

Peculiarities of absorption spectra of solid solutions of CsAg_2I_3 – CsCu_2I_3 complex compounds

V.K.Miloslavsky, O.N.Yunakova, E.N.Kovalenko*

V.Karazin National Kharkiv University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

*Kharkiv National University of Radio Electronics,
14 Lenin Ave., 61166 Kharkiv, Ukraine

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The low-frequency electron absorption spectra in thin films of $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ solid solutions have been investigated. At the fundamental band edge, two exciton bands A_0 and A_1 are observed, and the parameters thereof (spectral position, half-width and oscillator strength) have been found in the $0 \leq x \leq 1$ range. From the concentration dependence of those parameters, the A_0 and A_1 excitons have been established to be localized in the double chains consisting of tetrahedrons MI_4 ($\text{M} = \text{Ag}, \text{Cu}$) and being a structural elements of CsM_2I_3 crystal lattice. Experimental results are discussed assuming the hybridization Ag, Cu d -orbitals and I p -orbitals in the upper valence band of the compounds and dependence of hybridization on molar concentration x .

Исследованы низкочастотные электронные спектры поглощения в тонких пленках твердых растворов $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$. На краю фундаментальной полосы наблюдаются две экситонные полосы A_0 и A_1 , параметры которых (спектральное положение, полуширина и сила осциллятора) найдены в интервале $0 \leq x \leq 1$. По концентрационному ходу параметров установлена локализация A_0 и A_1 экситонов в двойных цепях, состоящих из тетраэдров MI_4 ($\text{M} = \text{Ag}, \text{Cu}$) и являющихся структурными элементами кристаллической решетки CsM_2I_3 . Результаты эксперимента обсуждены в предположении гибридизации d -орбиталей Ag, Cu и p -орбиталей I в верхней валентной зоне соединений и зависимости гибридизации от молярной концентрации x .

CsI and MI ($\text{M} = \text{Ag}, \text{Cu}$) compounds do not form solid solutions because of structural differences of their crystal lattices. But at certain molar concentrations, ternary complex compounds CsAg_2I_3 , Cs_2AgI_3 , CsCu_2I_3 and $\text{Cs}_3\text{Cu}_2\text{I}_5$ [1, 2] are formed in the CsI – MI system. The CsM_2I_3 crystal lattice is orthorhombic (space group D_{2h}^{17}) with 4 molecules per one unit cell [3, 4]. Cs_2AgI_3 has a similar lattice (space group D_{2h}^{17} including 4 molecules per one unit cell) [5]. Because of a large difference in the unit cell parameters, these crystals exhibit properties of quasi-one-dimensional structures. Structural elements, which in crys-

CsM_2I_3 represent double chains (in Cs_2AgI_3 single chains) consisting of MI_4 tetrahedrons and separated by Cs^+ ions at a large spacing, testify for the quasi-1D character.

The structure of electron bands and optical spectra in these compounds are investigated insufficiently. Research of intrinsic absorption bands in thin CsM_2I_3 films [6–8] testifies to localization of low-frequency excitons and electron excitations therein on the double chains. An additional information on localization of excitons is provided by absorption spectra of lattices containing extrinsic centers. So in [9, 10], it is estab-

lished that substitution of Rb^+ ions for Cs^+ influences only slightly the spectral position and half-width of low-frequency exciton absorption bands. This is a supplementary argument for exciton localization on double chains.

In this work, we have investigated the absorption spectra in thin films of $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ solid solutions at $0 \leq x \leq 1$. In this case, substitution Cu^+ ions for Ag^+ in double chains is expected as well as changed character of concentration dependence of exciton band parameters, since Cu^+ ions also form tetrahedral ion-covalent bond with I^- ions.

Thin films of $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ were prepared by evaporating melt of mixed pure CsI , AgI , CuI powders at the initial mixture molar composition corresponding to the molecule formula. The mixtures prepared included the whole range of x with step $\Delta x \approx 0.1$. The vapors were deposited onto quartz substrates transparent in UV region, the substrate temperature being 80°C . To measure the absorption spectra, the optimum film thickness ($h \approx 100$ nm) was selected, so that optical density D did not exceed 2 within the measured spectral range (2 to 6 eV). The film thickness was set by the mixture weight and monitored by a quartz measuring instrument.

