INVESTIGATION OF ENERGETIC STATES, DETERMINED BY Cu AND Cd IMPURITY ATOMS, AT SURFACE OF GaS AND GaSe MONOCRYSTALLINE LAYERS

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Abstract

The reflection, absorption, photoconductivity, and thermally stimulated luminescence (TSL) spectra of GaS:Cu and GaSe:Cu, Cd single crystals have been studied. As a result of these investigations, the energy diagram of GaS and GaSe crystals after doping was determined.

1. Introduction

The crystallization of GaS and GaSe binary compounds results in a stratified structure of S (Se)-Ga-Ga-S (Se) type. The S (Se)-Ga-Ga-S (Se) packing with predominant covalent bonds, while the bonds between different packings are of polarizational origin. The Ga atom is bound to another Ga atom, being surrounded by three S (Se) atoms placed on the top of a tetrahedron [1], inside a packing. The peculiarities of the chemical bonds between Ga-Ga and Ga-S(Se) inside a stratified packing and between different packings, determine the localization possibilities of the impurity atoms in these materials and, as a consequence, their energy spectrum.

The valence bonds at the surface of the stratified packing are closed, resulting in low concentration of surface states. This property along with suitable optical, photoelectrical, and luminescent properties determine the use of these materials in multilayered nanoelectrical devices [2, 3].

The Cu and Cd impurity atoms create two types of states: by removing the intrinsic defects from the metal sublattice inside a stratified layer, maintaining the surroundings of Ga atom and another being localized between the stratified packings. The latter ones form surface impurity centers, allowing the control of the energetic spectrum of the surface states.

As a result of the investigations on the optical, photoelectrical, and luminescent properties of the monocrystalline GaS: Cu and GaSe: Cu and Cd, having a concentration up to 0.50at%, the energy diagram of the impurity states caused by the impurity atoms, has been determined.

2. Experimental

The impurity atoms of 0.01at% up to 0.50at% Cu in GaS and 0.01at% up to 0.50at% Cu and Cd in GaSe, have been added to the initial mixture of main components. The variation of concentration of Cu and Cd atoms, determined by emission spectral analysis, is less than 5%

for GaSe single crystals. The 3247.5 Å and 3273.9 Å for Cu and 3261.06 Å and 3467.6 Å for Cd have been considered as analytical spectral lines.

The reflection spectra in 1÷6 eV spectral region and the absorption spectra in the fundamental absorption region at 78 and 293 K have been recorded by a spectrophotometric device, with a ~1 meV resolution for the entire energetic interval to be studied.

The absorption coefficient α has been determined from the optical transmission $T(\hbar\omega)$ and reflection $R(\hbar\omega)$ spectra of the monocrystalline layers with 0.1 μm up to 0.5 cm thickness, spectrum

$$\alpha(\hbar\omega)=\frac{1}{\alpha}\ln\frac{2T}{(1-R)^2-T^2+\sqrt{\left[(1-R)^2-T^2\right]+4T^2}} \qquad (1)$$

The photoconductivity spectral dependence of the GaS (Cu) and GaSe (Cu, Cd) single crystal layers at 78 and 29 K has been studied by using a diffraction grid (1200 mm^{-1} and 600 mm^{-1}) monochromator based device. The 1000 W Xe lamp was used as light source. The spectral resolution for photoconductivity measurements was ~2 meV in the 1.7÷3.6 eV range. The energy distribution of the incident beam has been measured by a Vth-1 thermoelement with a SiO_2 window. Its sensitivity was 4 V/W.

The samples for photoconductivity measurement have been cut out of single crystal slices, ~(0.01÷0.05)×3×6 mm^3, parallelepiped-shaped. The In electrodes were thermally evaporated on the lateral faces of the samples. The monochromatic light has been focused between the electrodes by using a system of lenses. The absence of EMF in closed circuit while illuminating the region adjacent to electrodes, was considered as a criterion of the absence of potential barrier between electrode and semiconductor. The spectral dependences have been referred to photon numbers and normalized.

