Exciton absorption spectra of thin films of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ ternary compounds

E. N. Kovalenko

Kharkiv National University of Radio Electronics, Kharkiv 61166, Ukraine E-mail: olena.kovalenko@nure.ua

O. N. Yunakova and N. N. Yunakov

Kharkiv National University, Kharkiv 61022, Ukraine E-mail: o.n.yunakova@gmail.com nnyunakov@ukr.net

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The absorption spectra of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films were studied in the 2–6 eV spectral and 90–450 K temperature ranges. The localization of excitons in $CuCl_4^{3-}$ structural elements of crystal lattice of compounds, three-dimensional nature of excitons in RbCu₂Cl₃ and two-dimensional nature of excitons in Rb₂Cu₃Cl₅ were established. The exciton spectra of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films were interpreted based on the transitions in the Cu⁺ ion.

Keywords: thin films, absorption spectra, excitons.

Interest in ternary compounds based on copper and alkali metal halides is due to their unusual properties and the possibility of their practical use. Some of them have high ionic conductivity [1-3] and can be used as solid electrolytes, others are good luminophores [4]. Compounds of the RbCl-CuCl system have been studied by many authors in order to identify compounds with high ionic conductivity. Thus, in Refs. 5, 6, superionic conductors RbCu₃Cl₄ and Rb₂Cu₃Cl₅ with high ionic conductivity at room temperature were found in the RbCl-CuCl system. Other studies suggest the different compositions for the superionic phase ---- $Rb_3Cu_7Cl_{10}$ [7], $Rb_4Cu_9Cl_{13}$ [8]. However, according to the phase diagram, RbCu2Cl3, Rb2Cu3Cl5, and Rb2CuCl3 compounds are formed in RbCl-CuCl system [9]. The RbCu₂Cl₃ compound has a high ionic conductivity $5 \cdot 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$ at room temperature [10, 11]. According to [12], the temperature dependences of the conductivity and thermal electromotive force of RbCu₃Cl₄ exhibit anomalies in the range 410-420 K possibly related to the phase transition. The phase transitions were not found in compounds of other compositions.

As far as we know absorption spectra of ternary compounds of the RbCl–CuCl system have not yet been studied. The absorption spectrum is a stable characteristic of a compound and is connected with its crystal structure. The parameters of the exciton bands [spectral position E_{ex} and halfwidth (FWHM) Γ] are sensitive to phase transitions [13, 14]. The temperature dependences $E_{ex}(T)$ and $\Gamma(T)$ can be used to determine the temperatures of phase transitions [13, 14], if any of these dependences are found in the studied compounds.

It is of interest to study the absorption spectra of thin films of compounds of the RbCl–CuCl system with various molar compositions in order to identify stable compounds of monophase composition, and to study their absorption spectra in a wide temperature range to reveal possible phase transitions.

In this work, the absorption spectra of $RbCu_2Cl_3$ and $Rb_2Cu_3Cl_5$ thin films are investigated in a broad spectral range of 2–6 eV and a temperature range of 90–480 K.

Experiment

Thin films $(RbCl)_{1-x}(CuCl)_x$ were prepared by evaporating a molten mixture of pure RbCl and CuCl powders of a given molar composition in a vacuum onto quartz substrates heated to 373 K, followed by annealing the films during an hour at a constant temperature. This method was previously used to obtain thin films of ternary compounds [13, 14] and is based on the fact that usually a melting point of ternary compounds is significantly lower than that