When evaporating a mixture, other binary and ternary compounds might be formed. In the CsI-AgI-CuI system under study, complex compounds Cs_2AgI_3 , $\text{Cs}_3\text{Cu}_2\text{I}_5$ and their solid solutions as well as $\text{Ag}_{1-x}\text{Cu}_x\text{I}_3$ ones may arise besides $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ films. All these compounds exhibit narrow and intense low-frequency exciton bands with spectral positions essentially different from those of exciton bands in CsAg_2I_3 (3.73 eV) [6, 7] and CsCu_2I_3 (3.89 eV) [8]. This difference allows to control the phase structure of films being studied directly by absorption spectra. Evaporation of a mixture of a defined stoichiometric composition, the absorption spectra have been found to be stable, and no impurity of other phases has been revealed.

The absorption spectra were measured at $T = 290$ and 90 K using a SF-46 spectrophotometer. To measure the spectra at liquid nitrogen temperature, the samples were placed in a vacuum cryostat with quartz windows. Transmission of bands was measured with respect to clean quartz substrates. At the data computer processing, the main attention was given to determination of low-frequency exciton band parameters. In the studied compounds, there are

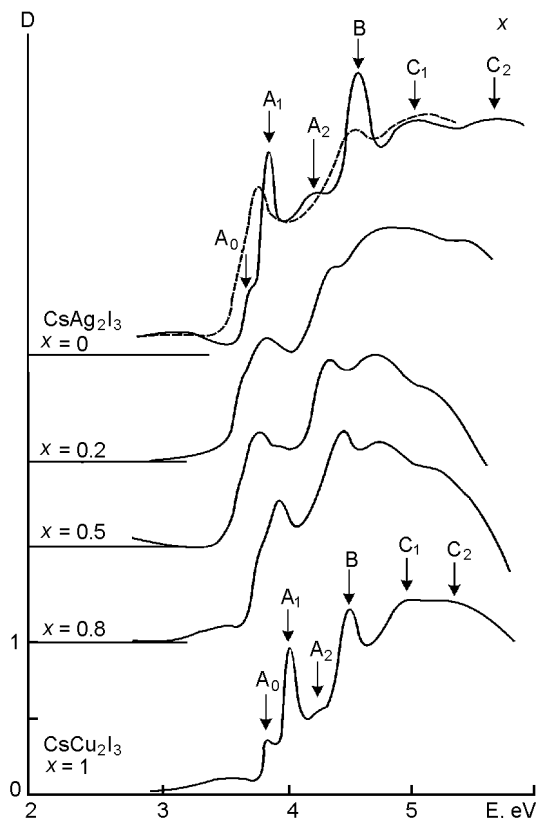


Fig. 1. Absorption spectra of thin $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ films at $T = 90$ K and $T = 290$ K (dotted line). Shift of the coordinate origin is marked by short horizontal axis.

two such bands (A_0 and A_1). The method [11] was used to process the experimental $D(E)$ dependence. Each band was approximated by a symmetric contour representing a linear combination of Lorentz and Gauss contours. The band parameters (spectral position E_m , half-width Γ , optical constants) were found by the best fitting of experimental and calculated contours.

The absorption spectra of some samples are shown in Fig. 1. The similarity of CsAg_2I_3 ($x = 0$) and CsCu_2I_3 ($x = 1$) spectra is well visible. In each of compounds, narrow A_0 and A_1 bands separated by a small interval, weak band A_2 and more intense band B are allocated. The last two bands are imposed on the continuous spectrum reaching a maximum at 5.2 eV. The absorption spectrum of CsCu_2I_3 is shifted a little with respect to that of CsAg_2I_3 towards higher frequencies (by 0.15 eV). The non-monotonous trend of $D(E)$ at $E < E_{A_0}$ is connected with light interference in the film transparent field of two compounds. At room temperature, A_0 , A_1 and B bands are broadened

