

# Triplet luminescence of cadmium centres in alkaline-earth fluoride crystals

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## Abstract

The emission and excitation spectra as well as decay of emissions of alkaline-earth fluoride crystals doped with CdF<sub>2</sub> were investigated in the 2–24 eV range at temperatures in the range 8–300 K. Emission bands at 4.2 and 3.5 eV, respectively, were found under excitation into the Cd absorption region in CaF<sub>2</sub>–Cd and SrF<sub>2</sub>–Cd crystals at low temperatures. Both emission bands have slow luminescence decay times of microsecond timescale. No Cd-related emission was found in BaF<sub>2</sub>–Cd crystals.

The calculations of the geometrical configurations of excited triplet Cd<sup>2+</sup> centres and the Cd-related electron transitions were carried out by using the *ab initio* Hartree–Fock method. The results of experiments and calculations lead us to the conclusion that the observed Cd<sup>2+</sup> emission bands are due to the triplet–singlet transitions from the Cd s-states to the nearest fluorine ions. The calculated energies are in good agreement with experimentally observed ones.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The performance of the fast BaF<sub>2</sub> scintillator crystals is strongly affected by slow self-trapped exciton emission. Cadmium impurity is known to decrease considerably the undesired exciton emission in BaF<sub>2</sub> fast scintillator [1]. However, the optical properties of Cd centres in alkaline-earth fluorides are still rather scarcely investigated.

Cadmium impurity is introduced into alkali halide crystals and into alkaline-earth fluorides as Cd<sup>2+</sup> ions [2–4]. Cadmium centres cause the strong absorption bands near exciton edges in alkali halide crystals [2] and also in alkaline-earth fluoride crystals [4]. But no separate absorption bands were observed in CaF<sub>2</sub> and SrF<sub>2</sub> crystals obviously due to overlap with exciton

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edges [4]. The nature of Cd absorption bands in alkali halides was tentatively ascribed to the formation of excitonic bands perturbed by Cd ions [2]. However, Radzhabov *et al* concluded that the Cd bands, having energy near 2 eV less than that of exciton absorption bands, are due to the transitions from the surrounding fluorines to the Cd ions [4]. No luminescence of Cd<sup>2+</sup> centres was found so far.

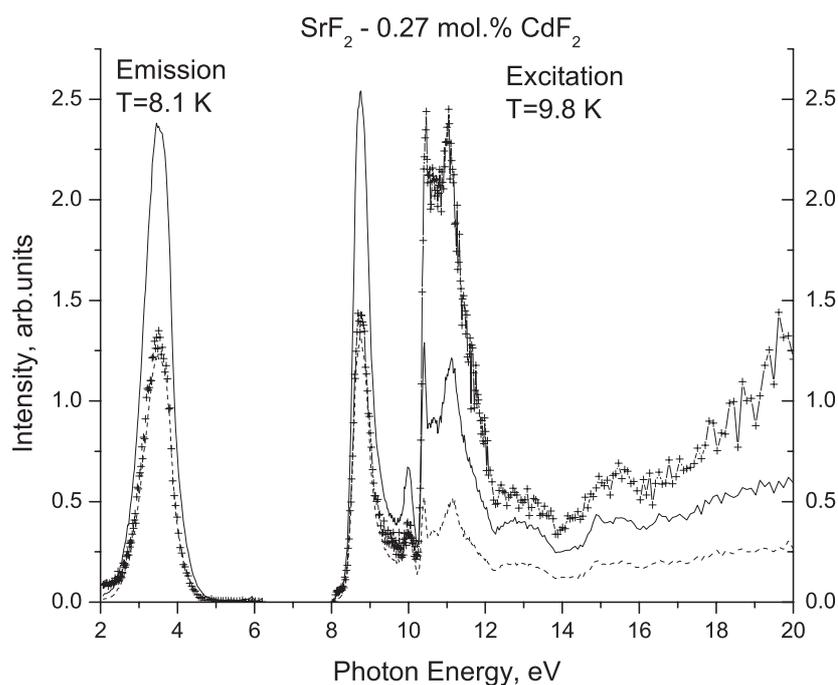
In this study, Cd-related emissions in CaF<sub>2</sub> and SrF<sub>2</sub> crystals at low temperatures were revealed. The optical excitation, emission and decay of luminescence were studied in BaF<sub>2</sub>, SrF<sub>2</sub>, CaF<sub>2</sub> doped with cadmium using vacuum ultraviolet radiation generated by conventional lamps and a storage ring (synchrotron). Unempirical Hartree–Fock calculations were performed to define the spatial structure of excited cadmium centres and origin of optical transitions.

