Cadmium centres in alkaline-earth fluoride crystals

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Strong absorption in the vacuum ultraviolet region near the exciton edge was observed in Cd doped CaF_2, SrF_2 and BaF_2 crystals. The Cd^{++} absorption band at 8.6 eV was observed in low doped BaF_2 crystals. In SrF_2 and CaF_2 the maximum of Cd^{++} band cannot be resolved due to stronger overlapping with exciton bands. The calculations of geometry of Cd^{++} and Cd^+ centres and Cd- related electron transitions were done using $ab-initio$ Hartree-Fock and density functional methods. The experimental and calculated results lead us to the conclusion that strong Cd^{++} absorption bands belong to allowed transitions from the nearest fluorides to the Cd^{++} ion. Lattice relaxation around Cd^+ centres, created by x-irradiation, and optical transitions of these centres were also calculated. The calculated energies are in good agreement with experimental ones.

1 Introduction

Cadmium impurities considerably decrease the unwanted exciton emission in BaF_2 fast scintillators [1]. However the optical properties of Cd^{++} defects in alkaline-earth fluorides have not been investigated.

Strong bands near the exciton absorption bands were observed in Cd- or Zn-doped NaCl, KCl, KBr, KJ crystals [2]. These bands were tentatively ascribed to those of excitons in the vicinity Cd or Zn ions. During x-ray irradiation new bands due to s-p transitions of single valence Cd or Zn centres, respectively, were observed in the ultraviolet region [2].

In this paper the optical absorption and excitation spectra were studied in BaF_2, SrF_2, CaF_2 doped with different concentrations of cadmium. $Ab-initio$ Hartree-Fock and density functional calculations were done to refine the spatial structure of cadmium centres and the details of optical transitions.

2 Experimental

The excitation and absorption spectra in the 4-12 eV region were measured with a grating vacuum monochromator VMR2. Cadmium impurity was added into the raw materials as CdF_2 in amount from 0.01 to 2 weight %. The crystals were grown in vacuum in a graphite crucible closed by a lid to prevent evaporation of CdF_2 [3][1]. The concentration of cadmium in BaF_2 and SrF_2 crystals was measured by atomic emission spectroscopy analysis [2].

$Ab-initio$ Hartree-Fock and density functional calculations of a molecular cluster containing a few shells around cadmium were done using Gamess [4] and PCGamess codes [5]. Calculations were done

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[1] All crystals were grown by V. Ivashechkin and A. Istomin in our laboratory

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

with LANL2 basis. For density functional calculations B3LYP exchange and correlation functionals were chosen. Lattice distortion around of Cd^{++} in SrF_2 was determined using the GUESS code [6]. Very similar lattice distortion was obtained also using the significantly faster Gamess geometry optimisation. In this case we chose a quantum cluster $CdF_8Sr_{12}F_{24}Sr_6$ with the Oh symmetry group. We surround the quantum cluster with three shells of alkaline-metal core pseudopotentials on sites of positive charges and additionally by three shells of potassium metal core pseudopotentials on sites of negative charges. Effective core potentials for fluorine F^- are not known. Potassium core potentials were used instead of those for fluorides because K^+ and F^- ions have almost equal ionic radiuses. Similar method was used for the calculation of various defects in MgO crystal [7], where a method of deriving of effective core potentials for negative and positive ions for using in crystal calculations is presented. During the geometry optimisation the positions of ions from the 5-th fluorine shell and 6-th alkali-metal shell as well as additional effective core potentials and point charges are frozen.

3 Results and discussion

3.1 Optical spectra

Strong absorption in the vacuum ultraviolet region below the respective exciton edges appear in BaF_2, SrF_2, CaF_2 doped with CdF_2 (Fig.1). The low energy wing of this band continuously shifts to lower energies with increasing cadmium concentration.
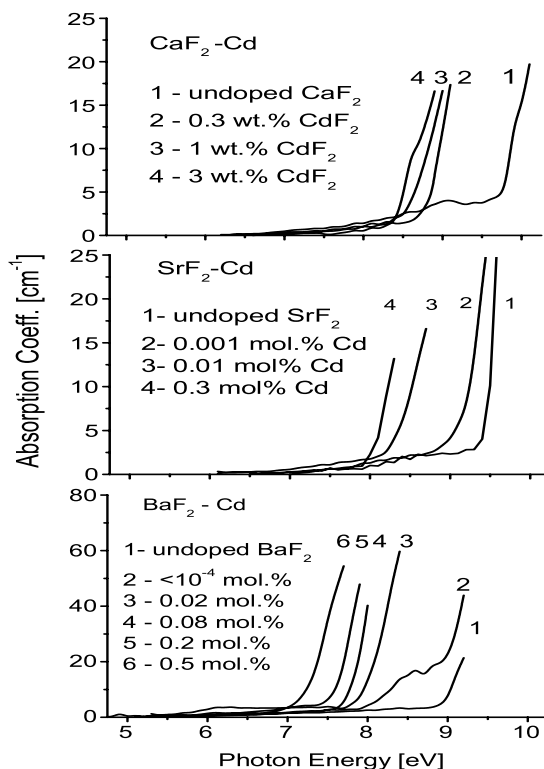