The localized energy states depending on the role they can have in the generation-recombination process could be recombination or capture ones. Depending on the technologic conditions they can change their role. The energies of capture levels have been determined by thermal stimulated luminescence. The methodology of the experiment considers the excitation of the sample with light having energy close to fundamental absorption edge for minimum temperature in a given experiment [4]. A Hg lamp with an average power of 500 W has been used as a light source. The wavelength has been selected by using optical filters from 312 up to 435 nm for GaS (Cu) and the excitation wavelength range has been extended up to 579 nm for GaSe. The heating rate varied from 0.1 $K\cdot s^{-1}$ up to ~ 1.5 $K\cdot s^{-1}$.

3. Results and discussion

a) GaS and GaS (Cu) crystals

The absorption spectral dependence of 0.50at% Cu GaS at 293 and 78 K in the fundamental absorption edge region is given in Figure 1 (curves 1 and 2 respectively). A comparison with the same dependences for undoped GaS crystals, curves 3 and 4, 293 and 78 K, respectively, indicate the presence of D_0 ($\hbar\omega_0$=2.31 eV) and D_1 ($\hbar\omega_1$=2.46 eV) bands for absorption coefficient $\alpha\leq$12 cm^{-1}, determined by Cu atoms. The GaS doping with Cu ($C\leq$0.5at%) [5] does not change the majority of charge carrier type (holes). One can assume that Cu atoms form acceptor states in the energy gap. The edge of the impurity absorption at 293 and 78 K can be equivalent to the energy position D_0 ($\hbar\omega_0$=2.31 eV) and D_1 ($\hbar\omega_1$=2.46 eV) particularities. The localization energy of the acceptor (Cu atom) estimated with a precision of the binding energy of indirect excitons (30 meV) [6], is equal to ~0.11 eV.

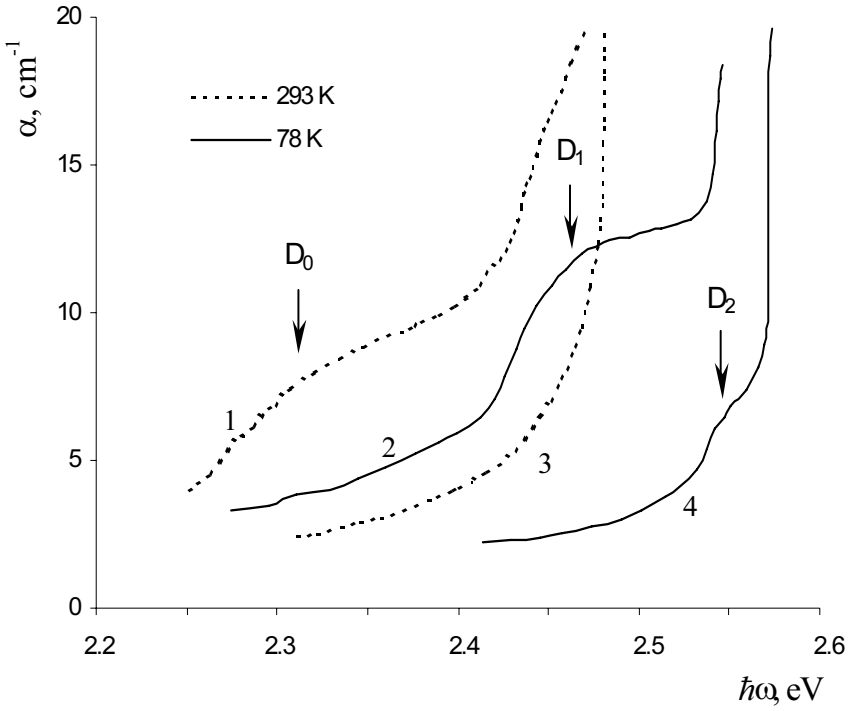


Figure 1. The absorption spectra for undoped (3, 4) GaS crystals and 0.50at% Cu doped GaS (1, 2) crystals at 293 and 78 K.

