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Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report results from a contract tasking Ioffe Institute as follows: The main aim of the project is to carry out basic research on optoelectronic properties of CdGeAs2 and (Zn,Cd,Hg)(Ga,Al,In)2(S,Se,Te)4 materials and to supply samples of these materials to the US AFRL/ML. This research include measurements of X-ray diffraction as well as spectra of polarized first- and second-order Raman scattering by lattice vibrations, photoconductivity, and photoluminescence measurements in a temperature range 77-300K mainly on the crystallographically oriented CdGeAs2, CdGa2S4 and HgGa2S4 single crystals - the most important representatives of these compounds. Results of these joint investigations will allow the research community to gain a new understanding of the crystalline structure and spectroscopic characteristics of the lattice perfection of these anisotropic group II-IV-V2 and II-III2-VI4 semiconductor compounds with ordered stochiometric vacancy. These materials will find uses as harmonic generators and tunable lasers in the infrared region of the spectrum.

15. SUBJECT TERMS
EOARD, Physics, Solid State Physics

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ISTC 2008p

Final
Project Technical Report
of ISTC 2008p

Study of Optoelectronic Properties of Anisotropic Semiconductor Compounds With Ordered Stochiometric Vacancy

(From 1 September 2001 to 31 August 2004 for 36 months)

Rud' Yurii Vasil'evich

(Project Manager)

Ioffe Physico-Technical Institute
RAS

August 2004

This work was supported financially by EOARD and performed under the contract to the International Science and Technology Center (ISTC), Moscow.

Study of Optoelectronic Properties of Anisotropic Semiconductor Compounds With Ordered Stochiometric Vacancy

(From 1 September 2001 to 31 August 2004 for 36 months)

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The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy

Keywords: anisotropic semiconductors, inelastic light scattering spectra, photoluminescence, photoconductivity, natural palechroism.

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I. PROJECT ACTIVITIES REPORT

1. Objectives of the Project

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy

2. Scope of Work and Technical Approach

We have grown and selected by preliminary optical and electrical measurements the high quality $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs2 crystals and in a temperature range from 77 to 300 K on the $CdGa_2S_4$ and Hg Ga_2S_4 single crystals.

We have performed also measurements of polarized luminescence spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector E_{rad} and tetragonal axis of the crystal c.

We have performed measurements of the temperature dependent polarized photoconductivity spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals with n-type conductivity.

We have performed also investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ in the temperature range 77-300K.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of $CdGeAs_2$ grown by low temperature crystallization

3. Summary of Project Technical Report (about 5 to 10 pages)

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs2 crystals and in a temperature range from 77 to 300 K on the $CdGa_2S_4$ and Hg Ga_2S_4 single crystals. All samples were oriented by x-ray measurements. The Raman scattering spectra have been measured for $CdGeAs_2$ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature Eg = 0.57 eV for $CdGeAs_2$) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. Excitation of the spectra for $CdGa_2S_4$ samples were performed by λ = 514.5 нм of argon laser and λ = 632.8 nm of He-Ne laser. The polarization vectors of the incident and scattered light were directed along [110] ($\perp$) and [112] ($\|$) for the parallel ($e_i \| e_s$) ($\perp\perp$) or crossed ($e_i \perp e_s$) ($\perp\|$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have shown that photoluminescence for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at E_{rad} II *c,* i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

We have performed measurements of polarized luminescence spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector E_{rad} and tetragonal axis of the crystal c. The same type of dependencies was observed for the coefficients of optical absorption for $CdGa_2S_4$ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have performed measurements of the temperature dependent polarized photoconductivity spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals with n-type conductivity The spectral dependencies of native photopleochroism coefficient P_N were determined when the temperature is reduced below 300 K.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ in the temperature range 77-300K.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of $CdGeAs_2$ grown by low temperature crystallization

4. Presentation of project results
   - List of published reports
     1. Annual Report, Project # 2008p, For 1 year (1 September 2001 – 31 August 2002).
     2. Annual Report, Project # 2008p, For 2 year (1 September 2002 – 31 August 2003).
     3. Final Report, Project # 2008p, For 3 year (1 September 2001 – 31 August 2004).

SUMMARY OF FINAL REPORT

Project # 2008p

1. Title of the Project / Final Report

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy

For 3 years

2. Contracting Institute

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5. Commencement Date, Duration

1 September 2001, 3 years

6. Objectives of the Project

Promoting integration of scientists of CIS states into the international scientific community;

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy

7. Scope of Work and Technical Approach

We have grown and selected by preliminary optical and electrical measurements the high quality $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs2 crystals and in a temperature range from 77 to 300 K on the $CdGa_2S_4$ and Hg Ga_2S_4 single crystals. The Raman scattering spectra have been measured for $CdGeAs_2$ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature Eg = 0.57 eV for $CdGeAs_2$) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the ***c***-axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] ($\perp$) and [112] ($\|$) for the parallel ($\boldsymbol{e_i} \parallel \boldsymbol{e_s}$) ($\perp\perp$) or crossed ($\boldsymbol{e_i} \perp \boldsymbol{e_s}$) ($\perp\|$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have performed measurements of polarized luminescence spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector $\boldsymbol{E_{rad}}$ and tetragonal axis of the crystal c. The same type of dependencies was observed for the coefficients of optical absorption for $CdGa_2S_4$ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation τ =19% and 14% for $CdGa_2S_4$ and $HgGa_2S_4$ crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor $II-III_2-VI_4$ compounds with ordered stoichiometric vacancy.

We have shown that photoluminescence for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\boldsymbol{E_{rad}}$ II ***c***, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

To solve the problem of detection low-level signals we have installed new photomultiplier tube with the InP/InGaAs photocathode (for spectral range 300 - 1700 nm), together with the new cooling system required for the tube (up to T = - 200°C) as well as an electronics for two-channel single photon counting system, developed and fabricated by us.

8a. Technical Progress

We have grown and selected by preliminary optical and electrical measurements the high quality $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs2 crystals and in a temperature range from 77 to 300 K on the $CdGa_2S_4$ and Hg Ga_2S_4 single crystals. The Raman scattering spectra have been measured for $CdGeAs_2$ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature Eg = 0.57 eV for $CdGeAs_2$) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the ***c***-axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (⊥) and [112] (||) for the parallel $(\boldsymbol{e_i} \parallel \boldsymbol{e_s})$ (⊥⊥) or crossed $(\boldsymbol{e_i} \perp \boldsymbol{e_s})$ (⊥||) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have performed measurements of polarized luminescence spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector $\boldsymbol{E}_{rad}$ and tetragonal axis of the crystal c as well as we. The same type of dependencies was observed for the coefficients of optical absorption for $CdGa_2S_4$ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

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We have shown that photoluminescence for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\boldsymbol{E}_{rad}$ II ***c***, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

Polarization dependent measurements of the photoconductivity spectra has been performed on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals, for the first time. These measurements were conducted with shining along the normal to (100) and (001) faces of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals, that allowed to determine the coefficient of the photopleochroism. Obtained results allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The photoconductivity spectra I^{II} and $I^{\perp}$ have maximum at $\hbar\omega^m$ = 2.23 eV for $HgGa_2S_4$ and $\hbar\omega^m$ =2.76 for $CdGa_2S_4$ which are essentially less then the band gap of these semiconductors. Therefore, the observed spectra can be attributed to the photoactive absorption with participation of lattice defects, located at the activation energies $E_D \approx 0.6$ eV (for $HgGa_2S_4$) and ≈0.8 eV (for $CdGa_2S_4$). The photoconductive bands in these crystals can be characterized also by full width at the half maximum $\delta \approx 0.38$ eV (for $CdGa_2S_4$) and $\delta \approx 0.4$ eV (for $HgGa_2S_4$). Large values of δ< as well as the bands asymmetry with long-wavelength tailing indicate on nonelementarily and, therefore, on the complex energetic spectra of the lattice defects of the crystals under the study. We show that in this group of the crystals with defect chalcopyrite structure exist phenomenon of native photopleochroism and azimutal dependencies of photoconductivity in agreement with the crystalline symmetry of these compounds.

Our measurements of the photoconductivity spectra of $CdGa_2S_4$ and $HgGa_2S_4$ compounds oriented in the (100) plane show that native photopleochroism coefficient in these crystals has additional sign in the range of the maximum of the photoconductivity and the maximum value of $P_N \approx 20\%$ for $HgGa_2S_4$ crystals and $P_N \approx 10\%$ for $CdGa_2S_4$.

It is important to note that we observe also strict decreases of the amplitude of P_N and an inversion of its sign in the range of the strict cut-off of the photoconductivity. The reason of such inversion can be connected as with the increase of the surface recombination velocity as well as with changing the selections rules with the changing of the incident photon energy in the range of strong interband absorption. For final selection between these possibilities it is need further study of interconnections of the polarization photoconductivity measurements and technological aspects of the growth processes of these ternary compounds.

Our study of the azimuthal dependencies of photoconductivity i_φ of the $CdGa_2S_4$ and $HgGa_2S_4$ single crystals allow to establish that the positive native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane. The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axisies [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the $HgGa_2S_4$ $CdGa_2S_4$ single crystals.

Our experimental search was also devoted toward study of electrical properties and optical absorption of the $HgGa_2S_4$ single crystals, study of contact properties of these crystals with some metals with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion.

We established that mechanical contact of pure metal layers of (In , Ni, Au, Ag) with the cleaved surface of the $HgGa_2S_4$ single crystals and further with chemically polished surface of electrically homogeneous $HgGa_2S_4$ give rectifying characteristics. Rectification determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 20$ V, reaches the values $K \approx 200$, that is the record value obtained up to now for the the n-$HgGa_2S_4$ single crystals. We find that direct and reverse current-voltage characteristics in the case of illumination shifts relatively darks in the direction of increasing direct and reverse currents. We show the real way of further improvement of the surface-barrier structure characteristics on the base of $HgGa_2S_4$ with solving size and crystal perfection problems.

