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# Exciton absorption spectrum of thin films of ternary compounds in the CsCl–CuCl system

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The absorption spectra of thin films $(CsCl)_{1-x}(CuCl)_x$ were studied at $T = 90$ K in the spectral range 2–6 eV. From the analysis of the spectra, the formation of $CsCu_2Cl_3$ and $Cs_2CuCl_3$ compounds in the CsCl–CuCl system was created. The $Cs_2CuCl_3$ compound is stable only in a vacuum; in air, it apparently decomposes into $CsCu_2Cl_3$ with a disordered crystal lattice and CsCl. The exciton spectrum of both compounds is interpreted on the basis of transitions in the $Cu^+$ ion. The one-dimensional character of excitons in $CsCu_2Cl_3$ and the two-dimensional character in $Cs_2CuCl_3$ were established.

Keywords: thin films, absorption spectra, excitons.

## 1. Introduction

Perovskites based on copper and alkali metal halides are attracting more and more attention of researchers due to their luminescent properties and increased ionic conductivity [1–7]. A few copper perovskites have crystal lattices with significantly different parameters [5, 6]. Such compounds can be good luminophores [1, 2] and can be used to create nontoxic optoelectronic devices.

Binary compounds CsCl and CuCl do not form solid solutions, but stable ternary compounds are formed in the CsCl–CuCl system at certain molar concentrations. $CsCu_2Cl_3$ is the most studied compound among the compounds formed in the CsCl–CuCl system. $CsCu_2Cl_3$ crystallizes into an orthorhombic lattice (space group *Cmcm*) with parameters $a = 9.5$, $b = 11.89$, and $c = 5.6$ Å, $z = 4$ [5, 6]. The structural element of the $CsCu_2Cl_3$ crystal lattice is double chains of $CuCl_4$ tetrahedra which are oriented along the short axis of the crystal [6]. The compound has a low ionic conductivity by Cu which is equal to $10^{-4}\ \Omega^{-1}\cdot cm^{-1}$ at 500 K [3–5].

The $Cs_3Cu_2Cl_5$ compound is also formed in the CsCl–CuCl system, according to [5]. The $Cs_3Cu_2Cl_5$ compound is isostructural to $Cs_3Cu_2I_5$ [9] with the orthotorhombic lattice parameters (space group *Pnma*) $a = 9.176$, $b = 10.505$, and $c = 13.141$ Å. The ionic conductivity of this compound by Cu is also low [5]. The formation of a stable phase $Cs_4Cu_5Cl_9$ in the CsCl–CuCl system is also likely [7], but this has not been experimentally verified.

Previously, only the absorption spectrum of $CsCu_2Cl_3$ thin films has been studied [8]. The absorption spectra of other compounds in the CsCl–CuCl system have not been studied. At the same time, the absorption spectra are a stable characteristic of the compound, which makes it possible to establish the formation of stable phases of ternary compounds from the spectra in the CsCl–CuCl system.

In this work, we have studied the absorption spectra of compounds $(CsCl)_{1-x}(CuCl)_x$ with different molar compositions in the spectral range 2–6 eV to reveal the formation of stable phases of ternary compounds in the CsCl–CuCl system and to study their exciton spectrum.

## 2. Experimental

Thin films of $(CsCl)_{1-x}(CuCl)_x$ were prepared by vacuum evaporation of a molten mixture of pure CsCl and CuCl powders with different molar compositions onto quartz substrates heated to 100 °C, followed by annealing the films with the same temperature during one hour. This method of obtaining thin films of ternary compounds is based on the fact that the melting temperature of ternary compounds is significantly lower than that of the initial components [8, 10]. The melt evaporation temperature for different phases was chosen to satisfy the condition to obtain the single-phase films without admixture of other phases of ternary compounds.

The phase composition of $(CsCl)_{1-x}(CuCl)_x$ thin films and their quality were defined by absorption spectra at $T = 90$ K. Such measurement turned out to be possible due to a qualitative difference in the absorption spectra of various compounds and a significant difference of spectral position of long-wavelength exciton bands in ternary compounds (4.33–4.84 eV) and in the initial components CuCl (3.3 eV) and CsCl (7.8 eV). The films with a stable spectrum for a given phase and the narrowest and most intense absorption bands were selected to study the exciton absorption spectra.

The absorption spectra were measured in the spectral range 2–6 eV at $T = 90$ and 290 K on an SF-46 spectrophotometer. The absorption spectrum in the region of long-wavelength exciton bands (3.1–5.4 eV), was measured at the temperature range 90–400 K. Films 300–350 nm thick were used to measure the absorption spectra. The film thickness was measured on an MII-4 interferometer.

