

Triplet luminescence of cadmium centres in alkaline-earth fluoride crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 5821

(<http://iopscience.iop.org/0953-8984/17/37/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 05:57

Please note that [terms and conditions apply](#).

Triplet luminescence of cadmium centres in alkaline-earth fluoride crystals

E Radzhabov^{1,3} and M Kirm²

¹ Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii street 1a, PO Box 4019, 664033 Irkutsk, Russia

² Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

E-mail: eradz@igc.irk.ru

Received 10 June 2005, in final form 4 August 2005

Published 2 September 2005

Online at stacks.iop.org/JPhysCM/17/5821

Abstract

The emission and excitation spectra as well as decay of emissions of alkaline-earth fluoride crystals doped with CdF₂ 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 CaF₂–Cd and SrF₂–Cd crystals at low temperatures. Both emission bands have slow luminescence decay times of microsecond timescale. No Cd-related emission was found in BaF₂–Cd crystals.

The calculations of the geometrical configurations of excited triplet Cd²⁺ 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 Cd²⁺ 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 BaF₂ scintillator crystals is strongly affected by slow self-trapped exciton emission. Cadmium impurity is known to decrease considerably the undesired exciton emission in BaF₂ 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 Cd²⁺ 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 CaF₂ and SrF₂ crystals obviously due to overlap with exciton

³ Author to whom any correspondence should be addressed.

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 Cd²⁺ centres was found so far.

In this study, Cd-related emissions in CaF₂ and SrF₂ crystals at low temperatures were revealed. The optical excitation, emission and decay of luminescence were studied in BaF₂, SrF₂, CaF₂ 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 CdF₂ 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 CdF₂ [5]. The achieved concentration of cadmium impurity in the crystals was several times lower than that added into the melt. Most measurements of BaF₂ and SrF₂ 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 CaF₂ 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 CaF₂–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 Δt after the arrival of the excitation pulse delayed by δt . 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 μ 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

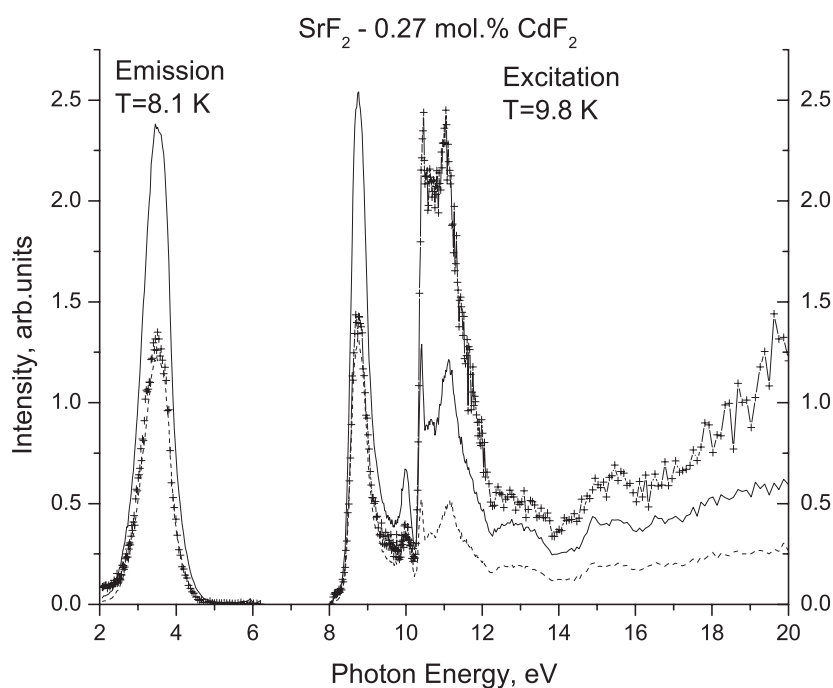


Figure 1. Emission and excitation spectra of SrF_2 -0.27 mol% CdF_2 crystal. Excitation spectra were measured for 3.54 eV emission light; the emission shown was excited by 8.74 eV photons. Spectra were recorded in time-integrated mode (solid lines), in the short-time window mode (symbols) and in the 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 Cd^{2+} absorption at room temperature. Absence of 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 CaF_2 and SrF_2 samples at lower temperatures (figures 1, 2). No additional emission was discovered in 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 CaF_2 . The dependence in 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 Cd^{2+} absorption bands and the intensity of these luminescence bands increases markedly with increasing Cd concentration.

