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# Study of generation-recombination processes of non-equilibrium charge carriers in single crystalline thin GaSe(Cu) films

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The generation-recombination processes of non-equilibrium charge carriers in undoped and Cu-doped (in the range 0.1-0.5 at.%.) single crystalline GaSe films with thickness *d* in the range 1.5-225 μm are investigated. Cu doping of GaSe crystals up to 0.5 at.% leads to an increase of electrical conductivity by over 4 orders of magnitude, as well to enhancement of impurity luminescence band (PL) and extension of photoconductivity spectral range. By studying PL and photonductivity spectra, for different excitation (photon) energies in temperature range (78-420) K, energies of localized states due to both Cu and accidental impurities are determined. By analysing temperature dependence of electrical conductivity and photoconductivity for undoped and Cu-doped films, the activation energy of acceptor levels in doped films was determined as 0.058 and 0.025 eV. Increasing Cu doping from 0.1 to 0.5 at.%. results in decreasing energy of acceptor levels up to ~0.02 eV. By analysing the impurity absorption and photoconduction at 78 K the energy of acceptor levels was determined as 12-15 meV greater than previously evaluated, depending on Cu concentration. For films with $d$<5 μm, the surface states concentration increased for Cu doping over 0.3 at.%.

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## 1. Introduction

Gallium selenide (GaSe) belongs to $A^{III}B^{VI}$ layered crystals, with a hexagonal unit cell. Each layer is composed of stratified packages of Se-Ga-Ga-Se type. The links between packages are accomplished by polarizational forces, while inside the package covalent bonds prevail [1]. By inserting impurity metal atoms of I-III groups into GaSe lattice, the native structural defects in the metal sublattice are liquidated, besides they can form an intermediary layer localized between halogen planes, resulting in nanostructured -Se-Ga-Ga-Se-Me- stratified packages [2]. The GaSe-based nanostructures prepared by impurity atoms intercalation show (likewise GaSe single crystals) photoelectric and radiative properties in the VIS spectral range [3]. At layer surface the valence bonds are practically closed [1], thus leading to low concentrations of surface states. This feature recommends utilization of $A^{III}B^{VI}$ materials as active elements in luminescent diodes (LEDs) and micro-lasers in VIS and NIR spectral domains [4, 5].

In a previous paper[6] we have reported the construction of a Fabry-Perot interferometer based on GaSe(Cu) single crystal.

In the present work we investigate the influence of Cu doping on the recombination-generation processes of charge carriers in GaSe crystals, by studying their optical, photoelectrical and radiative characteristics.

## 2. Experimental

The GaSe single crystals were grown from melt (Bridgmann's method) in a temperature gradient furnace. Cu atoms in proportions of 0.01-0.50 at.%. have been introduced into the initial element composition for the chemical synthesis. As resulted from the emission spectral analyze, the variation of Cu atoms concentration in GaSe single crystals was up to 5 at.%.

The crystalline structure of as-prepared crystals was examined by X-ray diffraction (XRD), by using a DRON-2 apparatus ($CuK_\alpha$ radiation, $\lambda$=0.15418 nm).

The spectral characteristics of photoluminescence (PL) of GaSe(Cu) crystals at 78 K have been recorded by a spectrophotometric installation including a monochromator with diffraction grating (1200 $mm^{-1}$ and 600 $mm^{-1}$) [8]. The excitation of PL was performed by using monochromatic radiations provided by a $N_2$ laser ($\lambda$=334 nm) and a DRS-500 filtered mercury lamp ($\lambda$=546 nm), respectively. In the calibration of respective installation, the spectrum of rodamine solution in ethanol was used as reference.

The energy spectrum of trapping states (surface capture levels) has been studied by using the method of thermally stimulated currents (TSC). In TSC method the sample (previously excited by a radiation corresponding to the depth of the fundamental absorption band) is heated at a constant rate $v_T=dT/dt$, ranged between 20 and 40 K/min. In the course of sample cooling from room temperature (293 K) to the nitrogen's boiling point (77.3 K), it was excited with photons of energy hν>2 eV; in this way, the capture levels are uniformly filled with electrons and reproducible results are obtained.

