

# Luminescence of $\text{Cu}^+$ and $\text{Cu}^{2+}$ Ions in CsBr Crystals

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The luminescence of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in CsBr:Cu and CsBr:CuBr<sub>2</sub> crystals, respectively, is investigated under excitation by synchrotron radiation in the CsBr fundamental absorption range at 10 K and 300 K. The existence of the luminescence bands of different origin: (i) the intrinsic radiative transition of  $\text{Cu}^+$  ions in the bands peaked at 2.61 eV and 2.23 eV, (ii) the recombination luminescence of  $\text{Cu}^{2+}$  ions in the bands peaked at 2.55 eV and 2.13 eV, (iii) the luminescence of excitons localized around  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in the band peaked at 3.08 eV and 3.38 eV, respectively, was found in CsBr:Cu and CsBr:CuBr<sub>2</sub> crystals. The energies of creation of exciton localized around  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions (6.06 eV and 6.09 eV, respectively, at 10 K) and excitons bound with these ions (5.83 eV and 5.99 eV at 300 K) were determined as well.

PACS numbers: 61.72.Hh, 76.30.Kg, 76.30.Lh, 76.70.Dx

## 1. Introduction

Copper ions in different charge states usually create the set of strongly localized states in ionic compounds [1]. This, in principle, may be used for development of the storage phosphors, working on the principle of photostimulated luminescence (PSL), and materials for thermoluminescent (TL) dosimetry [2]. The luminescence of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in CsBr crystals was studied in our previous papers [3, 4] by the traditional spectroscopic methods. In this work, we continue investigation of the nature of the luminescent centers created by copper dopant in CsBr host using the UV-VUV synchrotron radiation (SR) excitation.

Recently, UV-VUV excitation was applied to study the absorption and luminescence of  $\text{Cu}^{2+}$  ions in LiF [5] and absorption of  $\text{Cu}^+$  ions in LiCl crystals [6]. The luminescence of  $\text{Eu}^{2+}$  ions in CsBr:Eu host was also studied in our previous paper [7] and later in the CsBr:Eu<sup>2+</sup> needle image plates (NIP) [8] under excitation by SR in the CsBr fundamental absorption range. The creation of excitons localized around  $\text{Eu}^{2+}$  ions was noted [7]. In work [8] it was shown that photostimulable storage centers arise exclusively under the excitation of bands related to creation of the  $4p^55s$  excitons. These results can indicate that excitons localized around different types of dopants in CsBr host to the great extent are responsible for storage and PSL processes in this material.

## 2. Samples and experimental technique

The CsBr:Cu and CsBr:CuBr<sub>2</sub> crystals with dominant valence state of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  [3, 4], respectively, were chosen for investigation. These crystals were grown by the Bridgman–Stockbarger method from the CsBr salt of 5N purity and doped by adding the metallic Cu and

CuBr<sub>2</sub> bromide with a concentration of 0.5 mol%, respectively. At the same time, a small amount of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions can be also present in CsBr:Cu and CsBr:CuBr<sub>2</sub> crystals, respectively.

The luminescence of these crystals was investigated at 10 K and 300 K at the Superlumi station (HASY-LAB, DESY) under excitation by SR with an energy of 3.7–25 eV. The emission and excitation spectra were measured in the limits of SR pulse with a repetition time of 200 ns and a duration of 0.127 ns. The excitation spectra were corrected on the spectral sensitivity of the detection part and intensity of SR beam.

## 3. Experimental results and discussion

### 3.1. Luminescence of $\text{Cu}^+$ ions

The emission spectrum of the  $\text{Cu}^+$  ions in CsBr:Cu crystal at 300 K under excitation at 5.29 eV, in the range of high-energy absorption band related to partly allowed  $^1A_{1g} \rightarrow ^1T_{2g}$  transition of  $\text{Cu}^+$  ions [3, 4, 6, 9], presents the complex emission band in the visible range as a superposition of the two main sub-bands peaked at 2.61 eV and 2.23 eV (Fig. 1a, curve 1). The dominant high-energy emission band corresponds to the  $^1E \rightarrow A_{1g}$  radiation transitions [9]. In work [3] we also noted that as opposite to the typical one-component character of  $\text{Cu}^+$  emission [9], the luminescence spectrum of  $\text{Cu}^+$  ions in CsBr:Cu crystal under  $^1A_{1g} \rightarrow ^1T_{2g}$  band excitation consists also of second low-energy emission band peaked at 2.23 eV. The small-intensity bands peaked approximately at 2.5 eV and 2.13 eV in the spectra of CsBr:Cu crystal most probably are related to the luminescence of  $\text{Cu}^{2+}$  ions.