The reflection spectra next to fundamental absorption edge have been measured for GaS and GaS:Cu for $\vec{E} \perp \vec{c}$. As one can see in Figure 2, the reflection spectrum of GaS at 293 K consists of two bands A and C localized at ~2.50 eV and 3.25 eV. A similar band structure was noticed for $\vec{E} \perp \vec{c}$ polarization for GaS:Cu. The temperature decrease to 78 K results in slight shift of the peculiarity A to higher photon energy region, thermal expansion coefficient being equal to $\sim 6 \cdot 10^{-4}$ eV/K. The peculiarity C is localized at ~3.15 eV at 293 K and 3.25 eV at 78 K, and as it was shown in [7], it is caused by direct optical transitions in M point of Brillouin zone [8].

The reflection spectra in the fundamental absorption band edge region of β-GaS (1) and β-GaS:Cu (2) at 293 K is given in Figure 3. The maxima energies $R(\hbar\omega)$ are given in Table 1.

Table 1. The maximum energy of the reflection peaks of β-GaS and β-GaS(Cu) (eV)

Maxima index / Chemical compound	A	B	C	C*	D*	D	E	F
β-GaS	2.50	4.00	4.81	5.15	5.52	5.70	6.15	-
β-GaS(Cu)	-	3.95	4.80	-	-	5.70	6.20	6.7

The excess of Cu atoms is localized between the stratified packings, so the cleavage of the crystal will have a surface enriched with Cu atoms. These defects perturbate the energetic spectrum of the electronic states and can be revealed by reflection spectra. At the same time, the energy states created by Cu atoms on the GaS crystals surface as well as impurity atoms captured from atmosphere result in a decrease of C* and D* (Figure 3) peculiarities, but the F threshold (~6.7 eV) is amplified.

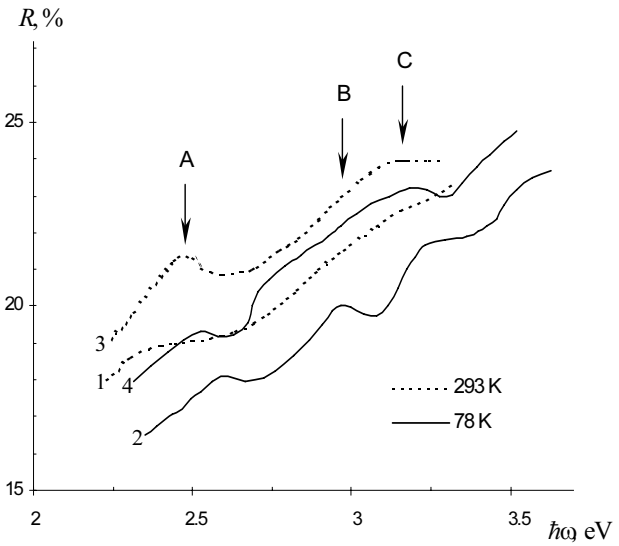


Figure 2. The reflection spectra of undoped β-GaS (3, 4) and β-GaS 0.50at% Cu doped (1, 2) crystals at 293 and 78 K for $\vec{E} \perp \vec{c}$ polarization.

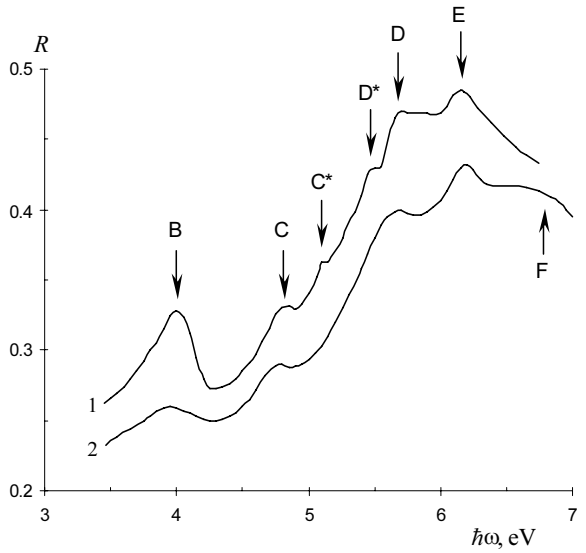


Figure 3. The spectral dependence of the reflection coefficient for β-GaS (1) and β-GaS: Cu (2) crystals at 293 K for $\vec{E} \perp \vec{c}$.

