

OPTICAL PROPERTIES OF CRYSTALS GaSe AND InSe DOPED WITH Cu

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The anisotropy of absorption spectra in the range of the margin of fundamental band of the crystals GaSe and InSe doped with Cu in the percentage quantities up to 0.5 % at. from which the implementation mechanism of the impurity atoms of Cu in the hexagonal crystal grating of the GaSe and InSe crystals and the localization energy of the impurity levels in the forbidden energetic band is studied.

Introduction

The compounds GaSe and β -InSe are crystallized in the stratified structure (symmetric spatial group D_{6h}). The crystalline grating of the compounds belonging to this structural type is formed by four stratified packages of X-M-M-X type. Each atom of Ga (In) belongs to the tetrahedral neighbor of the Se atoms and one atom of Ga (In) [1]. In the internal part of stratified package the ionic-covalent preponderant bonds are active, but the bonds between package are realized by polarization forces [2]. The presence of weak bonds between layers leads to the anisotropy of electronic states.

The impurity atoms in the stratified structures of $A^{III}B^{VI}$ type are localized in the space between stratified packages, modifying so the character of chemical bonds between layers. But the presence of impurity atoms in the space between the planes of halogen atoms (Se) leads also to the modification of energetic spectrum especially on the axis direction with the high symmetry C_6 .

The presence of vibration modes at low frequencies is among characteristic peculiarities of weak interaction, which correspond to the removing of atomic layers one with respect to another. The atoms from the interior of the stratified package at vibration do not remove one with respect to another. The presence of impurity atoms of Cu in the crystals GaSe and InSe with the modification of vibration spectrum of the crystalline grating leads to the formation of new energetic states in the forbidden energetic band.

Application in practice of GaSe and InSe crystals is determined by solution of the preparation problem of crystals with the electrical conductivity and energetic level diagram that will assure this.

The small mechanical deformations of the monocrystals lead to the increasing of the concentration of surface states. The energy of capture levels which are localized at $\sim 0.18 \div 0.05$ eV from the top of valence band modifies the character of absorption and photoconductivity in the range of absorption band margin.

Method of experiment

The crystals of GaSe and InSe were grown by Bridgman method from the elementary components Ga, In and Se which are pure spectral. The doping of the crystals GaSe and InSe with the Cu atoms in the concentrations from 0.01 up to 0.5% at was effected in the process of synthesis of the respective compounds. The samples of researches were obtained by

cleaving from the massive crystals and had the thickness in the limits from 0.1 up to 15 mm and the area $250 \div 350 \text{ mm}^2$. The cleaving is made in the direction perpendicular to the axis C_6 . As the result of cleaving the plan parallel surfaces at the atomic level are obtained.

In order to obtain the information about the absorption of linear light polarization on the direction $\vec{E} \parallel \vec{C}$, the light beam falls on the surface of crystal under the angle 45° .

The absorption spectra and reflection ones at the temperature of 78K and 293 K were recorded on the spectrophotometer installation with the monochromator MDR-2 with the energetic resolution of about 0.5 meV.

Experimental results and their explanation

The spectral dependence of absorption coefficient in the range of fundamental band margin of the crystals ε -GaSe special non-doped is presented in fig.1. The margin of absorption band is formed by excitonic absorption both in the polarization $\vec{E} \parallel \vec{C}$ (curve 1) and $\vec{E} \perp \vec{C}$ (curve 2). The states $n=1$ and $n=2$ are underlined clearly in both polarizations at the temperature of 78 K. The maxima of absorption excitonic lines $n=1$ and $n=2$ are localized at 2.105 and 2.106 eV.

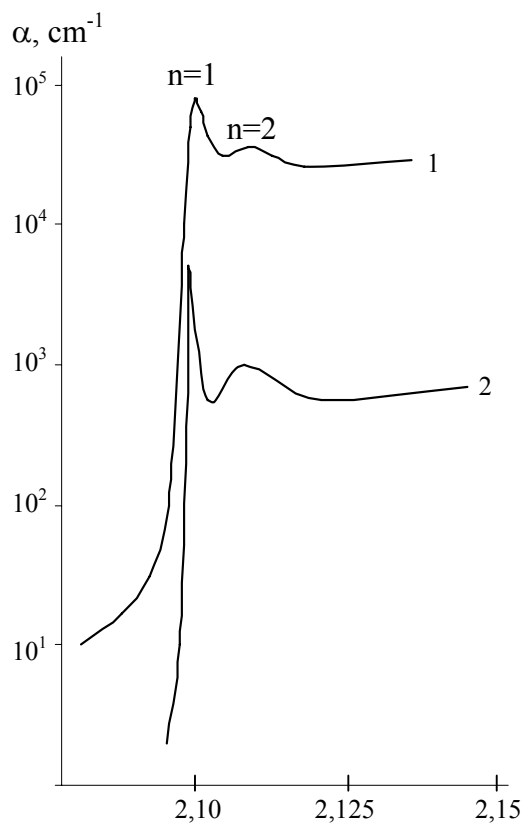


Fig.1. The absorption spectra of GaSe crystals in the polarization $\vec{E} \parallel \vec{C}$ (1) and $\vec{E} \perp \vec{C}$ (2), $T=78 \text{ K}$.

