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CONDENSED-MATTER SPECTROSCOPY

Cross Luminescence of BaF_2 Crystal: Ab Initio Calculation

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Abstract—Using ab initio methods and taking into account the lattice relaxation and polarization caused by the occurrence of the core hole, we have studied theoretically the cross luminescence in barium fluoride crystals in terms of the embedded-cluster approach. Two schemes of modeling of the core hole have been performed—in the form of an additional point charge and in the form of the 5*p* state of the barium ion. Calculations have been done both by the Hartree–Fock method and by the density functional method. We have showed that the deformation of the lattice caused by the occurrence of the core hole leads to states localized on fluorine ions of the nearest environment splitting off from the valence band of the BaF_2 crystal. The cross-luminescence bands at 5.7, 6.3, and 7.1 eV are caused by transitions from these localized states. We have also showed that the low-energy edge of the cross luminescence is formed by transitions from states that are localized on ions of the second coordination sphere.

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1. INTRODUCTION

Barium fluoride crystals stand out among alkali-earth fluorides because they possess such an important property as cross luminescence. The most significant feature of the electronic structure of the BaF_2 crystal is related to the value of the energy gap between occupied states of the anion and cation, which is more than two times smaller than the band gap. In this crystal the core–valence transitions (cross luminescence) were observed for the first time. These transitions make it possible to consider barium fluoride crystals as the most rapid known inorganic scintillators (with a decay time shorter than 1 ns) [1–4]. Basically, cross luminescence is of great interest as a form of optical transitions in solids. Therefore, during the 30-year period of investigations of cross luminescence, rather extensive experimental material has been accumulated. Thus, over the last decade, to study the intrinsic luminescence of barium fluoride, various types of excitation were used, such as vacuum ultraviolet radiation [5, 6], X rays [7, 8], synchrotron radiation [9–11], laser radiation [12], and electron beams [13, 14]. However, details of very interesting processes that proceed during the conversion of excitation energy into quanta of intrinsic luminescence remains to be clarified. In particular, it has not been clarified yet which role in the cross luminescence process is played by the relaxation of the lattice near the core hole [14–18], and the very question of the location of the core hole remains open [19, 20].

Answers to many questions can be given by theoretical investigations; however, there are only a few theoretical works devoted to the investigation of cross-luminescence barium-fluoride crystals. In the first work in this field, Ermakov et al. [21] calculated the density of states in occupied bands of alkali-earth fluorides using the method of expansion of the Green's function into a continued fraction. The authors of [22] performed LCAO calculations of the cluster $[Ba^{3+}F_8^-]^{5-}$. For cross luminescence, eight allowed transitions were obtained, which formed the radiation spectrum of the crystal. Good agreement between calculated and experimental luminescence spectra was obtained. It was assumed that the two luminescence bands in the BaF_2 crystal (at 5.6 and 6.4 eV) are caused by transitions from bonding and antibonding 2*p* fluorine orbitals, respectively. The authors of [23], using the self-consistent nonrelativistic method of Xα scattered waves, calculated the electronic structure of the molecular cluster $[CsCl_n]$ ($n = 6, 8, 12$). It was shown that the structure of the spectra of cross luminescence depends on the coordination number of anions in the crystal: one basic band is characteristic for the structure of rock salt $[AX_6]$ (such as RbF); two bands are characteristic for fluorite and CsCl $[AX_8]$. The shape of the calculated spectra agrees well with the experimental data for crystals with different coordination geometries.

All calculations in the works considered above were conducted using small clusters, i.e., under the assumption that the cross luminescence has a local character. The authors of [24] used a large cluster $[Ba_{19}F_{32}]^{+6}$ and the DV-Xα method to model the luminescence spectrum. Their calculated cross-luminescence spectrum reproduces three maxima of the experimental spectrum. They calculated that the main maximum, which is located at 5.6 eV, is predominantly formed by transitions from states localized on fluorine ions nearest to the central barium; i.e., core–valence transitions occur mainly between 5*p* orbitals of barium and 2*p* orbitals of fluorine ions nearest to it. Both higher-energy peaks (at 6.3 and 7.1 eV) are formed by transitions from states localized on fluorine ions of the second coordination sphere.