We find that photovoltage of the free motion in the surface-barrier structures on the base of *n*-$HgGa_2S_4$ single crystals is dominated under conditions of illumination of the structures from the side of barrier contacts. In this case the sign of the photovoltage always corresponds to the direction of the rectification in the structures and independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. These established facts on the structures obtained for the first time can be used as a base to connect rectification and photovoltaic effect with energy barrier at the contact of semiconductor with metal studied. Maximum value of the voltage photosensitivity achieved for the surface-barrier In-*n*-$HgGa_2S_4$ structures is $2 \cdot 10^3$ V/W at T=300 K.

We have measured spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier In-*n*-$HgGa_2S_4$ structures, It is found that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 0.8-3.8 eV. It is shown that the spectral parameter η at $\hbar\omega < 2.2$ eV strongly changes from structure to structure and may be used for the diagnostic of the material perfection. Under condition of illumination of from the substrate side at the photon energy range $\hbar\omega > 2.25$ eV in the η spectra appears sharp cut-off of the photosensitivity. This cut-off may indicate on increase of the optical absorption in the $HgGa_2S_4$ plate. It can be supposed that due to small length of a diffusion shift of the nonequilibrium charge carriers the concentration of the photogenerated carriers, which achieve the active area, with increasing the photon energy $\hbar\omega > 2.3$ eV begin to fall and, therefore, the quantum efficiency of photoconversion $\eta \rightarrow 0$. It is important to note that the cut-off spectral range of η under the condition of illumination of Shottky barriers from the substrate side is in an agreement with a beginning of sharp increase of the optical absorption coefficient α exactly at photon energy $\hbar\omega \approx 2.3$ eV. This value can be used as a preliminary estimation of the absorption edge E_G of this little known semiconductor. We show that the $\eta(\hbar\omega)$ spectra in the range of $\hbar\omega < 2.25$ eV are practically independent on illumination geometry of the surface-barrier structures that is due to the bulk nature of the charge carrier photogeneration in the $HgGa_2S_4$ crystals. The longwavelength edge of the photosensitivity of the surface-barrier structures in the range of $\hbar\omega < 2.2$ eV follows to the Fowler law and, therefore, is rectified in the coordinates $(\eta\hbar\omega)^{1/2}$ - $\hbar\omega$. From the extrapolation of the direct linear parts $\eta^{1/2} \rightarrow 0$ we obtain first estimation of the energy height of In-n-$HgGa_2S_4$ and Ag-n-$HgGa_2S_4$ structures $\varphi_D \approx 1.1$eV at T=300 K. We note, that for some barriers in the dependencies $(\eta\hbar\omega)^{1/2} - \hbar\omega$ revealed several direct linear parts and , correspondingly, several cut-off energies. This situation may reflect complicated nature of the energy band structure of the $HgGa_2S_4$ crystals.

The increase of the photoconductivity in the best surface-barrier structures at $\hbar\omega > 2.3$ eV under the condition of illumination of the structures from the barriers side can be related with the fundamental absorption in the $HgGa_2S_4$ crystals, that is not possible to detect by traditional absorption spectroscopy techniques on sush a small size samples. We find that the increase of the photoconductivity in the best surface-barrier structures at the photon energy range of 2.3-2.8 eV follows the $(\eta\hbar\omega)^{1/2} - \hbar\omega$ law. Extrapolation of this dependense $(\eta\hbar\omega)^{1/2} \rightarrow 0$ allows to estimate the energy of indirect interband optical transitions $E_G^{in} \approx 2.27$ eV for *n*-$HgGa_2S_4$ at T=300 K. More sharp increase of the photoconductivity in the surface-barrier structures at the photon energy range of $\hbar\omega > 2.8$ eV follows to the characteristic for the direct optical transitions quadratic $(\eta\hbar\omega)^2 - \hbar\omega$ law. Extrapolation of this dependense $(\eta\hbar\omega)^2 \rightarrow 0$ allows to estimate the energy of direct interband optical transitions $E_G^{dir} \approx 2.86$ eV for n-$HgGa_2S_4$ at T=300 K. So, in this work for the first time, the problem of creation of the photosensitive structure on the base of n-$HgGa_2S_4$ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of n-$HgGa_2S_4$ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

We have performed investigations of the contact phenomena of photosensitive surface-barrier structures on the base of the $CdGa_2S_4$ single crystals with n-type conductivity We study the stationary and light current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion in dependence of the geometry of excitation with a unpolarized irradiation.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ in the temperature range 77-300K

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of $CdGeAs_2$ grown by low temperature crystallization.

9a. Plan for Following Year(s) (in the case the original work plan has been significantly changed)

10a. References of papers and reports published.

1. Annual Report, Project # 2008p, For 1 year (1 September 2001 – 31 August 2002).
2. Annual Report, Project # 2008p, For 2 year (1 September 2002 – 31 August 2003).
3. Final Report, Project # 2008p, For 3 year (1 September 2001 – 31 August 2004).

FINAL TECHNICAL REPORT

1. Title of the Project / Number of Final Report

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy

For 3 years

2. Contracting Institute

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3. Participating Institutes

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E--mail: bairamov@mail.ioffe.ru

5. Commencement Date, Duration

1 September 2001, for 3 years

6a. Brief description of the work plan: objective, expected results, technical approach

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy.

According to the Work Plan we have conducted**:**

Task 1
Standard x-ray diffraction measurements on the CdGeAs2, CdGa2S4 and HgGa2S4 crystals, for determination homogeneity and the crystallographic orientation of the samples.

Task 2
Measurements of polarized Raman scattering by phonons (at room temperature on the CdGeAs2 and in a temperature range from 77 to 300 K on the CdGa2S4 and HgGa2S4)

for accomplishment the Raman selection rules, for determination symmetry and spectroscopic parameters (frequencies, linewidth, intensities) of phonon lines,

Task 3
Polarized photoluminescence measurements (on CdGa2S4 and HgGa2S4) in a temperature range from 77 to 300 K.

Task 4
Polarized photoconductivity measurements (on CdGa2S4 and HgGa2S4) in a temperature range from 77 to 300 K.

Task 5
Polarized photosensitivity measurements (in a temperature range from 77 to 300 K) of surface barriers on In/CdGa2S4 and In/HgGa2S4.

Task 6
Temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements for determination mobility, concentration, activation energy of impurity level, and degree of compensation,

We have grown and selected by preliminary optical and electrical measurements the high quality $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs2 crystals and in a temperature range from 77 to 300 K on the $CdGa_2S_4$ and Hg Ga_2S_4 single crystals. The Raman scattering spectra have been measured for $CdGeAs_2$ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature Eg = 0.57 eV for $CdGeAs_2$) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the ***c***-axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (⊥) and [112] (||) for the parallel ($\boldsymbol{e_i} \parallel \boldsymbol{e_s}$) (⊥⊥) or crossed ($\boldsymbol{e_i} \perp \boldsymbol{e_s}$) (⊥||) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

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which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III$_2$-VI$_4$ compounds with ordered stoichiometric vacancy.

We have shown that photoluminescence for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\boldsymbol{E}_{rad}$ II ***c***, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

To solve the problem of detection low-level signals we have installed new photomultiplier tube with the InP/InGaAs photocathode (for spectral range 300 - 1700 nm), together with the new cooling system required for the tube (up to T = - 200°C) as well as an electronics for two-channel single photon counting system, developed and fabricated by us.

7a. Technical progress during the 1 year of reference

- compliance with tasks and milestones as described in the work plan

  All works are on schedule.

- achievements of the first year

Multicomponent anisotropic semiconductor II-IV-V$_2$ ($CdGeAs_2$) and II-III$_2$-VI$_4$ (Zn,Cd,Hg)(Ga,Al,In)$_2$ (S,Se,Te)$_4$ compounds with ordered stoichiometric vacancy known as chalcopyrites and defect chalcopyrites or thiogallates, respectively. The most important representatives of these compounds are $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$.

The chalcopyrite structure $CdGeAs_2$ crystals have the symmetry with space group $D_{2d}^{12}(I\bar{4}2d)$ and the body centered tetragonal unit cell.

Single crystals of chalcopyrite type $CdGeAs_2$ have been grown by the improved low temperature directional crystallization technique from non-stoichiometric melts. This technique allows to grow crystals at the temperature range significantly below the temperature of chalcopyrite → sphalerite phase transition (~ 870 K). This situation may allow to perform crystallization of $CdGeAs_2$ compounds in the range of stability of the chalcopyrite structure, when the formation of the equilibrium sphalerite structure is forbidden. Therefore drastically decrease of deviation from the stoichiometry by minimizing concentration of Cd_{Ge} and Ge_{Cd} antisite defects should be achieved.

The defect chalcopyrites or thiogallates structure $CdGa_2S_4$ and $HgGa_2S_4$ crystals have the symmetry with space group $S_4^2(I\bar{4})$ with two formula units in the cell. There are no data in literature on the phase transition in the $CdGa_2S_4$ and $HgGa_2S_4$ crystals. Hence the question of formation of the antisite defects in these crystals remains open.

Therefore before starting the time-consuming x-ray measurements for crystallographic orientation of the $CdGeAs_2$, $CdGa_2S_4$ and $HgGa_2S_4$ samples, we have made preliminary mapping measurements, by using all of our planned experimental techniques to select high optical quality and homogeneity areas of the grown crystals. We performed such measurements of the optical absorption, photoelectric, photoluminescence and Raman scattering spectra, which allowed selecting high quality samples for our further measurements.

Our X-ray diffraction measurements have been carried out by employing the typical diffractometer DRON-2, equipped with the four-ring goniometer GUR- 5. The radiation source was MoK_{α} radiation. Monochromatization was achieved by using a pyrolytic graphite crystal.