Under excitation by SR, in the exciton range of 6.04–6.88 eV, the emission spectrum of CsBr:Cu crystal at 300 K (Fig. 1a, curves 1, 2) and at 10 K (Fig. 1b,

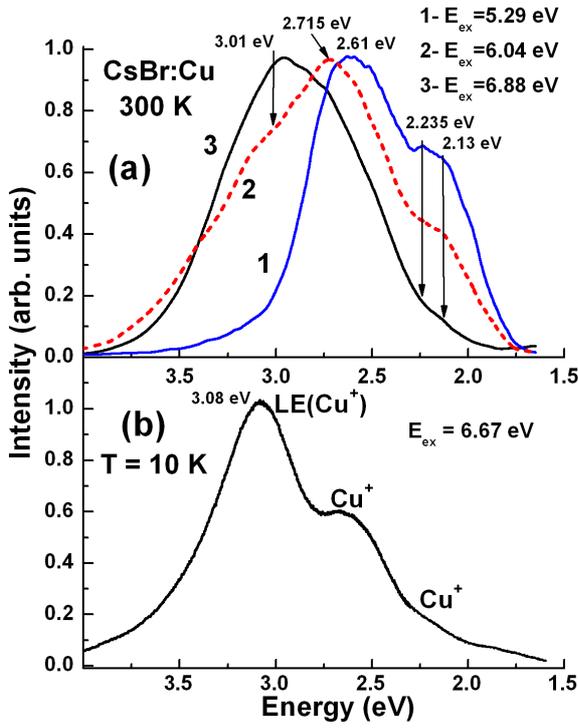


Fig. 1. Emission spectra (normalized) of CsBr:Cu crystals at 300 K (a) and 10 K (b) under excitation by SR in the range of absorption bands of  $\text{Cu}^+$  ions at 5.29 eV (1a), exciton range at 6.04 eV (2a) and range of interband transition at 6.88 eV (3a) and 6.67 eV (b).

curve 1) presents the dominant band peaked at 3.01 eV (3.08 eV at 10 K) corresponding to the emission of excitons localized around  $\text{Cu}^+$  ions.

The excitation spectra of two luminescence bands of  $\text{Cu}^+$  ions in CsBr:Cu crystal are shown in Fig. 2. The excitation spectrum of high-energy emission band consists of two bands in the CsBr transparency range peaked at 4.47 eV and 5.45 eV related to the  ${}^1A_{1g} \rightarrow {}^1E$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition of  $\text{Cu}^+$  ions. In the exciton range this spectrum contains the band peaked at 5.83 eV corresponding to the energy of formation of excitons bound with  $\text{Cu}^+$  ions. The shape of excitation spectrum of the low-energy band of the  $\text{Cu}^+$  luminescence changes in comparison with the same spectrum for the high-energy band (Fig. 2, curve 2). Specifically, the emission in this band is weakly excited in the fundamental absorption range (6.2–8.3 eV) and is more effectively excited in the wide band peaked approximately at 4.5–5.1 eV which strongly overlap with the low-energy absorption band of  $\text{Cu}^+$  ions. Most probably, this excitation band related to the formation of  $\text{Cu}^0$  state [10] corresponds to the charge transfer transition (CTT) between the ground state of  $\text{Cu}^0$  ions and bottom of conductive band.

The emission band peaked at 3.08 eV at 10 K, related to the luminescence of excitons localized around  $\text{Cu}^+$  ions, is excited mainly in the range of 5.5–6.2 eV (Fig. 2, curve 3) which confirms its exciton origin. The maximum

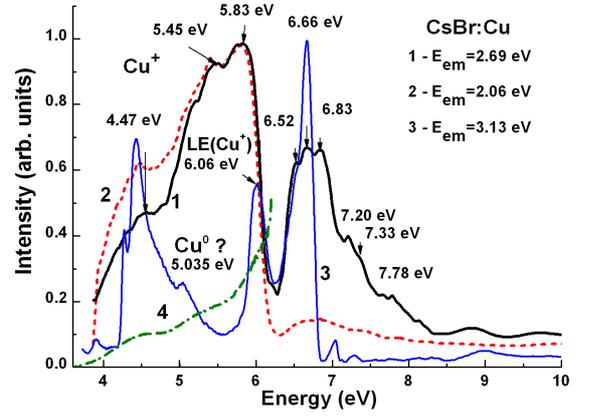


Fig. 2. Excitation spectra of  $\text{Cu}^+$  luminescence in the band peaked at 2.69 eV (1) and 2.06 eV (2) at 300 K and luminescence of excitons localized around  $\text{Cu}^+$  ions in the band peaked at 3.13 eV (3) at 10 K in CsBr:Cu crystal. Absorption spectra of CsBr:Cu crystal (4) are shown for comparison.

