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TRIPLET LUMINESCENCE OF CADMIUM CENTRES IN ALKALINE-EARTH FLUORIDE CRYSTALS

The emission and excitation spectra as well as decay of emissions of alkaline-earth fluoride crystals doped with CdF_2 were investigated in the 2-24 eV range at temperatures 8-300 K. Emission bands at 4.2 eV and 3.5 eV were found under excitation into Cd absorption region in CaF_2-Cd and SrF_2-Cd crystals at low temperatures, respectively. Both emission bands have slow luminescence decay times of microsecond time scale. No Cd-related emission was found in BaF_2-Cd crystals.

The calculations of the geometrical configurations of excited triplet Cd^{2+} centres and the Cd-related electron transitions were carried out by using *ab-initio* Hartree-Fock method. The results of experiments and calculations lead us to the conclusion that the observed Cd^{2+} emission bands are due to to the triplet-singlet transitions from the Cd s-states to the nearest fluorine ions. The calculated energies are in a good agreement with experimentally observed ones. Calculations of triplet Hg^{2+} and Zn^{2+} centres configurations and luminescence energies were done also. These centres could be effective exciton quenchers in BaF_2 and possibly in SrF_2.

Introduction

Performance of the fast BaF_2 scintillator crystals is strongly affected by slow self-trapped exciton emission. Cadmium impurity is known to decrease considerably the undesired exciton emission in BaF_2 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^{2+} 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_2 and SrF_2 crystals obviously due to overlap with exciton edges [4]. The nature of Cd absorption bands in alkali halides were 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^{2+} centres was found so far.

In this study Cd-related emissions in CaF_2 and SrF_2 crystals at low temperatures were revealed. The optical excitation, emission and decay of luminescence were studied in BaF_2, SrF_2, CaF_2 doped with cadmium using vacuum ultraviolet radiation generated by conventional lamps and storage ring (synchrotron). The unempirical Hartree-Fock calculations were performed to define the spatial structure of excited cadmium centres and origin of optical transitions. Preliminary results have been reported recently [15].

Experimental details

Cadmium impurity was added into raw materials for crystal growth as CdF_2 in amount from 0.01 to 2 weight %. High purity alkaline-earth fluorides powder or "melted" raw materials (better than 99.99 %) were used. The crystals were grown in vacuum in graphite crucible that was closed by a lid to prevent evaporation of CdF_2 [5]. The achieved concentration of cadmium impurity in the crystals was several times lower than added into the melt. Most measurements of BaF_2 and SrF_2 crystals were done with Cd concentration near 0.3 mol.% that was determined by atomic emission spectroscopy analysis of cadmium in the samples studied[1]. Concentration of Cd in CaF_2 crystals was not analysed. However, from the comparison of excitation spectra and from the shift of absorption edge in vacuum ultraviolet we estimate that the Cd concentration in the investigated sample of CaF_2-Cd was in the range of 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 10x10x2 mm.

The excitation, absorption spectra in the energy range of 4-12 eV and emission spectra in 2-6 eV were measured with grating vacuum monochromator VMR2 and grating monochromator MDR2. In addi-

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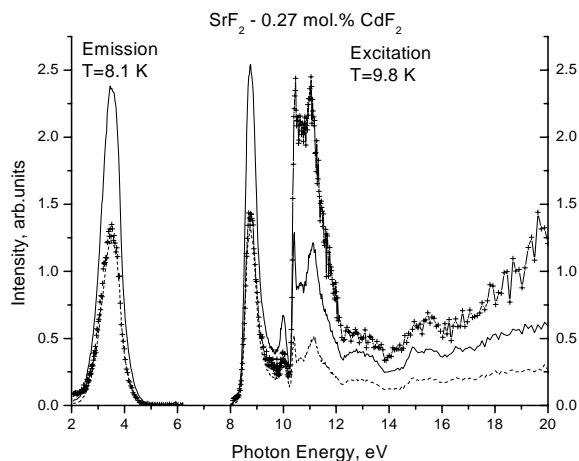[1] Concentration of Cd was analysed by I.Vasil'eva

