CONDENSED-MATTER SPECTROSCOPY

Absorption Spectra of Thin Layers of Solid Solutions $Cs_2(Cd_{1-x}Zn_x)I_4$

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Received June 16, 2009

Abstract—The excitonic absorption spectra of thin films of ferroelectric Cs_2CdI_4 and Cs_2ZnI_4 solid solutions are studied for the first time. It is found that, within the whole range of molar concentrations x, the spectra of $Cs_2(Cd_{1-x}Zn_x)I_4$ comprise two bands that originate from the bands of the two compounds. It is shown that the exciton transfer occurs most efficiently between the tetrahedrons CdI_4 and ZnI_4 along the **b** axis of the crystal. Unusual behavior of the concentration with regards to the maxima of long-wavelength excitonic bands $E_m(x)$ agrees well with the developed theory that takes into account dependence on x of the matrix element of the intertetrahedron exciton transfer and that is similar to the theory of Davydov's splitting in molecular crystals.

The search for new ferroelastic crystals is carried out, in recent years, mainly by varying properties of known compounds through purposely doping them with different impurities. Compounds Cs_2CdI_4 and Cs_2ZnI_4 are ferroelastics with incommensurate phase and very close parameters of the crystal lattice [1−5], which should favor formation of solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ over the whole range of concentrations.

The absorption spectra of Cs_2CdI_4 and Cs_2ZnI_4 have been studied previously [6−8]. It has been established that both compounds are direct band dielectrics, with the low-frequency excitons localized in the structural elements CdI_4^{2-} (ZnI_4^{2-}) of the compounds. With this localization, one should expect that the disordering in the sublattice $Cd_{1-x}Zn_xI_2$ of the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ should substantially change their absorption spectra. The absorption spectra of the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ have not been studied previously. They are of interest from the viewpoint of the theory of solid solutions and excitons in multicomponent compounds. In addition, the compounds Cs_2CdI_4 and Cs_2ZnI_4 reveal their layered nature in the types of bonding [2, 5−8], which imparts specific features to the spectra of $Cs_2(Cd_{1-x}Zn_x)I_4$. In this paper, we present the results of studying the absorption spectra of the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ within the range of concentrations $0 \le x \le 1$.

EXPERIMENTAL

Thin films of $Cs_2(Cd_{1-x}Zn_x)I_4$ were prepared by the vacuum evaporation of a mixture of powders CsI, CdI_2, and ZnI_2 with a specified molar composition onto a quartz substrate heated to 100°C using the method of [7]. The samples were annealed at the same temperature for an hour.

The quality and phase composition of the films were monitored by the absorption spectra measured at $T = 90$ K. It was possible due to a substantial difference between the spectral positions of the long-wavelength bands in $Cs_2(Cd_{1-x}Zn_x)I_4$ (4.65−4.8 eV), CdI_2 (4.03 eV [9]), ZnI_2 (4.48 eV [9]), and CsI (5.8 eV).

The absorption spectra were measured in films 100−150 nm thick using an SF-46 spectrophotometer in the spectral range 2−6 eV at $T = 90$ and 290 K. The thickness of the films was determined from the transmission spectra using the method of [10].