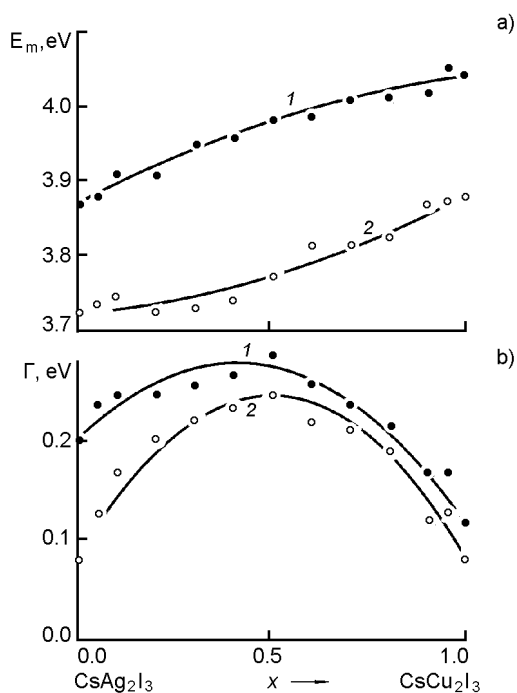


Fig. 2. Concentration dependences of spectral position $E_m(x)$ (a), and half-width $\Gamma(x)$ of A_0 (2) and A_1 (1) exciton bands (b) (points — experiment, solid curves — calculation using (1) and (2)).

and displaced to low E due to exciton-phonon interaction. The continuous background is not subjected to any appreciable change.

An appreciable broadening of A_0 and A_1 bands resulting in their apparent fusion, disappearance of A_2 band and broadening of B band is observed as the molar concentration increases in $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ solid solutions. However, the computer processing of A_0 and A_1 bands using the method [11] allows to determine more precisely their spectral position E_m using the maximum of imaginary part of dielectric permeability $\varepsilon_{2m} \equiv (2n\kappa)_{max}$, where n and κ are optical constants. As a result, it has been established that dependence $E_m(x)$ is nonlinear (Fig. 2) and answers to the law

$$E_m(x) = E_m(1)x + E_m(0)(1 - x) + bx(1 - x), \quad (1)$$

where $E_m(1) = 3.88$, $E_m(0) = 3.72$ and $b = -0.12$ eV for A_0 band, and $E_m(1) = 4.045$, $E_m(0) = 3.87$ and $b = +0.1$ eV for A_1 band, accordingly. The bend of $E_m(x)$ for A_0 band towards lower energy is typical of exciton bands in solid solutions of binary compounds, this phenomenon was repeatedly discussed theoretically and is associated with small-scale structure fluctuations in

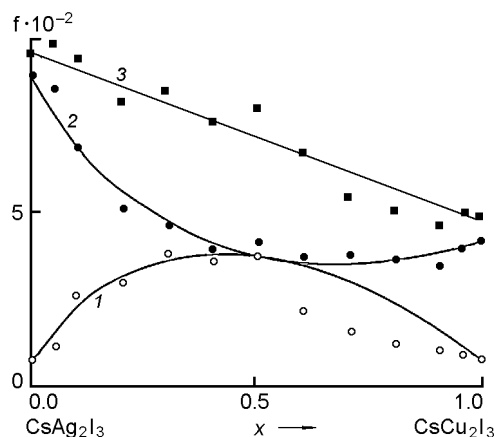


Fig. 3. Concentration dependences of oscillator strength of A_0 band (1) and A_1 one (2) function $f(x) = f_{A_0}(x) + f_{A_1}(x)$ (3): points — experiment, solid curves 1 and 2 — calculation using (8).

disordered solid solutions. However, the concentration-dependent bend of the A_1 band to higher energy is unusual and demands special discussion. The greatest divergence of A_0 and A_1 bands is observed at $x = 0.5$.