### 3. Results and discussion

The XRD patterns of GaSe samples show strong reflexions indexed as (004) and (0014) respectively, from which the parameters of the hexagonal lattice have been determined (Table 1).

*Table 1. The parameters of the hexagonal lattice of GaSe.*

| Cu concentration, at.% | 0.00 | 0.01 | 0.05 | 0.10 | 0.20 | 0.50 |
|---|---|---|---|---|---|---|
| *a*, Å | 3.752 | 3.752 | 3.757 | 3.765 | 3.767 | 3.767 |
| *c*, Å | 15.952 | 15.951 | 15.949 | 15.950 | 15.948 | 15.946 |

As estimated values of *a* and *c* parameters are seen to correspond to ε-GaSe polymorph [6].

As can be observed from Table 1, at Cu concentrations up to 0.1 at.%, the lattice parameters *a* and *c* virtually coincide with those of undoped GaSe crystals. So, we can state that Cu atoms, at low concentrations, do liquidate the structural defects from metal sublattice. A further increase in the Cu concentration results in an increase of the parameter *a*, which stabilizes itself at concentrations x≥0.20, while the parameter *c* is seen to vary only slowly against 15.950 Å throughout investigated concentration range.

The above results can be interpreted by taking into the account that the covalence radius of Cu is lesser than that of Ga, and thus by filling Ga vacancies with Cu atoms (relatively low proportions), the lattice practically doesn't change. Besides, the parameter *c*, corresponding to the "c" optical axis, which is normal to the layer (stratified package) surface, remains also unchanged during vacancies liquidation. At higher doping levels, the exceeding Cu atoms localize between Se planes, producing new hydrogen bonds between Se atoms from neighboring packages and thus contributing to a relatively small decrease of the *c* value in the case of GaSe (Cu) crystals.

In the domain of the fundamental absorption band, the absorption coefficient of GaSe crystals is seen to increase from (1-3)×$10^3$ $cm^{-1}$ at the red absorption edge, to a constant value ~6×$10^5$ $cm^{-1}$ for a photon energy of about 3.70 eV [9]. From this feature one can conclude that the generation-recombination process of non-equilibrium charge carriers takes place in a surface outer layer with thickness $1/\alpha_{min} \approx 0{,}5$ μm.

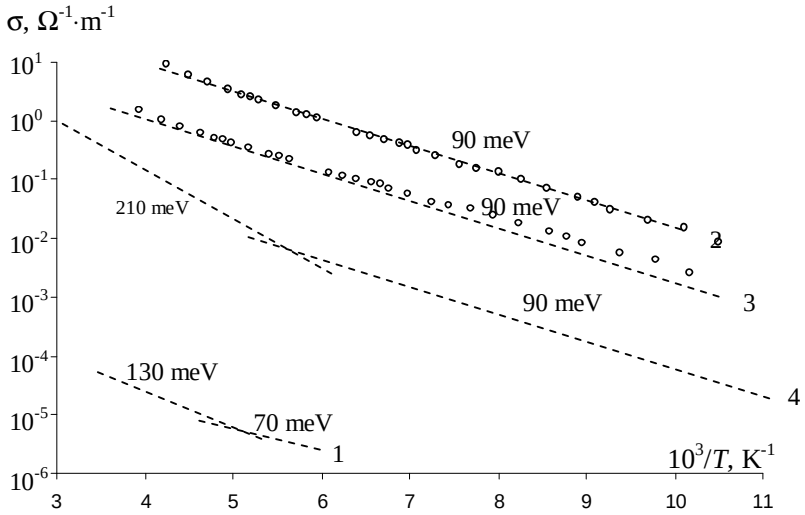


*Fig. 1. Temperature dependence of the dark electrical conductivity for undoped GaSe (1) and Cu-doped GaSe with Cu concentration 0.05 % at. (2), 0.10 % at. (3) and 0.20 %. at. (4).*

Fig. 1 shows the temperature dependences of the electrical conductivity, σ, for undoped (curve 1) and Cu-doped GaSe with impurity concentrations in the range 0.01-0.20 at.% (curves 2-4). As can be easily observed, the electrical conductivity exponentially increases with temperature. In both model based on bandgap representation and potential barrier model, this dependence can be described by the relation [10]

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{2kT}\right), \qquad (1)$$

were $E_a$ is the thermal activation energy of the acceptor states, $\sigma_0$ is a parameter depending on the semiconductor nature, k is the Boltzmann's constant, and T is the temperature.