The calculations done in all these works show qualitative agreement with experiment and quite accurately reproduce the shape and position of the cross-luminescence spectrum. It was shown in all the works that the valence band of the crystal is predominantly formed by 2*p* states of fluorine ions; i.e., the hybridization of the $5pBa^{2+}$ and $2pF^-$ states is insignificant, which distinguishes this crystal from other systems (e.g., CsCl and CsBr [25]). However, all these works suffer from a substantial drawback: they do not take into account the polarization and deformation of the crystal lattice, even though the luminescence time is sufficiently long in order for electron and ion relaxation of the environment of the Ba^{2+} ion, which contains the core hole, to occur.

The objective of this work is to investigate theoretically the cross luminescence in barium-fluoride crystal using ab initio methods of quantum mechanics in terms of the model of embedded molecular cluster taking into account the relaxation and polarization of the lattice caused by the occurrence of the core hole.

2. METHODOLOGY OF CALCULATIONS

Theoretical calculations were performed by the embedded cluster method using the GUESS software package [26]. In the crystal lattice, a quantum-mechanical cluster was separated that contained a defect and its nearest environment. Around this cluster, ~700 atoms were separated, which were described classically with pair potentials (the classical region). To correctly reproduce the Madelung potential inside the system, the quantum cluster and the classical region were surrounded by ~7000 point motionless charges. The GUESS software package does not determine the electronic structure of the quantum-mechanical cluster but calls up another quantum-chemical program (in our case, this is Gaussian 03 [27]) and adds classical terms for finding the total energy of the system.

All calculations were performed by ab initio methods, the choice of which is a rather nontrivial question. At present, the Hartree–Fock method and the method of the density functional (DFT) are the most widespread ab initio methods. On the one hand, in Hartree–Fock calculations, electronic states frequently proved to be overly localized and transition energies proved to be overestimated because this method does not take into account correlations. On the other hand, the majority of density functionals yield overly delocalized electronic states and, consequently, underestimated transition energies. The reason for this behavior is taking into account nonphysical "self-action" of the electron, i.e., the Coulomb interaction of the electron with its own electron density. For the majority of functionals, it is impossible to get rid of this artifact.

There are also hybrid functionals, which, along with Hartree–Fock terms, contain DFT terms. Thus, the B3LYP functional contains 20% of the Hartree–Fock exchange and 80% of the Becke exchange functional. This functional was developed for thermochemical calculations; however, it can also successfully be used in calculations of defects in solids. As far as the degree of localization/delocalization of the electron density is concerned, the B3LYP functional is prone to delocalize it. Based on calculations of the geometry and optical properties of point defects in CaF_2 and SrF_2 crystals that were performed in [28, 29], one can conclude that, to ensure the correct degree of delocalization, the functional should contain 40% of the Hartree–Fock exchange and 60% of the Becke exchange. Precisely this functional was used in calculations of cross luminescence in the BaF_2 crystal by the density functional method.

We used the standard Huzinaga D95 basis set for fluorine ions and the LANL2DZ basis with the LANL2 pseudopotential for barium ions (the Hay–Wadt pseudopotential with a small core [30]). Excited states and energies of optical transitions were calculated both by the configuration interaction method (CIS) and by the time-dependent DFT (TD DFT) method.

The occurrence of positive point charges near the boundary of the cluster may distort the electron density distribution of the ground state and configuration of excited one-electron states. To avoid this, positive point charges around the cluster are replaced by pseudopotentials. Several dozen classical barium ions were replaced by the LANL1 pseudopotential (the Hay–Wadt pseudopotential with a large core).

For the classical region, pair potentials are required. We used parameters of Buckingham pair potentials for the BaF_2 crystal from handbook [31] and slightly modified them for our purposes (Table 1). Namely, we adjusted them so that the equilibrium value of the lattice constant obtained in the classical calculation would coincide with a value of 6.4 Å rather than with the experimental value of 6.2 Å. The value of 6.4 Å is more consistent with that obtained in [32, 33] from the minimum of the total energy upon modeling a defect-free BaF_2 crystal. In addition, the parameters were adjusted such that the elastic and dielectric constants agree with experimental data.