of the excitation band peaked at 6.06 eV in the exciton range corresponds to energies of creation of such excitons. This emission is also excited in the band peaked at 4.47 eV most probably related to the CTT between the bottom of valence band and ground state of  $\text{Cu}^{2+}$  ions with subsequent formation of excitons localized around  $\text{Cu}^+$  ions. The band at 5.03 eV most probably is related to the formation of  $\text{Cu}^0$  state under condition of high-energy excitation by SR.

### 3.2. Luminescence of $\text{Cu}^+$ ions

The luminescence spectrum of  $\text{Cu}^{2+}$  ions in CsBr:CuBr<sub>2</sub> crystal at 300 K, under excitation with an energy of 4.09 eV in the strong absorption band of this crystal caused by  $\text{Cu}^{2+}$  dopant (Fig. 4, curve 3) [3, 4], consists of the dominant emission band of  $\text{Cu}^{2+}$  ions peaked at 2.49 eV with low-intensity bump in the low-energy side (Fig. 3b, curve 1). Besides the emission band of  $\text{Cu}^{2+}$  ions, under excitation of the CsBr:CuBr<sub>2</sub> crystal in the exciton range at 5.98 eV, we also observed two emission bands of  $\text{Cu}^+$  ions peaked at 2.71 eV and 2.55 eV (Fig. 1b, curve 2). The luminescence spectrum of CsBr<sub>2</sub> crystal under excitation at 6.76 eV in the fundamental absorption range presents the wide emission band peaked at 2.86 eV (Fig. 1b, curve 3). Probably, this band is a complex superposition of the emission of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions and the luminescence of excitons localized around  $\text{Cu}^{2+}$  and partly  $\text{Cu}^+$  ions.

More detailed separation of luminescence bands in CsBr crystals related to  $\text{Cu}^{2+}$  doping can be done at 10 K (Fig. 3b). Under excitation by SR at 7.07 eV in the onset of interband transitions, the emission spectrum of CsBr:Cu crystals in UV (4.0–3.0 eV) range shows the dominant emission of self-trapped excitons (STE) in the band peaked at 3.53 eV and luminescence band of  $\text{Cu}^{2+}$  ions at 2.55 eV in the visible range. Apart from the emis-

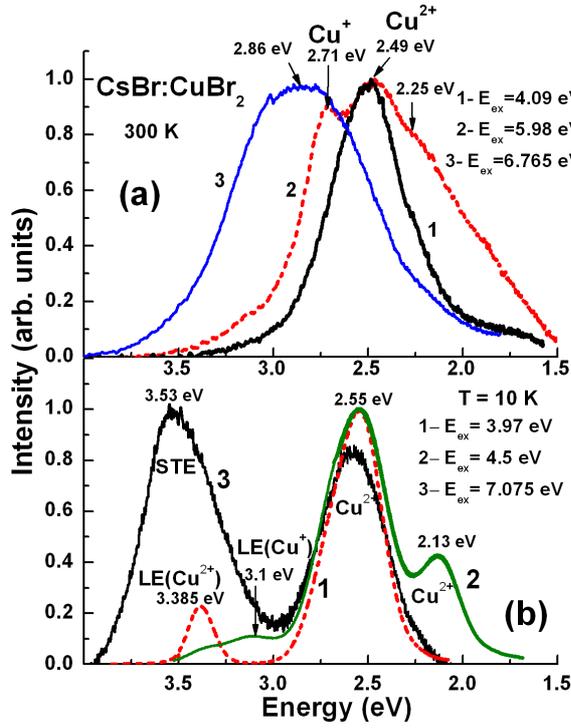


Fig. 3. Emission spectra (normalized) of  $\text{CsBr}:\text{CuBr}_2$  crystals at 300 K (a) and 10 K (b) under excitation by SR in the range of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ion absorption bands at 3.97 eV (1b) and 4.50 eV (1b), exciton range at 5.98 eV (2a) and in the interband transition range at 7.07 (3b) and 6.76 eV (3a).

sion of  $\text{Cu}^{2+}$  ions in the dominant band peaked at 2.55 eV and low-intensive band peaked at 2.13 eV, the luminescence of excitons localized around  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions in the bands peaked at 3.38 and 3.10 eV appears also in the emission spectrum of  $\text{CsBr}:\text{CuBr}_2$  crystals under excitation by SR with energies of 3.97 eV and 4.50 eV in the  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  absorption bands (Fig. 3b, curve 1 and 2, respectively).