For the $CdGeAs_2$ crystal we have found 6 crystallographic orientation, of as-grown surfaces, corresponding to (112), (112-), (101), (101-), (110) and (11-0). To monitor the body centered tetragonal unit cell of the $CdGeAs_2$ we found the following values for the parameters of the unit cell: a = (5.9403 ± 0.0002) Å and c = (11.2022 ± 0.0005) Å. One of the main structural parameter, characteristic for the chalcopyrite type compounds is tetragonal compression $h = (1 - c/2a)$, which deviates parameter c from the ideal ratio $c = 2a$. This value is very close to $h = 1$ among all chalcopyrite type compounds. In our case $h = 0.0571$ in good agreement with the literature data.

For the sample cut from the $CdGa_2S_4$ crystal the orientation of the sample on the main crystallographic surfaces (100), (001) and (010) was determined by using the following reflections found: 325, 215, 224, 226 and 316. For the determination of the parameters of unit cells the following reflections were used: 0.0.24, 14.0.0, 10.10.0, 10,0.20, 0.0.28 and 14.6.0. The following values for the parameters of the unit cell: a = (5.5460 ± 0.0003) Å and c = (10.1654 ± 0.0005) Å, which are also in good agreement with the literature data.

Task 2:

The chalcopyrite structure $CdGeAs_2$ crystals have the symmetry with space group $D_{2d}^{12}(I\bar{4}2d)$ and the body centered tetragonal unit cell with two formula units and, therefore, eight atoms. Therefore, there are 21 optical and 3 acoustical lattice vibrational branches with with the following representation for the Brillouin zone center with k=0

$$\Gamma = 1\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_4 + 6\Gamma_5 \quad \text{и} \quad 1\Gamma_4 + 1\Gamma_5.$$

With the splitting of infrared active modes Γ_4 and Γ_5 by the macroscopic long range electrostatic interaction into transverse and longitudinal components as well as taking into account that the Γ_2 modes are silent, one expects 22 Raman-active optical modes:

$$1\Gamma_1 + 3\Gamma_3 + 3\Gamma_4(LO) + 3\Gamma_4(TO) + 6\Gamma_5(LO) + 6\Gamma_5(TO).$$

The Raman scattering spectra have been measured for $CdGeAs_2$ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature Eg = 0.57 eV for $CdGeAs_2$) these measurements have been performed in the back-scattering configuration.

The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the ***c***-axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (⊥) and [112] (||) for the parallel $(\mathbf{e}_i \parallel \mathbf{e}_s)$ (⊥⊥) or crossed $(\mathbf{e}_i \perp \mathbf{e}_s)$ (⊥||) polarizations of the incident and scattered light, respectively.

For the both polarizations at the room temperature, corresponding spectra were also obtained for the anti-Stokes components of these spectra. This fact indicate that the all observed sharp lines are caused by the first-order Raman light scattering by optical phonons corresponding to the center of the Brillouin zone.

All these spectra also demonstrate clear polarization dependence and indicate that the vibrational modes are anisotropic. Moreover, the properly polarization behavior of the Raman scattering spectra obtained from the long-wavelength optical phonons and the sharpness of the lines with the deconvoluted values of full width at half intensity of 1-3 cm^{-1} as well as absence of background scattering indicated on high crystalline quality of the grown $CdGeAs_2$ single crystals.

In addition, the mapping measurements taken with a step of 0.3 mm showed a high reproducibility of all parameters of the spectra (scattering intensity, frequency shift, line width and polarization). These observations also indicate high homogeneity of the grown crystals.

The following measured frequencies (in cm^{-1}) together with the results of our interpretation of the symmetry of the all observed zone-center optical phonons are for $CdGeAs_2$ single crystals have been obtained:

66 - Γ_5(TO);
78 - Γ_4(TO);
94 - Γ_4(LO);
161 - Γ_5(LO);
193 - Γ_1;
202, 273, and 283 - Γ_5(LO).

The defect chalcopyrites or thiogallates structure $CdGa_2S_4$ crystals have the symmetry with space group $S_4^2(I\overline{4})$ with two formula units in the cell.

Such a structure can be considered as obtained from the sphalerite structure by adding ordered vacancies. It is intermediate between CdS, when Cd atoms occupies half of the tetrahedral voices of cubically packed S atoms, and α-Ga_2S_3, when Ga atoms occupies 1/3 of such voices. At the same time Cd and Ga atoms occupies 1/8 and ¼ of the tetrahedral voices.

There are 7 atoms in the unit cells of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals. The vibrational representation at the Γ point ($\kappa = 0$) can be given as

$$\Gamma = 3A + 6B + 6E.$$

These 15 optical modes are polar and Raman-active.

Our Raman measurements on $CdGa_2S_4$ crystals have been performed on the samples preliminarily crystallographically oriented by x-ray diffraction measurements sample on the main crystallographic surfaces (100), (001) and (010). The scattering spectra were excited at room temperature by using the argon laser line at 514.5 nm and 632.8 nm line of the He-Ne laser.

We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

Moreover measurements performed at low temperatures (up to T=77K) indicated that all these lines exhibited small intensity dependence as well as small frequency shifts (in the range 2-3 1/cm) indicating that all these lines corresponds to the first-order scattering by the Brillouin zone center optical phonons. These preliminary results are in good agreement with the infrared absorption data performed on $CdGa_2S_4$ crystals (V. Slivka et al, UPJ, 22,1951-1953, 1977).

The defect chalcopyrites or thiogallates structure $HgGa_2S_4$ crystals also have the symmetry with space group $S_4^2(I\overline{4})$ with two formula units in the cell. Similar Raman scattering measurements for these crystals were performed with spectral resolution of 3 cm^{-1} at room temperature by using the argon laser line at 514.5 nm and 632.8 nm line of the He-Ne laser. These measurements have revealed approximately 7 spectral lines. They are located in the spectral range of 60-750 cm^{-1}, namely, at 373, 416, 428, 446, 571, 576, and 750 cm^{-1} in the spectra with the both of excitations used indicating that they induced by the Raman scattering and not luminescence. The most intense lines have been observed also in the anti-Stokes spectra directly indicating that they are due to the optical phonons. There are no literature data on phonons in the $HgGa_2S_4$ crystals.

Our light scattering spectra for $CdGa_2S_4$ and $HgGa_2S_4$ crystals have been obtained by using the analog detection system under the linear scanning on wavelengths, which does not allow to obtain the spectra linear on wavenumber directly. Now we are finishing the works on connecting personal computer that will allow computer-controlled scanning of our double grating spectrometer SDL-1. Moreover, such a system will allow digital registration of the light scattering spectra.

In addition the low sensitivity of our photomultiplier does not allow to detect spectra with high signal/noise ratio. Therefore the full treatment of the obtained experimental data and final results on determination the phonon frequencies and their symmetry identification will be conducted after connecting the new photomultiplier with InP/InGaAs photocathode, Hamamatsu R5509-72 (currently we have purchased such a photomultiplier) and obtaining supplementary spectra which will be possible to process by using computer.

Task 3:

Early the photoluminescence spectra of $CdGa_2S_4$ compounds were investigated relatively in detail while there is only one publication about $HgGa_2S_4$. Polarization dependence for both crystals were not known. It evident that such studies can be interesting for clarification the nature of optoelectronic phenomena in such a multicomponent anisotropic semiconductors.

Photoluminescence was excited by the focused radiation (the excitation spot diameter was approximately 0.1 mm) of the He-Cd laser with excitation energy of $\hbar\omega_{exc} \approx 2.88$ eV and density of $P \approx 10^{19}$ quant /$cm^2 \cdot s$. Luminescence spectra were detected by using grating mochromator MDR-3 (LOMO) and photomultiplier PhEU-62. The spectral sensitivities of the monochromator and photomultiplier were corrected by the tungsten spectral lump. Spectral resolution was better than 1 meV.

Main results of measured for the first time polarized photoluminescence spectra can be formulated as following:

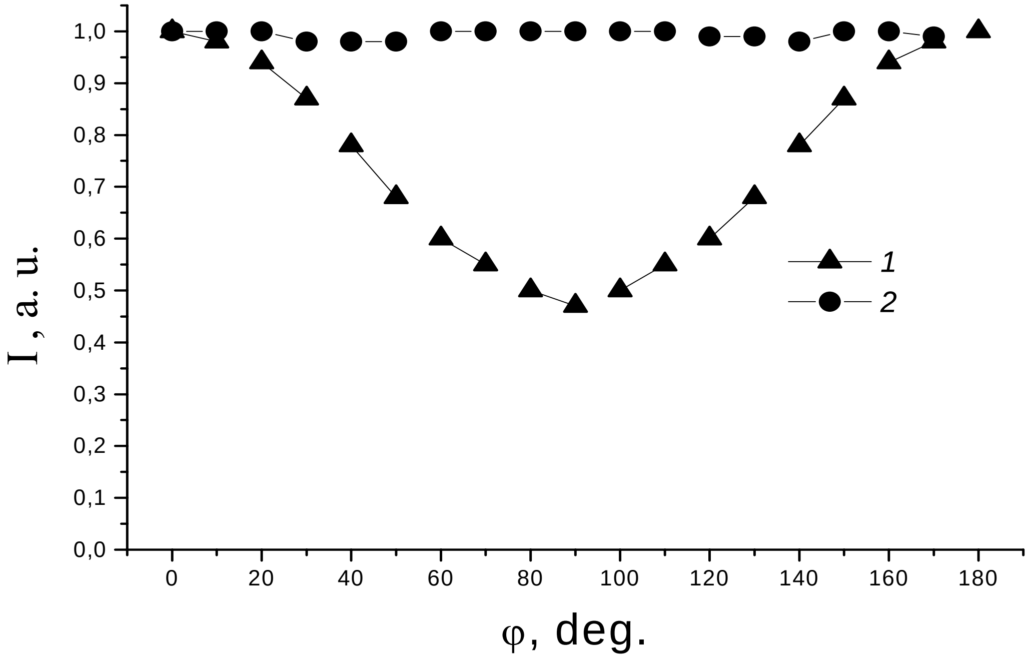


Fig.1. Polarization indicatrice of the PL intensity for CGS at $T = 300$ K.
$\hbar\omega = 2.0$ eV, Crystallographic directions for registration of the PL:
curve 1 – [100], curve 2 – [001]. Sample No. 4.

i) we have observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector $\boldsymbol{E}_{rad}$ and tetragonal axis of the crystal ***c.*** We find that the intensity dependence for the case of registration the radiation along the normal parallel to the (100) and (010) faces in the temperature range 77 – 300 K is described as

$$I_{\varphi} = I^{II} cos^2 \varphi + I^{\perp} sin^2 \varphi, \qquad (1)$$

where I^{II} and $I^{\perp}$ - are photoluminescence intensities for $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ and $\boldsymbol{E}_{rad}$ **c**, respectively. The same type of dependencies was observed for the coefficients of optical absorption for $CdGa_2S_4$ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions. This fact indicates that Kirkhgoff law on detailed correspondence between absorption and radiation processes is fulfilled for this new class of semiconductor materials.