The concentration-dependent change of half-width Γ for A_0 and A_1 bands (Fig. 2b) show to strong disorder of solid solutions. The dependence $\Gamma(x)$ for two bands is described by the formula

$$\Gamma(x) = \Gamma(0)(1 - x) + \Gamma(1)x + \beta x(1 - x), \quad (2)$$

where $\beta = 0.66$; 0.46 eV, $\Gamma(0) = 0.08$; 0.205 eV and $\Gamma(1) = 0.08$; 0.12 eV for bands A_0 and A_1 , respectively. The concentration-dependent broadening of the bands might be caused by large-scale fluctuations of structure, along with small-scale ones. The quantity β in two cases is $\beta = a(dE_m/dx)$.

The computer processing allows to determine also the oscillator strength of exciton bands. For the mixed contour,

$$f = \frac{mv}{4\pi e^2 h^2} \varepsilon_{2m} E_m \Gamma \left[1 - \alpha(1 - (\pi \ln 2)^{1/2}) \right], \quad (3)$$

where α is the fraction of the Gauss component of a contour, v is the volume per one atom M (Ag^+ , Cu^+), $\varepsilon_{2m} \equiv \varepsilon_2(E_m)$. The quantity v was calculated basing on the known values of CsAg_2I_3 lattice parameters ($a = 1.108$, $b = 1.374$, $c = 0.623$ nm) [3] and CsCu_2I_3 ones ($a = 1.03$, $b = 1.289$, $c = 0.607$ nm) [4] taking into consideration the number of ions in a cell, and assuming the Vegard rule

being valid for solid solutions. When calculating f , the contribution from the Gauss component to the total contour was taken into account; in solid solutions, $\alpha \approx 1$. Fig. 3 shows $f(x)$ for A_0 and A_1 bands. It is seen that at $x = 0$ and $x = 1$, $f_{A0} < f_{A1}$, however, as the concentration increases, f_{A0} rises, reaching a maximum at $x \approx 0.4$. At the same time, with change of x reduction of f_{A1} is observed. At $x \approx 0.4$, the oscillator strengths for two bands are almost leveled. At the same time, the total oscillator strength of two bands (taking into account the experimental errors) depends linearly on x and varies from $9.8 \cdot 10^{-2}$ at $x = 0$ up to $4.7 \cdot 10^{-2}$ at $x = 1$.

To interpret the absorption spectra of $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ it is necessary to take into consideration the following facts: a significant nonlinear concentration-dependent growth of half-width of A_0 and A_1 bands, defined by parameter β ; the concentration dependent "repulsion" of A_0 and A_1 bands (in CsAg_2I_3 , $\Delta E = E_{A1} - E_{A0} = 0.15$ eV, in CsCu_2I_3 , $\Delta E = 0.165$ eV, but at $x \approx 0.5$ $\Delta E = 0.21$ eV); low oscillator strength for A_0 band in comparison to A_1 band at $x = 0$ and 1 and leveling of their values at $x \approx 0.4$.

When discussing the trend of $\Gamma(x)$, it is reasonable to compare these dependences for $\text{Rb}_x\text{Cs}_{1-x}\text{Ag}_2\text{I}_3$ solid solutions [10] and in $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$. While for the first solutions, the deviation from linear dependence of $\Delta\Gamma$ does not exceed 0.025 eV, $\Delta\Gamma$ reaches 0.15 eV in the latter case, as is seen in Fig. 2b. This result shows no doubt that A_0 and A_1 bands are belonging to double chains and that disordered solid solutions are formed when Ag atoms become substituted by Cu therein. At the same time, the substitution by Rb^+ ions for Cs^+ does not bring any appreciable disturbance to the double chains.