The spectral distribution of GaS and GaS (Cu) the relative photoconductivity at 293 K (curves 3 and 1) and 78 K (curves 4 and 2) is given in Figure 4. The photoconductivity spectrum of GaS (78 K) consists of three pronounced maxima (A, B, D) at 308 nm ($\hbar\omega_1$=4.02 eV) (D), 405 nm ($\hbar\omega_3$=3.065 eV) (B) and 475 nm ($\hbar\omega_4$=2.61 eV) (A) and a peculiarity threshold shaped (C) at 378 nm ($\hbar\omega_2$=3.25 eV).

The A′ peculiarity (red edge of the fundamental absorption) keeps its shape with temperature increase from 78 K up to 293 K, but it shifts toward long wavelength region. The thermal shift coefficient being equal to $\sim 6 \cdot 10^{-4}$ eV/K correlates well with the indirect band gap coefficient determined from the absorption spectra.

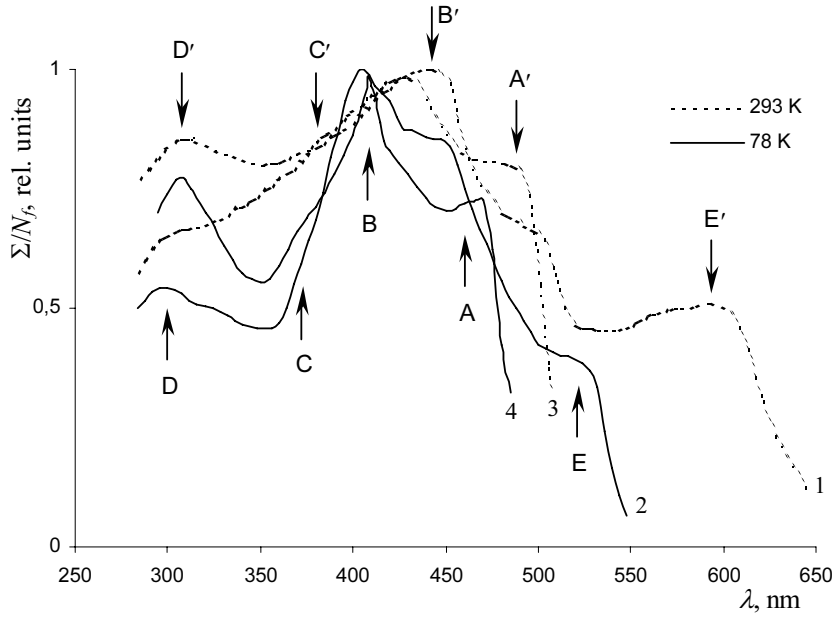


Figure 4. The photoconductivity spectral dependence for undoped GaS (3, 4) and Cu doped GaS (1, 2) at 293 K and 78 K.

By coming from the analysis of 1 and 2 (Fig. 4) Cu impurity atoms reveal a supplementary band localized at 450÷560 nm at 78 K and at 550÷650 nm at 293 K correlating well with D_1 from the absorption spectrum (Fig. 1). Considering the conformity between the absorption and photoconduction, one can assume that Cu atoms form localized states next to valence band top of GaS. The nonequilibrium charge carriers are generated in the conduction band as a result of indirect optical transitions from these levels. The localization energy of the Cu states, which determine the photoconductivity in the red spectral region, is 0.34 eV.

One can find reliable information on the low energy capture level position from the analysis of thermally stimulated luminescence. The experimental investigations on the thermoluminescent crystals demonstrated that the energy of the capture levels could be calculated if the position of thermoluminescent maximum is known [9]

$$E_t = \frac{A}{T_{\max}}, \tag{2}$$

where A is a characteristic constant.

The thermoluminescent spectra are localized in the 80÷240 K interval for β-GaS undoped as well as for Cu doped 0.01at% and 0.07at% (Fig. 5). The thermoluminescence of these crystals has been excited with the radiation with $\hbar\omega$>3.2 eV and 8 W/cm^2 beam density.