The dependence described by the Eq.1 not shows a sensitivity to the excitation radiation (unpolarized or changing the orientations of $\boldsymbol{E}_{rad}$ and photon energy $\hbar\omega_{exc}$. Only the rotations of the sample in the (100) and (010) planes that cause the changes of the space orientation of the axis ***c***, is accompanied by changing the electric field polarization vector of light wave in the photoluminescence spectra.

It is important to note that in the case of registration photoluminescence spectra from (001) plane when tetragonal axes of $CdGa_2S_4$ compound is collinear to the direction of registration the photoluminescence spectra became isotropic. All deviations of the registration direction from axis ***c*** cause to accomplishment of Kirhof law described by Eq. 1. At same time the ratio of intensities $I^{II} / I^{\perp}$ at the $\hbar\omega$ = const reaches the maximum value if the photoluminescence light is analyzed in the directions perpendicular to the collinear axes ***c***.

So, we have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation τ =19% and 14% for $CdGa_2S_4$ and $HgGa_2S_4$ crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III$_2$-VI$_4$ compounds with ordered stoichiometric vacancy.

ii) Spectral dependences of photoluminescence spectra for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the investigated temperature range have as a rule a form of a broad structureless bands. Table 2 shows typical values of the maximum of photoluminescence band $\hbar\omega^m$ at T = 300 and 77 K. These values are lower than the corresponding band gap. Therefore, the recombination radiation of these crystals is determined by transitions of electrons to the deep levels of

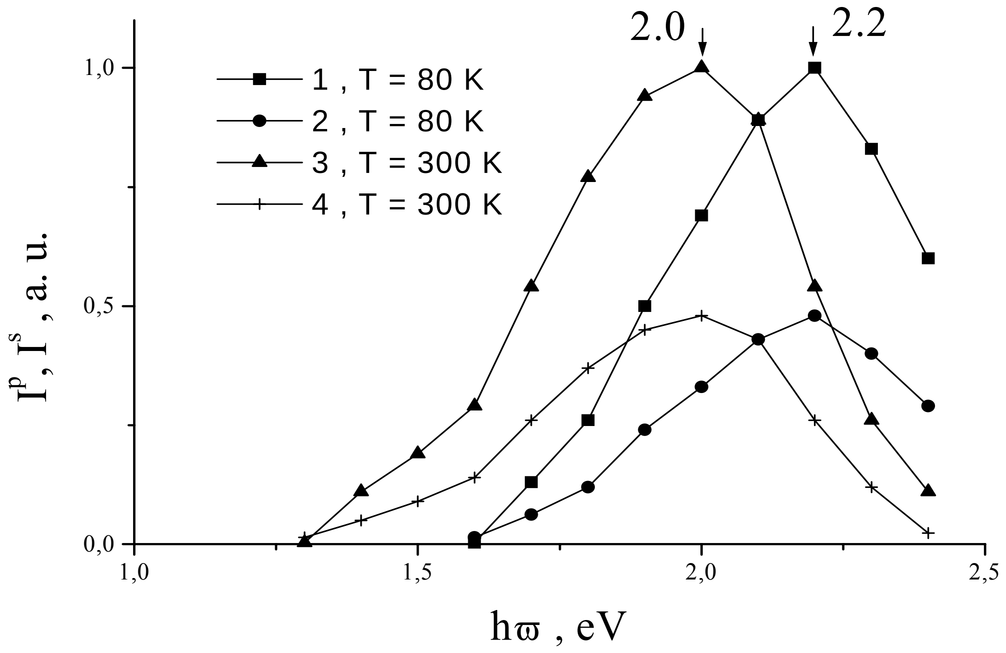


Fig.2. Spectral dependence of the PL intensity for CGS. The direction of the Pl detection is [100]. Temperature T: for curves 1 and 2 – 80 K, for curves 3 and 4 – 300 K. PL polarizations: cuerves 1 and 3 - E‖C (I^p) , curves 3 and 4 – E⊥C (I^s). Sample No. 10.

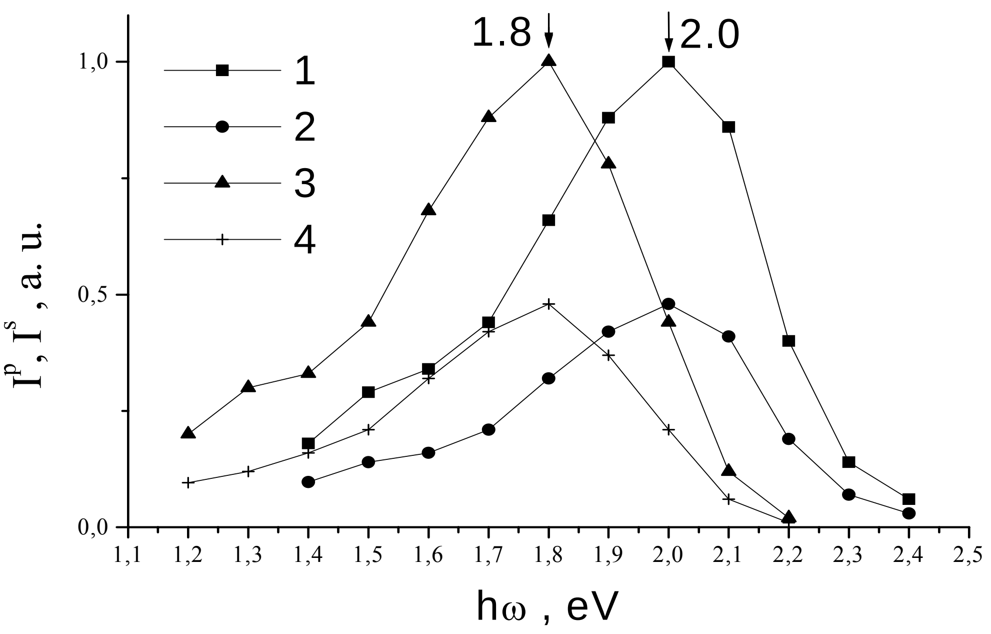


Fig.3. Spectral dependence of the PL intensity for HGS. The direction of the Pl detection is [100]. Temperature T: for curves 1 and 2 – 80 K, for curves 3 and 4 – 300 K. PL polarizations: cuerves 1 and 3 - E‖C (I^p) , curves 3 and 4 – E⊥C (I^s). Sample No. 6.

antisite defects, which are lower by 0.8 –1.0 eV than the band gap for the $HgGa_2S_4$ crystals and by 1.4 –1.6 eV for the $CdGa_2S_4$ crystals. Observed shifts for both crystals of the maximum of photoluminescence band to the low wavelength range indicate different contributions of deep levels to the recombination process.

We find that values of full width at half maximum $\delta_{½}$ are large that indicate on nonelementar character of recombination transitions. Note that observed broad photoluminescence bands for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals are in the range of high optical transparency, when $\hbar\omega^{m} < E_G$, thus they can be attributed to the recombination transitions with participation of the antisite levels.

With reduction of the excitation energy level, as a role, we find the increase of the long-wavelight contributions that cause the enhancement of the long-wavelength shoulders and red shift of the bands for both crystals. In some crystals we have observed also red shift of $\hbar\omega^{m}$ also of sort-wavelength shoulders. These observations form the base for conclusion that dominated processes are donor-acceptor recombination. Similar behavior of the photoluminescence spectra for both crystals indicate that donor and acceptor components can be related to the point defects in gallium and sulfur sub lattices.

Luminescence spectra emitted from (100) plane showed that the recombination radiation in the temperature range 77 – 300 K are partially polarized and dominated for $\boldsymbol{E}_{rad}$ || $\boldsymbol{c}$ polarization while the shape of the bands for both polarizations $\boldsymbol{E}_{rad}$ || $\boldsymbol{c}$ and $\boldsymbol{E}_{rad} \perp \mathbf{c}$ were the same as in the case of chalcopyrite crystals [2]. Therefore, the degree of polarization of the luminescence determined as