Table 1. Parameters of pair potentials

	A (eV)	ρ(Å)	C (eV Å^6)
Classical region			
Ba–Ba	6702	0.4105	0.37
Ba–F	1407	0.3285	0.27
F–F	2129	0.1084	88.95
Parameters for the interface region			
Ba_{iface}–Ba_{QM}	5500	0.4105	0.37
Ba_{iface}–F_{QM}	1450	0.3285	0.27
Parameters of the shell	Y(|e|)	k (eV Å^{-2})	
F	−1.9	19.53	

Note: A, ρ, and C are the parameters of the Buckingham potential $U(r) = A\exp(-r/\rho) - C/r^6$, Y is the shell charge, and k is the elastic constant.

3. RESULTS AND DISCUSSION

3.1. *Calculation of Cross Luminescence in the Cluster $[Ba_5F_8]^{+2}$*

As was noted above, there are several works devoted to theoretical investigation of cross luminescence in barium fluoride crystals. A substantial drawback of these works is that they do not take into account the lattice relaxation upon formation of a core hole at the central barium ion.

Assuming that the cross-luminescence process is local and determined by the cation and its nearest anion environment, to calculate the cross-luminescence process, it is sufficient to use a cluster that contains the barium ion and eight fluorine ions. However, for the cluster to be more stoichiometric, we added another four barium ions. As a result, we obtained the cluster $[Ba_5F_8]^{+2}$ with the D_{4h} symmetry (Fig. 1). In what follows, it will be shown that this cluster is convenient for calculation of the core hole in the form of an excited state, since, in this case, lattice relaxation processes do not reduce the cluster symmetry (upon appropriate choice of the excited state) and we can compare results of calculations.

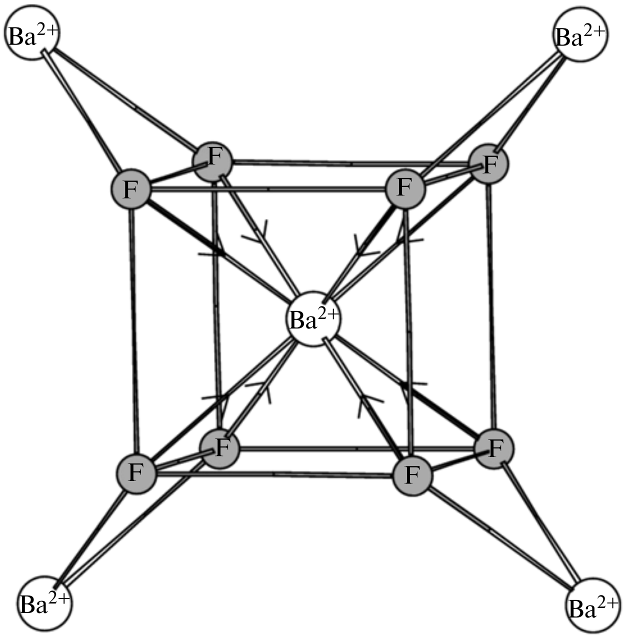

Fig. 1. Cluster $[Ba_5F_8]^{3+}$; arrows show directions of displacements of fluorine ions upon geometry optimization.

This series of calculations was performed both by the Hartree–Fock method and by the DFT method; in this case, transition energies were calculated, correspondingly, either by the CIS method (the configuration interaction taking into account single excitations) or by the TD DFT method.

Modeling of the core hole in the form of a positive point charge. Initially, we calculated the equilibrium geometry of the cluster $[Ba_5F_8]^{3+}$, which contains a core hole. The core hole is a high-lying excited state, which complicates the optimization of its geometry by the Hartree–Fock method or by the DFT method. Therefore, to optimize the geometry, we made the following assumption. Namely, we assumed that the core hole is strictly localized on the central barium ion; consequently, it acts on closely lying fluorine ions as an additional point positive charge that is located on the cation, which is transformed into Ba^{3+}. Therefore, we put an additional charge +1 on the core of the barium ion and admitted the relaxation of the cluster and the lattice. An additional point positive charge considerably deforms the nearest environment. Upon calculation by the Hartree–Fock method, nearest anions were displaced toward the central barium ion by 0.24 Å, which constitutes 8.7% of a ($a = 2.77$ Å is the Ba^{2+}–F^- distance in the defect-free crystal). Displacements of all the remaining ions did not exceed 0.05 Å. The relaxation energy (i.e., the difference between the total energies of the relaxed and nonrelaxed defects) for the hole on the central barium ion was 2.84 eV. Comparative data on calculation results by the Hartree–Fock and DFT methods are presented in Table 2.