Fig.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. Intensity of spectra in the short time window were increased by 14 times for the better comparison with other spectra. The emission band, corrected for spectral sensitivity of registration system, has a maximum at 3.5 eV and the half-width 0.8 eV

tion, emission and excitation measurements were carried out using a low temperature luminescence set-up SUPERLUMI designed for 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 tuneable in the energy range of 4-40 eV using a 2-m normal incidence monochromator with an optical slit width of 0.32 nm. Luminescence was analyzed with a 0.3-m imaging spectrograph SpectraPro308i (Acton Research Inc.). The optical slit width of the secondary monochromator was typically 2 nm. Data acquisition time was typically 2 seconds per each point. Discrimination between the fast and slow emissions was achieved by recording signals within the time window Δt after the arrival of excitation pulse delayed by δt. All spectra were measured in the time integrated mode, in the short time window (δt=1.2 ns and Δt=5.5 ns) and in the long time window mode (δt=47 ns and Δt=53 ns). Therefore for luminescence with decay longer than 1 μs 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 Madelung crystal field a few thousands of point charges around quantum cluster were introduced. However, the positive charges attract the cluster orbitals. This leads to appearing physically unrealistic states within the band gap. In order to prevent the unphysical escaping of molecular orbitals of 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.

Results

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 eV and 3.5 eV were revealed in CaF_2 and SrF_2 samples at lower temperatures, respectively (Fig.1, Fig.2). No additional emission was discovered in BaF_2 crystals at any temperatures. No these emission bands were observed in undoped crystals. 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 of 50-70 K in CaF_2. The dependence in SrF_2 is more complicated, showing two steps at 40-60 K 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 increase markedly depends on the Cd concentration. Undoubtedly, the emission bands at 4.2 eV in CaF_2-Cd and 3.5 eV in SrF_2-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 peaked at 4.35 eV.

Starting from exciting photon energies of 10 eV and above that, the emission band of SrF_2-Cd becomes different than the band of Cd^{2+} centres. Namely, the band shifts to higher energies by 0.1 eV.
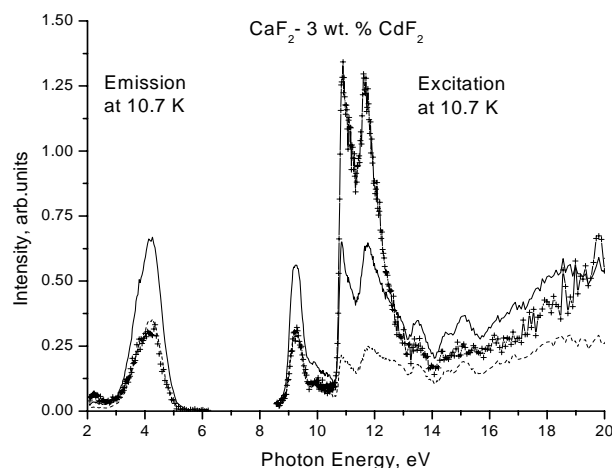
Fig.2 Emission and excitation spectra of CaF_2 -CdF_2 . Excitation spectra were measured for the 4.0 eV emission, emission spectra shown were excited by 9.25 eV photons. Spectra were recorded in time integrated mode (full lines), in the short time window (symbols) and in the long time window mode (dashed lines) as described in the text. Intensity of spectra in the short time window were increased by 12 times for the better comparison with other spectra

Therefore, the excitation spectrum above 10 eV (see Fig.1) corresponds to this new 3.6 eV band. It is well excited in the exciton region (see Fig.1). Moreover, the excitation spectra for emission recorded at 3.6 eV resembles to 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 decay of 3.5 eV and 4.2 eV emission bands in SrF_2 and CaF_2 possess decay times above 1 μ s. The luminescence of Cd^{2+} centres in SrF_2 crystal at 12 K has a decay time 33 μ 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.

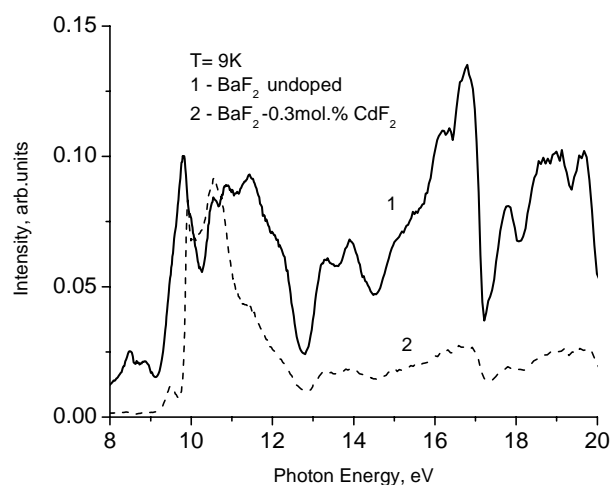Luminescence of the Cd perturbed excitons show apparent fast decay components of 7.5 and 7.3 ns in SrF_2 and in CaF_2 at 10 K, respectively. The initial intensity I_0 of the fast components are 10 times larger then that of the slow components. The fast and slow components of luminescence of singlet and triplet self-trapped excitons at nanosecond and microsecond time scale have been observed in all CaF_2, SrF_2, BaF_2 crystals [11, 12].