The excitation spectrum of the  $\text{Cu}^{2+}$  luminescence in  $\text{CsBr}:\text{CuBr}_2$  crystals is very complicated (Fig. 4). The excitation spectrum of high-energy band of the  $\text{Cu}^{2+}$  luminescence peaked at 2.55 eV at 300 K (Fig. 4a, curve 1) in  $\text{CsBr}$  transparency range consists of the intensive complex band peaked at 4.09 eV which coincides with the above mentioned strong absorption band of  $\text{Cu}^{2+}$  ions (Fig. 4a, curve 3). The fine structure of this band is observed at 8 K. Namely, this band at 8 K presents the superposition of three bands peaked at: 3.97, 4.20 and 4.59 eV (Fig. 4b, curve 2). In addition to these bands, other two high-energy bands peaked at 4.59 and 5.33 eV are also present in excitation spectrum of the  $\text{Cu}^{2+}$  luminescence at 8 K. The excitation spectrum of the  $\text{Cu}^{2+}$  luminescence in the low-energy band peaked at 2.13 eV (Fig. 4b, curve 3) differs from that for high-energy band peaked at 2.55 eV mainly due to the overlapping of the excitation spectra of the first band with the excitation

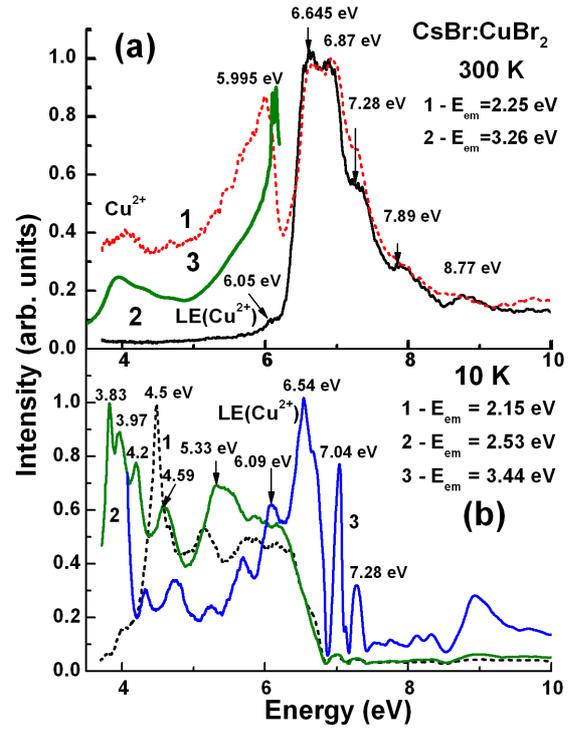


Fig. 4. Excitation spectra (normalized) of  $\text{Cu}^{2+}$  luminescence in the band peaked at 2.25 eV (1a) at 300 K, and 2.53 eV (2b) and 2.15 eV (1b) at 10 K, and luminescence of excitons localized around  $\text{Cu}^{2+}$  ions in the band peaked at 3.26 eV (2a) at 300 K, and 3.44 eV (3b) at 10 K in  $\text{CsBr}:\text{CuBr}_2$  crystal. Absorption spectrum of  $\text{CsBr}:\text{CuBr}_2$  crystal (3a) is shown for comparison.

spectrum of low-energy band of the  $\text{Cu}^+$  luminescence (Fig. 2, curve 2). Specifically, the dominant sharp band peaked at 4.50 eV, most probably can be related exactly to the excitation band of  $\text{Cu}^+$  ions (Fig. 2b, curve 1). The band in the 5.0–5.2 eV range can be related to  $\text{Cu}^0$  ions [10].

The dominant band peaked at 5.99 eV in the excitation spectrum of the  $\text{Cu}^{2+}$  luminescence in  $\text{CsBr}_2$  crystal at 300 K, in the exciton range corresponds to the energy of formation of excitons bound with  $\text{Cu}^{2+}$  ions. The band peaked at 6.09 eV in the excitation spectrum of the luminescence in  $\text{CsBr}_2$  crystal at 10 K, in the exciton range corresponds to the energy of formation of excitons bound with  $\text{Cu}^{2+}$  ions. The intensive bands at 6.64 and 6.87 eV in the fundamental absorption range are related to excitation of the  $\text{Cu}^{2+}$  emission via e/h recombination.