of the initial components. According to [9], the melting points of ternary compounds of the RbCl-CuCl system are $T_m = 703$ K for RbCu₂Cl₃, $T_m = 732$ K for Rb₂Cu₃Cl₅ and $T_m = 800 \text{ K}$ for Rb₂CuCl₃, the same for initial components are $T_m = 703$ K (CuCl) and $T_m = 988$ K (RbCl) [15]. Investigation of the absorption spectra of the thin films $(RbCl)_{1-x}(CuCl)_x$ (0.5 $\leq x \leq 0.66$) showed that in this concentration range only two compounds with a stable spectrum are formed — $RbCu_2Cl_3$ and $Rb_2Cu_3Cl_5$ (Fig. 1). At x > 0.66, the (RbCl)_{1-x}(CuCl)_x mixture upon heating sublimetes from the powder, similar to CuCl. Such films contain excess CuCl, as well as both phases of ternary compounds RbCu₂Cl₃ and Rb₂Cu₃Cl₅. Films RbCu₂Cl₃ were produced by evaporating a $(RbCl)_{1-x}(CuCl)_x$ mixture of stoichiometric composition (x = 0.66) in vacuum onto heated quartz substrates at the lowest possible temperature. Both compounds are present in the molten mixture of $(RbCl)_{1-x}(CuCl)_x$ (x = 0.6) powders due to the close values of the melting temperatures of Rb₂Cu₃Cl₅ and RbCu₂Cl₃. However, a crystalline precipitate remains at the bottom of the evaporator after evaporation at the lowest possible temperature of the liquid fraction of the melt, melting at



Fig. 1. Absorption spectra of RbCu₂Cl₃, Rb₂Cu₃Cl₅ and CsCu₂Cl₃ thin films at T = 90 (*1*) and 290 (*2*) K.

The quality of the films and their phase composition were monitored using the absorption spectra measured at 90 K. To study the absorption spectra films with the narrowest and most intense absorption bands were selected. Controlling the phase composition by absorption spectra is possible due to a significant difference in the spectral positions of long-wavelength exciton bands in the ternary compounds RbCu₂Cl₃ (4.21 eV), Rb₂Cu₃Cl₅ (4.36 eV) and in the initial components CuCl (3.3 eV) and RbCl (7.52 eV).

The absorption spectra were measured in the spectral range of 2–6 eV at T = 90 and 290 K using SF-46 spectrophotometer. In the region of long-wavelength exciton bands (3.5–4.9 eV), the absorption spectrum was measured in the temperature range of 90–450 K. To measure the absorption spectra, films with a thickness of 140–150 nm were used.

The dispersion of the refractive index $n(\lambda)$ in Rb₂Cu₃Cl₅ and RbCu₂Cl₃ thin films in the transparency region was determined by the interference method [16] using the transmission spectra. For this, decently thick films ($t \sim 600-1000$ nm) were used, in the transmission spectra $T(\lambda)$ of which there are several noticeable interference extrema in the transparency region.

The parameters of the long-wavelength bands A and B [the position E_m , half-width Γ and the value of the imaginary part of the permittivity at the maximum of the band $\varepsilon_{2m} = \varepsilon_2(E_m)$] were determined by the method [17], approximating the bands with a two-oscillator symmetric contour, which is a linear combination of the Lorentzian and Gaussian contours. The parameters of the exciton bands (E_m , Γ , and ε_{2m}) were selected such that the calculated and experimental contours were in the best agreement on the longwavelength slope of the band.

Results of the experiment and conclusions

The absorption spectra of $RbCu_2Cl_3$ and $Rb_2Cu_3Cl_5$ thin films at nitrogen and room temperatures are shown in Fig. 1. Two narrow intense bands A and B, a weak band B_1 and a wide short-wavelength band C can be observed in the spectra of $RbCu_2Cl_3$ and $Rb_2Cu_3Cl_5$ (the spectral position of the bands is given in Table 1).

With an increase in the temperature, the A and B bands shift to the long-wavelength part of the spectrum, broaden and weaken due to exciton-phonon interaction (EPI), which indicates their exciton origin. The band C is not very sensitive to temperature and, apparently, corresponds to interband transitions. After separating the A and B bands by a twooscillator contour, the bandgap values $E_{gB} = 4.66$, 4.84 eV