The parameters of the long-wavelength excitonic bands were determined using the method in [8] by approximating the bands by two-oscillator symmetric profiles with the shape intermediate between Lorentzian and Gaussian profiles (mixed profile). The mixed profile, being a linear combination of the Lorentzian and Gaussian profiles, does not differ substantially from the Voigt profile. The parameters of the excitonic bands (the position E_m, the halfwidth Γ, and the imaginary part of the permittivity at the peak of the exciton band $\varepsilon_{2m} \equiv \varepsilon(E_m)$) were chosen to provide the best fit between the calculated profile and the measured spectrum of the optical density $D = -\ln\tau$ at the long-wave-
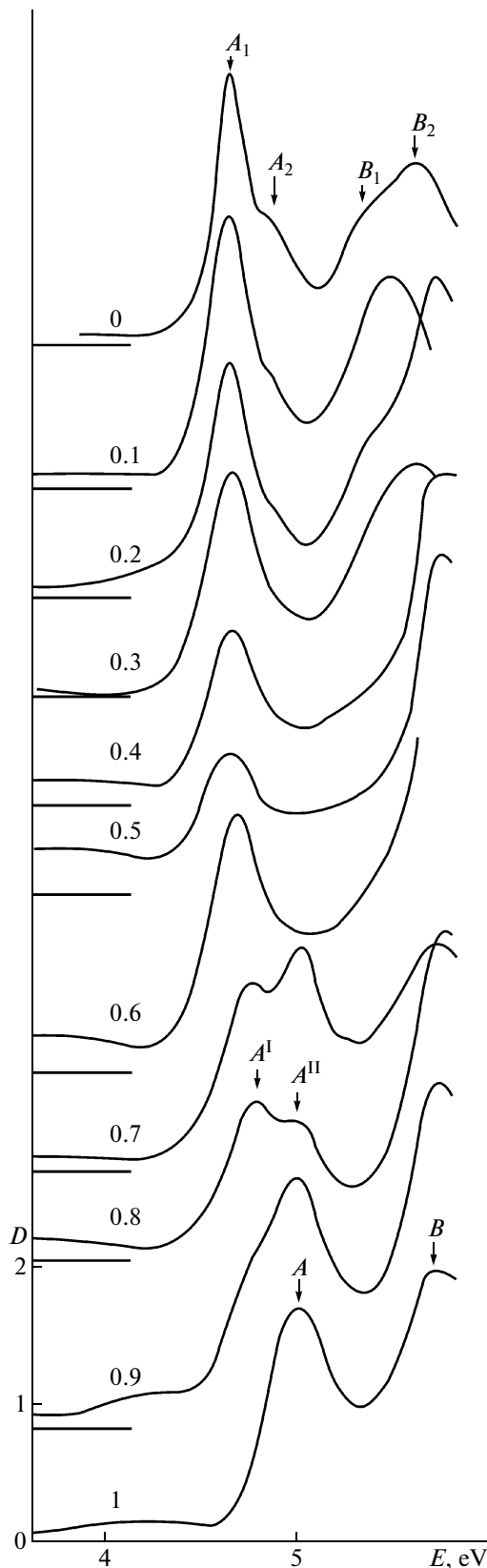
Fig. 1. Absorption spectra of thin films of solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ at different x ($0 \leq x \leq 1$) and $T = 90$ K.

length slope of the bands. The spectra were measured at 11 values of x with a step of $x = 0.1$.

EXPERIMENTAL RESULTS AND DISCUSSION

The absorption spectrum of Cs_2CdI_4 thin films (Fig. 1) reveals intense bands A_1 and A_2, which are located at the long-wavelength edge of the intrinsic absorption band at 4.64 eV and 4.89 eV (90 K). At shorter wavelengths of the spectrum, there are the bands B_1 and B_2, which are located at 5.25 and 5.6 eV, respectively. With increasing temperature, the A and B bands shift toward longer wavelengths, broaden and weaken in intensity due to the exciton–phonon interaction (EPE), which indicates their relation to excitons. The spectrum of Cs_2ZnI_4 ($x = 1$), in contrast to that of Cs_2CdI_4, reveals isolated excitonic A and B bands (5.04 and 5.73 eV), with the spectral interval between them $\Delta E_{A,B} = 0.725$ eV being controlled by the spin–orbit splitting of the upper valence band [8]. The large value of the halfwidth of the long-wavelength A band in Cs_2ZnI_4, $\Gamma(1) = 0.37$ eV, allows one to assume that, in this compound, as in Cs_2CdI_4, the A band exhibits splitting which is revealed, however, only as broadening of the band. With addition of the Cd impurity ($x = 0.9$), a weak low-frequency band splits off from the A band. The intensity of this band increases with the concentration of Cd^+ ions.

On the contrary, the intensity of the high-frequency A^{II} band decreases. As will be shown below, the low-frequency A^I band observed in the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ ($0.1 \leq x \leq 0.9$) is genetically related to the A_1 band in Cs_2CdI_4, while the high-frequency A^{II} band, to the A band in Cs_2ZnI_4. In the range $0.2 \leq x \leq 0.6$, due to the concentration broadening of the excitonic bands, the A^{II} band can be seen in the spectrum only as an asymmetry of the A^I band.