Excitation spectra

Strong excitation bands at 8.75 eV and 9.25 eV for the 3.5 and 4.2 eV emission bands were observed in SrF_2-Cd and CaF_2-Cd crystals, respectively (see Fig.1, 2). No other excitation bands were found at lower energies. The sharp onsets at 10.4 eV in SrF_2 and at 10.7 eV in CaF_2 shown on Fig.1, 2 and the following excitation at higher energies belong to the exciton states perturbed by Cd ion. The relative intensities of the short emission components become much higher in these regions (see Fig.1, 2).

The low energy edge of excitation spectra of exciton luminescence shifts apparently towards the 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_2 see Fig.3). Evidently, this shift is due to overlapping of exciton band with strong Cd^{2+} absorption band.

We did not find any emission of Cd^{2+} centres in BaF_2 crystals. Therefore, the position of the main absorption bands were taken from the respective absorption spectra peaked at 8.6 eV [4]. From the comparison of excitation spectra of undoped and Cd-doped BaF_2 crystals (Fig.3) one can conclude that the dip at 9.7 eV is due to the second Cd^{2+} absorption band. Similar to this we interpret analogous dips at 10.25 eV and 10.58 eV (see Fig.1, 2) are arising from the second Cd^{2+} absorption band in SrF_2 and CaF_2, respectively. The energetic positions of the observed Cd^{2+} bands in all three crystals are listed in Table 1.

Fig.3 Excitation spectra for exciton emission at 4.0 eV of BaF_2 -undoped (dashed line) and BaF_2 -0.27 mol.% of CdF_2 (solid line). Spectra were recorded in time integrated mode.

Calculations

Crystal	$E_{Cd^{++}}$ I	$E_{Cd^{++}}$ 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

Tabl.1 Energies in eV of Cd transitions in alkaline-earth fluoride crystals. Energies of Cd bands were taken from excitation spectra for CaF_2, SrF_2, BaF_2 at 10 K and from absorption spectra of BaF_2-Cd (8.6 eV band) at 295 K.

The calculation of absorption of Cd^{2+} 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 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 by 1-1.5 eV higher energies than that of the first bands in alkaline-earth fluorides (see Table 1). The calculated energies are near 1.5 times greater than experimental, which is usual for Hartree-Fock method.

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

Excitation into the first Cd^{2+} absorption band results in the electron transfer from the nearest fluorines to cadmium. The obtained defect can be considered as the Cd^{2+} 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 has a relatively long lifetime near Cd impurity ion also. It is reasonable to assume that the electron is trapped by Cd^{2+} 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 like generally in systems with the 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 CdF_8Me_{12} (Me is Ca, Sr, Ba). The second cluster has a central point between two F ions and contained 40 atoms. In 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 quantum cluster into region of positive point charges, we surrounded the cluster with a few shells of effective core potentials of appropriated metal.
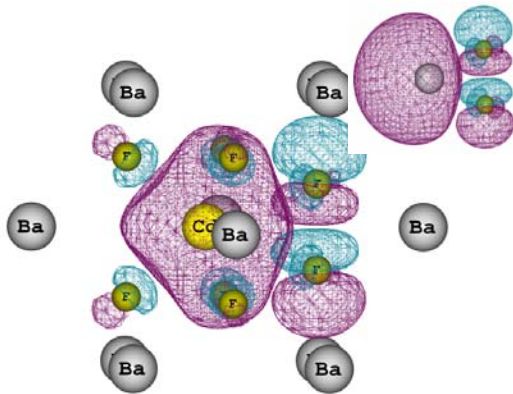

Fig.4 CdF_8Ba_{12} cluster with the optimised geometry. Two fluorine ions are brought together to the distance near 1.9 A between them, a central Cd ion moves to the opposite direction by few tenths of $\overset{\circ}{A}$. Other fluorine ions slightly shift outwards in respect of the centre of cluster. Two highest occupied molecular orbitals, having spins parallel are shown. One orbital is well localised on two nearest fluorine ions forming the F_2^- part and another orbital does the same on Cadmium forming the Cd^+ part. Inset (upper right corner) shows the triplet CdF_2 molecule with optimised geometry. Two highest occupied molecular orbitals are shown.