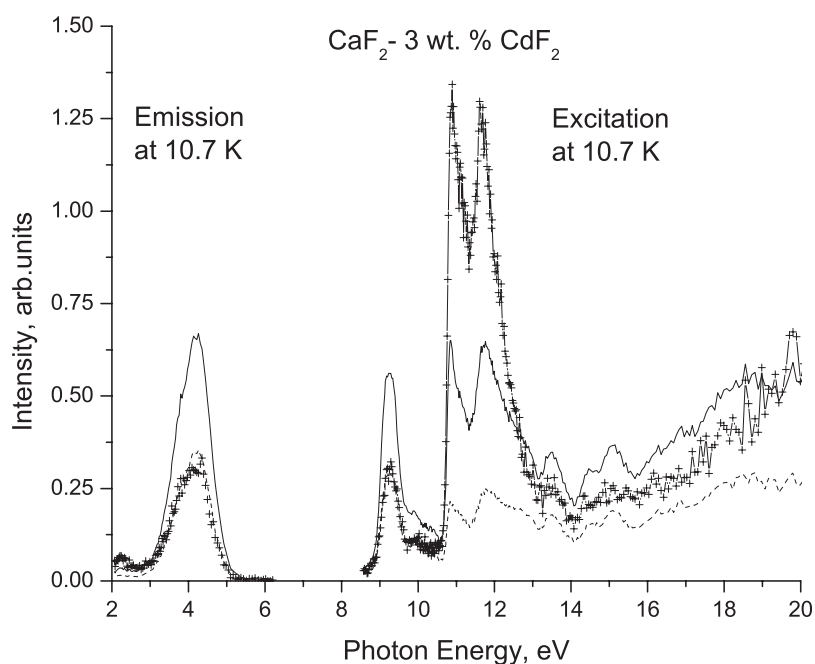


Figure 2. Emission and excitation spectra of $\text{CaF}_2\text{-CdF}_2$. Excitation spectra were measured for the 4.0 eV emission; the emission spectra shown were excited by 9.25 eV photons. Spectra were recorded in time-integrated mode (full lines), in the short-time window mode (symbols) and in the 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 Cd^{2+} centres. The emission band at 4.2 eV of Cd^{2+} centres in CaF_2 is rather close to the emission band of self-trapped excitons at 4.4 eV, whereas the 3.5 eV Cd^{2+} emission in 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 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 SrF_2 and CaF_2 possess decay times above 1 μs . The luminescence of Cd^{2+} centres in SrF_2 crystal at 12 K has a decay time 33 μs 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 SrF_2 and in 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 CaF_2 , SrF_2 , BaF_2 crystals [11, 12].

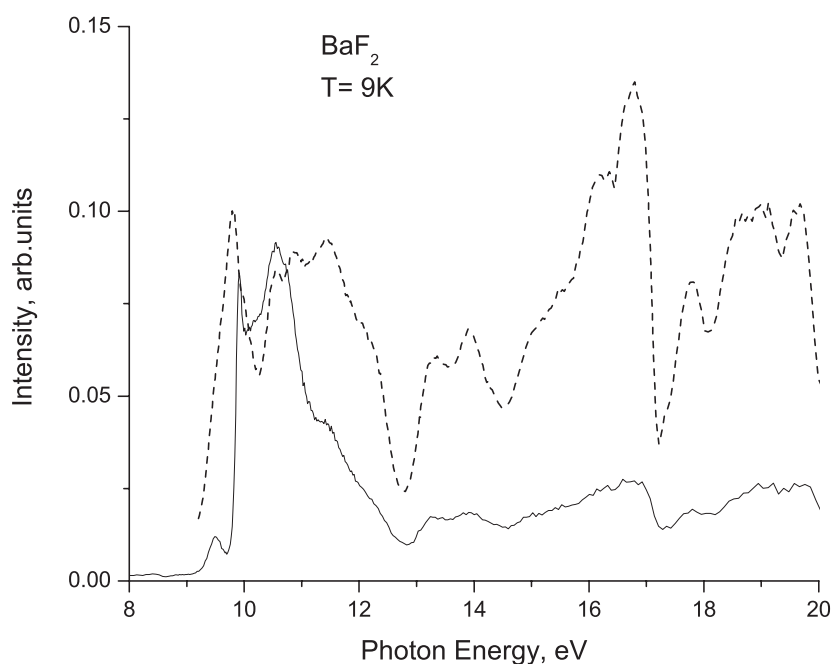


Figure 3. Excitation spectra for exciton emission at 4.0 eV of BaF₂-undoped (dashed line) and BaF₂-0.27 mol% of CdF₂ (solid line). Spectra were recorded in time-integrated mode.

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 SrF₂-Cd and CaF₂-Cd crystals, respectively (see figures 1, 2). No other excitation bands were found at lower energies. The sharp onsets at 10.4 eV in SrF₂ and at 10.7 eV in CaF₂ 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 BaF₂ see figure 3). Evidently, this shift is due to overlapping of the exciton band with the strong Cd²⁺ absorption band.