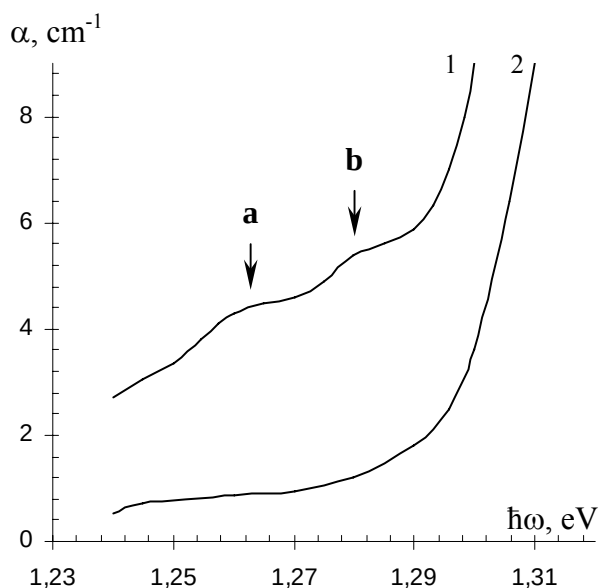


Fig.2. The margin of the absorption band of InSe in the polarization $\vec{E} \parallel \vec{C}$ (1) and $\vec{E} \perp \vec{C}$ (2), $T=78 \text{ K}$.

The ratio between the absorption coefficient in the maximum of excitonic line $n=1$ for the polarization $\overline{E} \parallel \overline{C}$ and respectively $\overline{E} \perp \overline{C}$ is equal to 17 which is the value that correlates better with the coefficient of anisotropy calculated from the effective mass equal to 16 [3]. This ratio for the line $n=2$ is greater by 1.7 times than for the line $n=1$. Such an increasing of anisotropy of absorption coefficient in the range of the line $n=2$ is possible because in this field the absorption for the lines $n \geq 2$ is add and also it is necessary to take into consideration that the optical transitions in the polarization $\overline{E} \parallel \overline{C}$ are permitted, but for $\overline{E} \perp \overline{C}$ are forbidden [2]. Also, the margin of absorption band of the crystals InSe special non doped is described by an exponential decreasing of the absorption coefficient with the energy of incident photons on the sample. The background absorption in the polarization $\overline{E} \perp \overline{C}$ is $\sim 0.75 \text{ cm}^{-1}$. In the polarization $\overline{E} \parallel \overline{C}$ at the energies $\hbar\omega < 1.29 \text{ eV}$, the absorption coefficient α decreases at $\sim 5.5 \text{ cm}^{-1}$ up to 2.5 cm^{-1} at the energy $\hbar\omega < 1.24 \text{ eV}$. Two maxima **a** and **b** (fig.2) are distinguished in this spectral domain respectively at 1.278 eV and 1.264 eV and the presence of these peculiarities is probably determined by the surface states, their concentration is considerable in the samples of GaSe and InSe which are studied in this polarization. The energetic levels of the surface states are localized at $\sim 42 \text{ meV}$ and 56 meV from the minimum of conduction band of the crystals InSe.

The absorption of light in the range $\hbar\omega < 1.26 \text{ eV}$ in the polarization $\overline{E} \parallel \overline{C}$ (in the crystals InSe (see fig.2, curve 1) can be interpreted as the process determined by indirect optical transitions, permitted by this polarization).

The doping of the crystals GaSe with the impurity atoms of Cu in the quantities up to 0.04% at. leads to the liquidation of the proper defects in the sub grating of metal which is the process that is manifested by the increasing of the intensity of excitonic line $n=1$ by 1.2 times, but for the line $n=2$ by ~ 3 times in the absorption spectra (fig.3) and 1.6 times for the line $n=1$ and 2.1 times for the line $n=2$ in the luminescence spectra. The intensity of impurity band in the absorption spectra is increased rapidly at the continuing increasing of the concentration of impurity atoms of Cu from 0.05 up to 0.1% at.