Table 1. Spectral position of absorption bands, bandgap width E_g , binding energy R_{ex} , and exciton radius a_{ex} in the studied compounds

| Compound | $E_{mA,}$ | $E_{mB,}$ | $E_{mB1,}$ | $E_{mC,}$ | $R_{\rm ex}$, | <i>Eg</i> , | $a_{\rm ex}$, |
|-----------------------------------|-----------|-----------|------------|-----------|----------------|-------------|----------------|
| | eV | eV | eV | eV | eV | eV | Å |
| RbCu ₂ Cl ₃ | 4.21 | 4.475 | 4.92 | 5.9 | 0.185 | 4.4 | 12.8 |
| $Rb_2Cu_3Cl_5$ | 4.36 | 4.63 | 5.08 | 6.2 | 0.21 | 4.57 | 11.5 |
| $CsCu_2Cl_3$ | 4.33 | 4.615 | 4.92 | 6.05 | | | |

and the exciton binding energy $R_{ex} = E_{gB} - E_{mB} = 0.185$, 0.21 eV for band B in RbCu₂Cl₃ and Rb₂Cu₃Cl₅, respectively, were found at the inflection point of the absorption edge. Assuming the equality of R_{ex} for bands A and B, we can find the values $E_g = E_{mA} + R_{ex} = 4.4$, 4.57 eV for RbCu₂Cl₃ and Rb₂Cu₃Cl₅, respectively.

Let us estimate the exciton radius in $RbCu_2Cl_3$ and $Rb_2Cu_3Cl_5$ thin films:

$$a_{\rm ex} = a_B \frac{R}{R_{\rm ex} \varepsilon_{\rm eff}},\tag{1}$$

where $a_B = 0.529 \cdot 10^{-8}$ cm is the Bohr radius, R = 13.6 eV is the Rydberg constant, ε_{eff} is the effective dielectric constant, $\varepsilon_0 < \varepsilon_{\text{eff}} < \varepsilon_{\infty}$, ε_0 is the optical dielectric constant, which determines the contribution of high-frequency excitations to ε_{eff} , ε_{∞} is static dielectric constant, $R_{\text{ex}} = 0.185$, 0.21 eV are the values of the exciton binding energy in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ determined above. The main contribution to ε_{eff} near the low-frequency exciton band is determined by ε_0 , therefore to estimate a_{ex} we use this limit of ε_{eff} . Unknown values of ε_0 were determined from the dispersion of the refractive index $n(\lambda)$ of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films in the transparency region (Fig. 2). The experimental dependences $n(\lambda)$ are well described by the Wemple singleoscillator model [18]:

$$\varepsilon_1 = n^2 = 1 + \frac{E_d E_0}{E_0^2 - E^2},\tag{2}$$



Fig. 2. The spectral dependence of the refractive index $n(\lambda)$ in thin films RbCu₂Cl₃ (1) and Rb₂Cu₃Cl₅ (2). Points represent experiment, solid curves represent calculation by Eq. (2).

where $E = \hbar \omega$, E_0 and E_d are the parameters of the oneoscillator model: E_0 determines the spectral position of the effective oscillator associated with interband optical transitions, $E_0 > E_g$; E_d is the dispersion energy, which characterizes the strength of interband transitions.

The processing of the experimental data $n(\lambda)$ in the coordinates $(n^2 - 1)^{-1}$ on E^2 by the least squares method allowed us to determine the values of $E_0 = 7.5$, 7.84 eV and $E_d = 15.17$, 15.22 eV for RbCu₂Cl₃ and Rb₂Cu₃Cl₅, respectively. The calculated dependences $n(\lambda)$ by Eq. (1) with the found values of E_0 and E_d are in good agreement with the experimental $n(\lambda)$ (Fig. 2). Extrapolation of the dependences $n(\lambda)$ to E = 0 gives the values of the optical dielectric constant $\varepsilon_0 = 1 + E_d/E_0 = 3.024$ and 2.942 in RbCu₂Cl₃ and Rb₂Cu₃Cl₅. The exciton radii in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ are $a_{ex} = 12.8$ and 11.5 Å, respectively. The obtained a_{ex} values indicate the excitation of intermediate bond excitons in the studied compounds.

In terms of the structure of the spectrum and the position of the main absorption bands, the spectra of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films differ significantly from the spectra of the initial components CuCl [19] and RbCl [20] and are close to the spectrum of the previously studied compound CsCu₂Cl₃ [21] (Fig. 1, Table 1). Excitons in CsCu₂Cl₃ are cationic, localized in the structural elements of the CuCl₄³⁻ crystal lattice, and their spectrum is interpreted based on the state of the Cu⁺ ion in a tetrahedral environment with Cl⁻ ions [21]. The cationic character of excitons in CsCu₂Cl₃ is also confirmed by studies of the luminescence spectra [22].