We did not find any emission of Cd²⁺ centres in BaF₂ 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 BaF₂ crystals (figure 3) one can conclude that the dip at 9.7 eV is due to the second Cd²⁺ 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 Cd²⁺ absorption band in SrF₂ and CaF₂, respectively. The energetic positions of the observed Cd²⁺ bands in all three crystals are listed in table 1.

3.3. Calculations

The calculations of absorption of Cd²⁺ 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 CaF₂, SrF₂, BaF₂ at 10 K and from absorption spectra of BaF₂–Cd (8.6 eV band) at 295 K.

Crystal	$E_{\text{Cd}^{2+}} \text{ (I)}$	$E_{\text{Cd}^{2+}} \text{ (II)}$
CaF ₂ :Cd ²⁺	9.25	10.58
SrF ₂ :Cd ²⁺	8.75	10.25
BaF ₂ :Cd ²⁺	≈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 Cd²⁺ absorption band results in electron transfer from the nearest fluorines to cadmium. The obtained defect can be considered as the Cd⁺ 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 Cd²⁺ forming the Cd⁺ 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⁺–V_k 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 CdF₈Me₁₂ (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. CdF₈Me₁₂ cluster. The calculations were performed for the cluster CdF₈Me₁₂ containing 21 atoms. The outer shell Me₁₂ 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 MeF₈Me₁₂ 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 F₂[−] is 1.94 Å in BaF₂, which is very close to that of the F₂[−] centre (1.91 Å) in the

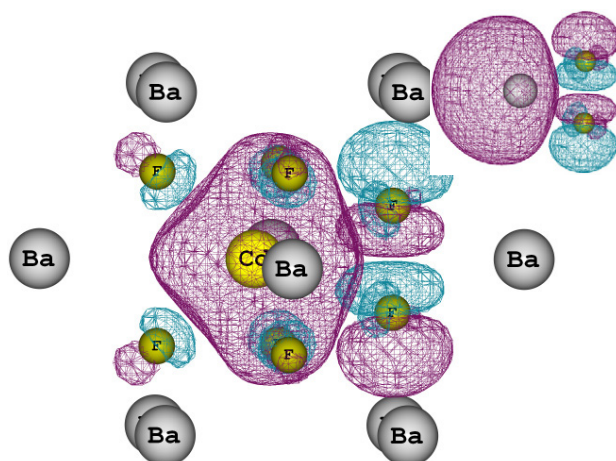


Figure 4. $\text{CdF}_8\text{Ba}_{12}$ cluster with the optimized geometry. Two fluorine ions are brought together to a distance near 1.9 Å between them; the central Cd ion moves to the opposite direction by a few tenths of an ångström. Other fluorine ions slightly shift outwards in respect of the centre 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 F_2^- part and the other orbital does the same on cadmium, forming the Cd^+ part. The inset (upper right corner) shows the triplet CdF_2 molecule with optimized geometry. Two highest occupied molecular orbitals are shown.

Table 2. Energies in eV of triplet–singlet luminescent transitions of 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 BaF_2). The Cd ion is shifted from its initial lattice site in the opposite direction in respect of the 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 Cd^+ ion in comparison with the original 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 F_2 , Me_2 and next F_8 ions were let

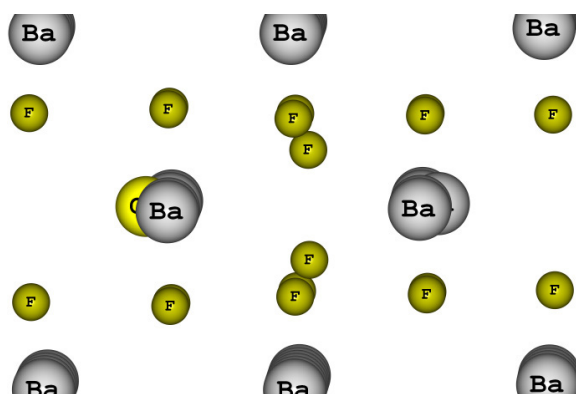


Figure 5. Central part of a $\text{CdBa}_{19}\text{F}_{20}$ quantum cluster with optimized geometry surrounded by 94 Ba effective core potentials.

