$ and $A^+: A^{2+}X^-_2$, the ions surrounding the impurities are described with the lattice-consistent wave functions obtained in the PI calculation of the pure crystal. With these assumptions, $E_t$ and $\chi$ reduce to a difference of effective energies

$$E_t = E_{\text{eff}}(X^0: A^{2+}X^-_2) - E_{\text{eff}}(X^-: A^{2+}X^-_2)$$

(5)

$$\chi = E_{\text{eff}}(A^{2+}X^-_2) - E_{\text{eff}}(A^+: A^{2+}X^-_2).$$

(6)

$E_{\text{eff}}(X^0: A^{2+}X^-_2)$ is the effective energy of a neutral halogen atom in an otherwise perfect crystal $A^{2+}X^-_2$, and a similar interpretation holds for the other effective energies (for details, consult refs. 28 and 56). $E_t$ gives the main contribution to $E_{gap}$, while $\chi$ only provides a small correction of magnitude $\sim 0.2$ eV, as in the previous calculation. The ΔSCF calculations are performed at the HF and uCHF levels; the second ones include, besides orbital relaxation effects, correlation corrections to the HF energy.

### C. Cross luminescence

We extend now the previous expressions to the calculation of $\Delta E_{VC}$, the energy difference between valence and core bands. In some $AX_2$ crystals (see section III.C below), the core band nearest to the valence band is associated to the outermost p-orbitals of the $A^{2+}$ cation, but in some others it is associated to the outermost s-orbitals of the $X^-$ anion (when the anionic s-eigenvalue is less negative than the cationic p-eigenvalue). Our first calculation is again a simple difference between energy eigenvalues (Koopmans’ approximation). For the first case:

$$\Delta E_{VC} = \epsilon_{mp}(X^-) - \epsilon_{n-1,p}(A^{2+}),$$

(7)

and in the second case:

$$\Delta E_{VC} = \epsilon_{mp}(X^-) - \epsilon_{ms}(X^-),$$

(8)

with a notation consistent with eq.(2). We can improve the calculation of $\Delta E_{VC}$ allowing for the relaxation of the hole states created in the curse of the CL process (see Fig. 1). We obtain first the core binding energy, $E_C$. Allowing for orbital relaxation, the expression for $E_C$ is similar to eq.(5):

$$E_C = E_{\text{eff}}(A^{3+}: A^{2+}X^-_2) - E_{\text{eff}}(A^{2+}: A^{2+}X^-_2),$$

(9)

if the core band is formed by the outermost cationic p-orbitals, or

$$E_C = E_{\text{eff}}(X^0(ms^1mp^6): A^{2+}X^-_2) - E_{\text{eff}}(X^-: A^{2+}X^-_2),$$

(10)

if the core band is formed by the outermost anionic s-orbitals (the notation $X^0(ms^1mp^6)$ indicates the electronic configuration of the halogen species after removing one electron from the ns orbital). $E_C$ is the energy necessary to remove an electron from the core band out of the crystal. By substracting from this energy the threshold energy of the crystal, given in eq.(5), we obtain the following approximation for the energy difference between core and valence bands:

$$\Delta E_{VC} = E_C - E_t.$$  

(11)

As before, the ΔSCF calculations are carried out at the HF and uCHF levels of theory.

### III. RESULTS AND DISCUSSION

An important part of the whole process involves to solve the electronic structure of the pure crystal. The
PI model is a general method for dealing with crystalline compounds of any spatial group, and the only inputs required are the spatial group and the lattice constants. CaF₂, SrF₂, BaF₂ and SrCl₂ adopt the fluorite structure (Pm3n in the international notation for spatial groups), MgF₂ a rutile-type structure (P4₂/mnm), CaCl₂ and CaBr₂ adopt distorted rutile structures (Pnma), MgCl₂ has the cadmium chloride structure (R3m), and MgBr₂, MgI₂ and CaI₂ the cadmium iodide structure (P53m). Finally BaCl₂, SrBr₂ and BaI₂ adopt the PbCl₂ structure (Pbnnm). The treatment of complicated crystalline structures is not a challenge for the PI calculations. Experimental geometries have been obtained from ref. 51, except those of BaCl₂, SrBr₂ and BaI₂, which have been taken from refs. 52, 53 and 54, respectively. In the Pbnnm structures the two anions are in slightly nonequivalent positions, so they have different eigenvalues and effective energies. To calculate the threshold energy in these cases we will take out from the crystal the least bound p-electron, which corresponds to an anion X⁻ in a definite site. In all the other cases, anions are in equivalent positions.