Experimentally, the question of the shape of the cross-luminescence spectrum is of interest, since, as distinct from the photoelectron spectrum of the valence band of the BaF_2 crystal, the cross-luminescence spectrum exhibits two main maxima (at 5.7 and 6.3 eV) and a weaker peak at 7.1 eV.

The energies and intensities of core–valence transitions were calculated as follows. Since the core hole on the 5p state of Ba^{2+} is a high-lying excited state, it is impossible to reach convergence for this state using the method of a self-consistent field, which was already mentioned above. Therefore, instead of calculation of the core hole state, we modeled hole states on different levels of the valence band and, after that, we calculated transitions from these states to the 5*p* core band of Ba^{2+}. The shape of the spectrum in this approach is determined by the probability of transitions from the core hole level to a set of local states that belong to the valence band of the crystal. There are 12 states that correspond to gerade irreducible representations (i.e., states for which the dipole transition matrix element will be nonzero). States 5*p* of the central barium ion became separated from the core band of the crystal, with one of these states being directed along the fourth-order symmetry axis, while the other two proved to be degenerate. This splitting is determined only by the choice of the quantum cluster and its symmetry. The energy of transitions to the nondegenerate state is 0.1–0.2 eV higher than the energy of transitions to the degenerate states, which does not introduce substantial errors to the calculated transition energies.

Figure 2 presents calculated cross-luminescence spectra. The intensity was normalized to that of the main maximum (at 5.7 eV) of the experimental spectrum. The cross-luminescence spectrum calculated by the configuration interaction method agrees well with experimental data. The transition energies calculated by the TD DFT method are overestimated on average by 1 eV compared to experimental data, and, in this case, the relaxation energy of the system and maximal displacements of fluorine ions proved to be somewhat higher than those calculated by the Hartree–Fock method. The calculated cross-luminescence spectra show two main maxima and qualitatively agree quite well with experiment in both cases.

Modeling of the core hole as a 5*p* state of the barium ion. The core hole is predominantly formed by 5*p* states of the Ba^{2+} ion; therefore, it is also necessary to take into account the Jahn–Teller effect, according to which the geometric configuration of atoms cannot be stable if the charge distribution is asymmetric. In order to consider how the Jahn–Teller effect affects the character of cross luminescence, it is necessary to calculate the equilibrium geometry for a system in which the hole is modeled as an excited state.

For calculations, we chose the 5*p* state of the central barium ion, which is directed along the fourth-order symmetry axis (010). The geometry of the excited state was optimized by the CIS method. For the DFT calculation, it is required to optimize the geometry of the excited state, the energy of which is calculated by the TD DFT method; however, our software package did not provide the possibility of this procedure.

Results of our calculations show that, in this geometry, the relaxation energy is lower by 1 eV than in the preceding case, being 1.9 eV (Table 3). The displacements of ions are also almost two times smaller than in the case of modeling of the hole as a point charge. In this case, the displacements of fluorine ions along axes (100) and (001) were 0.09 Å, while those along axis (010) were somewhat smaller, being 0.06 Å. However, basic features of the behavior of the cross luminescence spectrum calculated using different methods were retained. The transition energies calculated by the TD DFT method are on the average higher by 1.5 eV than those calculated by the CIS method, which show quite good agreement with experiment (Fig. 2).