The parameters of long-wavelength exciton bands [position $E_m$, half-width Γ and the value of the imaginary part of the permittivity at the band maximum $\varepsilon_{2m} = \varepsilon_2(E_m)$] were determined according to the method [11] by approximating the bands with two-oscillator and single-oscillator symmetric contours, which form a linear combination of the Lorentzian and Gaussian contours. The parameters of the exciton bands ($E_m$, Γ, and $\varepsilon_{2m}$) were found by best matching the experimental and calculated contours.

## 3. Results and discussion

### *3.1. Features of the absorption spectra of compounds formed in the* CsCl–CuCl *system*

The investigation of the absorption spectra of thin films $(CsCl)_{1-x}(CuCl)_x$ showed that one compound is formed at high concentrations of CuCl ($x = 0.66 \pm 0.05$) with a spectrum that is characteristic of $CsCu_2Cl_3$ [8] (Fig. 1, curves *1*). The highest quality $CsCu_2Cl_3$ films are obtained by evaporating the melt of a mixture of powders of molar composition at the lowest possible temperature. There is no admixture of other phases of ternary compounds and initial components in the absorption spectra of such films. $CsCu_2Cl_3$ films are non-hygroscopic. They are stored for a long time in air without changing the absorption spectrum. The absorption spectrum of $CsCu_2Cl_3$ ($T = 90$ K) shows long-wavelength A and B bands at 4.33 and 4.615 eV, a weak $B_1$ band at 4.84 eV, and a short-wavelength C band at 6.05 eV.

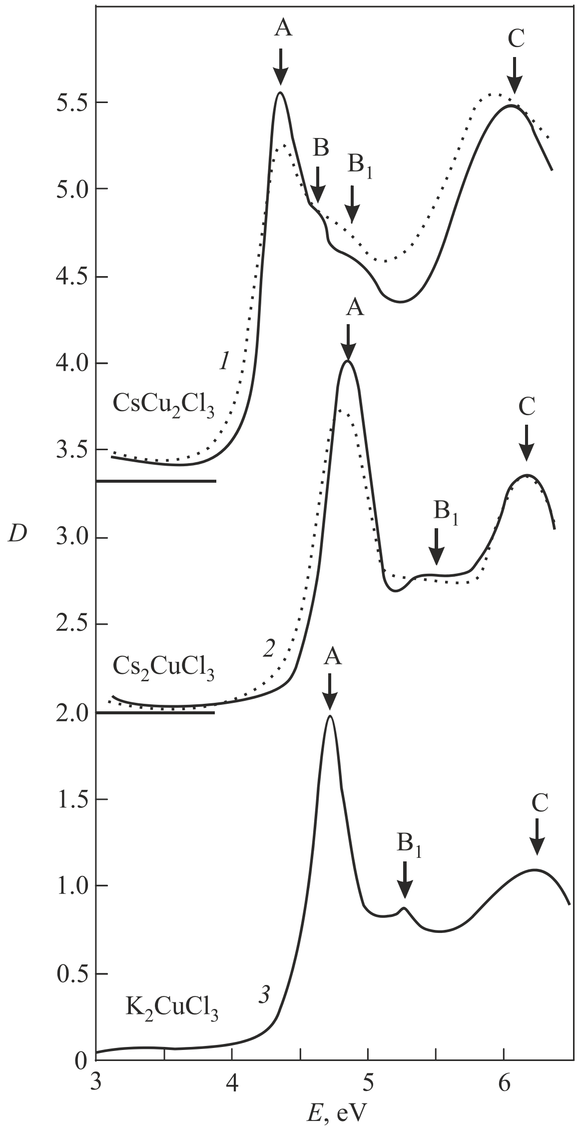

*Fig. 1.* Absorption spectra of thin films $CsCu_2Cl_3$ (*1*), $Cs_2CuCl_3$ (*2*), and $K_2CuCl_3$ (*3*) at $T = 90$ K (solid curve) and 290 K (dotted line).