$$P = (I^{II} - I^{\perp}) / (I^{II} + I^{\perp}), \tag{2}$$

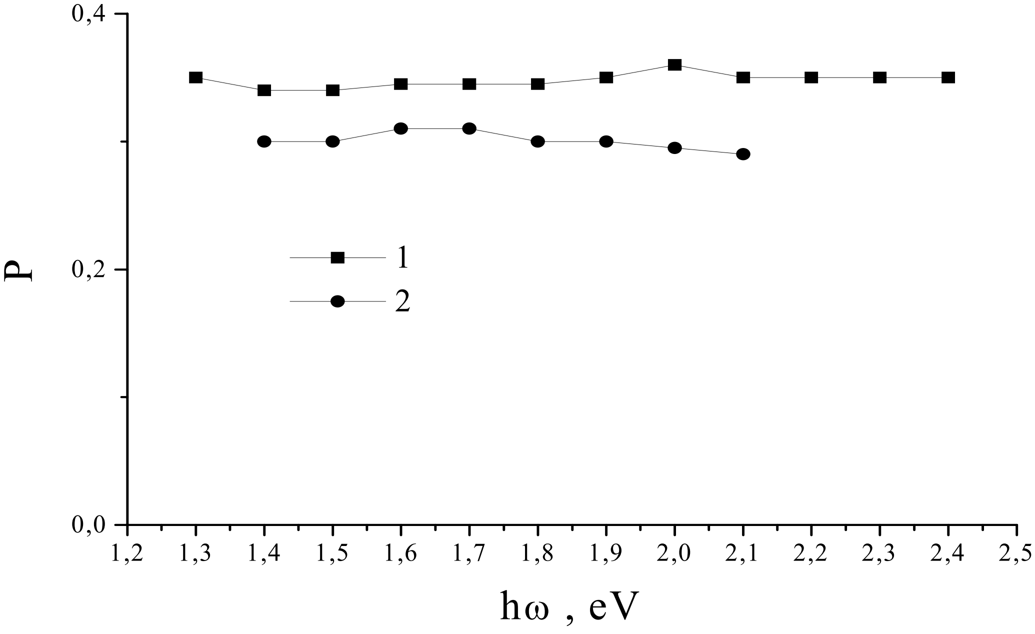
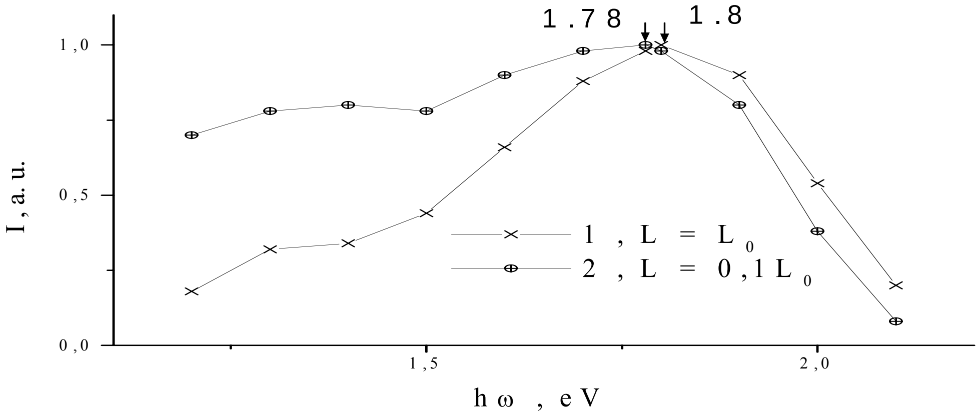


Рис. 4. Dependence of The PL spectra for HGS on en excitation energy. T = 80 K, Excitatation intensity L/L_0, in arbitrary units:
1 – 1.0, 2 – 0,1.

became positive $P > 0$ for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals. The result is in a good agreement with our polarized measurements of optical absorption coefficient n the same samples and theoretical calculations of the band gap of the multicomponent anisotropic semiconductors with ordered stoichiometric vacancy [3]. On the base of our polarized measurements the observed photoluminescence bands (Table 2) are connected with radiation transitions with participation of levels induced by Γ_1 and Γ_3 bands.

Fig. 5. Spectral dependence of the linear polarizatio P of PL
for CGS (curve 1, T = 80 K) and HGS (curve 2, T = 300 K).



The degree of polarization of the photoluminescence bands were practically constant and in addition independent on temperature. This may be he consequence of the high tetragonal deformation of crystalline lattices of these compounds (Table 1) and corresponding high values of the splitting of upper valence bands by the tetragonal crystal fields. Low values and absence of the P dispersion for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the investigated spectral range is not unexpected. These data are in agreement with the early-observed reduction of the anisotropy of oscillators, which take place in the case of radiation with participation of deep levels.

Therefore, photoluminescence for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\boldsymbol{E}_{rad}$ II $\boldsymbol{c}$, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

Table 1.

Physical properties for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals at T = 300 K.

Compound	Space group	Lattice constants *a* and *c*	τ %	.E_g eV
$HgGa_2S_4$	S_4^2	5.50 10.23	14	2.8
$CdGa_2S_4$	S_4^2	5.57 10.08	19	3.58

Table 2

Parameters of photoluminescence bands for the $CdGa_2S_4$ and $HgGa_2S_4$ crystals

Compound	300 K			77 K		
	$\hbar\omega^{m}$ eV	$\delta_{1/2}$ eV	P %	$\hbar\omega^{m}$ eV	$\delta_{1/2}$ eV	P %
$HgGa_2S_4$	2.0	0.45	0.3	1.8	0.4	0.3
$CdGa_2S_4$	2.2	0.5	0.35	2.0	0.45	0.35

[1] V. Yu. Rud’, Yu. V. Rud’, M.C. Ohmer, P.G. Schunemann. Semiconductors, **33**, 1317 (1999).

[2] Yu. V. Rud’, I. A. Mal’tseva. Semiconductors,, **19**, 870 (1977).

[3] V. L. Panutin, B. E. Ponedel’nikov, A.E. Rozenson, B.H. Chijikov. Phisika. Izvestia Vuzov, 8, 57 (1979).

9. Current technical status

- on schedule, behind, ahead

All works are on schedule.

- refining next year schedule if necessary

- recommendation for changes of the work plan, if necessary

10.Cooperation with foreign collaborators

- exchange of scientific material (information, computer codes and data, samples)

  We present Annual Reports, for 1 year (1 September 2001– 30 August 2002).

- signature of protocols (with short description)

- research carried out jointly

11. Problems encountered and suggestions to remedy

No

12. Perspectives of future developments of the research/technology developed

Attachment 1: Illustrations attached to the main text

Attachment 2: Other Information, supplements to the main text

Attachment 3: Abstracts of papers and reports published during the year of reference
Attachment 4: Information on patents and property rights.

III. ATTACHMENTS

I. Summary of personnel commitments for the year

Category I – 186 days and Category II – 185 days.

II. Equipment acquired during the year.

We have purchased new equipment – a photomultiplier with InP/InGaAs photocathode (Hamamatsu R5509-72).

Task 4 (part 1)

Photoconductivity of $CdGa_2S_4$ compounds were investigated starting from 1975 [1] and up to now not in detail [2-4] and only for nonpolarized light. As for $HgGa_2S_4$ there is no publications on this subject. Information about photoactive absorption on $HgGa_2S_4$ can be found only in one publication in which the results of the fabrication of photosensitive structures as well as the spectra of quantum efficiency of photoconversion η were presented [5]. In this publication also was used nonpolarized light, therefore the polarization dependences were not considered. It is evident that such studies with the linearly polarized light can be interesting for clarification the nature of optoelectronic phenomena in such a highly anisotropic $CdGa_2S_4$ and $HgGa_2S_4$ single crystals.

Photoconductivity spectra were detected by using grating mochromator SPM – 2. The spectral sensitivities of the monochromator and photomultiplier were corrected by the tungsten spectral lump. The spectra were measured at the constant and modulated excitations when the photoconductivity signal was proportional to the intensity of the incident light. They were corrected by the equal number of incident photons. Spectral resolution was better than 1 meV. All measurements were performed at the room temperature due to the long time relacsations detected with the reducing temperature gown to 77 K.

Measurements of the photoconductivity spectra were conducted with shining along the normal to (100) and (001) faces of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals, that allowed to measure the coefficient of the photopleochroism P_N [6], according to equation

$$P_N = (I^{II} - I^{\perp}) / (I^{II} + I^{\perp}) . \qquad (1)$$

Here I^{II} and $I^{\perp}$ are photocurrents for the incident polarization radiation $E||c$ and $E \perp c$, respectively.

Main results of measured for the first time polarized photoconductivity spectra of $CdGa_2S_4$ and $HgGa_2S_4$ crystals can be formulated as following:

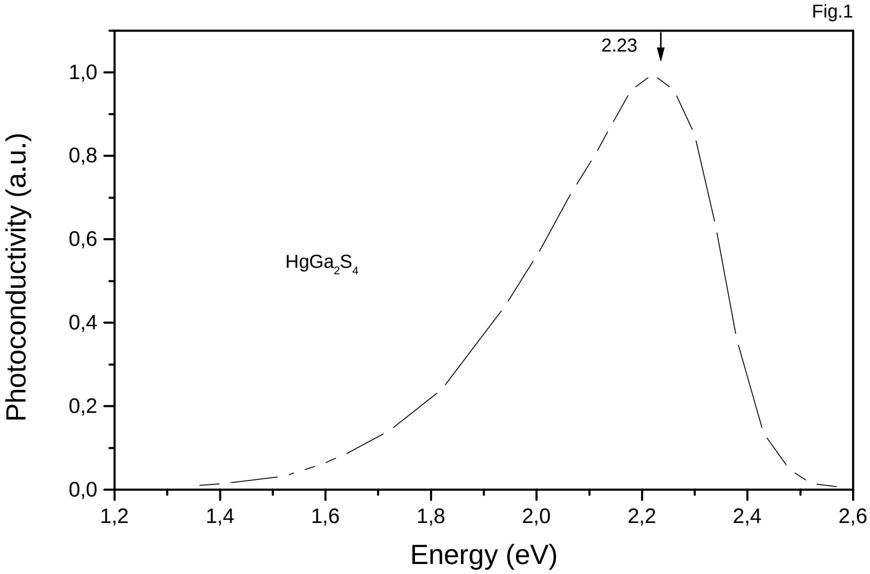


Fig.1. Spectral dependence of stationary photoconductivity of the $HgGa_2S_4$ single crystals (sample No. 7) at T=300 K for the nonpolarized excitation. Spectral resolution is better than 1 meV.