Table 2. Results of calculations in the cluster $[Ba_5F_8]^{3+}$; the core hole is modeled as a point positive charge

Parameter	Hartree–Fock method	DFT method	Experiment
Relaxation energy, eV	2.84	3.00	–
Maximal displacements of fluorine ions, Å	0.24	0.26	–
Positions of main maxima of cross luminescence, eV	5.4	6.4	5.7
	6.2	7.6	6.3

3.2. *Calculation of Cross Luminescence in the Cluster $[Ba_{13}F_{32}]^{-6}$*

The preceding calculations showed that quite good qualitative and quantitative agreement with experi-

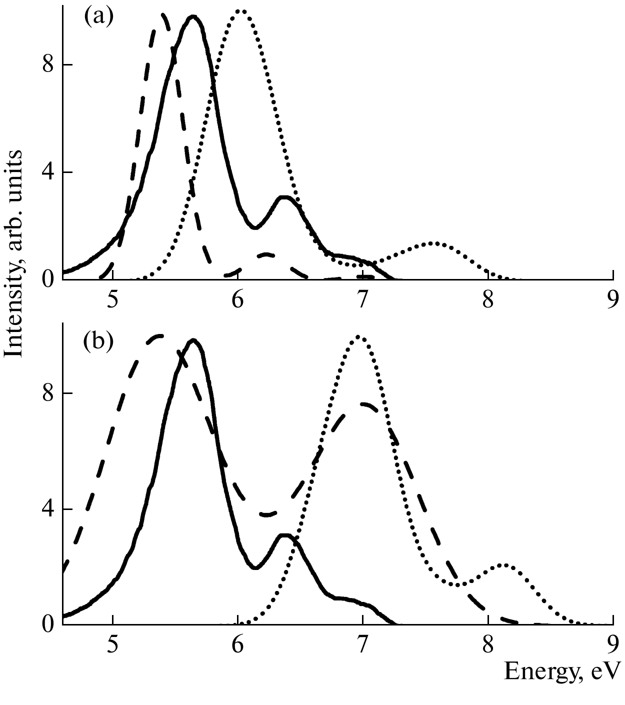

Fig. 2. Calculated cross-luminescence spectrum (dashed curve corresponds to the Hartree–Fock method, and dotted curve corresponds to the DFT method) in comparison with experimental data (solid curve): (a) the core hole was modeled as a point positive charge, and (b) the core hole was modeled as an excited state.

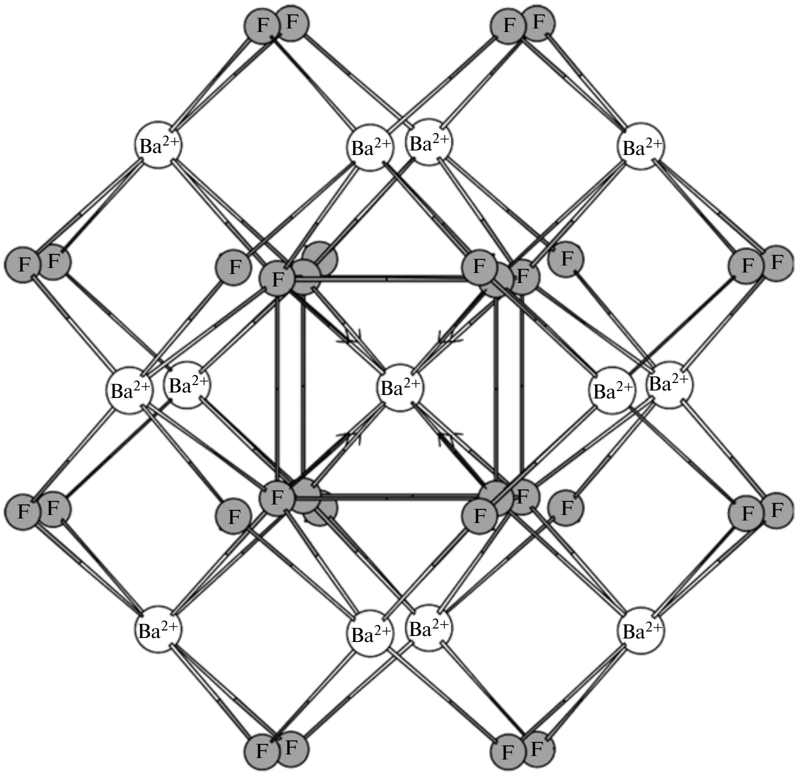

Fig. 3. Cluster $[Ba_{13}F_{32}]^{-6}$; arrows show directions of displacements of fluorine ions upon geometry optimization.

ment is achieved even with the use of the Hartree–Fock method and upon modeling the core hole as a point positive charge. However, in order to consider the question of the locality of the cross luminescence process, it is necessary to perform calculations in a cluster of a larger size. Therefore, for the following calculations, we used the cluster $[Ba_{13}F_{32}]^{-6}$ of the O_h symmetry (Fig. 3). For the calculations in this cluster, we used the Hartree–Fock method; excited states were calculated by the CIS method.