Evaporation of the powder mixture melt in the concentration range $0.3 \le x \le 0.4$ at high temperature also forms one compound with its characteristic absorption spectrum (Fig. 1, curves *2*). The absorption spectrum of this compound is simpler. An intense long-wave band A is observed at 4.84 eV, a weak band $B_1$ at 5.25 eV, and a short-wave band C at 6.1 eV in the spectrum at $T = 90$ K. As the temperature increases, the A and B bands in both compounds shift to the long wavelength region of the spectrum broaden and weaken due to the exciton-phonon interaction (EPI), which indicates their exciton origin. The C bands are not very sensitive to changes in temperature and, apparently, correspond to interband transitions. According to the structure and position of the absorption bands, the spectrum of the compound which is formed in the range $0.3 \le x \le 0.4$ is close to the spectrum of $K_2CuCl_3$ (Fig. 1, curve *3*) (see Table 1), which indicates that both com-

Table 1. Spectral position of absorption bands, band gap $E_g$ and binding energy $R_{ex}$ of excitons in compounds of the CsCl–CuCl system

| Compound | $E_{mA}$, eV | $E_{mB}$, eV | $E_{mB1}$, eV | $E_{mC}$, eV | $R_{ex}$, eV | $E_g$, eV |
|---|---|---|---|---|---|---|
| $CsCu_2Cl_3$ | 4.33 | 4.615 | 4.96 | 6.05 | 0.195 | 4.595 |
| $Cs_2CuCl_3$ | 4.84 | | 5.51 | 6.1 | 0.24 | 5.08 |
| $(CsCl)_{0.6}(CuCl)_{0.4}$ | 4.35 | 4.65 | 5.45 | 6.0 | 0.23 | 4.58 |
| $K_2CuCl_3$ | 4.7 | | 5.25 | 6.2 | | |
| $KCl:Cu^+$ | 4.75 | | 5.3 | | | |
| $RbCl:Cu^+$ | 4.7 | | 5.29 | | | |

pounds are isostructural. From the above, we assume that a $Cs_2CuCl_3$ compound is formed in the CsCl–CuCl system in this concentration range. Apparently, the structural elements of the crystal lattice of $Cs_2CuCl_3$, as well as $K_2CuCl_3$, are single chains of $CuCl_4$ tetrahedra. Such a simple spectrum with one intense long-wavelength exciton band is also characteristic of other isostructural $K_2CuCl_3$ compounds, for example, $M_2AgI_3$, M = K, Rb, Cs [12–14].

Thin films of $Cs_2CuCl_3$, like $CsCu_2Cl_3$, are non-hygroscopic. They are stored in vacuum for a long time without changes in the absorption spectrum. But when the films are stored in the atmosphere, the $Cs_2CuCl_3$ compound decomposes under the action of moisture from the air. The films remain optically smooth. They do not show scattering. The decay process is slow. Figure 2 shows the absorption spectra of a thin film $(CsCl)_{0.6}(CuCl)_{0.4}$ ($T$ = 90 K) at different stages of decomposition. The initial absorption spectrum of the $(CsCl)_{0.6}(CuCl)_{0.4}$ film corresponds to $Cs_2CuCl_3$ (Fig. 2, curve *1*). The long-wave band $A^{II}$ of another phase appears in the spectrum of the film $(CsCl)_{0.6}(CuCl)_{0.4}$ at $T$ = 90 K during decomposition, the intensity of the band A decreases, while the intensity of $B_1$, on the contrary, increases (Fig. 2, curve *2*). The decay process is completed after 2 months. The absorption spectrum of the film, which was obtained as a result of the decomposition of $Cs_2CuCl_3$, is similar to $Cs_2CuCl_3$ by structure, but is not identical to it. Possibly, this is the spectrum of the $Cs_3Cu_2Cl_5$ compound, whose synthesis and crystal structure, were reported in [5]. Otherwise, it can be the spectrum of $Cs_2CuCl_3$ with a highly disordered crystal lattice. Therefore, the compound obtained as a result of decomposition will be denoted as $(CsCl)_{0.6}(CuCl)_{0.4}$ from now on. The spectral position of the absorption bands in $(CsCl)_{0.6}(CuCl)_{0.4}$ is shown in the Table 1.