To interpret the absorption spectra of the studied compounds, let us turn to the structure of their crystal lattices. The crystal structure of compounds in the RbCl–CuCl system has been studied by many authors [8, 23–25]. So, according to [23], the Rb₂Cu₃Cl₅ compound crystallizes into a cubic lattice with the parameter a = 21.213 Å. The chains of CuCl₄ tetrahedra are structural elements of the crystal lattice of Rb₂Cu₃Cl₅ [23].

The crystal structure of RbCu₂Cl₃ was studied in [24], but the authors were unable to determine the type of lattice. In [24], the formation of RbCu₂Cl₃ was discovered in the range of CuCl molar concentrations from 0.65 to 0.69. A detailed description of the crystal structure of the compound Rb₄Cu₉Cl₁₃ (molar concentration of CuCl is 0.69), which is close in molar composition to RbCu₂Cl₃, is given in [8, 25]. According to [8, 25], Rb₄Cu₉Cl₁₃ has rhombohedral symmetry (space group $R\overline{3}c$) with lattice parameters a = 19.54 Å, $\alpha = 84.43^{\circ}$ and 12 molecules per unit cell. Cu⁺ ions in the Rb₄Cu₉Cl₁₃ lattice are distributed over 11 sets of tetrahedral positions surrounded by Cl⁻ and one set of positions with threefold coordination relative to Cl⁻ [8, 25]. Since at high CuCl concentrations in the RbCl-CuCl system, only one compound $RbCu_2Cl_3$ is formed [9, 24], which exists in the CuCl concentration range of 0.65-0.69 [24], the above description of the crystal structure can be attributed to RbCu₂Cl₃.

The double chains of $CuCl_4$ tetrahedra oriented along the short axis of the crystal are the structural elements of the crystal lattice in $CsCu_2Cl_3$ [26].

Common to the crystal lattices of all three compounds is the arrangement of Cu^+ ions in a tetrahedral environment by $C\Gamma$ ions with a slight shift of Cu^+ from the center of the tetrahedron [8, 23, 25]. Apparently, the absorption spectra of the RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films, as the spectrum of CsCu₂Cl₃, are due to transitions in the Cu⁺ ion.

Low-frequency excitations of the free Cu⁺ ion correspond to the transition ${}^{1}S_{0} \rightarrow {}^{1}D_{2}$. As for the Cu⁺ ion located in the center of the tetrahedron, ${}^{1}S_{0}$ transforms into ${}^{1}A_{1}$ and the fivefold degenerate state ${}^{1}D_{2}$ splits into levels ${}^{1}T_{2}$ and ${}^{1}E$. According to the selection rules for the local group T_d [21, 26], the optical transition to a lower level 1T_2 is allowed, but the transition ${}^{1}A_{1} \rightarrow {}^{1}E$ is prohibited. Since the Cu⁺ ion in the lattices of the studied compounds is somewhat displaced from the center of the tetrahedron, the local group decreases to C_{2V} . Under the action of a weak axial intracrystalline field, the prohibition on the transition ${}^{1}A_{1} \rightarrow {}^{1}E$ is partially lifted, and the level ${}^{1}T_{2}$ is split into components. Therefore, the intense exciton bands A and B in the studied compounds, such as in CsCu₂Cl₃, correspond to the transition ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$, and the weak B₁ band corresponds to the transition ${}^{1}A_{1} \rightarrow {}^{1}E$.

Based on the above reasoning, we can conclude that excitons in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ are localized in the CuCl₄³⁻ structural elements of the crystal lattice. For a given localization, the top of the valence band in the studied compounds, such as in CuCl, is formed by the 3*d* states of the Cu⁺ ion and by the 3*p* states of the Cl⁻ ion, whereas the conduction band is formed by the 4*s* states of the Cu⁺ ion.