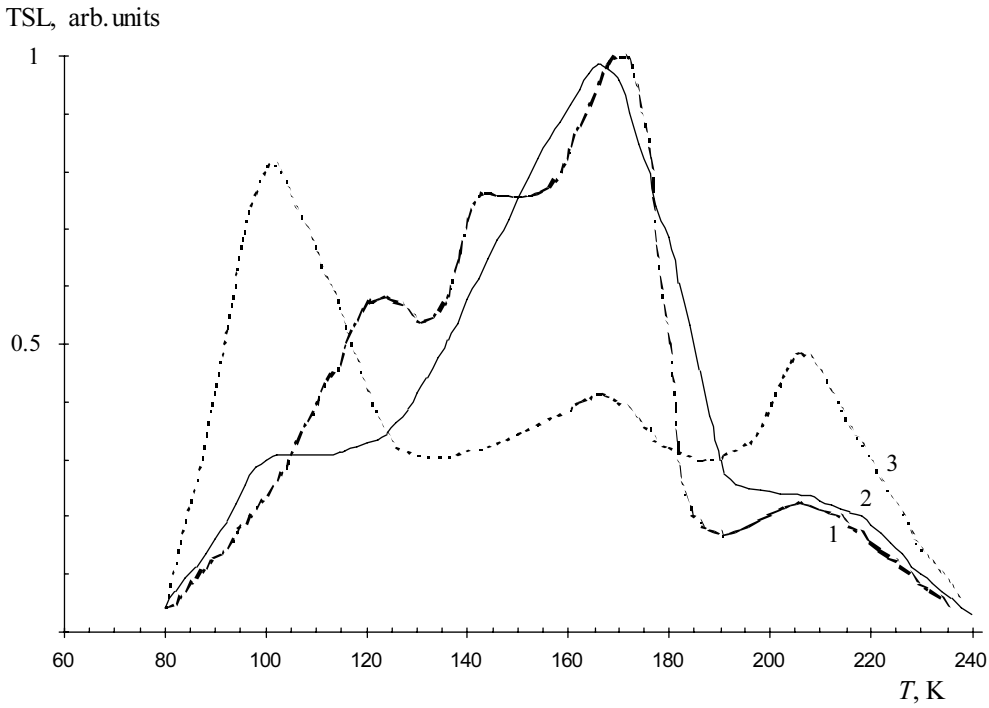


Figure 5. The thermostimulated luminescence temperature dependence for undoped β-GaS (1) and Cu 0.01at% (2) and 0.07at% (3) doped GaS crystals.

As one can see from Fig. 5 (1), the thermoluminescent spectrum of the starting β-GaS crystals consists of four bands with maxima at 122 K, 141 K, 170 K, and 202 K, which correspond to four types of electron capture levels at 0.26 eV, 0.30 eV, 0.36 eV, and 0.43 eV, respectively, from the bottom of the conduction band. The Cu impurity atoms create a new arrangement of the capture levels (Fig. 5, curves 2 and 3).

As it follows from the analysis of curves 1 and 2 (Fig. 5), one can conclude that 0.01at% Cu atoms create three capture levels for electrons in β-GaS band gap, at 0.22 eV, 0.35 eV, and 0.44 eV higher than the valence band top.

The increase of Cu concentration up to 0.07at%, results in an essential change of the structure of I_{TSL} (T) dependence. 120 K band became predominant, but 166 K band is atenuated and the high temperature band is amplified. As a consequence, 0.22 eV, 0.35 eV, and 0.44 eV capture levels are active.

b) GaSe and GaSe (Cu, Cd) crystals

The reflection spectra of monocrystalline GaSe and GaSe (Cu, Cd) (0.01÷0.50at%) have been studied at 293 K from the natural surfaces oriented perpendicular to hexagonal axis C_6.

Low intensity bands are revealed in the reflection spectra of GaSe (Cu) (Fig. 6), localized in the green spectral region (2.5÷2.9 eV). The bands have intensities depending on the quantity of impurity atoms in GaSe. In the 3÷6 eV region, two principal maxima E_2 and E_5 appear, localized in 3.74÷3.77 eV and 4.98÷5.08 eV, respectively.