We calculated the equilibrium geometry of the cluster $[Ba_{13}F_{32}]^{-6}$, which contains the core hole as a point positive charge on the central barium ion. After the optimization of the geometry, the nearest anions were displaced toward the central barium ion by 0.24 Å, which constitutes 8.7% of the value of a (a = 2.77 Å is the Ba^{2+}–F^- distance in the defect-free crystal). Displacements of all the remaining atoms do not exceed 0.05 Å. Relaxation energy E_{rlx} was 2.97 eV.

Table 3. Results of calculations in the cluster $[Ba_5F_8]^{3+}$; the core hole is modeled as an excited state

Parameter	Hartree–Fock method	DFT method	Experiment
Relaxation energy, eV	1.9	–	–
Maximal displacements of fluorine ions, Å	0.14	–	–
Positions of main maxima of cross luminescence, eV	5.4 7.0	7.0 8.1	5.7 6.3

As a result of the geometry optimization, the positions of energy levels of neighboring ions were changed with respect to bands of the defect-free barium fluoride crystal. The displacement of anions led to a situation in which a number of states localized near the core hole were split off from the valence band, and the spacing between the occupied states of the anion and cation was decreased, which resulted in a shift of the cross-luminescence spectrum toward the low-energy range, as was observed in experiment [15, 16, 18]. These parameters were estimated from one-electron energies, which, in the majority of cases, do not yield complete agreement with experiment. However, we did not aim at estimating the energetic parameters of the crystal (this can be done with more reliable calculation methods, such as, e.g., the periodic model [33, 34]), but rather we wanted to estimate the influence of the lattice relaxation on these parameters.

After the optimization of the geometry, 24 states that correspond to 2*p* states of the eight fluorine ions nearest to the central barium ion (these fluorine ions were denoted as F_{NN}) were split off from the states of the valence band that are formed by 2*p* orbitals of anions. It is these states that are responsible for the for-

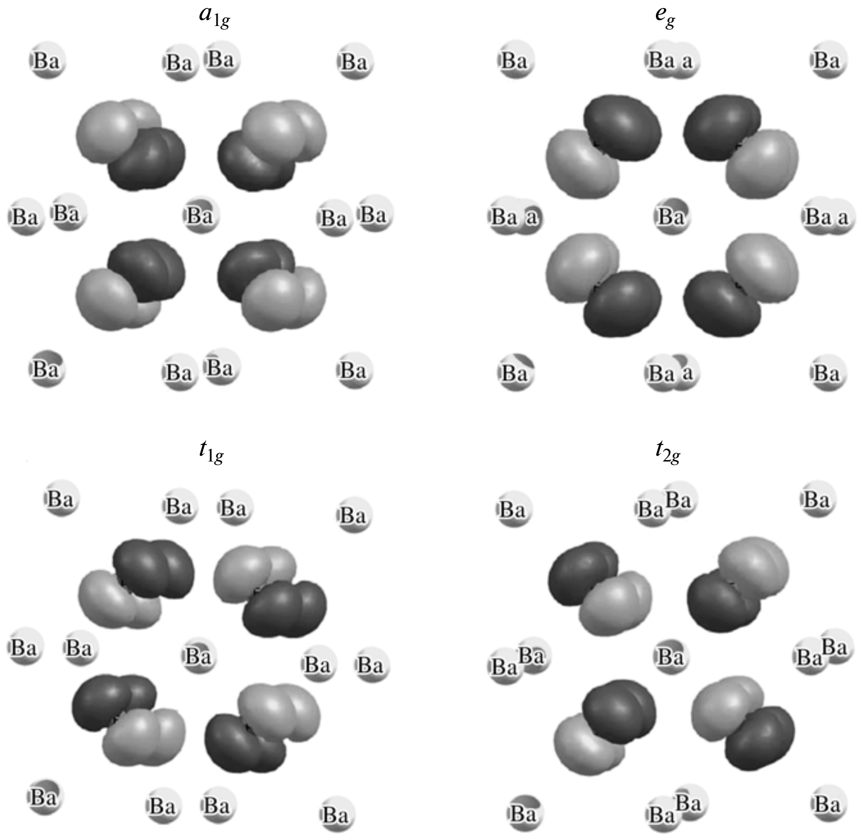

Fig. 4. States of the valence band of the BaF_2 crystal that correspond to the irreducible representations a_{1g}, e_g, t_{1g}, and t_{2g} of the O_h symmetry group. Only the nearest environment of the central barium ion is shown (8 fluorine ions and 12 barium ions).