Fig. 1 Absorption spectra of CaF_2, SrF_2 and BaF_2 crystals doped with different amounts of cadmium at room temperature. The concentration of cadmium in CaF_2 are not analysed yet. Therefore we present the cadmium concentration in raw material CaF_2. Based on analysis for BaF_2 and SrF_2 we estimate that concentration of Cd in CaF_2 crystals should be at least ten times less then that in raw material.

No new emission bands were observed under illumination into Cd^{++} vacuum ultraviolet bands. The emissions were absent at room temperature and at 80 K. Absence of Cd^{++} luminescence is in line with the fact that cadmium impurity effectively quenches exciton luminescence. The influence of cadmium impurity on exciton luminescence will be presented in a separate paper.

The low energy edge of excitation spectra of exciton luminescence shows an apparent shift to higher energy with increasing of Cd concentration. The shift becomes 0.3-0.4 eV when the Cd concentration reach 0.1 mol. %. No exciton emission was observed with illumination into the Cd absorption region. Evidently, this shift is due to overlapping of the exciton band with the strong Cd absorption band. Taking the left wing of the Cd band from the absorption spectrum and right wing from the excitation spectrum we may estimate the position of the band maximum as a mean value from the left and right wing energies. The estimated peaks of Cd^{++} absorption bands in all three crystals are shown in Table 1.

3.2 Cd^{++} centres calculations

Calculations of Cd clusters show that a new level appears in the band gap. The level wavefunction consists mainly of the 5s cadmium level. The new level is separated from alkaline-metal conduction band states by a few eV. Geometry optimisation calculations show that ions from the first shell of fluorine and the second shell of the alkaline-earth metal are shifted toward the Cd. This is not surprising because of the small ionic radius of the cadmium ion. Displacements obtained by Hartree-Fock calculations agree well with those obtained by density functional calculations. The calculated displacements of the nearest fluorine are 0.02, 0.11, 0.23 for CaF_2, SrF_2, BaF_2, respectively. The distances between the cadmium and fluorine from first shell in CaF_2, SrF_2 and BaF_2 become very close to those in CdF_2 (R=2.33 Å) after geometry optimisation. Therefore the calculated displacements can be considered as realistic.

The transition energies and oscillator strengths of transitions were calculated for the optimised geometry of the cluster. The calculated band gap energy overestimates the experimental band gap energy by 1.3-1.4 times (Table 1). Based on experimental E_g energies we correct the calculated position of the Cd bands (see Table 1). The corrected values of calculated Cd bands are larger than the experimental positions of bands by 0.7 - 1.2 eV. There is rather good general agreement between calculated and observed transitions. Oscillator strengths of allowed transitions from the three filled t_{1u} fluorine states to the empty a_{1g} Cd state have values from 0.47 to 0.67. The energy differences between Cd transitions and band gap transitions are largest for BaF_2 and smallest in CaF_2. According to this a maximum of Cd absorption band was observed in BaF_2 and was not observed in CaF_2 and SrF_2, due to closeness to the exciton absorption edge.

Therefore the experimentally observed Cd band should belong to charge transfer transitions from the surrounding fluorine to the cadmium 5s levels.

Table 1 Energies in eV of transitions in Cd doped alkaline-earth fluoride crystals. E_g - band-to-band transitions (exp.-experimental and calc. - calculated), E_{Cd++} - transitions from valence band to Cd level, f_{Cd++} - oscillator strength of transitions from each of three T_{1u} valence band states to A_{1g} Cd states. Calculated E_{Cd} were corrected by (E_g exp./E_g calc.)