A. Band gaps

Results of the calculated band gaps of fifteen alkaline-earth dihalide crystals are presented in Table I. We give the calculated gaps at three different levels of theory and compare these with experimental results whenever they are available. We have collected the experimental results from several sources. The ∆CHF gaps from eq. (2) show the expected behavior in ionic solids, namely, the band gap decreases when moving down the periodic table along the alkaline-earth (halogen) column, leaving fixed the halogen (alkaline-earth) ion. The influence of a different spatial symmetry does not affect at all these trends, so it seems that its effect on band gap energies is small. Comparison to experimental values shows a systematic overestimation of the gap. The gaps obtained by the ∆SCF(HF) procedure are smaller than those calculated by subtracting eigenvalues. Re-evaluation of correlation, the band gap energies change in the correct direction both for fluorides and chlorides, increasing the gap in the first group and decreasing it in the second group. The larger response of the anionic density cloud to correlation effects is also responsible for this improvement. On the other hand, ∆Eₜ at this level but not in the previous calculation is the main reason responsible for this effect. The influence of orbital relaxation on ∆Eₜ is rather negligible. We observe for the ∆SCF(HF) method an underestimation of the band gap energies of fluorides but still an overestimation for chlorides. Inclusion of Coulomb correlation effects is crucial to achieve quantitatively good results, as the ∆SCF(uchf) calculations show. Upon inclusion of correlation, the band gap energy change in the correct direction both for fluorides and chlorides, increasing the gap in the first group and decreasing it in the second group. The larger response of the anionic density cloud to correlation effects is also responsible for this improvement. On the other hand, ∆Eₜ remains practically unchanged, as before.

Theoretical studies of CaF₂ and MgF₂ have been carried out by Catti et al. using CRYSTAL, an ab initio periodic Hartree-Fock program. They have obtained ground state properties, like equilibrium geometries or elastic constants, and also have shown the calculated band structure for these crystals. The band gap energies obtained are 21 eV and 20 eV for CaF₂ and MgF₂, respectively. The HF approximation tends to overestimate the gap in ionic crystals. At first sight, it seems that these results should be compared to our ∆CHF calculation, which, although still overestimating the gap, gives closer agreement with experiment. However, both calculations should not be directly compared. In ref. the gap is identified with the energy difference between the highest occupied and the lowest unoccupied orbitals, that is a LUMO – HOMO calculation. In our ∆CHF calculation, while E₁ can be identified still with the HOMO, χ cannot be identified with the LUMO anymore, as it is the eigenvalue (with opposite sign) of an occupied orbital. We think that this fact, together with the appropriate inclusion of diffuse basis functions in the description of the conduction state to simulate delocalization (diffuse valence orbitals on cations were not included in the above mentioned works) are the main reasons for our improvement over their results. This shows that even an energy difference between eigenvalues can be a quite good approximation when the conduction state is more realistically described.

More recently, Ikeda et al. have calculated the band gaps of CaF₂, SrF₂ and BaF₂ by using active clusters of different sizes embedded in a field of point charges representing the Coulomb potential created by the crystals. The electronic structure of those active clusters is solved by the use of the discrete variational (DV) Xα method. The band gaps obtained by Ikeda et al. show some dependence on the size of the active cluster employed, but for a fixed cluster size, show the correct trend, that is a systematic decrease of the band gap when changing the cation size from Ca²⁺ to Ba²⁺. A meaningful quantitative comparison with our set of results is not direct, because their calculation identifies the gap with a difference between one-particle electronic levels (like our ∆CHF calculation), but including correlation effects at the same time footing as exchange through the Xα model. Nevertheless, the gaps they obtain with the (F₇A₄)⁺ cluster are almost identical to our most accurate ∆SCF(uCHF) results.