The concentration behavior of the spectral position [$E_m(x)$] of the long-wavelength excitonic bands A^I and A^{II} in $Cs_2(Cd_{1-x}Zn_x)I_4$ is also unusual (Fig. 2a); namely, the dependence $E_m(x)$ reveals a region of inflection and increases with x. Within the experimental error, the position of the low-frequency band does not change up to $x = 0.5$, and then shows a steep rise at $0.5 \leq x \leq 0.8$ with a maximum of dE_m/dx at $x \approx 0.65$. On the contrary, the maximum of dE_m/dx for the high-frequency band is observed at $x \approx 0.4$. This dependence is not observed for excitonic bands of solid solutions of binary compounds, in which the deviation from the linear dependence $E_m(x)$ is the greatest at $x = 0.5$. However, as follows from Fig. 2b, the difference between the two frequencies $\Delta E_m(x)$ is the greatest at $x = 0.5$ and is more symmetric with respect to this point. It is also noteworthy that, at $x = 0$ and 0.1, the
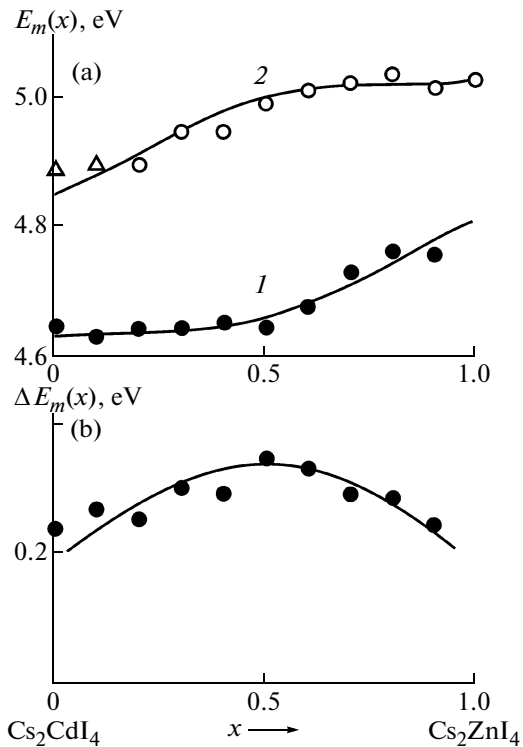
Fig. 2. Concentration dependence of (a) spectral position $E_m(x)$ and (b) difference $\Delta E_m(x)$ between spectral positions of (*1*) the long-wavelength excitonic A^I and (*2*) A^{II} bands in the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$: (dots) experiment and (solid curves) calculations by Eq. (4).

Fig. 3. Concentration dependence of halfwidth $\Gamma(x)$ of long-wavelength excitonic bands (*1*) A^I and (*2*) A^{II} in solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$: (dots) experiment and (solid curves) calculations by Eq. (1).

spectrum reveals a weak A_2 band at 4.89 eV, which is inherent to Cs_2CdI_4.

As expected, the halfwidth of the bands is the greatest at $x = 0.5$ (Fig. 3) and can be well described by the dependence

$$\Gamma(x) = \Gamma(1)x + \Gamma(0)(1 - x) + \alpha x(1 - x), \qquad (1)$$

where $\Gamma(0) = 0.17$ and 0.2 eV, $\Gamma(1) = 0.24$ and 0.29 eV, $\alpha = 0.5$ and 0.3 eV for the A^I and A^{II} bands, respectively.

In one of the earlier papers [11] devoted to the theory of exciton spectra of inorganic compounds, a criterion has been proposed for dividing the spectra into two types, i.e., persistence and amalgamation. Optical spectra of the first type reveal two bands inherent in the compounds A and B, remaining distinguishable over the whole range of variation of x for the substitutional solution $A_{1-x}B_x$. Spectra of the second type show a single band with a position dependent on x. As the criterion for distinguishing between the spectra, one can use the ratio $\rho = \Delta/T$ [11], where $\Delta = E_A - E_B$ and T is the bandgap width. According to [11], persistence-type spectra are formed at $\rho \geq 0.5$ and those of the amalgamation type are formed at $\rho < 0.5$. The amalgamation-type spectra are observed in solid solutions
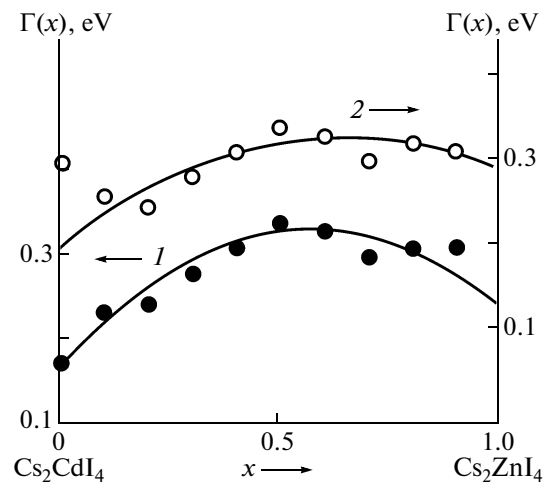
of semiconductor or some dielectric binary compounds, while those of the persistence type are formed in wide bandgap dielectrics. In our case, $\Delta = 0.4$ eV and, as will be shown below, $T \ll 0.2$ eV; i.e., the criterion for the persistence-type spectrum is evidently satisfied ($\rho > 2$). It is noteworthy that the analysis of the concentration dependence of the persistence-type spectra was performed in [11] at $\rho \leq 0.8$, and the case of large ρ has not been considered.