Fig.2

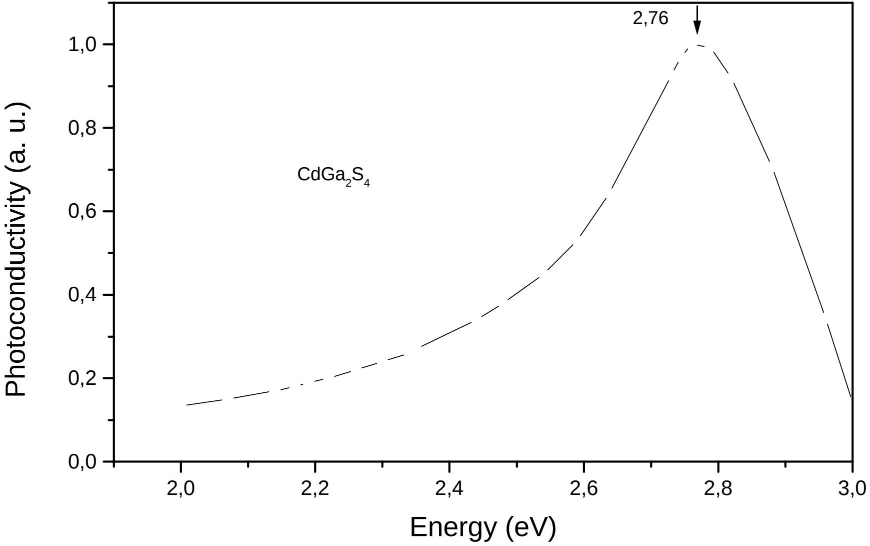


Fig. 2. Spectral dependence of stationary photoconductivity of the $CdGa_2S_4$ single crystals (sample No. 3) at T=300 K for the nonpolarized excitation. Spectral resolution is better than 1 meV.

1. Figure 1 and 2 show typical of stationary photoconductivity of the $HgGa_2S_4$ $CdGa_2S_4$ single crystals< respectively at T = 300 K. The photoconductivity spectra I^{II} and $I^{\perp}$ have maximum at $\hbar\omega^m$ = 2.23 eV for $HgGa_2S_4$ and $\hbar\omega^m$ =2.76 for $CdGa_2S_4$ which are essentially less then the band gap of these semiconductors [7]. Therefore, the observed spectra can be attributed to the photoactive absorption with participation of lattice defects, located at the activation energies $E_D \approx 0.6$ eV (for $HgGa_2S_4$) and ≈0.8 eV (for $CdGa_2S_4$). The photoconductive bands in these crystals can be characterized also by full width at the half maximum $\delta \approx 0.38$ eV (for $CdGa_2S_4$) and $\delta \approx 0.4$ eV (for $HgGa_2S_4$). Large values of δ< as well as the bands asymmetry with long-wavelength tailing indicate on nonelementarily and, therefore, on the complex energetic spectra of the lattice defects of the crystals under the study.

2. Polarized photosensitivity for the both crystals for the case of registration the radiation along the normal parallel to the (100) is characterized by $I^{II} > I^{\perp}$, while the azimuthal dependencies of the photocurrents follow to the periodical low

$$I_{\varphi} = I^{II} \cos^2 \varphi + I^{\perp} \sin^2 \varphi, \tag{2}$$

where I^{II} and $I^{\perp}$ - are photocurrents for $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ and $\boldsymbol{E}_{rad}$ **c**, and φ is the azimuthal angle between the polarization of the electric field vector $\boldsymbol{E}_{rad}$ and tetragonal axis of the crystal ***c*.** If we turn now to the photoresponse from the (001) plates it does not changes with the azimuthal angle and azimutal dependence turns to the direct line. These results indicate that in these group of the crystals with defect chalcopyrite structure exist phenomenon of native photopleochroism and azimutal dependencies of photoconductivity are in agreement with the crystalline symmetry of these compounds.

3. Spectra of the polarized photoconductivity for the $HgGa_2S_4$ for the both cases of the incident radiation polarizations have the same spectral shape (Fig. 3)

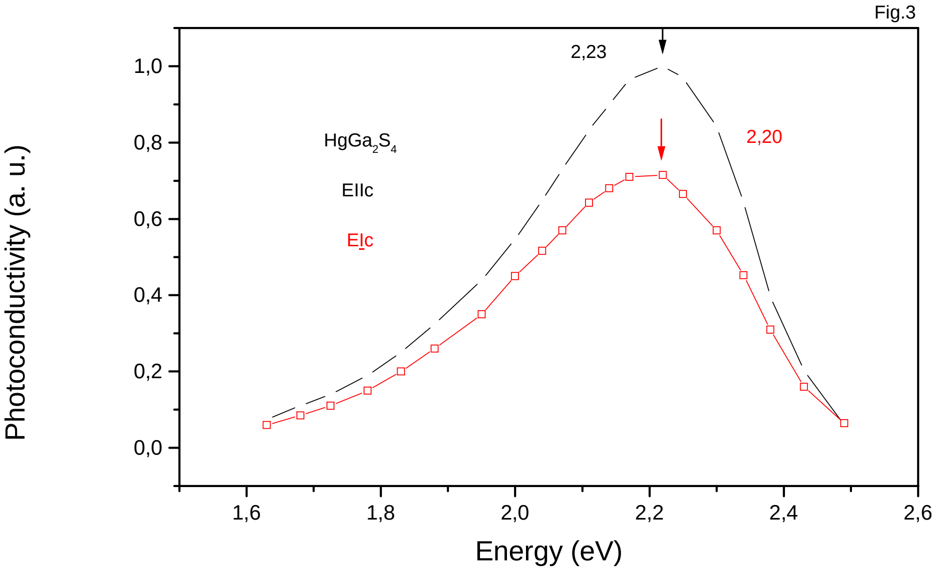


Fig. 3. Spectral dependencies of the stationary photoconductivity of the $HgGa_2S_4$ single crystals (sample No. 5, orientation of the plate – (100)) at T=300 K (the incident radiation polarizations are E||c and E ⊥c).

The main observed features can be formulated as following: The maximums of the photoconductivity bands for the both polarizations are realized at the approximately equal values of the incdinet photon energy and, therefore, the poarization splitting of the impurity band does not appear. Thus, the polarization of radiation control mainly the value of the photoconductivity in the way that in the range of long-wavelength shoulder for the maximum of photoconductivity inequality $I^{II} > I^{\perp}$ is satisfied. In the range of long-wavelength shoulder for the maximum of photoconductivity appears shoulder at $\hbar\omega = 2.37$ eV for E ⊥c. This leads to the positive sign of the maximum polarization difference of photoconductivity $\Delta = I^{II} - I^{\perp}$ and its maximum is localized in the range of the photoconductivity maximum. The sign of the polarization difference of maximum photoconductivity allows to look for selection rules of optical transitions, responsible to the maximum photoconductivity of the $HgGa_2S_4$ single crystals .

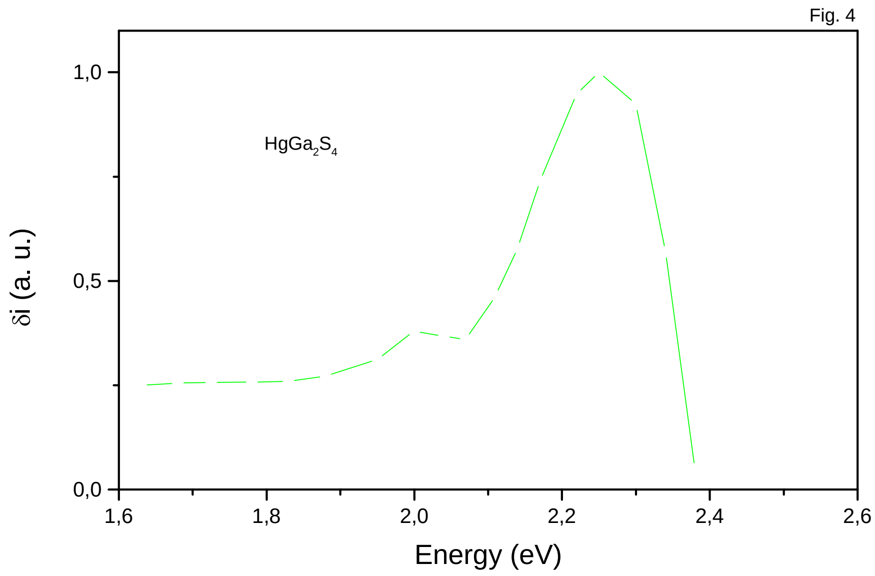


Fig. 4. Spectral dependencies of the polarization difference of photoconductivity of the HgGa$_2$S$_4$ single crystals (sample No. 5, orientation of the plate – (100)) at T=300 K.

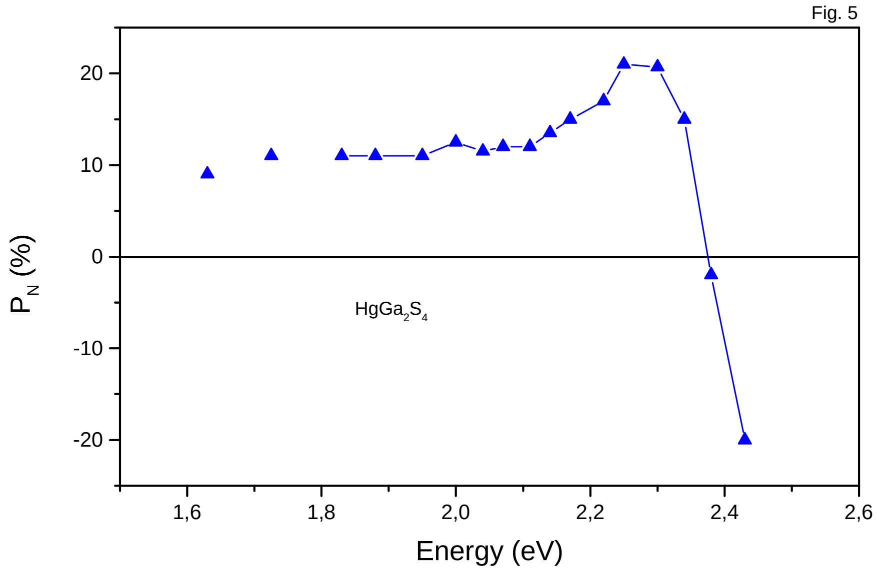


Fig. 5. Spectral dependencies of the coefficient of native photopleochroism of the HgGa$_2$S$_4$ single crystals (sample No. 5, orientation of the plate – (100)) at T=300 K.