In temperature range (78-300) K, the electrical conduction of undoped GaSe crystals is determined by two acceptor levels located at ~70 meV and 130 meV, respectively, toward the top of the valence band.

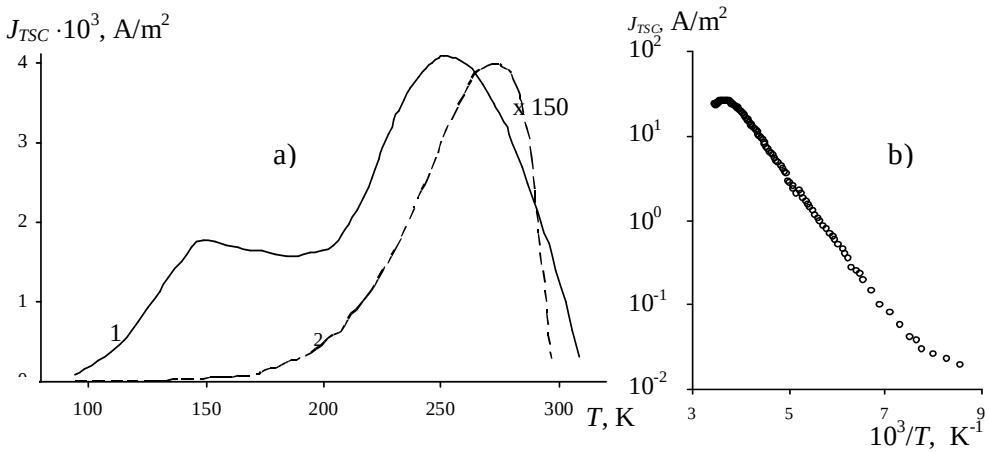


*Fig. 2. a) Temperature dependence of TSC for ε-GaSe samples with thickness 225 μm (1) and 5 μm (2). b) Semilogarithmic plot for the sample with thickness 5 μm.*

Cu-doping of ε-GaSe crystals up to 0.1 at.% leads to the formation of a new acceptor level, located at about 90 meV toward the top of the valence band. One can consider that by destroying the structural defects in the metal sublattice (inside the stratified package), Cu atoms fill up the acceptor levels with energies of 70 and 130 meV, and create a new acceptor level assembly with an average energy of 90 meV.

By increasing the concentration of Cu over 0.20 at.%, the level by 90 meV maintains, besides a new type of deep localized states, positionned at 210 meV against the top of the valence band, shows up. This is a deep acceptor level, produced by Cu impurity atoms, located between halogen plans of neighbouring packages.

The photoelectric and photoluminescent properties, whose efficiency is determined by the mechanisms of generation and recombination of non-equilibrium charge carriers, are strongly influenced by the nature and concentration of the shallow levels-capture levels. By analysing the thermally stimulated currents (TSC) and photoluminescence (PL), the characteristics of these levels are to be determined.

Fig. 2a presents the temperature dependence of TSC for two samples of undoped single crystalline GaSe, with different thicknesses. In the case of larger thickness (~225 μm), the TSC curve shows two bands with maximum at about 150 K and 250 K respectively, while in the case of small thicknesses (~5 μm), it contains a single one.

As was mentioned above, the structural defects are localized inside the stratified packages, as well as between halogen planes forming level assemblies with quite different energies. It is well established [7] that at the stratified package's surface the valence bonds are closed, which leads to a low density of surface states. Consequently, an increasing sample thickness must result in a band attenuation for the states localized at packages interfaces. By comparing curves 1 and 2 (Fig. 2a), one can conclude that the lower temperature band is produced by the capture states accumulated at interfaces between halogen planes, while the higher temperature band is due to the thermal ionization of the capture levels localized inside the stratified package.

In Fig. 2b the temperature dependence of TSC for the thinnest sample (5 μm) is presented. As can be seen, in temperature interval (~150-250) K, the experimental data are fitted by a straight line.