The unit cell of CsAg_2I_3 and CsCu_2I_3 contains two nonequivalent double chains separated by ions Cs^+ at the spacing $b/2$ equal 0.687 and 0.644 nm, respectively. The lower conductivity band in these compounds is formed by 5s and 4s orbitals of Ag and Cu [6–8]. Assuming on the basis of a tight-binding method the equality of their radii r_0 to atomic radii (0.144 and 0.128 nm), we obtain small values of the resonance integrals constructed on atomic s-orbitals of nonequivalent double chains $\{J \propto \exp(-b/2r_0) = 0.007\}$ as compared to integrals in single

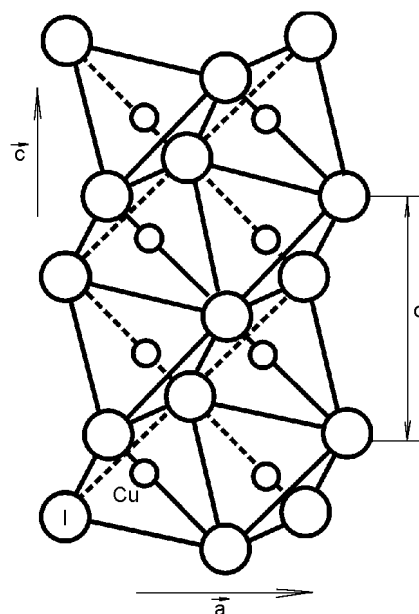


Fig. 4. Structure of double chain in CsM_2I_3 crystal lattice ($M = \text{Ag}, \text{Cu}$).

chains $\{J \propto \exp(-c/2r_0) = 0.096\}$. It follows therefrom that the excitons are distributed over one double chain only (1D excitons) and that exciton transition between nonequivalent chains is hardly probable.

This conclusion allows to study electron conditions in compounds using irreducible representations of the wave vector site group which governs the double chains (like the study of lattice fluctuations in complex crystals [12]), instead of irreducible representations of the wave vector group of the crystal (crystal class D_{2h}). As the double chains in CsAg_2I_3 and CsCu_2I_3 will consist of MI_4 tetrahedrons, the double chain site group is a subgroup of the tetrahedron group T_d ($43m$). In binary compounds ($\gamma\text{-AgI}$ and CuI), the site group coincides with crystal class T_d [13]. However, in double chains (Fig. 4), the site group will consist of elements E and σ_z (axis $z \parallel c$). The one-dimensional irreducible representations A' and A'' and respective basis functions ($x, y; xy; x^2 - y^2$, etc.) and ($z, yz; xz$, etc.), respectively, correspond to this group $C_s(m)$. The kind of functions permits mixing of I ion 5p orbitals with 4d (3d) orbitals of Ag (Cu) ion in the upper valence band.

Similar to binary compounds ($\gamma\text{-AgI}$ and CuI), the lower conductivity band has an energy minimum in the center of one-dimensional Brillouin zone ($k_z = 0$). We assume that the upper valence band has a maximum also at the point $k_z = 0$. This is

specified by absence of appreciable tails at $E < E_{A0}$ in the absorption spectrum appearing at indirect transitions. As noted above, difference of D from 0 at $E < E_{A0}$ is caused by interference in a thin film. Existence of two exciton bands separated by a small spacing testifies that the upper valence band will consist of two close subbands which the exciton absorption bands A_0 and A_1 are genetically connected to. Difference in oscillator strength of A_0 and A_1 bands ($f_{A0} \ll f_{A1}$ при $x = 0; 1$) specifies a considerable admixture of d -orbitals in the upper subband.

Following [13, 14], let the normalized wave functions in subbands at $k_z = 0$ be written as

$$\psi = c_1\phi_p + c_2\phi_d, \quad c_1^2 + c_2^2 = 1. \quad (4)$$

For A' representations, $\phi_p \equiv p_x \propto x$, $\phi_d \equiv d_{x,y} \propto xy$, similar functions can be written for A'' representations. The solution of Schrodinger equation with the one-electronic Hamilton operator H_0 (without taking into account spin-orbital interaction) gives the following system of equations for coefficients c_1 and c_2 :

$$\begin{aligned} c_1(H_p - E) + c_2H_{pd} &= 0, \\ c_1H_{pd} + c_2(H_d - E) &= 0, \end{aligned} \quad (5)$$

where the matrix elements constructed on p - and d -orbitals are as follows:

$$\begin{aligned} H_p &= \langle \phi_p | H_0 | \phi_p \rangle, \quad H_d = \langle \phi_d | H_0 | \phi_d \rangle, \\ H_{pd} &= H_{dp} = \langle \phi_p | H_0 | \phi_d \rangle. \end{aligned}$$