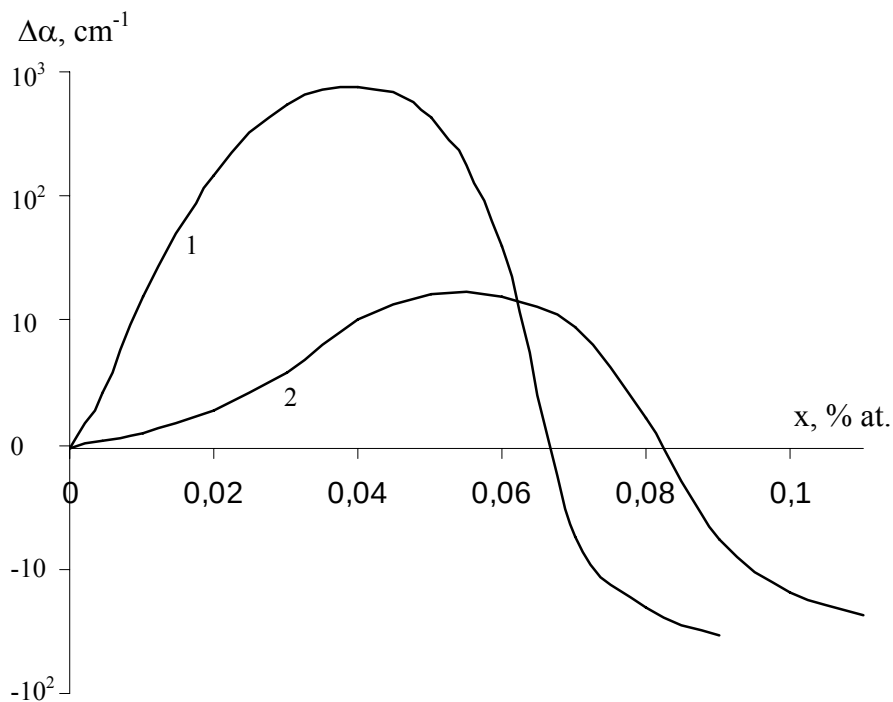


Fig.3. The variation of absorption coefficient of percentage concentration of copper in GaSe (1) and InSe (2) in the maximum of excitonic line $n=1$.

The impurity absorption reaches the value of about 12 cm^{-1} at the concentration of Cu of the order 0.08% at. Although the mechanism of electrical conductivity and the type of majority charge carriers in the process of doping of the crystals of ϵ -GaSe is not changed we can consider that the impurity atoms of Cu create in the forbidden band of the gallium monoselenium the acceptor levels. So, the impurity level that forms the threshold A^* (fig.4b) is localized at $\sim 50 \text{ meV}$ from the top of the valence band.

The impurity copper of InSe as in the GaSe leads to the liquidation of the defects in the sub grating of the metal for small concentrations ($x < 0.06 \text{ \% at.}$). As we can see from fig.3 (curve 2) the absorption coefficient in the center of excitonic line slowly increases with the increasing of doping concentration, although the variation of absorption coefficient with the concentration is distinguished more weakly than in the GaSe (curve 1).

The light absorption spectra of the InSe crystals special non doped (curve 1) and doped with Cu up to 0.06% at. (curve 2) are presented in fig.4a. The presence of impurity atoms of Cu leads to the decreasing of absorption coefficient in the field of excitonic line $n=1$, modifies the character of dependence $\alpha(\hbar\omega)$ on the band of small energies of the excitonic line and forms a supplemental band of absorption in the range $1.26 \div 1.30 \text{ eV}$. The absorption coefficient in the impurity band of the crystals InSe (Cu) is of the same order of value ($18 \div 20 \text{ cm}^{-1}$) as for the crystals GaSe for which the atoms of Cu consist $\sim 0.08 \text{ \% at.}$ (fig.4b).