CdF_8Me_{12} cluster

The calculations were performed for the cluster CdF_8Me_{12} containing 21 atoms. The outer shell Me_{12} remain frozen, while the coordinates of Cd and fluorine ions were optimised to obtain the lowest total energy of the cluster. The usability of such cluster for geometry optimisation was verified by a calculation of pure MeF_8Me_{12} cluster. As a result of calculation the initial coordinates of fluorine ions did not change more than 0.01 Å. Recently such cluster was successfully used in simulations of Cu ions in 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 localised on two fluorine sites and other unpaired electron is localised on the cadmium. The obtained
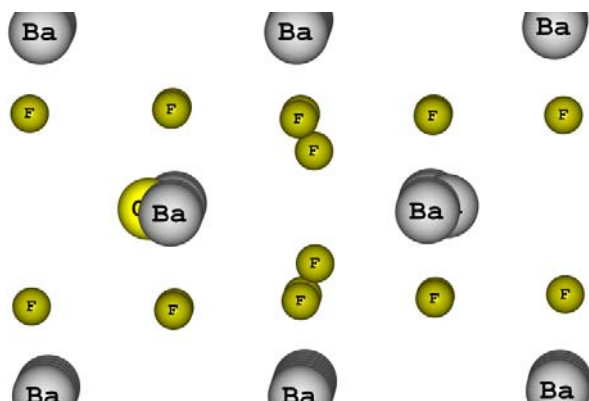
Fig.5 Central part of $CdBa_{19}F_{20}$ quantum cluster with optimised geometry surrounded by 94 Ba effective core potentials

internuclear distance of the F_2^- is 1.94 Å in BaF_2 that is very close to that of the F_2^- centre 1.91 Å in the 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 (Fig.4). The distances from the Cd to surrounding fluorine ions are slightly increased, obviously due to 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 use the relaxed coordinates of cluster ions, obtained in the course of optimisation of triplet state geometry, and calculate the total energy of singlet state. In this way we can estimate the energy of triplet-singlet luminescent transition. The calculated energies are collected in the table 2 together with experimentally observed energies.

$CdMe_{19}F_{20}$ cluster

To verify the results obtained so far we increased the cluster in such way that the created V_k -centre become a centre of cluster. The cluster centred on the V_k centre formed contains 40 atoms. It was chosen to simulate symmetry around the V_k centre. During optimisation of geometry the F_2, Me_2 and next F_8 ions were let free while other atoms were fixed on their equilibrium lattice sites. We obtained qualitatively similar results for the geometry of optimised configuration. However, in this cluster the formed Cd^+ ion pushes the F_2^- outwards from its equilibrium position (Fig.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 experimental ones. As next step we introduce 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 remain freezed during geometry optimisation. All calculations for three different clusters show that one of spins is well localised on the cadmium ion while the same happens with another spin being always localised 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 Fig.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 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).

Zn^{2+} and Hg^{2+} centres

The calculation for largest clusters and appropriated point charges were repeated for Zn and Hg centres. Both metal ions have similar outer shells as cadmium. Zinc has less ionic radius then cadmium and Hg has larger radius than Cd. We calculate the luminescence from both centres by similar way as luminescence from cadmium centres (Fig. 6).

Optimised geometry of Zn and Hg centres are similar to that of Cd-centres. The shift from site position is growth in a row of Hg, Cd, Zn. Obviously the shift is due to exchange interaction in triplet

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 optimised triplet state and singlet state with the same ion coordinates. Results were obtained for the following clusters: CdF_8Me_{12} (I) and $F_2CdMeF_8Me_4F_{10}Me_{14}$ (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 $_{emission\ exper.}$
CaF_2 :Cd^{2+}	6.1	5.0	4.0	4.2
SrF_2 :Cd^{2+}	5.2	4.3	3.5	3.5
BaF_2 :Cd^{2+}	3.1	2.1	1.6	not found

centre. The larger distance between both electrons with parallel spins the less exchange interaction energy. The Cd-centre has smallest total displacements of all ions from original sites. The Hg and especially Zn centres have larger total displacements in triplet state. In parallel wit this the energies of transitions in Zn and Hg-centres less than that of Cd- centres for particular crystal lattice (see Fig. 6).

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 Cd^{2+} band in all alkaline-earth fluorides. Moreover, we found the shift of excitation edge for exciton emission to higher energies due to the strong Cd-related absorption in CaF_2, SrF_2, BaF_2 (for example of BaF_2 see Fig.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 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 (SrF_2-Cd) and 4.2 eV (CaF_2-Cd) belong to the reverse radiative transitions from Cadmium to nearest fluorine ions.