As one can see from Fig. 7 (curve 1), the reflection spectrum of undoped GaSe consists of well contoured E_2 and E_5 band with maxima at 3.75 eV and 5.08 eV, and four particularities E_0' (2.73 eV), E_1 (3.35 eV), E_3 (4.25 eV), and E_6 (5.20 eV) are less pronounced.

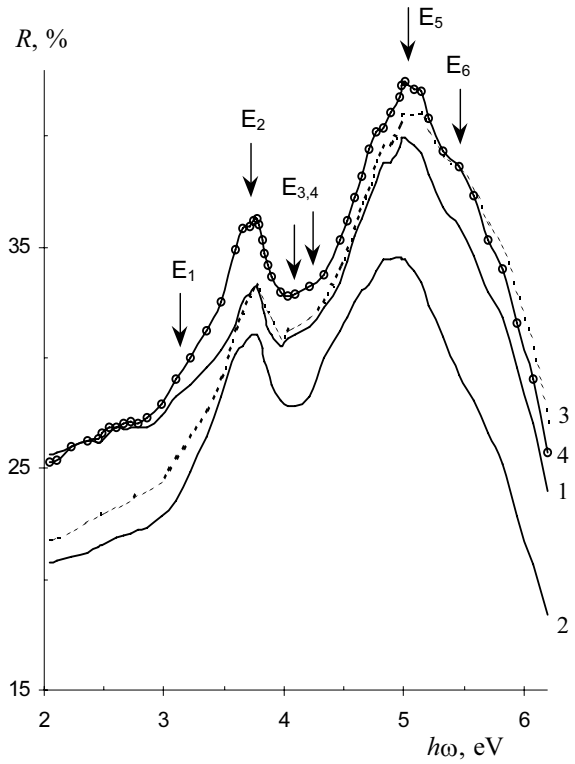


Figure 6. The influence of concentration of the Cu impurity atoms on the reflection spectra of GaSe. The concentration of Cu atoms in GaSe crystal, at%: 1 – 0.05; 2 – 0.10; 3 – 0.20; 4 – 0.50.

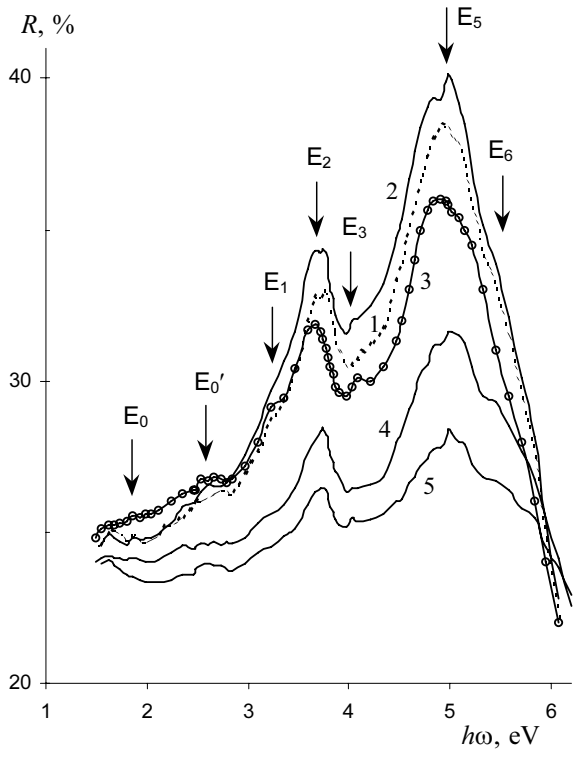


Figure 7. The influence of concentration of the Cd impurity atoms on the reflection spectra of GaSe. The concentration of Cd atoms in GaSe crystal, at%: 1 – 0.00; 2 – 0.05; 3 – 0.10; 4 – 0.20; 5 – 0.50.