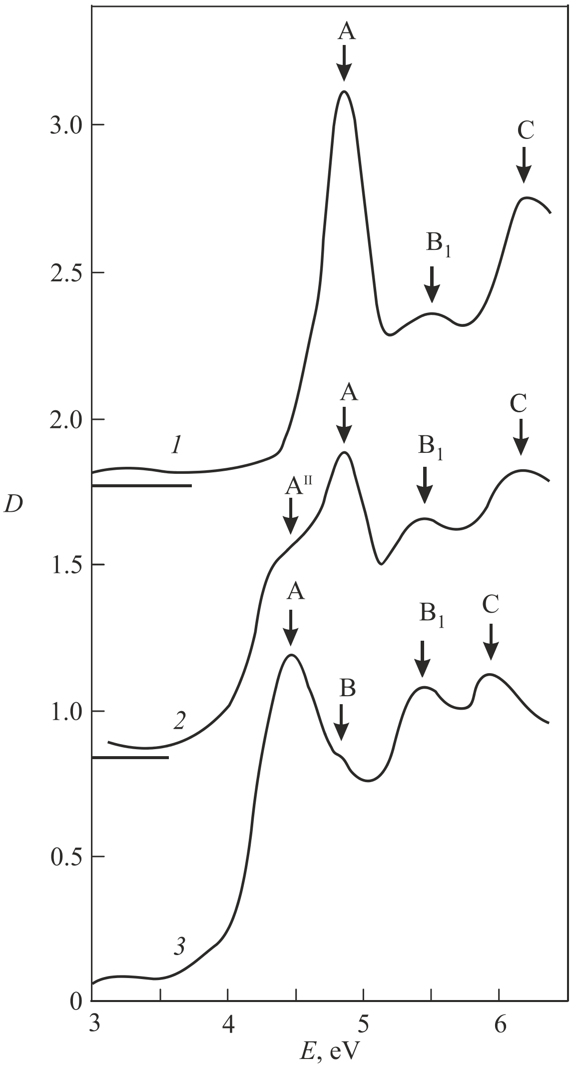

*Fig. 2.* Absorption spectrum of a thin film of $Cs_2CuCl_3$ at different stages of decomposition in air: initial film (*1*), after 7 days of storage in air (*2*), after a month (*3*).

To interpret the absorption spectra of $Cs_2CuCl_3$, $CsCu_2Cl_3$, and $(CsCl)_{0.6}(CuCl)_{0.4}$, let us turn to the structure of their crystal lattices. Presumably, the structural elements of the crystal lattice of $Cs_2CuCl_3$, as well as $K_2CuCl_3$ [5], are single chains of $CuCl_4$ tetrahedra. As noted above, $CuCl_4$ tetrahedra in the $CsCu_2Cl_3$ lattice form double chains oriented along the short axis of the crystal [6]. The molar composition of the $(CsCl)_{0.6}(CuCl)_{0.4}$ film corresponds to $Cs_3Cu_2Cl_5$. According to [5], this compound crystallizes into an orthorhombic lattice (space group *Pnma*) with parameters $a$ = 9.18, $b$ = 10.51, and $c$ = 13.14 Å, $z$ = 4. The structural elements of lattices of this type are double chains oriented along the **a** axis of the crystal. The chains are a sequence of trigonal bipyramids consisting of Cl tetrahedra. Each bipyramid forms a $Cu_2Cl_5^{3-}$ complex. The Cu atoms in the bipyramid are not equivalent. One Cu atom is located inside the lower tetrahedron, the second is displaced to one of the faces of the upper tetrahedron [9]. Similarity of the crystal lattices of all studied compounds is the tetrahedral environment of Cu atoms by Cl atoms.

As noted above, the absorption spectrum of $Cs_2CuCl_3$ thin films with the simplest structure (Fig. 1) is similar to that of $K_2CuCl_3$ [15]. In terms of the structure of the spectrum and the position of absorption bands, it is also similar to the spectra of impure $Cu^+$ ions in KCl and RbCl [16] (see Table 1). All this points to the common origin of

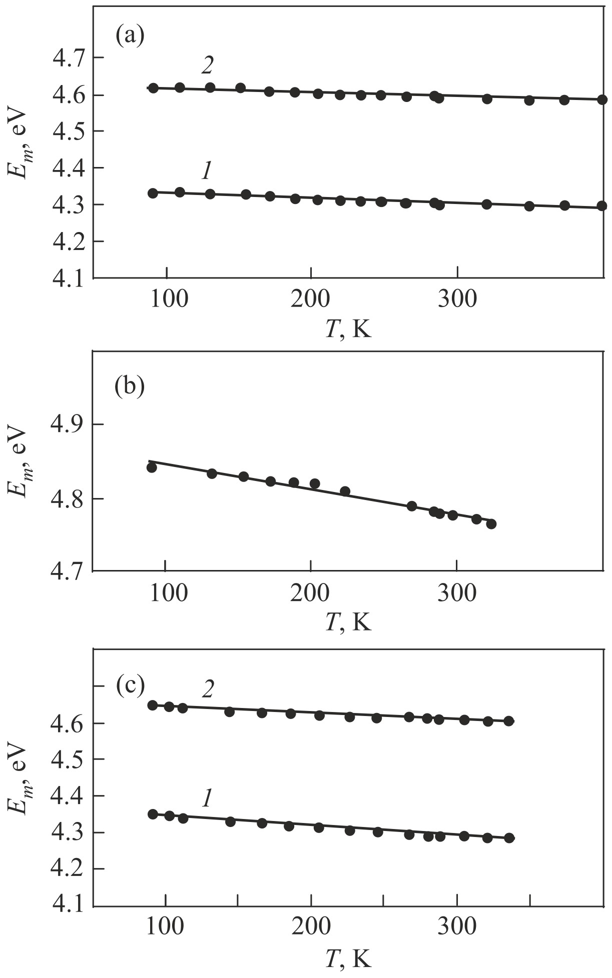

*Fig. 3*. Temperature dependencies of the spectral position $E_m(T)$ of long-wavelength exciton bands A (*1*) and B (*2*) in thin films $CsCu_2Cl_3$ (a), $(CsCl)_{0.6}(CuCl)_{0.4}$ (c), and band A in $Cs_2CuCl_3$ (b).