## 2. Experimental details

Cadmium impurity was added into raw materials for crystal growth as CdF<sub>2</sub> in amounts from 0.01 to 2 wt%. High-purity alkaline-earth fluoride powders or ‘melted’ raw materials (better than 99.99 %) were used. The crystals were grown in vacuum in a graphite crucible that was closed by a lid to prevent evaporation of CdF<sub>2</sub> [5]. The achieved concentration of cadmium impurity in the crystals was several times lower than that added into the melt. Most measurements of BaF<sub>2</sub> and SrF<sub>2</sub> crystals were done with Cd concentration near 0.3 mol%, which was determined by atomic emission spectroscopy analysis of cadmium in the samples studied. The concentration of Cd in CaF<sub>2</sub> crystals was not analysed. However, from the comparison of excitation spectra and from the shift of the absorption edge in vacuum ultraviolet we estimate that the Cd concentration in the investigated sample of CaF<sub>2</sub>–Cd was in the range 0.1–0.3 mol%. The crystals were cleaved in air before mounting onto the sample holder attached to the cold finger of a flow-type liquid He cryostat. Samples have typical dimensions 10 mm × 10 mm × 2 mm.

The excitation, absorption spectra in the energy range 4–12 eV and emission spectra in the range 2–6 eV were measured with a grating vacuum monochromator VMR2 and grating monochromator MDR2. In addition, emission and excitation measurements were carried out using a low-temperature luminescence set-up SUPERLUMI designed for the VUV spectral region, located in HASYLAB at DESY (Hamburg, Germany) [6]. Photons generated by a bending magnet of the storage ring DORIS (5 MHz repetition rate) are tunable in the energy range 4–40 eV using a 2 m normal incidence monochromator with an optical slit width of 0.32 nm. The luminescence was analysed with a 0.3 m imaging spectrograph SpectraPro308i (Acton Research Inc.). The optical slit width of the secondary monochromator was typically 2 nm. The data acquisition time was typically 2 s per each point. Discrimination between the fast and slow emissions was achieved by recording signals within the time window  $\Delta t$  after the arrival of the excitation pulse delayed by  $\delta t$ . All spectra were measured in the time-integrated mode, in the short-time window mode ( $\delta t = 1.2$  ns and  $\Delta t = 5.5$  ns) and in the long-time window mode ( $\delta t = 47$  ns and  $\Delta t = 53$  ns). Therefore for luminescence with decay longer than 1  $\mu$ s the ratio between intensities of short and long components is near 0.1 using the chosen time windows. The larger ratio points to the presence of the short decay components. But both measurements show rather similar spectra.

*Ab initio* Hartree–Fock calculations of molecular clusters were done using Gamess [7] and PCGamess codes [8]. To represent the Madelung crystal field a few thousands of point charges around the quantum cluster were introduced. However, the positive charges attract the cluster orbitals. This leads to the appearance of physically unrealistic states within the