Since the kinetics of non-equilibrium charge carrier release from the capture and recombination levels are unknown, the temperature dependence of the current density in the initial stage can be expressed in the form [11]:

$$J = A\cdot\exp\left(-\frac{E_i}{kT}\right), \qquad (2)$$

where A is a constant independent on temperature, and $E_i$ denotes the average energy of the capture levels for non-equilibrium charge carriers. According to Eq. (2), by plotting logJ=f($10^3$/T) dependence in the beginning domain (100-150 K) of curve 1 (Fig. 2a), from its slope the average energy of the initial capture levels has been determined as 0.32 eV.

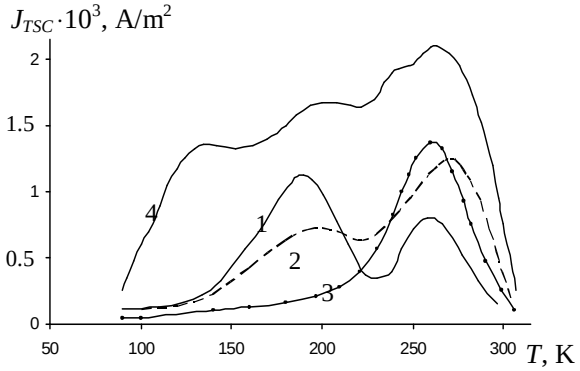


*Fig. 3. Temperature dependence of TSC for Cu-doped GaSe.1 – 0.01 % at.; 2 – 0.05 % at.; 3 – 0.10 % at.; 4 – 0.50 % at.*

The temperature dependence of the TSC, $J_{TSC}$=f(T), for Cu-doped GaSe samples with an impurity amount in the range (0.01-0.50) at.% is showed in Fig. 3. As evidenced in this figure, the $J_{TSC}$=f(T) curves show several bands with well outlined maxima. The temperature positions of TSC peaks from Fig. 3 are then introduced in the Bube formula [10]

$$E = T_m / A, \quad (3)$$

where E denotes the energy of the capture level, $T_m$ is the peak temperature, and A is a constant depending on the material's nature, in order to obtain the energy of respective level.

As determined energies of the capture levels for undoped and Cu-doped samples are listed in Table 2.

*Table 2. The energies of the capture levels for undoped and Cu-doped GaSe crystals.*

| Cu concentration, at.% | 0.00 | 0.01 | 0.05 | 0.10 | 0.20 | 0.50 |
|---|---|---|---|---|---|---|
| Energy of the capture levels, eV | 0.32 | 0.38 | 0.40 | - | 0.28 | 0.26 |
| | 0.51 | 0.52 | 0.54 | 0.52 | 0.49 | 0.40 |
| | | | | | | 0.47 |
| | | | | | | 0.53 |

By analysing these experimental results one can see that the capture level with (average) energy by 0.52 eV is present in overall concentration range. Moreover, if one admit that the area of a $J_{TSC}$=f(T) band is proportional with the concentration of the trapped charge carriers, then the nature of these levels could be related to the defects produced by halogen atoms. Besides, the level at 0.32 eV (pure GaSe) approaches the level at 0.52 eV for Cu concentrations of 0.01 and 0.05 at.%, and is seen to disappear for 0.10 at.%. Cu. One can conclude that the level by 0.32 eV in undoped GaSe is determined by the structural defects inside the stratified package (metal sublattice), and at increased Cu concentrations they are liquidated.

For further increased Cu concentrations, from 0.01 to 0.50 at.%, new capture levels, located at 0.26-0.28 eV, as well as 0.40 and 0.47 eV, turn up. By taking into account the XRD analyses, one can suppose that the last two levels are produced by Cu atoms present between halogen planes.

The spectral dependences of photoluminescence (PL) for GaSe(Cu) crystals at 78 K are presented in Fig. 4. Since the structure of the PL spectrum indicates the diagram of the recombination levels, that are also created by accidental crystal impurities, the analysis of undoped GaSe spectrum (Fig. 4, curve 1) is necessary. The spectrum is composed of two bands, one characterized by a structured contour located by 2.09-2.10 eV, while the other, a broad band, is of impurity nature and is positionned at ~2.03 eV. The first band is spitted in two components peaked at 2.092 and 2.097 eV.