mation of the main maxima of the cross luminescence spectrum. From the uppermost core band of the crystal, a group of states that correspond to the three 5*p* states of the central barium ion were also split off. Specific features of the energy level diagram are similar to those that were observed in cluster calculations of CsCl and CsBr crystals [25]; namely, the states of the valence band are divided into two groups (low-energy group I and high-energy group II). Therefore, one can expect that two main maxima will appear in the theoretical cross-luminescence spectrum.

In the dipole approximation, the transitions $a_{1g} \rightarrow t_{1u}$, $e_g \rightarrow t_{1u}$, $t_{1g} \rightarrow t_{1u}$, and $t_{2g} \rightarrow t_{1u}$, for which the transition matrix elements are nonzero, to the hole state t_{1u}, which is almost completely localized on the central barium ion and which corresponds to the irreducible representation t_{1u} of the O_h symmetry group, are allowed. There are 12 states that correspond to gerade irreducible representations. These are one a_{1g} state, two e_g states, three t_{1g} states, and six t_{2g} states (Fig. 4). The transition energies and oscillator strengths calculated for these states are presented in Table 4.

However, the energies of transitions from gerade states, which correspond to the 2*p* states of F_{NNN} ions (i.e., fluorine ions of the second coordination sphere), lie lower on the energy scale than those for transitions that correspond to cross luminescence. We failed to calculate hole states on these levels by the self-consistent field method; however, the transition energies can be estimated as follows. Let there be *n* states and let the transition energies from the first state to all the remaining ones be known (we denote them as $E_{1 \rightarrow 2}$, $E_{1 \rightarrow 3}$, ... $E_{1 \rightarrow n}$). The energy of the transition between states *m* and *n* can then be defined as follows: $E_{m \rightarrow n} = E_{1 \rightarrow n} - E_{1 \rightarrow m}$. The transition energies from F_{NNN} ions to the core band of the crystal were calculated pre-

Table 4. Basic characteristics of core–valence transitions calculated in the cluster $[Ba_{13}F_{32}]^{-6}$

Group of states	Transition	Transition energy, eV	Oscillator strength
F_{NN} I	$t_{2g} \longrightarrow t_{1u}$	5.38	0.2976
	$e_g \longrightarrow t_{1u}$	5.43	0.0151
	$a_g \longrightarrow t_{1u}$	5.47	0.4977
F_{NN} II	$t_{2g} \longrightarrow t_{1u}$	6.28	0.1027
	$t_{1g} \longrightarrow t_{1u}$	6.98	0.0445
F_{NNN}		4.35	0.0139

cisely in this way. The transition matrix elements (and oscillator strengths) were calculated based on the data of the output file of the program—the table of the configuration interaction and the list of molecular orbitals. This technique was verified in calculations of the cross-luminescence spectrum. The results almost completely coincide with those obtained using the method of calculation of the hole density on each state of the valence band. The calculation results show that the low-energy edge of cross luminescence can be caused by transitions from states of fluorine ions that are located in the second coordination sphere of the central barium ion.

It should be noted that the results of our calculations disagree with the results obtained in [22, 24]. The authors of [22] (calculation in the cluster $[Ba^{3+}F_8^-]^{5-}$) obtained only 8 states from which transitions to the core band are allowed, although in our calculations, there are 12 such states. The authors of [24] (calculation in the cluster $[Ba_{19}F_{32}]^{+6}$) did not take into account transitions from states that correspond to the irreducible representation t_{1g} of the O_h group, although transitions from these states to the hole state t_{1u} are also allowed. In addition, in that work, calculations in which were performed without taking into account the lattice relaxation, it was stated that only the main cross-luminescence maximum (at 5.7 eV) is caused by transitions from states that are localized on the nearest fluorine ions. The remaining two cross-luminescence maxima, which lie at higher energies (6.3 and 7.1 eV), are obtained as a result of transitions from states that are localized on fluorine ions of the second coordination sphere, with the states a_{1g} and e_g being also involved in the formation of these maxima. However, according to our results, all three cross-luminescence maxima are formed by transitions from fluorine ions of the nearest environment, while states localized on more distant fluorine ions form the low-energy edge of the cross luminescence.