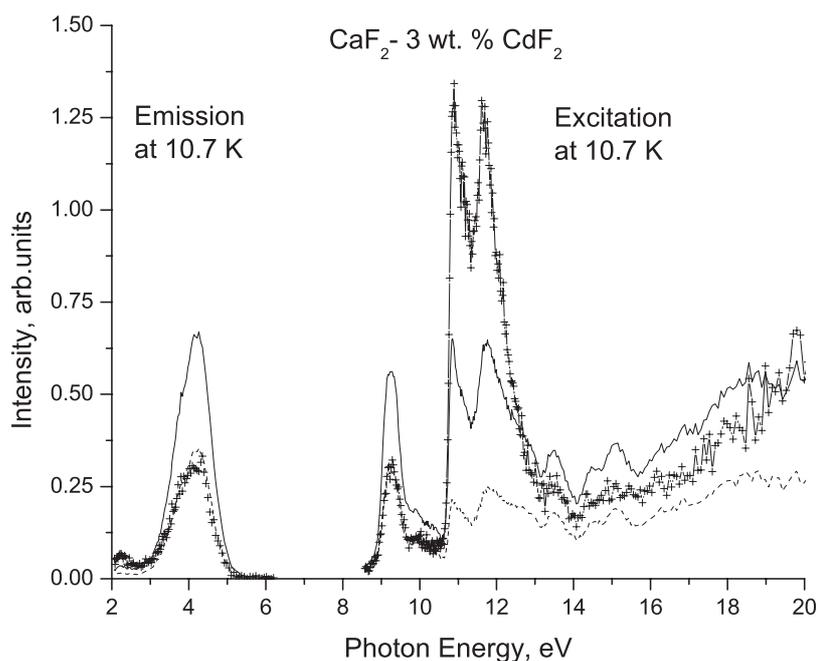
**Figure 1.** Emission and excitation spectra of  $\text{SrF}_2$ -0.27 mol%  $\text{CdF}_2$  crystal. Excitation spectra were measured for 3.54 eV emission light; the emission shown was excited by 8.74 eV photons. Spectra were recorded in time-integrated mode (solid lines), in the short-time window mode (symbols) and in the long-time window mode (dashed lines) as described in the text. The intensity of spectra in the short-time window was increased by 14 times for better comparison with other spectra. The emission band, corrected for spectral sensitivity of the registration system, has a maximum at 3.5 eV and half-width 0.8 eV.

band gap. In order to prevent the unphysical escaping of molecular orbitals of the quantum cluster to the region of point charges, the quantum cluster was surrounded with several shells of alkaline-metal effective core potentials on sites of positive charges.

### 3. Results

#### 3.1. Emission spectra

No new emission bands were observed under excitation in the region of  $\text{Cd}^{2+}$  absorption at room temperature. Absence of  $\text{Cd}^{2+}$  luminescence is in accordance with the fact that the cadmium impurity effectively quenches exciton luminescence under x-ray excitation. However, the new emission bands at 4.2 and 3.5 eV, respectively, were revealed in  $\text{CaF}_2$  and  $\text{SrF}_2$  samples at lower temperatures (figures 1, 2). No additional emission was discovered in  $\text{BaF}_2$  crystals at any temperature. The emission bands were not observed in undoped crystals. The intensity of these emission bands increased with increasing concentration of cadmium impurity. The temperature quenching of the observed emission bands took place in the temperature range 50–70 K in  $\text{CaF}_2$ . The dependence in  $\text{SrF}_2$  is more complicated, showing two steps at 40–60 and 90–150 K. These emission bands can be excited in the region of  $\text{Cd}^{2+}$  absorption bands and the intensity of these luminescence bands increases markedly with increasing Cd concentration.



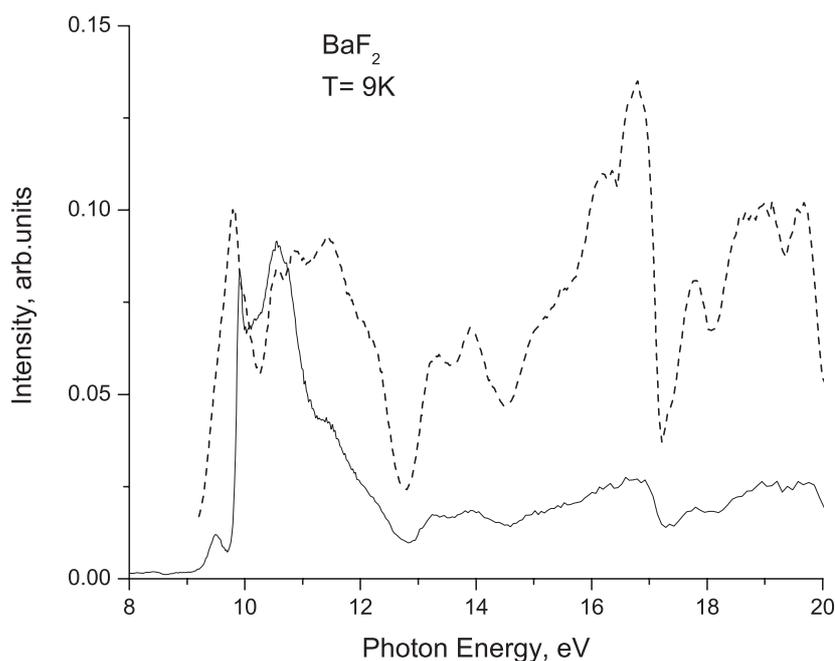
**Figure 2.** Emission and excitation spectra of  $\text{CaF}_2\text{-CdF}_2$ . Excitation spectra were measured for the 4.0 eV emission; the emission spectra shown were excited by 9.25 eV photons. Spectra were recorded in time-integrated mode (full lines), in the short-time window mode (symbols) and in the long-time window mode (dashed lines) as described in the text. The intensity of spectra in the short-time window was increased by 12 times for better comparison with other spectra.