It is relevant to point up that the splitting between the exciton line's components, due to both GaSe polymorphism and spin-orbit interaction of the excitons in the state n=1, is of the order of 2 meV [11] and, consequently, smaller than the previous one, equal to 5 meV. Besides, the energy of the optical phonons (LO mode), which are able to interact with the excitons, is equal to 25 meV [7], so that the component at 2.092 eV can't be associated with the phonon repetition of the line at 2.097 eV. From the above reasons one can admit that the line at 2.092 eV is due to the radiative annihilation of the excitons by ionizing centres in the ε-GaS crystal, and their binding energy is equal to ~5 meV.

Taking into consideration that holes are the majority charge carriers in both undoped and Cu-doped GaSe crystals (up to 0.0 at.%), the band by 2.03 eV can be assigned to the luminescent recombination of the non-equilibrium charge carriers from the conduction band with the holes located at the acceptor levels by 90 meV (toward the top of the valence band).

As is evidenced in Fig. 4, Cu impurity atoms do modify the structure of the radiative spectrum. The dynamics of the PL spectrum in the case of doped ε-GaSe crystals, in function of Cu concentration, is to be disscused bellow.

For a concentration of 0.05 at.%, the line of the radiative annihilation of the free excitons in the state n=1 (hν=2.098 eV) is outlined, and the line n=2 (the feature C in Fig. 4) practically overlaps the first one. Besides, the band B at 2.065 eV, registered for a Cu concentration of 0.01 at.%, merges the exciton line n=1, thus becoming an intense band with broadened base. Also, the impurity band, which is characteristic to undoped GaSe crystals, is evidenced (Fig. 4).

In this way, at low concentrations (~0.05 at.%), the peak of the impurity band displaces toward higher energies by ~30 mV as against respective band in undoped crystals, while the outer band has three components with maxima at 2.088, 2.098 and 2.113 eV. The maximum by 2.098 eV corresponds to the radiative annihilation of the free excitons in the state n=1, while the (weak) feature at 2.113 eV can be associated with the radiative annihilation of the excitons in the state n = 2. The last two features coincide (as energy position) with respective lines from the absorption spectra of ε-GaSe crystals at low temperatures. The particularity with energy 2.088 eV can be associated with the radiative annihilation of the bond excitons (binding energy equal to ~10 meV).