Before discussing the spectra under study, let us consider some specific features of the crystal lattices of Cs_2CdI_4 and Cs_2ZnI_4. At room temperature, both compounds have an orthorhombic crystal lattice with the parameters $a = 1.074$ nm, $b = 0.846$ nm, and $c = 1.485$ nm [1, 2] for Cs_2CdI_4 and $a = 1.086$ nm, $b = 0.82$ nm, and $c = 1.464$ nm [3−5] for Cs_2ZnI_4 with the number of molecules per unit cell $z = 4$. With decreasing temperature to 90 K, both compounds experience a succession of phase transitions (paraphase ⟶ incommensurate phase ⟶ ferroelectric phase with monoclinic and triclinic lattices) [1−5]. Detailed structural studies of the monoclinic and triclinic lattices in Cs_2CdI_4 at low temperatures showed [1] that the parameters a, b, and c of the triclinic lattice weakly differ (within one percent) from those of the orthorhombic phase, and the angles between **a**, **b**, and **c** deviate from 90° by less than 12′. Therefore, the low-temperature triclinic lattice can be considered as a slightly distorted orthorhombic lattice with $z = 4$.

Both compounds belong to the layered crystals of the β-K_2SO_4 type with layers perpendicular to the **c** axis and the tetrahedrons CdI_4 and ZnI_4 lying in the **ab** plane. The lengths of the bonds d_{Cd-I} in Cs_2CdI_4 are 0.274–0.313 nm; i.e., the tetrahedrons are slightly dis-

torted and d_{Cd-I} is noticeably smaller than the sum of the Pauling's ionic radii ($d_{Cd-I} = 0.313$ nm), which indicates a certain contribution of covalent bonding. Between the tetrahedrons in the layers, as well as in the interlayer gaps, the Cs^+ ions are arranged with $d_{Cs-I} = 0.385–0.428$ nm, which is close in value to the sum of the ionic radii ($d_{Cs-I} = 0.385$ nm). The structure of the Cs_2ZnI_4 crystals is less studied [3–5] and detailed data about d_{Zn-I} in the tetrahedrons are not available.

Since the smallest parameter of the unit cell is aligned along the **b** axis, one should expect that the translational exciton transfer is the most efficient along this direction. Between equivalent tetrahedrons, there is a tetrahedron, which is slightly displaced with respect to the axis, with the interval for Cs_2CdI_4 being $d_{Cd–Cd} = 0.546$ nm according to our estimate. It is likely that, in Cs_2ZnI_4, this interval is smaller. As follows from the Frenkel model, the exciton transfer between adjacent nonequivalent tetrahedrons should result in Davydov's splitting of excitonic bands [12]. The existence of the weaker peak A_2 at 4.89 eV in the spectrum of Cs_2CdI_4 (Fig. 1) is likely associated with Davydov's splitting; the interval $E_{A2}-E_{A1}$ is 0.25 eV. Because of the difference ($d_{Cd–Cd} = 0.85$ nm and $d_{Cd–Cd} = 0.546$ nm) between equivalent and nonequivalent tetrahedrons, one should expect that the bandgap width in Cs_2CdI_4 is $T \ll 0.2$ eV. Two points in Fig. 2a, i.e., at $x = 0$ and $x = 0.1$, are related to Davydov's splitting. Unfortunately, we failed to detect the splitting in Cs_2ZnI_4; however, the nonelementary nature of the A_1 band in this compound is implicitly evidenced by its large halfwidth (0.37 eV) compared to that in Cs_2CdI_4 (0.18 eV).