Cd atoms in GaSe exhibit a higher influence on the electronic states. The 0.05-0.50at% Cd doped GaSe reflection spectra are given in Fig. 7 (curves 2-5). The energies corresponding to the component bands of the reflection spectrum of these crystals are given in Table 2. As one can observe from the given Table, at the increase of Cd atom concentration in GaSe, the

E_5 maximum shifts to higher energy region with an ~8 meV/at% rate. A well pronounced threshold at 5.453 eV (E_6) is brought out better along with Cd atom concentration increase. One can find such structure of R ($\hbar\omega$) dependence in the reflection of the GaSe:Cu 0.20 and 0.50at% (Fig. 6, curves 3 and 4). The difference is that the peculiarity is less revealed and shifted by 0.246 eV to lower energies.

Table 2. The photon energies (eV) corresponding to the position of particularities of the reflection spectra.

Chemical compound GaSe (Cd), at%	E_0	E'_0	E_1	E_2	E_3	E_5	E_6
0.00	1.860	2.728	3.35	3.75	4.25	5.08	5.579
0.05	1.860	2.604	3.224	3.658 3.744	4.029	4.959	5.455
0.10	1.860	2.666	3.224	3.658	4.091	4.890	5.579
0.20	1.860	2.666	3.224	3.744	4.029	4.984	5.453
0.50	-	2.604	3.348	3.744	4.091	5.009	5.510

The typical TSL of GaSe:Cu and GaSe:Cd are given in Fig. 8 and 9, respectively.

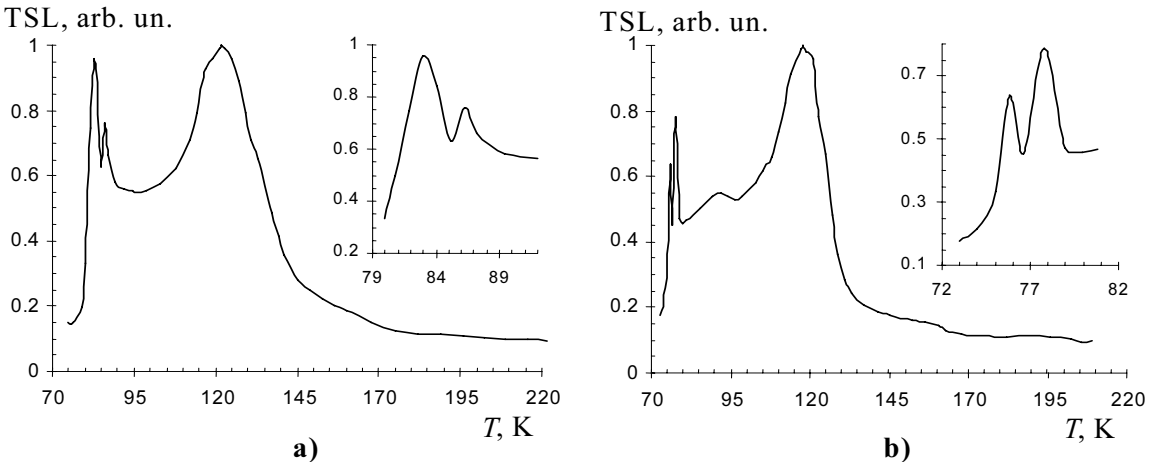


Figure 8. The influence of concentration of the Cu impurity atoms on the structure of TSL of Cu doped GaSe with 0.05at% (a) and 0.50at% (b).