#### 4. Discussion and conclusions

The possible reasons for the existence of two bands of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  emission in  $\text{CsBr}$  crystal are as follows: (i) the existence of *on-* and *off-centre* configurations of the relaxed excited state of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions due to very large difference of the ionic radius of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions (0.77 Å and 0.73 Å, respectively) in sixfold coordi-

nation and  $\text{Cs}^+$  cations (1.67 Å) [7], (ii) the formation of the dimer or other complex  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  centers [6]. The existence of both considered models in Cu-doped alkali-halides has been discussed in works [6, 10–12]. In our opinion, both of these models can be realized also in  $\text{CsBr:Cu}$  and  $\text{CsBr:CuBr}_2$  crystals. The close form of excitation spectra for the low- and high-energy emission bands of  $\text{Cu}^+$  ions (Fig. 2, curves 1 and 2) supports mainly the first mentioned model. At the same time, due to large concentration of copper dopant the formation of dimer centers is not excluded in the crystals under study. Very rich and complicated shape of the excitation spectra of the  $\text{Cu}^{2+}$  luminescence and exciton luminescence of  $\text{CsBr:CuBr}_2$  crystals in the host transparency range (3.7–6.0 eV) and exciton range (6.0–7.2 eV) mostly supports the last assumption.

The spectral identification of all mentioned excitation bands of the  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  luminescence in  $\text{CsBr:Cu}$  and  $\text{CsBr:CuBr}$  crystals presents the complicated task and will be performed in a separate paper. We only note here that the three bands (4.2–3.83 eV, 4.59 eV and 5.33 eV) in the excitation spectra of  $\text{CsBr:Cu}^{2+}$  crystals at 10 K can be assigned to the CTT in the  $(\text{CuBr}_6)^{4-}$  complexes formed in the alkali-halide crystals. The observed absorption and excitation spectra can be explained by taking into account the mixing of two  $t_{1u}$  molecular orbitals of ligands which consist of  $p_\pi$  and  $p_\sigma$  halogen orbitals. The transitions in  $(\text{CuX})^{4-}$  complexes from the ground  $^1E_g$  state to the excited  $^2T_{1u}\sigma$  and  $^2T_{1u}\pi$  states, respectively, are responsible for the high-energy and low-energy sets of excitation bands.

Based on the presented experimental results, the scheme of levels of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in  $\text{CsBr}$  host is shown in Fig. 5.

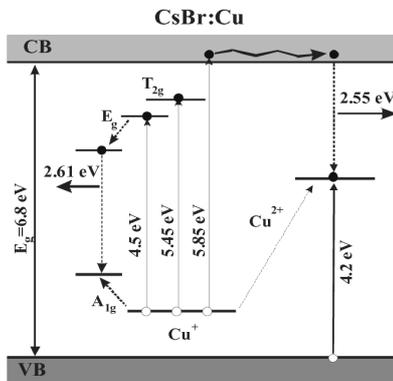


Fig. 5. Scheme of levels of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in  $\text{CsBr}$  host and possible mechanism of excitation of their luminescence.

Concluding, existence of the luminescence bands of different origin (intrinsic radiative transition of  $\text{Cu}^+$  ions, recombination luminescence of  $\text{Cu}^{2+}$  ions and luminescence of excitons localized around  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions) was found in  $\text{CsBr:Cu}$  and  $\text{CsBr:CuBr}_2$  crystals. This

reflects the complicated character of formation of the luminescence centers in  $\text{CsBr}$  host due to copper doping, which can participate in the storage or TL processes in such phosphors. The energy scheme of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in the  $\text{CsBr}$  host in the 3.7–10 eV range, and related with them low energy excitation, were clarified using the absorption and excitation spectra of luminescence of these ions under excitation by synchrotron radiation. Apart the intrinsic and charge-transfer transition related to the  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions we confirm in this work the existence of excitons localized around these ions and determined their energy of creation to be equal to 6.06 eV and 6.09 eV at 10 K, respectively. The radiative decay of such excitons results in the luminescence in the band peaked at 3.08 eV and 3.385 eV, respectively. We also found that the energy of creation of excitons bound with the  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  equals 5.83 eV and 5.99 eV at 300 K, respectively. Radiative annihilation of such type excitons results in the  $\text{Cu}^+$  emission in the band peaked at 2.61 eV and 2.235 eV, and  $\text{Cu}^{2+}$  emission in the bands peaked at 2.55 eV and 2.13 eV. The doublet character of these bands can be related to both — formation of the *off-centre* configuration of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions and creation of Cu-based dimer centers.

## Acknowledgments

The work was performed in the framework of HASYLAB II-20090087 research project.

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