Finally, in accordance with the sign of Δ the coefficient of native photopleochroism of the HgGa$_2$S$_4$ single crystals, as is evident from the Fig. 5, also has positive sign in the range of the long-wavelength maximum of photoconductivity. The maximum value P_N≈20% is achieved near the $\hbar\omega = 2.37$ eV. It important to note that there is also strict decreases of the amplitude of P_N and an inversion of its sign in the range of the strict cut-off of the photoconductivity. The reason of such inversion can be connected as with the increase of the surface recombination velocity as well as with changing the selections rules with the changing of the incident photon energy in the range of strong interband absorption. For final selection between these possibilities it is need further study of interconnections of the polarization photoconductivity measurements and technological aspects of the growth processes of these ternary compounds.

4. Fig. 6 shows typical dependencies of the stationary photoconductivity of the (100) plate of the $CdGa_2S_4$ single crystals at $T = 300$ K for polarized light

Fig. 6

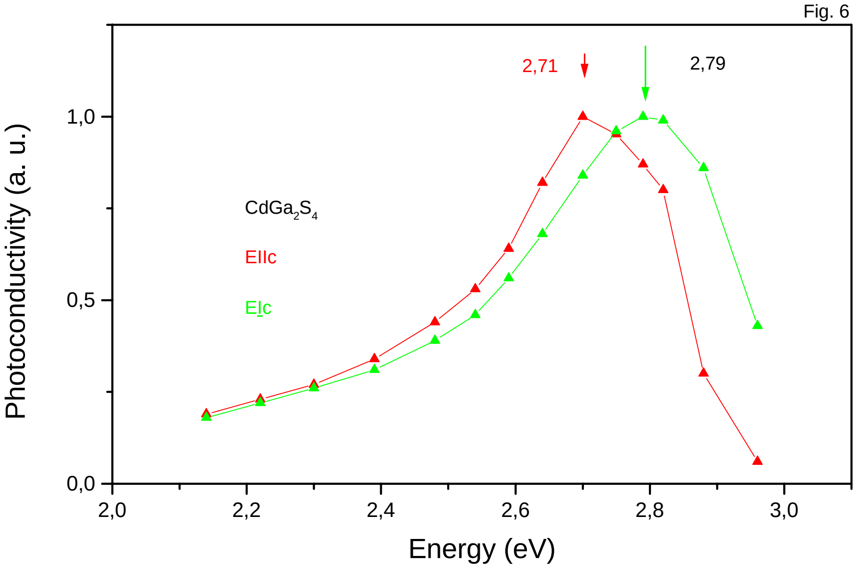


Fig. 6. Spectral dependencies of the stationary photoconductivity of the $CdGa_2S_4$ single crystals (sample No. 3, orientation of the plate – (100)) at T=300 K (the incident radiation polarizations are $E||c$ and $E \perp c$).

In principle, observed dependencies and features of polarization photoconductivity in this material are close to that observed for $HgGa_2S_4$. At the same time, for linear excitation polarization for $CdGa_2S_4$ we have found more pronounced polarization splitting of photoconductivity spectra $\Delta\hbar\omega = 0.1$ eV. In particular this can be the consequence of the high tetragonal deformation of crystalline lattices of the $CdGa_2S_4$ with respect to that of the $HgGa_2S_4$. As a result, at $\hbar\omega < 2.75$ eV the photoconductivity obey the inequality of $I^{II} > I^{\perp}$ as for the $HgGa_2S_4$ while at $\hbar\omega < 2.75$ eV these inequality transforms to the form of $I^{II} < I^{\perp}$. As a result in the spectra of the polarization difference of photoconductivity (Fig. 7) and the coefficient of the photopleochroism P_N of the $CdGa_2S_4$ single crystals

Fig. 7

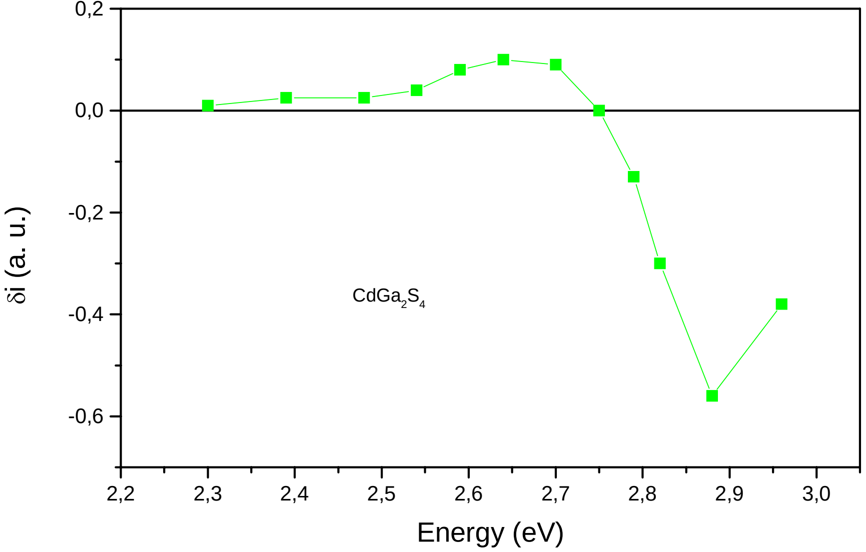


Fig. 7. Spectral dependencies of the polarization difference of photoconductivity of the $CdGa_2S_4$ single crystals (sample No. 3, orientation of the plate – (100)) at T=300 K.

Fig. 8

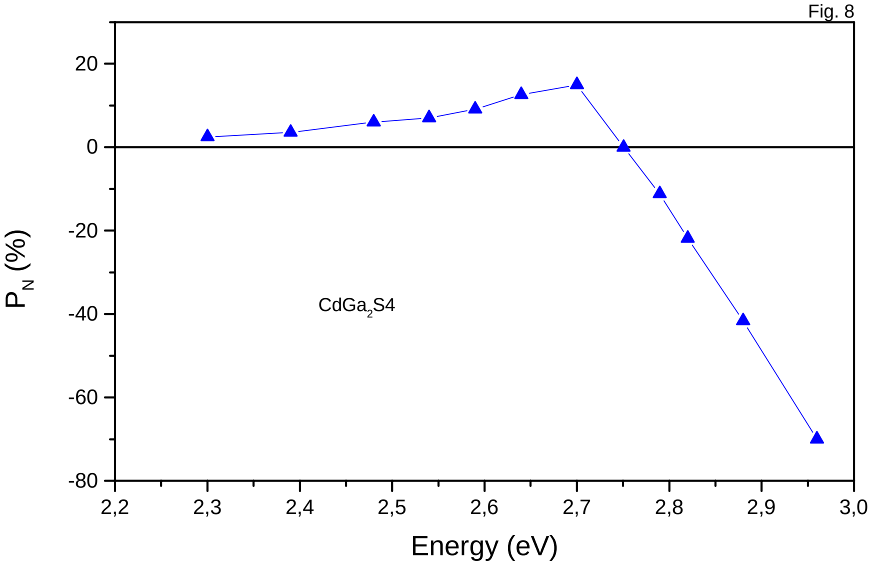


Fig. 8. Spectral dependencies of the coefficient of native photopleochroism of the $CdGa_2S_4$ single crystals (sample No. 5, orientation of the plate – (100)) at T=300 K.

appeared nontypical for the isotropic media the photoisotropic point at which $\Delta\equiv 0$, and correspondingly $P_N\equiv 0$.

As in the case of the $HgGa_2S_4$ crystals, the reason of the observed inversion of The sign of the native photopleochroism from the positive to the negative in the range of short-wavelength cut-off of the photoconductivity can be connected as with the increase of the surface recombination velocity of photogenerated pairs as well as with the appearance of optical transitions with other selection rules changing the selections rules. This question requires further special study.

5. So, polarization dependent measurements of the photoconductivity spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals, for the first time, allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The observed dependencies are rather complicated and may depend on the nature of the lattice defects and also on presence of close lying energies of the optical transitions that have different selections rules.

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Task 4 (part 2)

Our measurements of the photoconductivity spectra of $CdGa_2S_4$ and $HgGa_2S_4$ compounds oriented in the (100) plane show that native photopleochroism coefficient in these crystals has additional sign in the range of the maximum of the photoconductivity and the maximum value of $P_N \approx 20\%$ for $HgGa_2S_4$ crystals and $P_N \approx 10\%$ for $CdGa_2S_4$.

This anisotropy of the photoconductivity revealed in the range of impurity absorption by the lattice defects. We study the characteristic of local distribution of the experimental polarized indicatris of the potoconductivity by varying the exciting light position along the (100) plane.

It was essential to obtain information about the homogeneity of the samples studied. Therefore in contrast to our earlier measurements we have used focused linearly polarized beam. The diameter of the focus was in the range 0.2-0.3 mm.

We measured the polarized dependencies of the photoconductivity i_φ on the azimuthal angle φ between the polarization of the electric field vector $\boldsymbol{E}_{rad}$ and tetragonal axis of the crystal ***c*.**

Figure 1 shows typical examples of the azimuthal dependencies of photoconductivity i_φ of the for one of the $CdGa_2S_4$ single crystal sample under the fixed photon energy excitation $\hbar\omega_{exc}$, that corresponds to the maximum value of native photopleochroism coefficient P_N.

With shifting the position of 0.2 mm light beam exciting the photoconductivity we have found that experimental curves obey to the theoretical dependencies

$$I_\varphi = I^{II} \cos^2 \varphi \; + I^{\perp} \sin^2 \varphi, \qquad (2)$$

where I^{II} and $I^{\perp}$ - are photocurrents for $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ and $\boldsymbol{E}_{rad} \perp \boldsymbol{c}$. For the 5x5 mm^2 photoaccepting plane usually about 30 photoconductivity excitation points were measured.

It was found that the positions of the photoconductivity maximum always corresponds to the $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$**,** while potoconductivity minimum always observed for the $\boldsymbol{E}_{rad} \perp \boldsymbol{c}$ case.