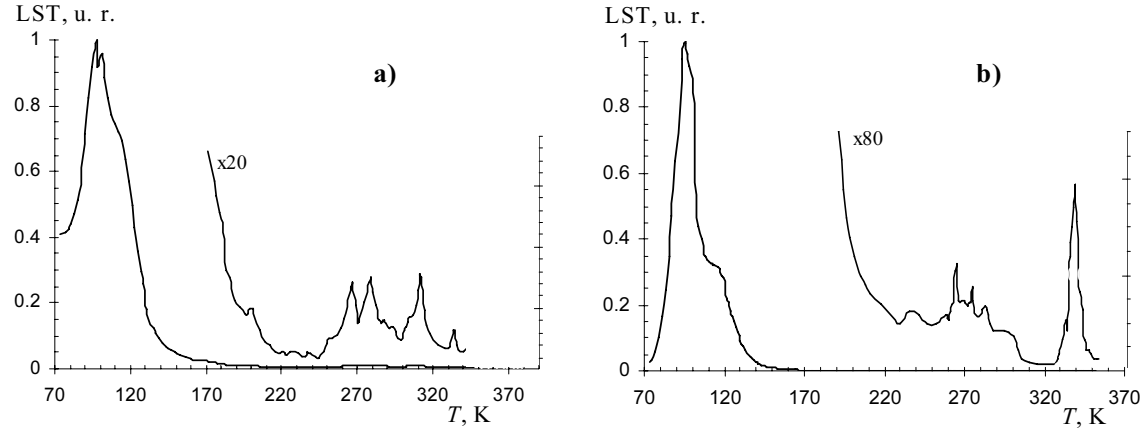


Figura 9. The influence of concentration of the Cd impurity atoms on the structure of TSL of Cd doped GaSe with 0.05at% (a) and 0.10at% (b)

The energies of the capture levels, determining the complex structure of TSL spectra for GaSe and GaSe: Cu and Cd, are given in Table 3.

Table 3. The energies of the capture levels created by Cd and Cu impurity atoms in GaSe crystals.

Chemical compound		Temperature *T*, K Energy *E*, eV
GaSe: Cd	0.05	98; 101; 266; 279; 312; 366 0.189; 0.196; 0.516; 0.541; 0.604; 0.710
	0.10	95; 113; 263; 280; 337 0.185; 0.218; 0.509; 0.544; 0.654
	0.20	98; 289; 310; 326; 348 0.189; 0.561; 0.601; 0.633; 0.676
	0.50	105; 127 0.204; 0.246
GaSe: Cu	0.05	83; 122 0.161; 0.236
	0.10	75; 77; 84; 96 0.145; 0.148; 0.163; 0.185
	0.20	98; 174 0.189; 0.337
	0.50	76; 78; 92; 118 0.147; 0.150; 0.178; 0.228

As one can see from this Table, the increase of the Cd concentration in GaSe from 0.10 to 0.50at% results in the shift of the energy of the 0.185 eV capture level to higher energies by ~19 meV. The decrease of capture state concentration at 0.50at% Cd in GaSe can be attributed to the formation of the compounds with closed valence bonds at the GaSe surface.
The Cu atoms create a large spectrum of capture levels with energies 0.16÷0.34 eV in the monocrystalline GaSe.

4. Conclusions

The Cu atoms in (0.50 at%) in GaS determine acceptor levels with the energy of ~0.11 eV, optically active, perturbating the edge of absorption by formation of an absorption band with maximum at 2.31 eV at 293 K and 2.46 eV at 78 K. The presence of the acceptor levels formed by Cu atoms results in shift to lower energies of the edge of photoconductivity, at room temperature as well as at low temperatures.

The electronic states of GaS crystals with energies in the 3.5÷6 eV range are weakly affected by Cu impurities. The latter ones intensify electronic transitions in $\hbar\omega < 3.5$ eV range and especially for $\hbar\omega \approx 6.7$ eV by forming bonds of Cu-S, Cu-Ga-S type.

The energies of the recombination and capture levels created by Cu atoms in GaS have been determined from the analysis of PL and TSL spectra.

Considering that Cu atoms with the concentration less than 0.05 at% amplify the structure of the reflection spectra of GaSe monocrystalline layers, one can conclude that the latter ones, having a covalent radius smaller than that of the Ga atoms, remove the defects in the metal sublattice. The Cd atoms $C \geq 0.10$ at% with a higher covalent radius are predominantly

localized between the stratified packings and at the surface of the sample, resulting in the attenuation of the R ($\hbar\omega$) peculiarities.

The Cu atoms form optically active recombination levels in GaSe as well as a large set of capture levels localized in the 0.14÷0.23 eV energy interval, while the Cd atoms with concentration less than 0.50at% create deep capture levels with energy up to 0.68 eV.

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