There are another two questions that should be discussed before we pass on to the final conclusions of this work. The calculated spectra shown in Fig. 2a show a rather uncharacteristic feature, namely, energies calculated by the DFT method prove to be about 1 eV higher than those calculated by the CIS method, whereas, when we discussed the drawbacks of these methods, we pointed out that they show quite a reverse behavior; namely, the DFT methods underestimate transition energies, while the CIS method overestimates them. A second, somewhat paradoxical, feature of our results is that the best agreement with experiment was obtained in the most rough approximation (small cluster, core hole as a point charge, and the CIS method), whereas more accurate methods only worsen this result. Here, it is necessary to point out once more that the core hole is a high-lying excited state, any exact calculation of which is a rather complicated problem and requires involving methods that take into account higher-order correlations (e.g., methods of coupled clusters in the CCSD(T) and CCSDTQ approximations, ADC methods of the third or higher orders). In our case, the application of these methods is unacceptable because of their unreasonably higher computational cost; thus, even the cluster Ba_5F_8 is too large for them. Therefore, the exact calculation of transition energies cannot be the goal of this work, we are interested in qualitative features of the cross-luminescence spectrum and in the assignment of bands of this spectrum to particular electronic transitions. In this case, the CIS and TD DFT methods, which we used, are capable of yielding a qualitatively correct pattern even if the error in determining transition energies is very large (more than 1 eV). Notably, the relative intensity of optical transitions is a more reliable characteristic than their energy, which makes it possible to quite reliably interpret calculated and experimental bands in the spectrum.

Therefore, we obtained a rather good agreement with experiment by modeling the core hole as a point positive charge on the central barium ion. Processes of electron and ion polarization and lattice deformation, which were induced by the core hole, resulted in the "separation" of a region in the crystal, which contains the central Ba^{2+} ion and its nearest environment (eight F^- ions). Energetically, this led to the formation of a set of local states related to 2*p*-states of anions from the nearest environment. Estimated energies of transitions from states localized on ions of the second coordination sphere (F_{NNN}) allow us to conclude that these states are responsible for the occurrence of the cross-luminescence low-energy edge.

4. CONCLUSIONS

We have shown that the cross-luminescence spectrum calculated in the geometry of a localized core hole agrees well with experimental data. After the optimization of the geometry, states that correspond to states of fluorine ions from the nearest environment are split off from the valence band of the crystal. These states participate in the cross-luminescence process, with the main maximum being formed by transitions from states that correspond to the irreducible representations a_{1g}, e_g, and t_{2g} of the O_h symmetry group. Higher-lying energy maxima are formed by transitions from the t_{1g} and t_{2g} states. It should be noted that these results disagree with conclusions of [24], according to which more distant fluorine ions participate in the formation of high-energy maxima of cross luminescence. We note that our work was implemented taking into account the polarization and deformation of the environment of the Ba^{2+} ion on which the core hole was modeled. We used two calculation methods (Hartree–Fock and DFT) and clusters of different sizes. Therefore, we can state that our results are more reliable.

The lattice relaxation induced by the core hole results in considerable displacements of anions, which causes local states to split off not only from the valence band of the crystal ($2p$ states of F_{NN} ions), but also from its core band ($5p$ state of Ba^{3+}). The energy interval between the split-off core and valence states proves to be smaller than the spacing between the core and valence bands of the defect-free crystal, as a consequence of which the spectrum is shifted toward the low-energy range compared to data of UV spectroscopy [18].

Transitions from states localized on fluorine ions of the second coordination sphere with respect to the barium ion on which the core hole is located form the low-energy edge of cross luminescence, which is observed in experiments [15, 16, 18].

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