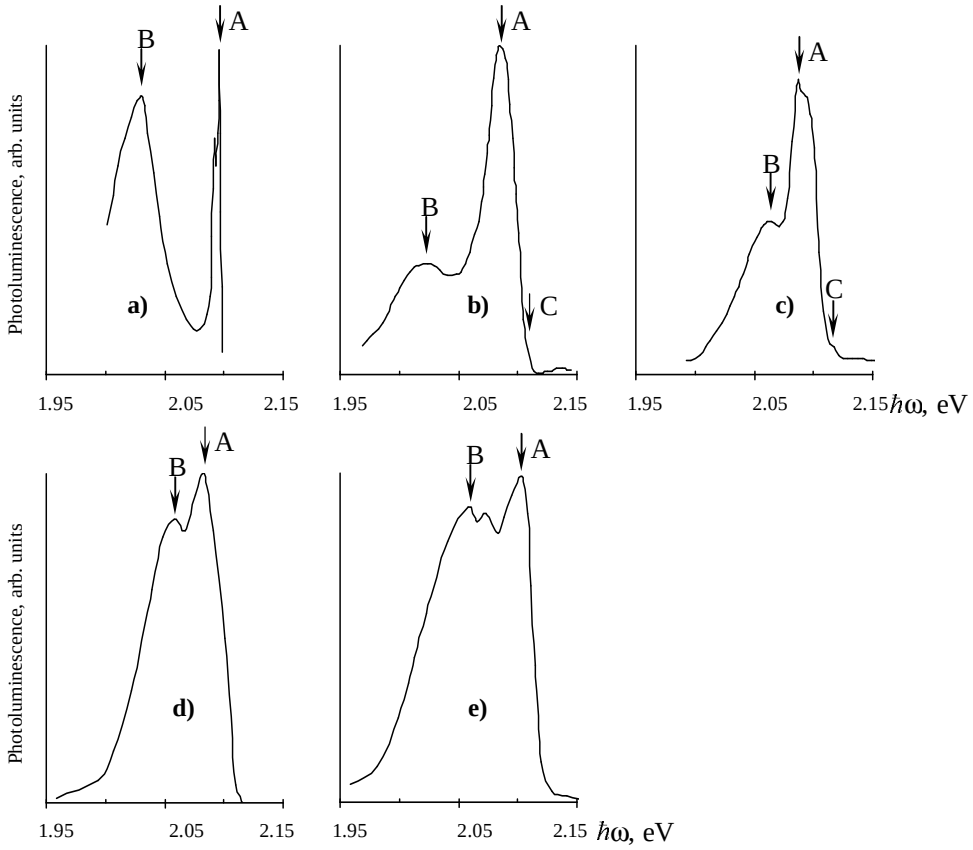


*Fig. 4. Spectral distribution of PL for undoped (a) and Cu-doped GaSe (b – 0.05 at.%; c – 0.10 at.%; d – 0.20 at.%; e – 0.50 at.%) at temperature 78 K.*

By comparing curves a and b from Fig. 4, one can state that Cu doping up to 0.05 at.% results in the elimination of structural defects and thus stimulates crystallizationn of ε-GaSe. In this way, GaSe crystals with 0.01 at.% Cu, grown by Bridgman method, are single phase and contain the ε polymorph.

An increased Cu concentration up to 0.20 at.% result in an enhanced impurity PL, as can be seen in curves *d* and *e*. Cu addition leads to the increase in the concentration of recombination levels localized by 60-65 meV against the top of the valence band.

Further increasing Cu concentration up to 0.50 at.%, the band of free excitons gradually extinguishes, but a new band with maximum at 2.073 eV shows up, which is displaced toward lower energies by ~26 meV as compared with the line of the free excitons. It is associated to the radiative annihilation of free excitons, accompanied by LO phonon emission, with an energy of ~26 meV [7].

The energy of the recombination levels contributing in the PL bands *a* and *b* coincides with the average thermal activation energy of respective level and can be determined by analysing the thermal quenching of respective bands.

In the case of the recombination bands the thermal quenching of PL is described by [13]

$$\ln\left(\frac{I_0}{I_T}-1\right)=f\left(T^{-1}\right), \tag{4}$$

where $I_T$ and $I_0$ denote the peak PL intensitiy at temperature T and its maximal value, respectively.

At increased tempeartures above 78 K, the intensity of the exciton band decreases, while the impurity band *b* initially increases and reaches the peak value at about 150 K, afterwards it quenches exponentially.

The dependences of the peak intensity for the bands *a* and *b* in function of the reciprocal temperature (eq. (4)) are presented in Fig. 5, for two Cu concentrations. For low Cu concentrations, the energy of thermal ionization of the band *a* is about 26 meV and is in good agreement with the binding energy of the electron-hole pair, as determined from the exciton absorption spectra [13]. The respective recombination level is localized at ~105 meV above the valence band.