Undoubtedly, the emission bands at 4.2 eV in  $\text{CaF}_2\text{-Cd}$  and 3.5 eV in  $\text{SrF}_2\text{-Cd}$  belong to the  $\text{Cd}^{2+}$  centres. The emission band at 4.2 eV of  $\text{Cd}^{2+}$  centres in  $\text{CaF}_2$  is rather close to the emission band of self-trapped excitons at 4.4 eV, whereas the 3.5 eV  $\text{Cd}^{2+}$  emission in  $\text{SrF}_2$  is more displaced from the self-trapped exciton emission peak at 4.35 eV.

Starting from exciting photon energies of 10 eV and above that, the emission band of  $\text{SrF}_2\text{-Cd}$  becomes different from the band of  $\text{Cd}^{2+}$  centres. Namely, the band shifts to higher energies by 0.1 eV. Therefore, the excitation spectrum above 10 eV (see figure 1) corresponds to this new 3.6 eV band. It is well excited in the exciton region (see figure 1). Moreover, the excitation spectra for emission recorded at 3.6 eV resembles that of the self-trapped exciton emission. Our tentative assignment is that this 3.6 eV band arises from radiative decay of exciton states perturbed by Cd impurity.

At 10 K the decays of the 3.5 and 4.2 eV emission bands in  $\text{SrF}_2$  and  $\text{CaF}_2$  possess decay times above 1  $\mu\text{s}$ . The luminescence of  $\text{Cd}^{2+}$  centres in  $\text{SrF}_2$  crystal at 12 K has a decay time 33  $\mu\text{s}$  under 8.7 eV excitation. Rather long decay times indicate that the radiative transitions should be from the triplet excited state to the singlet ground state.

The luminescence of the Cd perturbed excitons shows apparent fast decay components of 7.5 and 7.3 ns, respectively, in  $\text{SrF}_2$  and in  $\text{CaF}_2$  at 10 K. The initial intensity  $I_0$  of the fast components is 10 times larger than that of the slow components. The fast and slow components of luminescence of singlet and triplet self-trapped excitons at nanosecond and microsecond timescales have been observed in all  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  crystals [11, 12].



**Figure 3.** Excitation spectra for exciton emission at 4.0 eV of BaF<sub>2</sub>-undoped (dashed line) and BaF<sub>2</sub>-0.27 mol% of CdF<sub>2</sub> (solid line). Spectra were recorded in time-integrated mode.

### 3.2. Excitation spectra

Strong excitation bands at 8.75 and 9.25 eV for the 3.5 and 4.2 eV emission bands were observed in SrF<sub>2</sub>-Cd and CaF<sub>2</sub>-Cd crystals, respectively (see figures 1, 2). No other excitation bands were found at lower energies. The sharp onsets at 10.4 eV in SrF<sub>2</sub> and at 10.7 eV in CaF<sub>2</sub> shown in figures 1, 2 and the following excitation at higher energies belong to the exciton states perturbed by Cd ions. The relative intensities of the short emission components become much higher in these regions (see figures 1, 2).

The low-energy edge of the excitation spectra of exciton luminescence shifts apparently towards higher energy with increase of Cd concentration. The shift becomes as high as 0.3–0.4 eV when the Cd concentration reaches 0.1 mol% for all three crystals (for BaF<sub>2</sub> see figure 3). Evidently, this shift is due to overlapping of the exciton band with the strong Cd<sup>2+</sup> absorption band.