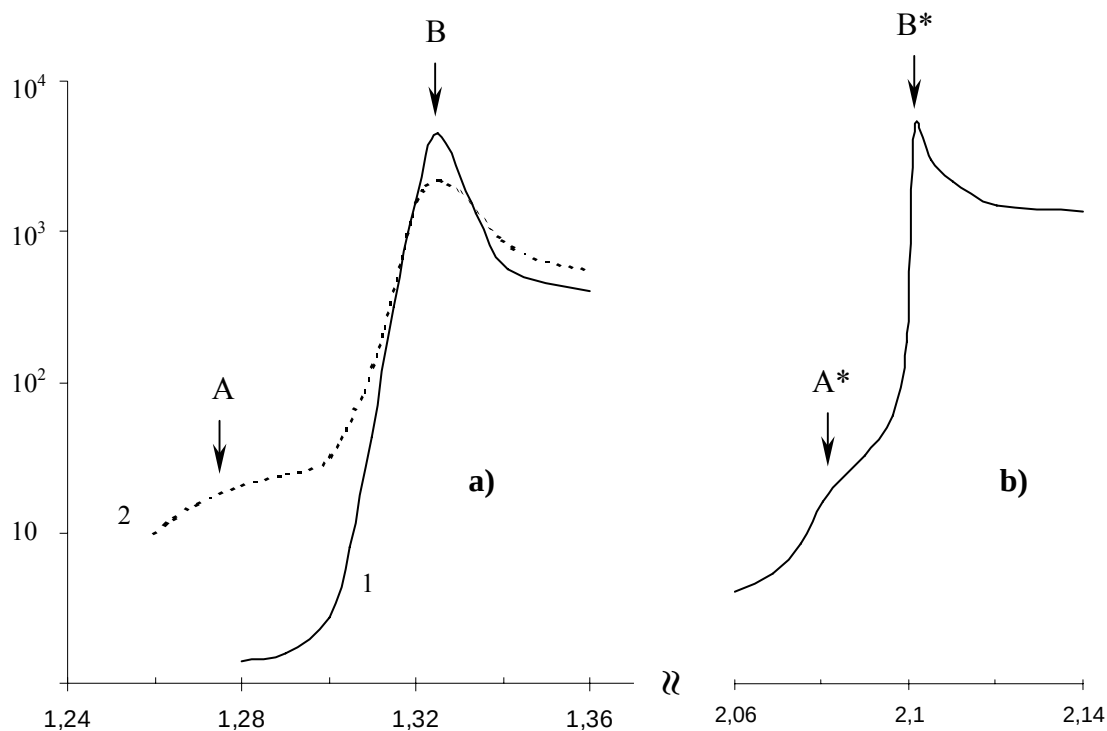


Fig.4. The spectral dependencies of the absorption coefficient of the photon energy in the range of absorption band margin for the crystals InSe (a) and GaSe (b) at the temperature $T=78\text{K}$.

The copper in the quantities greater than 0.05% at. both in the crystals GaSe and InSe screens the hole-electron bonds leading so to the liquidation of the line $n=2$. But a weak increasing of the absorption coefficient of the light at the energies from the fundamental

absorption band is determined by band – band optical transitions and the impurity levels of Cu localized at ~ 58 meV from the top of valence band in the crystals ϵ -GaSe.

The impurity absorption band in the crystals InSe (Cu) does not differ from those of GaSe by the form. The absorption coefficient in the field of energies 1.25 eV is increased by ~ 1.3 times with the increasing of the concentrations of Cu atoms from 0.05% at. up to 0.1% at. Though, for the quantities of Cu atoms included in the limits from 0.01% up to 0.1% at. the type of major charge carriers is not changed, the character of absorption of the light in the range of the margin of fundamental band allows to suppose that in the same time with the creation of the supplemental donor levels the atoms of Cu create also the acceptor levels in the forbidden band of the compound InSe localized at ~ 0.07 eV from the top of the valence band.

Conclusions

The value of the absorption coefficient in the center of excitonic line at the temperature of 78K and the influence of incident light polarization on the dependence $\alpha(\hbar\omega)$ in the range of fundamental band absorption band margin was established from the analysis of absorption spectra of the crystals ϵ -GaSe special non doped with Cu. The increasing of absorption coefficient in the range $\hbar\omega > 2.1$ eV in the polarization $\overline{E} \parallel \overline{C}$ with respect to $\overline{E} \perp \overline{C}$ polarization is influenced by the increasing of the probability of respective optical transitions.

The impurity atoms of Cu at small concentrations (Cu < 0.04% at.) in the GaSe and < 0.06% at. in the InSe liquidate the defects in the sub grating of the metal, and so that the intensity of excitonic absorption is increased. At bigger concentrations, both in the GaSe and InSe the impurity atoms of Cu screen the hole-electron interaction contributing so to the decreasing of absorption coefficient in the excitonic line. The process of screening of the excitonic bonds by impurity atoms of Cu both in the GaSe and InSe has the tendency to saturation.

The dissolved copper in the GaSe crystals creates the acceptor levels, the average energy of which is ~ 58 meV, but in the crystals InSe the acceptor levels are formed with the donor levels, average energy of which is about 70 meV.

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