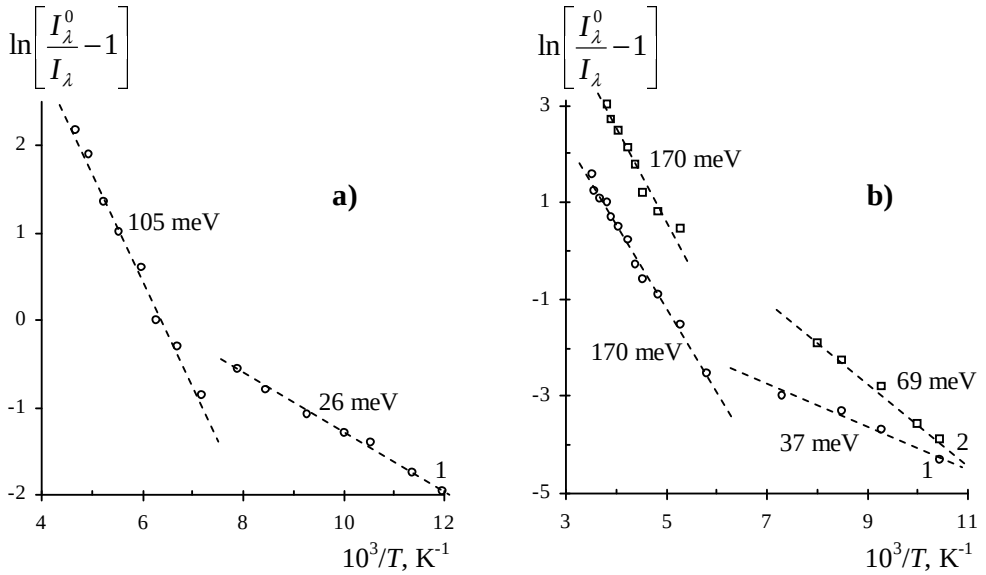


*Fig. 5. Temperature dependence of the peak PL intensity for bands A (1) and B (2) in GaSe(Cu) crystals. Cu, % at.: 0.05 (a) şi 0.10 (b). Indicated are the values of the activation energy.*

Increasing Cu doping of GaSe up to 0.50 at.%, the exciton band probably merges the impurity band and forms a mixt band. The average energy of the respective impurity level is equal to only ~11 meV toward the top of the valence band. For this reason the nature of quenching for the band *a* at increasing temperature coincides with PL quenching of the free excitons in undoped or low-doped (x≤0.05 at.%) GaSe crystals. The average energy of the recombination level created by Cu atoms (0.50 at.) is around 0.17 eV.

## 4. Conclusions

Cu-doping of GaSe crystals at low concentrations, up to 0.10 at.%, doesn't change the parameters *a* and *c* of the hexagonal lattice, equal to 3.752 and 15.952 Å, respectively. Increasing Cu concentration up to 0.50 at.% results in an increase of the *a* value by ~0.015 Å, while those of *c* decreases by ~0.006 Å. Consequently, Cu atoms initially fill up Ga vacancies, afterwards localize between halogen planes of consecutive stratified packages.

The electrical conductivity of GaSe(Cu) crystals depends on both temperature and Cu concentration. In temperature range (78-330) K, it exponentially varies with temperature and thermal activation energy of the acceptor levels. The accidental impurities produce two acceptor levels in the GaSe forbidden band, with a thermal ionization energy of about 70 and 130 meV, respectively. The copper atoms, at low concentrations, under 0.10 at.%, create a new acceptor level with an average energy of 90 meV. For increased Cu concentrations, up to 0.50 at.%, a second, deep level turns up, with a thermal activation energy of 210 meV. It is produced by Cu atoms localized between stratified packages.

The generation-recombination processes of the non-equilibrium charge carriers are determined by the density of the surface (capture) states in GaSe(Cu) crystals. These are localized either inside the stratified packages or at their surface.

From the analyze of TSC the energies of the capture levels for undoped and Cu-doped up to 0.50 at.% have ben determined. At increased Cu concentration up to 0.05 at.%, the average energy of the surface levels increases; for higher concentrations (0.20 at.% and 0.50 %at.), a new energy band diagram is effective.

GaSe and GaSe(Cu) crystals are red luminescent materials. The PL spectrum contains two bands, excitonic and impurity, respectively. The impurity PL band is produced by radiative recombination of the charge carriers from the conduction band and holes localized at the recombination level with an energy of 90 meV (against the top of the valence band).

The complex structure of the outer PL line is due to the radiative annihilation of free excitons in the state n=1 (the peak at 2.098 eV) and n=2 (the peak at 2.113 eV), as well as of bond excitons (by ionizing centres) with a binding energy of ~10 meV.

By analyzing the temperature dependence of PL intensity, it was found the average ionization energy of free excitons: ~26 meV. Besides, Cu atoms create a recombination level with an energy of ~105 meV.

For higher Cu concentrations of 0.50 at.%, a recombination level with an energy of 11 meV is formed. The corresponding PL band overlaps the exciton band,

turning into a mixted band. At the same time a recombination level localized at 170 meV (against the top of the valence band) turns up.

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