the spectra of $Cs_2CuCl_3$, $K_2CuCl_3$ and impure $Cu^+$ ions in alkali halide crystals. Consequently, the spectrum of $Cs_2CuCl_3$, like that of $K_2CuCl_3$ [15], is due to transitions in the $Cu^+$ ion. Low-frequency excitations of the free $Cu^+$ ion correspond to the transition ${}^1S_0 \to {}^1D_2$. For the $Cu^+$ ion located at the center of the tetrahedron the state ${}^1S_0$ passes into ${}^1A_1$, and 5-fold degenerate state ${}^1D_2$ splits into levels ${}^1T_2$ and ${}^1E$. According to the selection rules for the local group $T_d$, optical transition to a lower level ${}^1T_2$ is allowed, but the transition ${}^1A_1 \to {}^1E$ is prohibited. Since the $Cu^+$ ion is slightly displaced from the center of the tetrahedron in the lattices of the studied compounds [5], the local group decreases to $C_{2v}$. Under the action of a weak axial intracrystalline field the transition ${}^1A_1 \to {}^1E$ prohibition is partially lifted, and the level ${}^1T_2$ is split into components. Respectively, the intense exciton band in $Cs_2CuCl_3$, as in $K_2CuCl_3$, corresponds to the transition ${}^1A_1 \to {}^1T_2$, while the weak band $B_1$ corresponds to the transition ${}^1A_1 \to {}^1E$.

The more complex exciton spectrum of the $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ compounds is due to the more complex structure of the crystal lattices of these compounds. Additional interaction between the $CuCl_4$ tetrahedra in the double chains of the $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ crystal lattices leads to a shift of the exciton bands to the low-frequency region of the spectrum and splitting into components [8]. The appearance of intense exciton B bands in both compounds is associated with the Davydov splitting of exciton bands, which arises during the interaction of single chains of $CuCl_4$ tetrahedra in a double chain [8]. In this case, the position of the exciton bands is determined by the equation

$$E_{ex}^{\pm} = E_{ex}^{0} \pm \frac{1}{2}\Delta E_D , \tag{1}$$

where $E_{ex}^{0}$ is the excitation energy of an exciton in a hypothetical single chain. The value of $\Delta E_D = E_B - E_A = 0.285$ and 0.3 eV in $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$, respectively.

The absorption spectra of $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ are similar by the structure of the spectrum but differ in the position and intensity of the exciton bands. The main difference is in the intensity of the $B_1$ band. In $CsCu_2Cl_3$, as in $Cs_2CuCl_3$, the weak $B_1$ band corresponds to a partially allowed transition ${}^1A_1 \to {}^1E$. The high intensity of the $B_1$ band in $(CsCl)_{0.6}(CuCl)_{0.4}$ indicates an allowed transition. Previously, high-intensity $B_1$ bands were observed in the spectra of the four-component compounds $CsCu_2Cl_2I$ and $CsCu_2ClI_2$ [8]. The structural elements of the crystal lattices of these compounds, as well as $CsCu_2Cl_3$, are double chains of $CuHal_4$ tetrahedra. Partial disordering in the $CuHal_4$ tetrahedra, which consist of Cl and I ions, leads to a decrease in the local group of such tetrahedra to $C_{3v}$. In this case, the level ${}^1T_2$ is split into sublevels ${}^1A_1$ and ${}^1E$, optical transitions to which from the ground state ${}^1A_1$ are allowed in the dipole approximation. The intense exciton $B_1$ bands in these compounds correspond to the transition ${}^1A_1 \to {}^1A_1$ [8]. The positions of two $Cu^+$ ions are not equivalent in the crystal lattice of $Cs_3Cu_2Cl_5$. One $Cu^+$ ion is surrounded by four $Cl^-$ ions, the second $Cu^+$ by is surrounded by three $Cl^-$ ions [5]. In addition, the decomposition of $Cs_2CuCl_3$ in the formed lattice $(CsCl)_{0.6}(CuCl)_{0.4}$ results in partial disordering. This is evidenced by the significantly larger half-width of the exciton bands in $(CsCl)_{0.6}(CuCl)_{0.4}$ compared to $CsCu_2Cl_3$ and $Cs_2CuCl_3$ (Fig. 4). All this, apparently, leads to a decrease in the local group to $C_{3v}$ and to a splitting of the level ${}^1T_2$ into sublevels ${}^1A_1$ and ${}^1E$. The intense exciton $B_1$ band in $(CsCl)_{0.6}(CuCl)_{0.4}$, as in $CsCu_2Cl_2I$ and $CsCu_2ClI_2$ [8], corresponds to the allowed transition ${}^1A_1 \to {}^1A_1$.