We did not find any emission of Cd<sup>2+</sup> centres in BaF<sub>2</sub> crystals. Therefore, the positions of the main absorption bands were taken from the respective absorption spectra have a strong band at 8.6 eV [4]. From the comparison of excitation spectra of undoped and Cd-doped BaF<sub>2</sub> crystals (figure 3) one can conclude that the dip at 9.7 eV is due to the second Cd<sup>2+</sup> absorption band. Similarly to this, we interpret analogous dips at 10.25 and 10.58 eV (see figures 1, 2) as arising from the second Cd<sup>2+</sup> absorption band in SrF<sub>2</sub> and CaF<sub>2</sub>, respectively. The energetic positions of the observed Cd<sup>2+</sup> bands in all three crystals are listed in table 1.

### 3.3. Calculations

The calculations of absorption of Cd<sup>2+</sup> centres [4] were extended towards higher energies. It was found that 2–3 eV above the main absorption transition there is a second weaker Cd-related

**Table 1.** Energies in eV of Cd transitions in alkaline-earth fluoride crystals. Energies of Cd bands were taken from excitation spectra for CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> at 10 K and from absorption spectra of BaF<sub>2</sub>–Cd (8.6 eV band) at 295 K.

Crystal	$E_{\text{Cd}^{2+}} \text{ (I)}$	$E_{\text{Cd}^{2+}} \text{ (II)}$
CaF <sub>2</sub> :Cd <sup>2+</sup>	9.25	10.58
SrF <sub>2</sub> :Cd <sup>2+</sup>	8.75	10.25
BaF <sub>2</sub> :Cd <sup>2+</sup>	≈8.6 [4]	9.7

band. The transitions mainly occur from fluorine states to cadmium atomic p-levels. These results correlate with the excitation spectra recorded. The second Cd bands were found to have 1–1.5 eV higher energies than those of the first bands in alkaline-earth fluorides (see table 1). The calculated energies are nearly 1.5 times greater than experimental values, which is usual for the Hartree–Fock method.

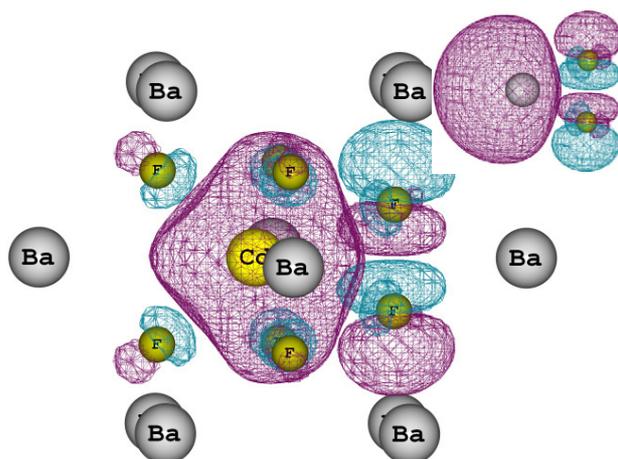
Based on the results that the Cd luminescence has a slow decay time, one can conclude that emission appears due to triplet–singlet transitions. This motivates the optimization of geometry of the Cd cluster in order to obtain the correct spatial configuration of the Cd defect in the excited triplet state, which can explain the large Stokes shift.

Excitation into the first Cd<sup>2+</sup> absorption band results in electron transfer from the nearest fluorines to cadmium. The obtained defect can be considered as the Cd<sup>+</sup> ion with a nearest hole. This defect has a rather long lifetime of tens of microseconds before its radiative recombination. The most important experimental fact is that the electron–hole pair also has a relatively long lifetime near the Cd impurity ion. It is reasonable to assume that the electron is trapped by Cd<sup>2+</sup> forming the Cd<sup>+</sup> centres, both of which are known to be stable defects [4]. Also very fast self-trapping of the holes is very probable, as happens generally in systems with strong exciton–phonon coupling [12]. Therefore, we propose the pair of nearest Cd<sup>+</sup>–V<sub>k</sub> centres as a potential candidate for the long-lived triplet Cd defect to be validated by calculations.