B. Cross luminescence

Now we turn to the calculation of the energy differences involved in cross luminescence processes. We show in Table II the energy eigenvalues (with opposite sign) of the core orbitals nearest to the valence band, for four representative crystals. We note that the outermost core band is formed by cationic alkaline-earth p-states in SrF₂, BaF₂ and BaCl₂, and by anionic halide s-states in SrCl₂. So the energy of the core band level (E₁C) is, in the Koopmans’ approximation, identified with the 3s eigenvalue of Cl⁻ in SrCl₂, with the 5p eigenvalue of Ba²⁺ in BaF₂ and BaCl₂ and with the 4p eigenvalue of Sr²⁺ in SrF₂. The energy differences ∆EVC are shown
at three levels of theory in Table III, together with experimental results for fluorides as given in ref. [14]. The $\Delta_{HF}$ calculation underestimates $\Delta E_{VC}$ in these materials, because the Koopmans’ approximation overestimates the threshold energy $E_t$ more than $E_C$. We can appreciate this item more clearly when passing from the $\Delta_{HF}$ to the $\Delta$SCF(HF) calculation. Here, contrary to the band gap calculation (see Table I), $\Delta E_{CV}$ increases in SrF$_2$, BaF$_2$ and BaCl$_2$, showing that anionic orbital relaxation effects are more important than cationic ones: both $E_t$ and $E_C$ are lower than in the $\Delta_{HF}$ calculation, but the lowering of $E_t$ is more important, resulting in an increasing of $\Delta E_{CV}$. In SrCl$_2$, such behaviour is not observed, and this is due to the fact that the core band is an anionic band. The $\Delta$SCF(HF) result lowers slightly the magnitude of $\Delta E_{VC}$ for this crystal. This effect is very small, however, showing that the error in applying Koopmans’ approximation is nearly the same for $E_t$ and $E_C$ in this case. The $\Delta$SCF(HF) results include orbital relaxation, and the different relaxations of core and valence holes are responsible for all the effects discussed. Finally, the effect of Coulomb correlation ($\Delta$SCF(uCHF) column) is, except for BaCl$_2$, very small, showing that the corrections introduced in the calculation of $E_t$ and $E_C$ are similar, and tend to cancel out in the energy difference. Then it seems that correlation tends to shift occupied bands by a rather constant amount with respect to the conduction band, leaving energy differences between occupied bands unaffected, at least for fluorides.

In the fifth column of Table III we show the possibility of occurrence of CL in these crystals. As we explained in the introduction, if the energy difference $\Delta E_{VC}$ between the valence and the outermost core band is smaller than the energy gap $E_{gap}$ between conduction and valence bands, then it is possible to observe CL. This condition holds in BaF$_2$, so we can assert that CL is possible, as it has been experimentally observed [28,29]. Regarding SrF$_2$, we obtain that $\Delta E_{VC}$ is larger than $E_{gap}$ by 1.7 eV, so cross luminescence is not predicted by our calculations. The situation is even more unfavourable for SrCl$_2$ and BaCl$_2$ crystals (for which we obtain a value for $\Delta E_{VC}$ larger than the corresponding band gap energy by 8 eV) as well as for the rest of AX$_2$ crystals not shown in Table III. The combination of fluorine and barium, which gives the most ionic compound between those studied in this work, gives a favourable limiting case for CL applications. Barium is the cation with the smallest ionization potential in the alkaline-earth series, so it is easier to remove an electron from the 5p orbital of Ba$^{2+}$ than from other alkaline-earth cations. This leads to a lower value of $E_C$ for barium compounds. On the other hand, fluorides show the largest band gap energies between alkaline-earth dihalides systems (as in simple alkal halide crystals [4]), because it is more difficult to remove an electron from a F$^-$ anion than from any other halide anion. As a consequence, the difference in eq.(11) is the lowest in magnitude.

The cluster model calculations performed by Ikeda et al. [14] lead to the same conclusions, although the specific value obtained for $\Delta E_{VC}$ again depends a little on the size of the active cluster. They obtain a band gap for BaF$_2$ which is 3 eV larger than $\Delta E_{VC}$, so their calculations predict also the occurrence of cross luminescence for BaF$_2$. The band gap of CaF$_2$ is smaller than the energy difference between the valence and core bands. For SrF$_2$, the values of $E_{gap}$ and $\Delta E_{VC}$ are similar, again in agreement with our results.

IV. CONCLUSIONS

We have calculated the band gap energies of fifteen alkaline-earth dihalide AX$_2$ crystals. For some of these crystals we have also calculated the energy difference between core and valence bands in order to study the possibility of cross luminescence (CL) processes. We have followed two different ways to estimate these quantities: first, we have taken differences between energy eigenvalues, and next we have carried out $\Delta$SCF calculations, both at the HF level and with inclusion of correlation effects. To this end we have used the Perturbed Ion (PI) model, supplemented with some additional assumptions to deal with an electron at the bottom of the conduction band. This is a cluster-type model which achieves full lattice-cluster consistency. Correlation effects have been included using a model proposed by Clementi [44]. Within the PI model we can deal with crystals of any spatial point group symmetry without any problem. The significance of an accurate estimate of the band gap energy in these crystals as a preliminary requirement for the study of luminescence properties has been pointed out, as well as the importance of the energy difference between core and valence bands in the CL process. The calculation of the last quantity is possible because our calculation is an all-electron calculation and does not invoke any approximations like frozen-core treatments. Orbital relaxation of the core hole is also allowed. However, one has to recognize that our method gives no dispersion for the core or valence bands so the applicability is restricted to cases when these bands are narrow enough.