The bandgap $E_g$ in the studied compounds was determined from the inflection point of the absorption edge after the separation of the exciton *A* band by a single oscillator contour in $Cs_2CuCl_3$ and the separation of the A and B bands by a two oscillator contour in $CsCu_2Cl_3$ and in $(CsCl)_{0.6}(CuCl)_{0.4}$. In $Cs_2CuCl_3$ and in $(CsCl)_{0.6}(CuCl)_{0.4}$ the values of $E_{gB}$ for the exciton B band were first found

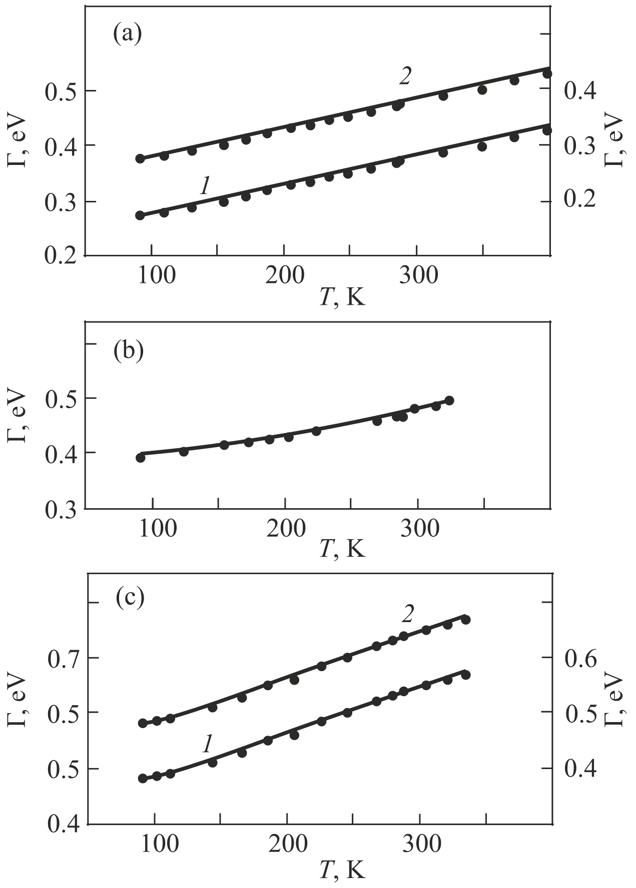

*Fig. 4*. Temperature dependencies of the half-width Γ(*T*) of long-wavelength exciton bands A (*1*) and B (*2*) in thin films of $CsCu_2Cl_3$ (a), $(CsCl)_{0.6}(CuCl)_{0.4}$ (c), and band A in $Cs_2CuCl_3$ (b). Experiment (points), calculation (solid curves) by Eqs. (3), (4) (a), (c) and Eqs. (3), (5) (b).

from the inflection point of the absorption edge and, accordingly, the exciton binding energy is $R_{\text{ex}} = E_{gB} - E_{mB}$. Assuming the equality of $R_{\text{ex}}$ for bands A and B, we determined $E_g = E_{mA} + R_{\text{ex}}$ in these compounds. The obtained values of $E_g$ and exciton binding energies $R_{\text{ex}}$ are given in Table 1.

### *3.2 Exciton-phonon interaction in the compounds* $CsCu_2Cl_3$, $Cs_2CuCl_3$, *and* $(CsCl)_{0.6}(CuCl)_{0.4}$

In $CsCu_2Cl_3$, the distance between $Cu^+$ ions along the short axis of the crystal is much smaller than the distance between the double chains of tetrahedra [5]. Accordingly, the transfer of exciton energy along the short axis is the most energetically favorable. Consequently, the energy bands and excitons in $CsCu_2Cl_3$ seem to have a quasi-one-dimensional character. To establish the nature of the energy bands and excitons in the compounds $Cs_2CuCl_3$, $CsCu_2Cl_3$, and $(CsCl)_{0.6}(CuCl)_{0.4}$, we studied the exciton-phonon interaction (EPI) in them. To achieve this, the absorption spectrum of the studied compounds was measured in the region of long-wavelength exciton bands in the temperature range 90–400 K.