It should be noted that the spectral positions of the absorption bands in Rb₂Cu₃Cl₅ and CsCu₂Cl₃ are close (see Table 1), while in RbCu₂Cl₃ the absorption edge is shifted to longer wavelengths by 0.15 eV relative to Rb₂Cu₃Cl₅. Such shift and a lower value of E_g indicate a lower ionicity of RbCu₂Cl₃ compared to Rb₂Cu₃Cl₅. Possible, the lower ionicity of RbCu₂Cl₃ is due to the presence in the crystal lattice of a compound of Cu⁺ ion positions with threefold coordination relative to Cl⁻ [8, 25].

Temperature dependence of the long-wavelength exciton absorption bands parameters in RbCu₂Cl₃ and Rb₂Cu₃Cl₅

The absorption spectra of thin films of the RbCu₂Cl₃ and Rb₂Cu₃Cl₅ compounds in the region of long-wavelength exciton bands were measured in the temperature range of 90–450 K. There are no features indicating the presence of phase transitions in the temperature dependences of the spectral position $E_m(T)$ (Fig. 3) and FWHM $\Gamma(T)$ (Fig. 4) of bands A and B in both compounds.

The A and B bands in RbCu₂Cl₃ are linearly shifted to the long-wavelength region of the spectrum with an increasing temperature with $dE_{mA}/dT = -(2.86 \pm 0.05) \cdot 10^{-4} \text{eV/K}$



Fig. 3. The temperature dependences of the spectral position $E_m(T)$ of long-wavelength excitons A (1) and B (2) bands in RbCu₂Cl₃ (a) and Rb₂Cu₃Cl₅ (b) thin films.

and $dE_{mB}/dT = -(1,98 \pm 0.05) \cdot 10^{-4} \text{ eV/K}$, whereas for RbCu₂Cl₃ with $dE_{mA,B}/dT = -(2.34 \pm 0.05) \cdot 10^{-4} \text{ eV/K}$ (Fig. 3). The long-wavelength shift of exciton bands with increasing *T* in the studied compounds is due to EPI, the coefficients of the temperature shift are characteristic of ionic crystals by the order of magnitude, which include the studied compounds.

In ionic crystals the interaction of excitons with longitudinal optical (LO) phonons predominates, which also leads to broadening of exciton bands with increasing *T*. The value of the exciton-phonon component $\Gamma_{ex-ph}(T)$ in the total FWHM of the exciton band $\Gamma(T)$ depends on the dimension of excitons. According to the theory [27], the broadening of the exciton band due to the exciton-phonon interaction $\Gamma_{ex-ph}(T)$ for excitons of various dimensions (d = 1, 2, 3) is defined as

$$\Gamma_{\text{ex-ph}}(T) \approx \left[\frac{\pi D^2}{\gamma (d/2)(2\pi B)^{d/2}}\right]^{\frac{2}{4-d}},$$
(3)

where $\gamma(d/2)$ is the gamma function depending on *d*, *B* is the width of the exciton band, $D^2 = 0.5C^2\hbar\omega_{LO}$ cth $(\hbar\omega_{LO}/2kT)$, $\hbar\omega_{LO} = 25.1$ and 24.8 meV are the energies of LO phonons in RbCu₂Cl₃ and Rb₂Cu₃Cl₅, $C^2/2$ is the lattice relaxation energy upon exciton excitation. We estimated the unknown

values of $\hbar\omega_{LO}$ in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ by linear interpolation over the values $\hbar\omega_{LO} = 27.2$ meV in CuCl [19] and $\hbar\omega_{LO} = 21.2$ meV in RbCl [20].

The total FWHM of the exciton bands $\Gamma(T)$ is determined by the residual broadening $\Gamma(0)$ contribution due to lattice defects and $\Gamma_{ex-ph}(T)$. The shape of exciton bands A and B in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films is close to Gaussian. In this case, the total FWHM $\Gamma(T)$ is equal to

$$\Gamma(T) = \left[\Gamma^{2}(0) + \Gamma^{2}_{\text{ex-ph}}(T)\right]^{1/2},$$
(4)

where $\Gamma_{ex-ph}(T)$ is described by Eq. (3) with an unknown factor *Q* independent on *T*. Processing of the experimental dependences $\Gamma_A(T)$ and $\Gamma_B(T)$ using Eq. (3) for different *d* gives the best agreement between the calculation and experiment at d = 3 for RbCu₂Cl₃ and d = 2 for Rb₂Cu₃Cl₅ (Fig. 4). FWHM of bands A and B coincide for Rb₂Cu₃Cl₅, therefore, in Fig. 4(b), only one dependence $\Gamma_{A,B}(T)$ common for both bands is given. For RbCu₂Cl₃ (d = 3)