The correct choice of the quantum cluster for calculations is an important but not a trivial problem. We performed calculations for three different clusters to obtain more reliable results. The first cluster contained the central Cd ion and two shells around cadmium CdF<sub>8</sub>Me<sub>12</sub> (Me is Ca, Sr, Ba). The second cluster has a central point between two F ions and contained 40 atoms. In the third case we surrounded the second cluster by 2000 point charges, in order to add the Madelung potential to the quantum cluster chosen. To prevent unphysical escaping of the orbitals of the quantum cluster into the region of positive point charges, we surrounded the cluster with a few shells of effective core potentials of appropriated metal (Ca, Sr or Ba).

**3.3.1. CdF<sub>8</sub>Me<sub>12</sub> cluster.** The calculations were performed for the cluster CdF<sub>8</sub>Me<sub>12</sub> containing 21 atoms. The outer shell Me<sub>12</sub> remained frozen, while the coordinates of the cadmium and fluorine ions were optimized to obtain the lowest total energy of the cluster. The usability of such a cluster for geometry optimization was verified by a calculation of the pure MeF<sub>8</sub>Me<sub>12</sub> cluster. As a result of the calculation the initial coordinates of fluorine ions did not change by more than 0.01 Å. Recently such a cluster was successfully used in simulations of Cu ions in an off-centre configuration substituted into alkaline-earth halide crystals [9].

The calculation of the triplet state with equilibrium coordinates of ions did not converge. However, a slight mutual shift of two nearest fluorine ions resulted in a calculation converging to the situation where a hole (or one unpaired electron) is localized on two fluorine sites and other unpaired electron is localized on the cadmium. The obtained internuclear distance of the F<sub>2</sub><sup>−</sup> is 1.94 Å in BaF<sub>2</sub>, which is very close to that of the F<sub>2</sub><sup>−</sup> centre (1.91 Å) in the



**Figure 4.**  $\text{CdF}_8\text{Ba}_{12}$  cluster with the optimized geometry. Two fluorine ions are brought together to a distance near 1.9 Å between them; the central Cd ion moves to the opposite direction by a few tenths of an ångström. Other fluorine ions slightly shift outwards in respect of the centre of the cluster. Two highest occupied molecular orbitals, having spins parallel, are shown. One orbital is well localized on two nearest fluorine ions forming the  $\text{F}_2^-$  part and the other orbital does the same on cadmium, forming the  $\text{Cd}^+$  part. The inset (upper right corner) shows the triplet  $\text{CdF}_2$  molecule with optimized geometry. Two highest occupied molecular orbitals are shown.

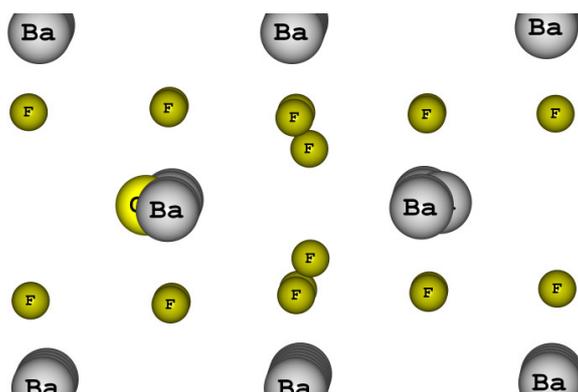
**Table 2.** Energies in eV of triplet–singlet luminescent transitions of  $\text{Cd}^{2+}$  centres in alkaline-earth fluoride crystals. Calculated energies obtained as the differences between total energies of geometry optimized triplet state and singlet state with the same ion coordinates. Results were obtained for the following clusters:  $\text{CdF}_8\text{Me}_{12}$  (I) and  $\text{F}_2\text{CdMeF}_8\text{Me}_4\text{F}_{10}\text{Me}_{14}$  (II), and similar cluster but surrounded with the 94 metal effective core potentials and 2000 point charges (III).

Crystal	$E$ (I) calc.	$E$ (II) calc.	$E$ (III) calc.	$E$ emission exper.
$\text{CaF}_2:\text{Cd}^{2+}$	6.1	5.0	4.0	4.2
$\text{SrF}_2:\text{Cd}^{2+}$	5.2	4.3	3.5	3.5
$\text{BaF}_2:\text{Cd}^{2+}$	3.1	2.1	1.6	Not found

respective crystal lattice ( $V_k$  centre in  $\text{BaF}_2$ ). The Cd ion is shifted from its initial lattice site in the opposite direction in respect of the  $\text{F}_2^-$  centre (figure 4). The distances from the Cd to surrounding fluorine ions are slightly increased, obviously due to the bigger radius of the  $\text{Cd}^+$  ion in comparison with the original  $\text{Cd}^{2+}$  ion. The calculation with the density functional (DFT) approach using the B3LYP functional does not lead to the picture described above, obviously due to the well-known problem with  $V_k$  centre simulations [10].