Overall we have obtained a rather good estimation of the energy band gaps, with a computational effort which is much less than that required by any other cluster multicenter approach or by standard band structure methods. Gaps compare quantitatively well with experimental results whenever they are available, and favourably to previous theoretical calculations for fluorides. The CL mechanism has been predicted as possible only in BaF$_2$, in agreement with the experimental observations.

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1) G. Blasse and B. C. Grabmaier: Luminescent Materials (Springer Verlag. Berlin, 1994).
Captions of figures

Figure 1
Schematic view of the cross luminescence process.
TABLE I. Calculated band gaps, compared to available experimental values. SPG gives the spatial point group of the crystal, in the international notation. $\Delta \epsilon_{HF}$ is a difference between one-particle orbital energy eigenvalues. $\Delta \text{SCF}$ refers to a difference between the total energies of the crystal in appropriate electronic states (see text). All energies are given in eV.

| Crystal | SPG         | $\Delta \epsilon_{HF}$ | $\Delta \text{SCF(HF)}$ | $\Delta \text{SCF(uCHF)}$ | Exp. |
|---------|-------------|-------------------------|--------------------------|---------------------------|------|
| MgF$_2$ | $P4_2/mnm$  | 14.3                    | 10.8                     | 12.8                      | 12.4$^a$ |
| CaF$_2$ | $Fm3m$     | 12.7                    | 10.0                     | 11.9                      | $12.0^b$ |
| SrF$_2$ | $Fm3m$     | 12.4                    | 9.7                      | 11.5                      | $11.1^b$ |
| BaF$_2$ | $Fm3m$     | 12.0                    | 9.2                      | 11.0                      | $10.5^b$ |
| MgCl$_2$| $R3m$      | 10.7                    | 9.2                      | 7.9                       | 7.5$^c$ |
| CaCl$_2$| $Pnmm$     | 10.2                    | 9.1                      | 8.0                       | $6.9^c$ |
| SrCl$_2$| $Fm3m$     | 9.6                     | 8.5                      | 7.4                       | 7.5$^c$ |
| BaCl$_2$| $Pbnm$     | 8.9                     | 7.8                      | 6.8                       | $7.0^c$ |
| MgBr$_2$| $P3m1$     | 10.5                    | 9.3                      | 7.6                       | -     |
| CaBr$_2$| $Pnmm$     | 9.7                     | 9.0                      | 6.7                       | -     |
| SrBr$_2$| $Pbnm$     | 8.5                     | 8.0                      | 6.5                       | -     |
| BaBr$_2$| $Pnma$     | 8.3                     | 7.7                      | 6.0                       | -     |
| MgI$_2$ | $P3m1$     | 9.9                     | 9.2                      | 7.2                       | -     |
| CaI$_2$ | $P3m1$     | 9.2                     | 8.4                      | 6.3                       | -     |
| BaI$_2$ | $Pbnm$     | 8.1                     | 7.4                      | 5.4                       | -     |

$^a$: Ref. 57
$^b$: Ref. 46
$^c$: Ref. 58

TABLE II. One-particle orbital energy eigenvalues for the outermost p-orbital of the $A^{2+}$ cation and the outermost s-orbital of the $X^-$ anion. All energies are given in eV.

| Crystal | $\epsilon(A^{2+})$ | $\epsilon(X^-)$ |
|---------|---------------------|------------------|
| SrF$_2$ | 23.6 (4p)           | 36.9 (2s)        |
| BaF$_2$ | 17.7 (5p)           | 36.3 (2s)        |
| SrCl$_2$| 27.0 (4p)           | 25.6 (3s)        |
| BaCl$_2$| 20.4 (5p)           | 24.9 (3s)        |

TABLE III. Energy differences between the upmost core band level and the valence band level calculated from different theoretical methods (as in Table I), and possibility of cross luminescence (CL). All energies in eV.

| Crystal | $\Delta \epsilon_{HF}$ | $\Delta \text{SCF(HF)}$ | $\Delta \text{SCF(uCHF)}$ | CL | Exp. |
|---------|-------------------------|--------------------------|---------------------------|----|------|
| SrF$_2$ | 11.2                    | 13.2                     | 13.2                      | no | ?    |
| BaF$_2$ | 5.7                     | 7.8                      | 7.7                       | yes| yes  |
| SrCl$_2$| 16.0                    | 15.8                     | 15.4                      | no | -    |
| BaCl$_2$| 11.4                    | 12.2                     | 14.8                      | no | -    |