$$\Gamma_{\text{ex-ph}}(T) = Q \operatorname{cth}^2 \left(\hbar \omega_{LO} / 2kT \right)$$
(5)

and for $Rb_2Cu_3Cl_5$ (d = 2)

$$\Gamma_{\text{ex-ph}}(T) = Q \operatorname{cth} \left(\hbar \omega_{LO} / 2kT \right).$$
(6)



Fig. 4. The temperature dependences of FWHM $\Gamma(T)$ of longwavelength exciton A (*1*) and B (*2*) bands in RbCu₂Cl₃ (a) and Rb₂Cu₃Cl₅ (b) thin films. Points represent experiment, solid curves represent calculation by Eqs. (4), (5) (a) and Eqs. (4), (6) (b).

Processing of the $\Gamma_A(T)$ and $\Gamma_B(T)$ dependences for RbCu₂Cl₃, linear in the Γ^2 coordinates on cth₄ ($\hbar \omega_{LO}/2kT$), and the $\Gamma_{A,B}(T)$ dependence for Rb₂Cu₃Cl₅, linear in the Γ^2 coordinates on cth² ($\hbar \omega_{LO}/2kT$), by the least squares method gives the values of $\Gamma_A(0) = (0.39 \pm 0.003)$ eV, $\Gamma_B(0) =$ $= (0.41 \pm 0.002)$ eV, $Q_A = (0.052 \pm 0.0006)$ eV, $Q_B =$ $= (0.031 \pm 0.0005)$ eV and $\Gamma_{A,B}(0) = (0.3 \pm 0.003)$ eV and $Q_{A,B} = (0.11 \pm 0.005)$ eV. The calculated dependences $\Gamma(T)$ by Eqs. (4)–(6) with the found values of $\Gamma(0)$ and Q are in good agreement with the experimental ones in both compounds.

Conclusion

Analysis of the absorption spectra of thin films $(\text{RbCl})_{1-x}(\text{CuCl})_x$ (T = 90 K) found the formation of two compounds — RbCu₂Cl₃ and Rb₂Cu₃Cl₅ — with a stable spectrum in the concentration range $0.5 \le x \le 0.66$ (Fig. 1).

The absorption spectra of the RbCu₂Cl₃ and Rb₂Cu₃Cl₅ thin films were studied in the spectral range of 2–6 eV at T = 90 and 290 K. It was found that excitons in both compounds are cationic. The exciton spectra of the compounds are due to transitions in the Cu⁺ ion in the tetrahedral environment of Cl⁻. The top of the valence band in RbCu₂Cl₃ and Rb₂Cu₃Cl₅, as in CuCl, is formed by the 3*d* states of the Cu⁺ ion and the 3*p* states of the Cl⁻ ion, whereas the conduction band is formed by the 4*s* states of the Cu⁺ ion.

Analysis of the temperature dependences of FWHM of the long-wavelength exciton bands A and B found a threedimensional character of excitons in $RbCu_2Cl_3$ and two-dimensional character in $Rb_2Cu_3Cl_5$.

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Екситонні спектри поглинання тонких плівок потрійних сполук RbCu₂Cl₃ та Rb₂Cu₃Cl₅

E. N. Kovalenko, O. N. Yunakova, N. N. Yunakov

Досліджено спектр поглинання тонких плівок RbCu₂Cl₃ та Rb₂Cu₃Cl₅ в області спектру 2–6 еВ та температурному інтервалі 90–440 К. Встановлена локалізація екситонів в CuCl₄^{3–} структурних елементах кристалічної гратки сполук, тривимірний характер екситонів в RbCu₂Cl₃ та двовимірний в Rb₂Cu₃Cl₅. Екситоний спектр тонких плівок RbCu₂Cl₃ та Rb₂Cu₃Cl₅ трактується виходячи з переходів в ioнi Cu⁺.

Ключові слова: тонкі плівки, спектри поглинання, екситони.