Then we used the relaxed coordinates of cluster ions, obtained in the course of optimization of the triplet state geometry, and calculated the total energy of the singlet state. In this way we can estimate the energy of the triplet–singlet luminescent transition. The calculated energies are collected in table 2 together with experimentally observed energies.

**3.3.2.  $\text{CdMe}_{19}\text{F}_{20}$  cluster.** To verify the results obtained so far we increased the cluster in such way that the created  $V_k$ -centre became the centre of a cluster. The cluster centred on the  $V_k$  centre formed contains 40 atoms. It was chosen to simulate the symmetry around the  $V_k$  centre. During optimization of the geometry the  $\text{F}_2$ ,  $\text{Me}_2$  and next  $\text{F}_8$  ions were let



**Figure 5.** Central part of a  $\text{CdBa}_{19}\text{F}_{20}$  quantum cluster with optimized geometry surrounded by 94 Ba effective core potentials.

free while other atoms were fixed on their equilibrium lattice sites. We obtained qualitatively similar results for the geometry of the optimized configuration. However, in this cluster the  $\text{Cd}^+$  ion formed pushes the  $\text{F}_2^-$  outwards from its equilibrium position (figure 5). The energies of triplet–singlet transitions, obtained for this configuration, are also shown in table 2. The calculated energies are 1–2 eV higher than the experimental ones. As a next step we introduced a few thousands of point charges around the quantum cluster. In these calculations the point charges, core potentials and metal outer shell of the quantum cluster remained frozen during geometry optimization. All calculations for the three different clusters show that one of the spins is well localized on the cadmium ion while the same happens with another spin being always localized on the  $\text{F}_2^-$  centre. As the  $\text{Cd}^+$  ion formed is larger than the initial  $\text{Cd}^{2+}$ , the surrounding fluorine ions shift away from the cadmium. As a result of mutual interaction, the  $\text{F}_2^-$  centre also moves from the central position (see figure 5). The shift from the central position increases in a row from  $\text{BaF}_2$  to  $\text{CaF}_2$ . All geometrical rearrangements are explained by the creation of a  $\text{Cd}^+-\text{V}_k$  centre pair. The obtained transition energies are very close to experimental energies of triplet–singlet luminescence bands in  $\text{CaF}_2$  and  $\text{SrF}_2$  (table 2).

#### 4. Discussion

The peak position of the Cd or Zn absorption band closest to the exciton edge is strongly dependent on the host crystal ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{KI}$ ) but is not very sensitive to the impurity. These facts suggest that this band may be due to the exciton absorption band perturbed by the neighbouring Cd or Zn impurity [2]. However, we do not observe exciton emission under excitation into the  $\text{Cd}^{2+}$  band in any of the alkaline-earth fluorides. Moreover, we found a shift of the excitation edge for exciton emission to higher energies due to the strong Cd-related absorption in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  (for the example of  $\text{BaF}_2$  see figure 3). Calculations show that the transitions from the valence band to Cd states should be 1–2 eV less than inter-band transitions [4]. Therefore, it was concluded that the  $\text{Cd}^{2+}$  bands are due to the transitions from the top of valence band, arising from the fluorine states, to the Cd 5s states [4]. Due to the charge transfer nature of the transition, its energy is strongly dependent on the host crystal. Based on the excitation spectra we conclude that the observed emission bands at 3.5 eV ( $\text{SrF}_2\text{-Cd}$ ) and 4.2 eV ( $\text{CaF}_2\text{-Cd}$ ) belong to the reverse radiative transitions from cadmium to nearest fluorine ions.