The absence of Cd-related luminescence in BaF_2 crystal may have the following reason. The Cd-related luminescence in BaF_2 may be quenched even at liquid helium temperature. According to simple model the relative Stokes shift (luminescence energy divided by absorption energy) should not be less than 0.5 [13]. The model based on assumption that configuration coordinates of ground and excited states describes by similar parabolas. The luminescence can be observed when the crossover point of excited and ground configuration curves lies at higher energy than transition point of 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_2, SrF_2, respectively, and estimated value for Stokes shift is 0.19 for BaF_2 (see table 1 and 2). Stokes shift depends on lattice relaxation in triplet state. The looser lattice the larger Stokes shift. Definitely, the relative Stokes shift 0.19 is too small to observe luminescence. Another model, which also well explain the existence and absence of F-centre luminescence, based on
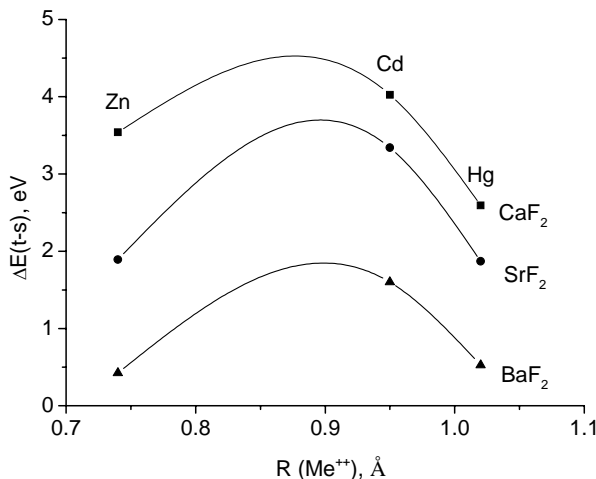
assumption that the system always reach the minimum of excited configuration curve and the absence of luminescence is due to horizontal vibronic tunneling to ground configurational curve [14]. The correspondence between the two different models is not surprising: Lowering the crossover point implies 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 tunneling rate [14]. In any cases the calculated lattice relaxation around triplet Cd centre in BaF_2 is significantly larger then relaxation in CaF_2, SrF_2 and absence of luminescence in BaF_2 is very reasonable.

Fig.6 Energies of triplet-singlet luminescent transitions of Zn^{2+}, Cd^{2+} and Hg^{2+} centres in alkaline-earth fluoride crystals. The curves connected calculated points are shown only for convenience.

Calculations performed confirm that the triplet Cd^{2+} centre can be considered as an unit formed from the Cd^+ ion together with the nearest F_2^- 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 calculated the properties of CdF_2 molecule also. The singlet state of molecule is a linear chain with the Cd ion between two fluorine ions. The molecule in triplet state transforms into configuration consisting of the Cd^+- F_2^- pair (see Fig. 4). The charge and spin distributions of triplet CdF_2 molecule and triplet Cd^{2+} centre are very similar. However, the calculated distance from Cd to the cental line of the F_2^- is 1.96 Å for CdF_2 molecule and 2.6-2.8 Å for triplet Cd^{2+} centre in alkaline-earth fluorides. This discrepancy is explained by the fact that in the CdF_2

molecule the geometrical centre of 5s Cd shell is about 0.6 Å farther from the line connecting two fluorine ions (F_2^-) than the position of Cd nucleus itself. The geometrical centre of 5s Cd orbital and position of Cd nucleus is very close in these crystals (see Fig. 4).

According to our calculation the Zn- and Hg-centres have small energies of triplet-singlet luminescence transitions (see Fig. 6) and can be considered as exciton luminescence quenchers in BaF_2 (and possibly in SrF_2 also).

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 were 3.5 eV and 4.2 eV observed at low temperatures under excitation into Cd impurity region in SrF_2 and CaF_2, respectively, and are assigned to the triplet-singlet luminescence transitions of Cd defects. Optimised geometrical configuration of the triplet state of the Cd^{2+} centre can be considered as the Cd^+-F_2^- (V_k) pair or the CdF_2 triplet molecule. Luminescent transitions occur from the Cd^+ 5s-state to the σ_u state of F_2^-. The calculated energies of triplet-singlet transitions of Cd^{2+} centre are in good agreement with the experimental transition energies observed for CaF_2 and SrF_2.

Investigation of excitation spectra allow us to find the maxima of the first and second Cd absorption bands in CaF_2, SrF_2 and that of the second band in BaF_2 (see Table 1).

Acknowledgment

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