The transfer of excitons in the solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ is possible between the tetrahedrons CdI_4 and ZnI_4, which is similar to the transfer of excitons between nonequivalent tetrahedrons in pure compounds. Keeping in mind this similarity, we can make use of the approach developed for the interpretation of Davydov's splitting. Consider the Schrödinger equations that take into account transfer of excitons between the adjacent tetrahedrons CdI_4 and ZnI_4,

$$(\hat{H}_1 + \hat{V}_{12})\psi = E\psi, \tag{2a}$$

$$(\hat{H}_2 + \hat{V}_{21})\psi = E\psi. \tag{2b}$$

Here, $\hat{H}_1$ and $\hat{H}_2$ are the Hamiltonians used to find excitonic states in Cs_2CdI_4 and Cs_2ZnI_4, respectively, and to take into account the transfer of excitons between equivalent and nonequivalent tetrahedrons $CdI_4 \longrightarrow CdI_4$ or $ZnI_4 \longrightarrow ZnI_4$ in solid solutions, while the operators $\hat{V}_{12}$ and $\hat{V}_{21}$ take into account the transfer of excitons between CdI_4 and ZnI_4. The wave function ψ belongs to excitons in the solid solution

and is a linear combination of the wave functions in pure compounds as follows:

$$\psi = c_1\psi_1 + c_2\psi_2, \tag{3}$$

where the normalization condition imposes the restriction upon the coefficients c_1 and c_2 of $c_1^2 + c_2^2 = 1$. At $\hat{V}_{12} = \hat{V}_{21} = 0$, Eqs. (2) yield the eigenenergies E_1 and E_2 for excitons in the two compounds with allowance for Davydov's splitting. Generally speaking, these equations depend on the excitonic wave vector **K**. However, taking into account that the width of the excitonic zones is small and that they are revealed in the excitonic absorption bands upon wave vector conservation **K** = **q** (**q** is the photon wave vector), the dependence $E(\mathbf{K})$ may be neglected assuming that $\mathbf{K} = 0$.

To find the energy levels of system (2), let us multiply Eqs. (2a) and (2b) by ψ_1^* and ψ_2^*, respectively and integrate them assuming that the integrals of $\langle\psi_1|\psi_2\rangle$ and $\langle\psi_{1,2}|\hat{H}_{1,2}|\psi_{2,1}\rangle$ vanish. As a result, we obtain the system of homogeneous equations for c_1 and c_2,

$$c_1(E_1 - E) + c_2V_{12} = 0, \tag{4a}$$

$$c_2(E_2 - E) + c_1V_{21} = 0. \tag{4b}$$

A nontrivial solution of this system gives a secular equation that yields the energy eigenvalues of the two excitons,

$$E_{\pm} = (1/2)[E_1 + E_2 \pm \sqrt{(E_1 - E_2)^2 + 4V_{12}V_{21}}]. \tag{5}$$

Here, the energies V_{12} and V_{21} are the matrix elements of the operators $\hat{V}_{12}$ and $\hat{V}_{21}$: $V_{12} = \langle\psi_1|\hat{V}_{12}|\psi_2\rangle$ and $V_{21} = \langle\psi_2|\hat{V}_{21}|\psi_1\rangle$.

For the molar concentrations $x = 0$ and 1, the matrix elements V_{12} and V_{21} vanish, which indicates that they depend on x in the solid solution $Cs_2(Cd_{1-x}Zn_x)I_4$,

$$V_{12} = x(1-x)\beta_{12}, \tag{6a}$$

$$V_{21} = x(1-x)\beta_{21}, \tag{6b}$$

where the energies β_{12} and β_{21} are assumed to be independent of x and equal to each other. Taking into account Eqs. (6), the energy difference $\Delta E = E_+ - E_-$ of the two excitons should be the greatest at $x = 0.5$, which is confirmed by the experimental data (Fig. 2b).