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 Cd^+ ion formed pushes the 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 F_2^- centre. As the Cd^+ ion formed is larger than the initial Cd^{2+} , the surrounding fluorine ions shift away from the cadmium. As a result of mutual interaction, the F_2^- centre also moves from the central position (see figure 5). The shift from the central position increases in a row from BaF_2 to CaF_2 . All geometrical rearrangements are explained by the creation of a Cd^+-V_k centre pair. The obtained transition energies are very close to experimental energies of triplet–singlet luminescence bands in CaF_2 and 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 (NaCl , KCl , KBr , and 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 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 CaF_2 , SrF_2 , BaF_2 (for the example of 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 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 BaF₂ crystal may have the following reason. The Cd-related luminescence in BaF₂ 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 CaF₂, SrF₂, respectively, and the estimated value for Stokes shift is 0.19 for BaF₂ (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 BaF₂ is significantly larger than the relaxation in CaF₂, SrF₂, and the absence of luminescence in BaF₂ is very reasonable.

Calculations performed confirm that the triplet Cd²⁺ centre can be considered as an unit formed from the Cd⁺ ion together with the nearest F₂⁻ 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 CdF₂ 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⁺-F₂⁻ pair (see figure 4). The charge and spin distributions of the triplet CdF₂ molecule and triplet Cd²⁺ centre are very similar. However, the calculated distance from Cd to the central line of the F₂⁻ is 1.96 Å for the CdF₂ molecule and 2.6–2.8 Å for the triplet Cd²⁺ centre in alkaline-earth fluorides. This discrepancy is explained by the fact that in the CdF₂ molecule the geometrical centre of the 5s Cd shell is about 0.6 Å farther from the line connecting the two fluorine ions (F₂⁻) 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 SrF₂ and CaF₂, respectively, and these are assigned to the triplet–singlet luminescence transitions of Cd defects. The optimized geometrical configuration of the triplet state of the Cd²⁺ centre can be considered as the Cd⁺-F₂⁻ (V_k) pair or the CdF₂ triplet molecule. Luminescent transitions occur from the Cd⁺ 5s-state to the σ_u state of F₂⁻. The calculated energies of triplet–singlet transitions of Cd²⁺ centre are in good agreement with the experimental transition energies observed for CaF₂ and SrF₂.

Investigation of excitation spectra allow us to find the maxima of the first and second Cd absorption bands in CaF₂, SrF₂ and that of the second band in BaF₂ (see table 1).

Acknowledgments

The authors would like to thank Alex Granovsky for the modification of PCGameSS code, which allowed us to introduce more than 100 point charges around the quantum cluster. The authors are grateful to V Ivashechkin and A Istomin for the growth of crystals and to I Vasil'eva for the determination of Cd concentrates in SrF₂ and BaF₂ crystals. Marco Kirm gratefully acknowledges support by the Estonian Science Foundation (grant no 6538). Experiments with synchrotron radiation were supported by the European Community—Research Infrastructure Action under the FP6 'Structuring the European Research Area' Programme (through the Integrated Infrastructure Initiative 'Integrating Activity on Synchrotron and Free Electron Laser Science').

References

- [1] Rogulis U, Trokss J, Veispals A, Tale I, Kulis P and Springis M 1995 *Radiat. Eff. Defects Solids* **135** 859
- [2] Jain S C and Radhakrishna S 1968 *Phys. Rev.* **172** 972
- [3] Jain S C, Sootha G D and Jain R K 1968 *J. Phys. C: Solid State Phys.* **1** 1220
- [4] Radzhabov E A, Egranov A V, Nepomnyashchikh A I, Mysovskii A and Kurobori T 2005 *Phys. Status Solidi c* **2** 388
- [5] Radzhabov E, Istomin A, Nepomnyashikh A, Egranov A and Ivashechkin V 2005 *Nucl. Instrum. Methods A* **537** 71
- [6] Kirm M, Lushchik A, Lushchik C, Nepomnyashikh A I and Savikhin F 2001 *Radiat. Meas.* **33** 515
- [7] Schmidt M W, Baldrige K K, Boatz J A, Elbert S T, Gordon M S, Jensen J J, Koseki S, Matsunaga N, Nguyen K A, Su S, Windus T L, Dupuis M and Montgomery J A 1993 *J. Comput. Chem.* **14** 1347
- [8] Granovsky A, <http://classic.chem.msu.su/gran/gamess/index.html>
- [9] García Fernandez P, Aramburu J A, Barriuso M T and Moreno M 2004 *Phys. Rev. B* **69** 174110
- [10] Gavartin J L, Sushko P V and Shluger A L 2003 *Phys. Rev. B* **67** 035108
- [11] Becker J *et al* 1998 *Proc. 3rd Int. Conf. on Excitonic Processes in Cond. Matter* vol 98-25 ed R T Williams and W Yen, pp 415–9
- [12] Song K S and Williams R T 1993 *Self-Trapped Excitons* (Berlin: Springer)
- [13] Bartram R H and Stoneham A M 1975 *Solid State Commun.* **17** 1593
- [14] Matteis F D, Leblans M, Joosen W and Schoemaker D 1992 *Phys. Rev. B* **45** 10377