Non-trivial solution of the system of equations (5) gives (using the secular equation) the energy levels in upper (E_1) and lower (E_2) subbands at $k_z = 0$:

$$E_{1,2} = \frac{1}{2}[H_p + H_d \pm \sqrt{(H_d - H_p)^2 + 4H_{pd}^2}]. \quad (6)$$

Substitution of E_1 and E_2 into (5) allows to calculate the contribution from p - and d -orbitals to wave function ψ . At small matrix element H_{pd} ($H_{pd} \ll |H_d - H_p|$) we deal, under account for $c_1^2 + c_2^2 = 1$ in the upper subband,

$$\begin{aligned} c_1 &= \frac{H_{pd}}{[(H_d - H_p)^2 + H_{pd}^2]^{1/2}}, \\ c_2 &= \frac{H_d - H_p}{[(H_d - H_p)^2 + H_{pd}^2]^{1/2}}. \end{aligned} \quad (7)$$

The prevalence of the contribution from d -orbitals in the upper subband of the valence band is seen from (7). Substitution of E_2 in (5) gives opposite result ($c_1 > c_2$, c_1 and c_2 are exchanged). This conclusion is in accordance with the experimental data, since the optical interband transition between even d and s states is forbidden, thus defining the small oscillator strength of A_0 band. On the contrary, since the contribution from p -states prevails in the lower subband, oscillator strength of A_1 band exceeds almost by one order that for A_0 band, both in CsAg_2I_3 , and in CsCu_2I_3 .

As follows from Figs. 1, 2, 3, the parameters of exciton bands change in solid solutions. As it was mentioned, the spacing $\Delta E = E_{A1} - E_{A0}$ increases with x , and at $x \approx 0.5$, ΔE attains its maximal value, approximately 1.3 times as much than at $x = 0; 1$. Assuming dependence of ΔE on the concentration divergence of levels for two subbands E_1 and E_2 at $k_z = 0$, we have, basing on (6), $\Delta E = [(H_d - H_p)^2 + 4H_{pd}^2]^{1/2}$. Thus, the matrix elements H_d , H_p and H_{pd} depend on x . It follows from the concentration dependence of the oscillator strength for two exciton bands (Fig. 3) that the matrix element H_{pd} defining the mixing of p - and d -states depends on x most heavily, and inequality $|H_p - H_d| \gg H_{pd}$, being valid at $x = 0$ and 1, is broken due to increase of H_{pd} . For direct allowed transitions, the oscillator strength of exciton bands is proportional to squared matrix element of dipole moment constructed on wave functions ψ and ϕ_s at $k_z = 0$. It follows therefrom that $f(x) \propto c_1^2(x)$. From (5) and (7), it follows that the increase of H_{pd} at small x defines the increase of oscillator strength for A_0 band and simultaneous decrease of the A_1 band. For the lower subband, as follows from the calculation of c_1 at $E = E_2$, c_1 decreases with rising H_{pd} . These conclusions are in agreement with the data of Fig. 3. Approximation of dependences $f(x)$ by formula of type (1) in the whole x range agrees poorly with experiment. The empirical formula gives a somewhat better agreement:

$$f(x) = f(0)(1 - x^m) + f(1)x^m + bx^m(1 - x^m), \quad (8)$$

where for A_0 band $f(0) = f(1) = 0.8 \cdot 10^{-2}$, $b = 0.1$; for A_1 band, $f(0) = 9 \cdot 10^{-2}$, $f(1) = 4.02 \cdot 10^{-2}$, $b = -0.1$. The determination accuracy of oscillator strength for A_0 and A_1 bands in solid solutions in the range where x provides the greatest p - d hybridization of

states ($x \approx 0.4-0.5$), $\Delta f = \pm 10^{-3}$ is almost three times smaller than at $x = 0; 1$ ($\Delta f = \pm 0.3 \cdot 10^{-3}$). For two bands, we have determined the exponent $m = 0.8$ by fitting of the calculated curve to experimental one at $x < 0.4$. The formula (8) agrees well with concentration dependence $f(x)$ for A_1 band in the whole x range within the error limits of the quantity determination (Fig. 3) and gives almost linear course of total oscillator strength $f(x) = f_{A_0}(x) + f_{A_1}(x)$. However, the calculated $f_{A_0}(x)$ is not in agreement with experiment at $x > 0.6$.