Crystal	E_g exp.	E_g calc.	E_{Cd++} calc.	f_{Cd++}	E_{Cd++} corr.	E_{Cd++} exp.
CaF_2:Cd^{2+}	11.5[a]	14.76	13.76	0.67	10.7	≈ 9.5
SrF_2:Cd^{2+}	10.9[a]	14.77	13.26	0.63	9.8	≈ 9.0
BaF_2:Cd^{2+}	10.7[a]	13.80	12.10	0.47	9.3	≈ 8.6

3.3 Cd^+ centres

A known band of Cd^+ ions at 4.08 eV [1] was observed in Cd-doped BaF_2 crystals after x-irradiation at room temperature. The band was stable at room temperature and completely disappeared after annealing at 500^oC. The height of 4.08 eV band was proportional to Cd concentration. No bands in the the visible region were created by x-irradiation at room temperature. A comparison of F, V_k and Cd^+ absorption bands

appeared in pure BaF_2 and BaF_2-Cd after x-irradiation allow us to conclude that the oscillator strength of Cd^+ band is closed to the strength of F band. The oscillator strength of the F band is in the range 0.5-0.8 in many crystals. Similar Cd^+ bands were observed at 3.96 eV and at 3.8 eV in x-irradiated SrF_2 and CaF_2 crystals, respectively. The maxima of the Cd^+ absorption bands shift to higher energies by 0.03 eV and the widths of bands remain the same when the temperature decreased from 295 K to 80 K. No emissions were observed in Cd doped CaF_2, SrF_2, BaF_2 under illumination into Cd^+ bands at 80 K. The Cd^+ absorption bands can be photobleached at 80 K.

According to our calculations the fluorines from first shell around the Cd^+ ion move outward from the cadmium ion. Shifts from the equilibrium site are 0.19, 0.09, 0.055 $\mathring{A}$ for CaF_2, SrF_2 and BaF_2, respectively. The alkali metals from second shell are slightly shifted to the cadmium, obviously due to attraction to effective negative charge of cadmium. To check the validity of the geometry optimisation we calculate the isotropic hyperfine constants of the Cd unpaired electron on nearest fluorine nuclei. The calculated hyperfine constants satisfactory agree with experimental hyperfine constants (see Table 2). Therefore, the calculated geometry of the Cd^+ defects is realistic.

Table 2 Parameters of Cd^+ centres in alkaline-earth fluoride crystals. The energy values are given in eV. E_{Cd+} - 5s-5p transitions in Cd^+ ions, f_{Cd+} - oscillator strength for each of three A_{1g} - T_{1u} Cd^+ transitions. Experimental position of Cd^+ bands were taken from paper [3]. Calculated and experimental isotropic hyperfine constant α_{iso} of Cd electron with nearest fluorine nuclei expressed in gauss. Experimental constants were taken from [9]

Crystal	α_{iso} calc.	α_{iso} exp.	E_{Cd+} calc.	f_{Cd+}	E_{Cd+} exp.
CaF_2	100	140.4	4.56	0.34	3.80
SrF_2	73	111	4.67	0.36	3.95
BaF_2	53	79	4.76	0.36	4.08

The calculated transition energies overestimated the experimental energies by 1.2 times (see Table 2). The calculation results reflect the right tendency in Cd s-p transitions as a function of the crystal lattice. Therefore we may definitely conclude that the bands near 4 eV in x-irradiated MeF_2-Cd belong to 5s-5p transition in Cd^+ ions.

References

[1] U. Rogulis, J. Trokss, A. Veispals, I. Tale, P. Kulis, and M. Springis, Radiat. Eff. Defects Solids **135**, 859 (1995).
[2] S.C. Jain and S. Radhakrishna, Phys. Rev. **172**,972 (1968).
[3] A.I. Nepomnyashchikh, E.A. Radzhabov, A.V. Egranov, V.F. Ivashechkin, A.S. Istomin, and T. Kurobori, Radiat. Meas. (2004), to be published
[4] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J.A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).
[5] A. Granovsky http://classic.chem.msu.su/gran/gamess/index.html
[6] V.B. Sulimov, P.V. Sushko, A.H. Edwards, A.L. Shluger, and A.M. Stoneham, Phys. Rev. B **66**, 024108 (2002),
[7] V. Luana, J.M. Recio, A.M. Pendas, M.A. Blanco, L. Pueyo, and R. Pandey, Phys. Rev. B **64**, 104102 (2001).
[8] R. Lindner, R.T. Williams, and M. Reichling, Phys. Rev. B **63**, 5110 (2001).
[9] V.F. Krutikov, N.I. Silkin, and V.G. Stepanov, Phys. Solid States **18**, 2958 (1976).