The absence of Cd-related luminescence in BaF<sub>2</sub> crystal may have the following reason. The Cd-related luminescence in BaF<sub>2</sub> may be quenched even at liquid helium temperature. According to a simple model the relative Stokes shift (luminescence energy divided by absorption energy) should not be less than 0.5 [13]. The model is based on the assumption that the configuration coordinates of ground and excited states are described by similar parabolas. The luminescence can be observed when the crossover point of excited and ground configuration curves lies at higher energy than the transition point of the excited configuration curve. The model well explains the absence of F-centre luminescence in ionic crystals [13]. The relative Stokes shifts for Cd luminescence are 0.45, 0.40 for CaF<sub>2</sub>, SrF<sub>2</sub>, respectively, and the estimated value for Stokes shift is 0.19 for BaF<sub>2</sub> (see tables 1 and 2). The Stokes shift depends on lattice relaxation in the triplet state. The looser the lattice the larger the Stokes shift. Definitely, the relative Stokes shift 0.19 is too small for luminescence to be observed. Another model, which also well explains the existence and absence of F-centre luminescence, is based on the assumption that the system always reach the minimum of the excited configuration curve and the absence of luminescence is due to horizontal vibronic tunnelling to the ground configurational curve [14]. The correspondence between the two different models is not surprising: lowering the crossover point implies an increased overlap between the vibrational wave functions of the ground and the excited state with the same energy, which is a crucial factor in the horizontal vibronic tunnelling rate [14]. In all cases the calculated lattice relaxation around the triplet Cd centre in BaF<sub>2</sub> is significantly larger than the relaxation in CaF<sub>2</sub>, SrF<sub>2</sub>, and the absence of luminescence in BaF<sub>2</sub> is very reasonable.

Calculations performed confirm that the triplet Cd<sup>2+</sup> centre can be considered as an unit formed from the Cd<sup>+</sup> ion together with the nearest F<sub>2</sub><sup>-</sup> self-trapped hole. Atomic spin densities are near 1 on Cd and near 0.5 on each of fluorine ions. Atomic charges are near 1 on Cd and near 0.5 on each of fluorine ions. For comparison we also calculated the properties of the CdF<sub>2</sub> molecule. The singlet state of the molecule is a linear chain with the Cd ion between two fluorine ions. The molecule in the triplet state transforms into a configuration consisting of the Cd<sup>+</sup>-F<sub>2</sub><sup>-</sup> pair (see figure 4). The charge and spin distributions of the triplet CdF<sub>2</sub> molecule and triplet Cd<sup>2+</sup> centre are very similar. However, the calculated distance from Cd to the central line of the F<sub>2</sub><sup>-</sup> is 1.96 Å for the CdF<sub>2</sub> molecule and 2.6–2.8 Å for the triplet Cd<sup>2+</sup> centre in alkaline-earth fluorides. This discrepancy is explained by the fact that in the CdF<sub>2</sub> molecule the geometrical centre of the 5s Cd shell is about 0.6 Å farther from the line connecting the two fluorine ions (F<sub>2</sub><sup>-</sup>) than the position of the Cd nucleus itself. The geometrical centre of the 5s Cd orbital and the position of the Cd nucleus are very close in these crystals (see figure 4).

## 5. Conclusion

We carried out a comprehensive investigation of Cd-doped alkaline-earth crystals at various temperatures by means of luminescence techniques in vacuum ultraviolet. New emission bands at 3.5 and 4.2 eV were observed at low temperatures under excitation into the Cd impurity region in SrF<sub>2</sub> and CaF<sub>2</sub>, respectively, and these are assigned to the triplet–singlet luminescence transitions of Cd defects. The optimized geometrical configuration of the triplet state of the Cd<sup>2+</sup> centre can be considered as the Cd<sup>+</sup>-F<sub>2</sub><sup>-</sup> (V<sub>k</sub>) pair or the CdF<sub>2</sub> triplet molecule. Luminescent transitions occur from the Cd<sup>+</sup> 5s-state to the σ<sub>u</sub> state of F<sub>2</sub><sup>-</sup>. The calculated energies of triplet–singlet transitions of Cd<sup>2+</sup> centre are in good agreement with the experimental transition energies observed for CaF<sub>2</sub> and SrF<sub>2</sub>.

Investigation of excitation spectra allow us to find the maxima of the first and second Cd absorption bands in CaF<sub>2</sub>, SrF<sub>2</sub> and that of the second band in BaF<sub>2</sub> (see table 1).

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