As the temperature increases, the long-wavelength exciton bands in all three compounds are linearly shifted to the low-frequency region of the spectrum and broaden due to EPI (Figs. 3 and 4). The temperature shift coefficients of bands A and B in $CsCu_2Cl_3$ are $dE_{mA}/dT = -(1.21 \pm 0.08)\times$ $\times 10^{-4}$ eV/K and $dE_{mB}/dT = -(1.13 \pm 0.08)\cdot 10^{-4}$ eV/K, bands A in $Cs_2CuCl_3$ with $dE_{mA}/dT = -(3.42 \pm 0.1)\cdot 10^{-4}$ eV/K, in $(CsCl)_{0.6}(CuCl)_{0.4}$ with $dE_{mA}/dT = -(2.73 \pm 0.08)\cdot 10^{-4}$ eV/K and $dE_{mB}/dT = -(1.82 \pm 0.08)\cdot 10^{-4}$ eV/K. In order of magnitude, the coefficients of the temperature shift of the exciton bands in the studied compounds are characteristic of ionic crystals, which include the studied compounds.

The interaction of excitons with longitudinal optical (LO) phonons predominates in ionic crystals. The greatest temperature changes in the parameters of exciton bands in ionic crystals occur at $\hbar\omega_{LO} \le kT$. We estimated the unknown values of the energy of LO phonons $\hbar\omega_{LO}$ in $CsCu_2Cl_3$, $Cs_2CuCl_3$, and $(CsCl)_{0.6}(CuCl)_{0.4}$ from the known values $\hbar\omega_{LO} = 24.8$ meV in CuCl [17] and $\hbar\omega_{LO} = 19.1$ meV in CsCl [18]. Taking into account the molar composition of compounds in $CsCu_2Cl_3$ $\hbar\omega_{LO} \sim 22.85$ meV, in $Cs_2CuCl_3$ $\hbar\omega_{LO} \sim 21$ meV and in $(CsCl)_{0.6}(CuCl)_{0.4}$ $\hbar\omega_{LO} \sim 21.4$ meV.

The EPI leads to an increase in the half-width of the exciton bands with increasing temperature. The exciton-phonon component $\Gamma_{\text{ex-ph}}(T)$ in the total half-width of the exciton band Γ(*T*) depends on the dimension of the excitons. According to the theory [19] the broadening of the exciton band due to the exciton-phonon interaction $\Gamma_{\text{ex-ph}}(T)$ for excitons of different dimensions *d* (*d* = 1, 2, 3) is defined as

$$\Gamma_{\text{ex-ph}}(T) \approx \left[\frac{\pi D^2}{\gamma(d/2)(2\pi B)^{d/2}}\right]^{\frac{2}{4-d}}, \qquad (2)$$

where γ(*d*/2) is the gamma function depending on *d*, *B* is the width of the exciton band and $D^2 = 0.5C^2\hbar\omega_{LO}\times$ $\times \coth(\hbar\omega_{LO}/2kT)$, $\hbar\omega_{LO}$ is the energy of LO phonons in the studied compounds, $C^2/2$ is the lattice relaxation energy upon exciton excitation.

The full half-width of the exciton bands Γ(*T*) is determined by the contribution to it of the residual broadening Γ(0) due to lattice defects and $\Gamma_{\text{ex-ph}}(T)$. The shape of long-wavelength exciton bands in thin films of the studied compounds is close to Gaussian. In this case, the full half-width of the exciton band Γ(*T*) is equal to

$$\Gamma(T) = \left[\Gamma^2(0) + \Gamma^2_{\text{ex-ph}}(T)\right]^{1/2}, \qquad (3)$$

where $\Gamma_{\text{ex-ph}}(T)$ described by Eq. (2) with an unknown factor *Q*, which does not depend on *T*. Processing of the experimental dependencies Γ(*T*) of long-wavelength exciton bands in the studied compounds using Eq. (2) for different *d* gives the best agreement between the calculation and experiment at *d* = 1 in $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$, and *d* = 2 in $Cs_2CuCl_3$ (Fig. 4). In the compounds $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ (*d* = 1)

$$\Gamma_{\text{ex-ph}}(T) = Q\,\coth^{1/2}(\hbar\omega_{LO}/2kT) \tag{4}$$

and in $Cs_2CuCl_3$ ($d = 2$)