At constant E_1 and E_2 (independent of x), the energies of the excitonic bands in the solution should be minimum for the low-frequency band and maximum for the high-frequency band at $x = 0.5$. However, the experimental dependence E_+ and E_- on x (Fig. 2a) contradicts this statement. From this, we have the dependence of E_1 and E_2 on x and, therefore, $\Sigma E = E_1 + E_2$. The quantity ΣE can be found from the experi-

mental data on E_+ and E_- and from Eq. (5), since $E_+ + E_- = E_1 + E_2$. Processing of this dependence in the interval $0.1 \leq x \leq 0.9$ shows that, within the experimental error, ΣE increases linearly with x,

$$\Sigma E = \Sigma E(0) + \alpha x, \qquad (7)$$

where $\Sigma E(0) = 9.5 \pm 0.02$ eV and $\alpha = 0.36 \pm 0.03$ eV. Then, assuming linear dependence of terms in the sum on x with the same slope and using the known values $E_2(0) = 4.64$ eV and $E_1(1) = 5.04$ eV, we have

$$E_1(x) = 4.86 + (0.18 \pm 0.02)x \text{ eV},$$
$$E_2(x) = 4.64 + (0.18 \pm 0.02)x \text{ eV}. \qquad (8)$$

It follows from this that the difference $\Delta E = E_1 - E_2$ hardly depends on x at all and equals 0.22 eV. Using this value along with $\Delta' E = E_+ - E_- = 0.34$ eV at $x = 0.5$ and Eqs. (5) and (6), we established a good agreement between the calculated dependence $\Delta' E(x)$ and experimental data (Fig. 2b). Thus, we have found that $\beta = 0.5$ eV. The calculation of the concentration dependences of the spectral positions of the long-wavelength excitonic bands by Eq. (5) with allowance for Eqs. (6) and (7) at $\beta = 0.5$ eV yields good agreement with the experimental data (Fig. 2a).

The reason for the growth of $E_1(x)$ and $E_2(x)$ with concentration is not quite clear and we can only make some reasonable guesses about it. This growth is likely to be related to a change of the parameter b of the unit cell with x in solid solution. Let us assume that the adjacent tetrahedrons arranged along the **b** axis are connected between themselves by bridging ions I^-, and this bond is not destroyed in solid solution. Then, when concentration of the tetrahedrons ZnI_4 noticeably exceeds that of CdI_4, the period of some chains of ZnI_4 appears to be close to $b = 0.82$ nm in Cs_2ZnI_4, which leads to extension of the tetrahedrons CdI_4 located between the chains, i.e., to an increase in d_{Cd-I}. However, it is known that the growing interatomic distance leads to increasing share of the long-range ionic bonding in the general ionic–covalent interaction. We assume that increasing share of ionic bonding leads to a short-wavelength shift of the low-frequency band with increasing x. At the same time, as the concentration of the tetrahedrons CdI_4 increases ($x < 0.5$), some of their chains have the period close to $b = 0.846$ nm in Cs_2CdI_4. As a result, the interaction of the ends of chains with tetrahedrons ZnI_4 leads to their compression, an increase in the share of the covalent bonding in them, and eventually to a shift of the high-frequency excitonic band towards lower energies. To test this hypothesis, one should measure the shift of the excitonic bands induced by hydrostatic pressure, although, as far as we know, such studies have not yet been performed for Cs_2CdI_4 and Cs_2ZnI_4.

CONCLUSIONS

The absorption spectra of excitons in thin films of solid solutions $Cs_2(Cd_{1-x}Zn_x)I_4$ were found to belong to the persistence type according to the classification of [11]. Analysis of the spectra revealed two excitonic bands genetically related to the bands of Cs_2CdI_4 and Cs_2ZnI_4. Both bands shift nonmonotonically towards higher frequencies with increasing x, with the inflection points in the dependence $E_m(x)$, which is symmetric with respect to $x = 0.5$, but the frequency difference between these bands is the greatest at $x = 0.5$ and the dependence $\Delta E_m(x)$ is symmetric with respect to this point. A theory was developed that accounts for this spectral shift with increasing x accompanying the exciton transfer between the tetrahedrons CdI_4 and ZnI_4 in the solution. The theory takes into consideration the dependence of the transfer operator on x and certain experimental data pertaining to crystal structure and excitonic operators of the starting compounds. The results of calculations based on the formulas thus obtained agree well with the experimental data to within experimental errors.

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Translated by V. Zapasskiĭ