The reason for m deviation from 1 towards smaller values and the incomplete agreement between of calculated and experimental $f(x)$ at $x > 0.6$ consists in our opinion in the film preparation technology. During the $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ evaporation from the melt, a partial decomposition of AgI is possible [15], i.e. the molar x' percentage in films is expected to be higher than x in the initial mixture ($x' = x^{0.8}$). As the melting temperature of copper-containing ternary compounds is higher than for those containing AgI [1], evaporation temperature rises at $x > 0.6$, that results in reduction of Ag content due to more intense decomposition of AgI.

The mixing of p - and d -states is typical of Ag and Cu halides with tetrahedral binding between metal and halogen atoms. In contrast to the III-V and II-VI compounds with the same binding type, strong mixing of p - and d -states in AgI and CuI is defined by closeness of d -levels in Ag^+ and Cu^+ ions to p -levels of I^- . Since in the studied compounds the low-frequency area of the fundamental band is connected with excitation in the double chains consisting of Ml_4 tetrahedrons, the mixing of p - and d -states therein is inevitable.

In disordered $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$ solid solutions, the hybridization of p - and d -states increases, thus affecting the nonlinear trend of $\Delta E(x)$ and $f(x)$ for A_0 and A_1 bands. The reason is the appearance of tails in state density $g(E)$ in the valence band of solutions. The quantity $g(E) \propto \exp[-(E_m - E)/E_0]$ decreases exponentially with reduction E as well as $E_0 \propto [x(1-x)]^n$, $n = 2, 1, 1/2$ [16]. At a small spacing between levels in two subbands ΔE at $x = 0; 1$, the appearance of a tail in $g(E)$ in the lower subband results in overlapping allowed states in two subbands, that, in turn, promotes increase of the matrix element $H_{pd}(x) \propto [x(1-x)]^n$ and

possible reduction of $H_p(x)$ and $H_d(x)$ due to lower density of states in the centers of subbands.

To conclude, the complex compounds CsAg_2I_3 and CsCu_2I_3 are unique due to the crystal lattice structure (double chains of Ml_4 tetrahedrons), the formation possibility of solid solutions and the localization of quasi-one-dimensional excitons in double chains. These excitons generate at A_0 and A_1 exciton bands at the fundamental band edge; the parameters of those bands depending on impurity concentration or temperature are easy to study. The results presented in this work provide a base for further theoretical and an experimental investigations in energy spectra of electrons and excitons in those compounds by improvement of the sample preparation technique and development of methods for calculation of CsAg_2I_3 and CsCu_2I_3 band structure.

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Особливості спектрів поглинання твердих розчинів комплексних сполук CsAg_2I_3 – CsCu_2I_3

В.К.Милославський, О.Н.Юнакова, Е.Н.Коваленко

Досліджено низькочастотні електронні спектри поглинання у тонких плівках твердих розчинів $\text{Cs}(\text{Ag}_{1-x}\text{Cu}_x)_2\text{I}_3$. На краю фундаментальної смуги спостерігаються дві екситонні смуги A_0 і A_1 , параметри яких (спектральне положення, напівширина та сила осцилятора) знайдено в інтервалі $0 \leq x \leq 1$. З концентраційного ходу параметрів встановлено локалізацію A_0 і A_1 екситонів у подвійних ланцюгах, що складаються з тетраедрів MI_4 ($M = \text{Ag}, \text{Cu}$) і є структурними елементами кристалічної ґратки CsM_2I_3 . Результати експерименту розглянуто у припущенні гібридизації d -орбіталей Ag, Cu і p -орбіталей I у верхній валентній зоні сполук та залежності гібридизації від молярної концентрації x .