$$\Gamma_{\text{ex-ph}}(T) = Q\,\coth(\hbar\omega_{LO}/2kT). \tag{5}$$

The processing of the linear dependencies $\Gamma_A(T)$ and $\Gamma_B(T)$ in $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ by the least squares method gives the values $\Gamma_A(0) = (0.12 \pm 0.004)$ and $(0.27 \pm 0.05)$ eV, $\Gamma_B(0) = (0.12 \pm 0.004)$ and $(0.27 \pm 0.05)$ eV, and $Q_A = (0.023 \pm 0.001)$ and $(0.37 \pm 0.002)$ eV, $Q_B = (0.023 \pm 0.001)$ and $(0.37 \pm 0.002)$ eV in $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$, respectively. Dependence of $\Gamma_A(T)$ on $\coth^2(\hbar\omega_{LO}/2kT)$ in $Cs_2CuCl_3$ is linear in the $\Gamma^2$ coordinates on $\coth^2(\hbar\omega_{LO}/2kT)$. Processing it by the least squares method gives the values $\Gamma_A(0) = (0.37 \pm 0.003)$ eV and $Q_A = (0.11 \pm 0.001)$ eV. The calculated dependencies $\Gamma(T)$ according to Eqs. (3)–(5) with the found values of $\Gamma(0)$ and $Q$ are in good agreement with the experimental ones in the studied compounds (Fig. 4).

The analysis of the temperature dependencies $\Gamma(T)$ of the long-wavelength exciton bands showed that the exciton bands and excitons in the compounds $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ are one-dimensional and two-dimensional in $Cs_2CuCl_3$. For $CsCu_2Cl_3$ such a conclusion is valid and consistent with the structure of the crystal lattice, but the one-dimensional character of excitons in $(CsCl)_{0.6}(CuCl)_{0.4}$ does not agree with the crystal structure of $Cs_3Cu_2Cl_5$ given in [5]. It is possible that the decomposition of $Cs_2CuCl_3$ results in the formation of an isostructural compound $CsCu_2Cl_3$, but with a strongly disordered lattice. This assumption is supported by the significantly larger residual broadening of the A and B exciton bands in $(CsCl)_{0.6}(CuCl)_{0.4}$ compared to $CsCu_2Cl_3$, as well as the appearance of an intense $B_1$ band in the spectrum of $(CsCl)_{0.6}(CuCl)_{0.4}$. Additional verification of the crystal structure of the compound with the molar composition $Cs_3Cu_2Cl_5$ is required to make a final conclusion.

## 4. Conclusion

The analysis of the absorption spectra of thin films $(CsCl)_{1-x}(CuCl)_x$ $0.3 \le x \le 0.66$ ($T = 90$ K) confirmed the formation of two compounds $CsCu_2Cl_3$ and $Cs_2CuCl_3$ with a stable spectrum in this concentration range (Fig. 1). Both compounds are non-hygroscopic. $CsCu_2Cl_3$ is a stable compound, while $Cs_2CuCl_3$ is only stable in a vacuum. In air, $Cs_2CuCl_3$ decomposes into $CsCu_2Cl_3$ with a disordered crystal lattice and CsCl.

The absorption spectra of thin films $CsCu_2Cl_3$, $Cs_2CuCl_3$, and $(CsCl)_{0.6}(CuCl)_{0.4}$ were studied in the spectral range 2–6 eV at $T = 90$ and 290 K.

An analysis of the temperature dependencies of the half-widths of long-wavelength exciton bands confirmed a one-dimensional character of excitons in $CsCu_2Cl_3$ and $(CsCl)_{0.6}(CuCl)_{0.4}$ and a two-dimensional character in $Cs_2CuCl_3$.

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## Екситонний спектр поглинання тонких плівок потрійних сполук у системі CsCl–CuCl

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Досліджено спектри поглинання тонких плівок $(CsCl)_{1-x}(CuCl)_x$ ($T = 90$ К) у спектральному інтервалі 2–6 еВ. З аналізу спектрів встановлено утворення в системі CsCl–CuCl сполук $CsCu_2Cl_3$ та $Cs_2CuCl_3$. Сполука $Cs_2CuCl_3$ є стійкою тільки у вакуумі, в повітрі вона розпадається, вірогідно, на $CsCu_2Cl_3$ з розупорядкованою кристалічною граткою та CsCl. Екситонний спектр обох сполук трактується виходячи з переходів у іоні $Cu^+$. Встановлено одновимірний характер екситонів у $CsCu_2Cl_3$ та двовимірний у $Cs_2CuCl_3$.

Ключові слова: тонкі плівки, спектри поглинання, екситони.