This means that all ranges of the surfaces studied are similar. In such a case the observed spread of the measured values for the photoconductivity ratio in each of n-zone, where n is the natural sequence of numerical numbers, corresponding to the number of the excitation, $\Delta_n = i^{//}_n / i^{\perp}_n$ can be related to positional ordering in the range of n-zone.

The measured Δ_n values for the $CdGa_2S_4$ single crystal sample show the spread of the photoconductivity ratio in the range 1.25 – 1.45. This spread matches to the native photopleochroism coefficient P_N in the range 11 –18% at T + 300 K.

Figure 2 shows typical examples of the azimuthal dependencies of photoconductivity i_φ of the for one of the $HgGa_2S_4$ single crystal sample that also has the (100) orientation for photoacceptance plane.

Curves 1 and 2, as in the case of $CdGa_2S_4$ single crystals, cover the whole range of the Δ_n from the minimal up to the maximal for the all samples used.

Typical average photoaccepance square was 3x3 mm^2 when we able to measure up to 20 photoconductivity excitation zones.

The main result of our analyses of the changes of local distribution of the polarized indicatris of the potoconductivity i_φ and ratio Δ_n by scanning the exciting light position along the (100) plane is that the all angels at which maximum values of the photoconductivity is observed corresponds to the polarization the $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$**,** while potoconductivity minimum observed only for the $\boldsymbol{E}_{rad} \perp \boldsymbol{c}$ case.

The spread of the photoconductivity ratio for the $HgGa_2S_4$ single crystals is in the range 1.4 – 1.7 that means that the native photopleochroism coefficient P_N for the $HgGa_2S_4$ single crystals reaches the range 17 –25% at T + 300 K.

In summary, our study of the azimuthal dependencies of photoconductivity i_φ of the $CdGa_2S_4$ and $HgGa_2S_4$ single crystals allow to establish that the positive the native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane. The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axisies [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the $HgGa_2S_4$ $CdGa_2S_4$ single crystals.

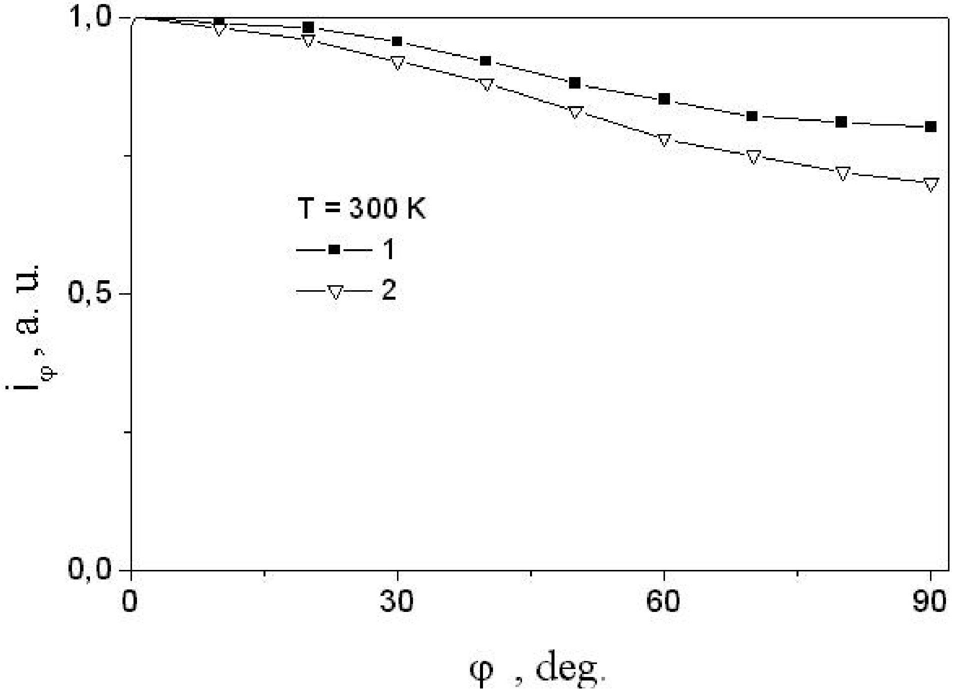

Fig. 1. Azimutal dependence of stationary photoconductivity i_φ of the $CdGa_2S_4$ single crystals at T=300 K (Sample No. 5, curve 1 – excitation range of the photoconductivity with the minimal value of the polarization ratio $\Delta_n \approx 1.25$, curve 2 – excitation range with the maximal value of the polarization ratio $\Delta_n \approx 1.43$, the excitation photon energy $\hbar\omega_{exc}$= 2.7 eV, solid curves are the theoretical dependencies according to the Eq. 1, points are experimental data).

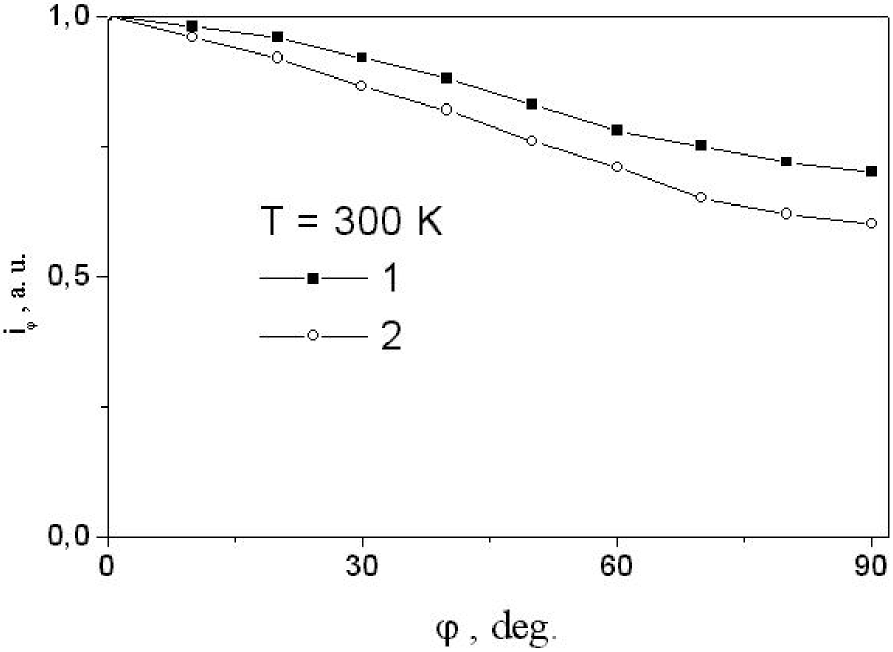

Fig. 2. Azimutal dependence of stationary photoconductivity i_φ of the $HgGa_2S_4$ single crystals at T=300 K (Sample No. 11, curve 1 – excitation range of the photoconductivity with the minimal value of the polarization ratio $\Delta_n \approx 1.41$, curve 2 – excitation range with the maximal value of the polarization ratio $\Delta_n \approx 1.67$, the excitation photon energy $\hbar\omega_{exc}= 2.7$ eV, solid curves are the theoretical dependencies according to the Eq. 1, points are experimental data.

Task 4 (part 3)

Our experimental search performed allowed to find lowohmic nonrectified contacts that together with the high resistance of the $CdGa_2S_4$ and $HgGa_2S_4$ compounds permitted to conduct measurements of the photoconductivity spectra of the both compounds. As a result we were able to detect the photoconductivity spectra of the $HgGa_2S_4$ down to T = 77 K and for the $CdGa_2S_4$ down to T = 150 K.
The main results are following:

Figure 1 and 2 show typical spectral dependencies of the stationary photoconductivity i_φ of the for electrically homogeneous $CdGa_2S_4$ and $HgGa_2S_4$ single crystals. For the both cassis $i_\varphi \sim L$, the density of incident polarized excitation. This situation vase the base for normalizing the photoconductivity signal to the equal number of the incident photons. We note that the surface mapping measurements with the diameter of the laser focus of 0.2 mm did not show any photovoltage that additionally indicate sufficiently high homogeneity of the samples measured. We note also that the spectra presented in Figs. 1

and 2 are well reproduced that also indicate that there are no “frozen” photoconductivity in our samples.

2. The spectra of the stationary of photoconductivity presented in Figs. 1 for the n-$HgGa_2S_4$ show broad structureless features (curves 1 and 2). Full widths at the half maximum (FWHM) $\delta_{1/2} \approx 400$ meV and practically independent on the temperature in the range 77-300 K as well as on orientation of the polarization of the electric field vector $\boldsymbol{E}_{rad}$ along the tetragonal axis of the crystal $\boldsymbol{c}$**.** With reduction temperature down to 80 K, as a rule, the photoconductivity 2-2.5 times increased with the shift of the maximum energy position to the short wavelength with a linear law with a speed of $\beta \approx - 5 \cdot 10^{-4}$ eV/K. This value is close to the temperature coefficient of the band gap E_G for the diamond like crystals [1]. The absolute maximum of the photoconductivity of the $HgGa_2S_4$ single crystals are realized at the energies sufficiently lower the band gap of the $HgGa_2S_4$. Therefore, the observed photoconductivity should be connected to the photoactive absorption from deep levels of lattice defects and possibly also to “psevdodirect” interband transitions [2]. Appearance of the sharp longwavelength maximum at LNT (Fig. 1 curve 4) indicate on the increase of the role of the deep centers located at ~ 1.1 eV from one of the free zones.

From the Fig. 1 it also is evident that the observed photoconductivity at T = 300 K in the excitation photon energy range $\hbar\omega_{exc} < 2.38$ eV is dominated for the $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ polarization, while for the energies higher then this value the influence of the polarization of the incident excitation is changed to the opposite. The existence of the photoisotropic point $\hbar\omega_I$ in the spectra of the $HgGa_2S_4$ single crystals can be related to the change of the selection rules for the corresponding optical transitions or due to the increased influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. The latter become active with the shift of the absorption zone at near the surface range, as it was observe early in the case of the III-V compounds [3].

The spectral dependence of the native photopleochroism coefficient P_N for the typical the $HgGa_2S_4$ crystals is given in the Fig. 3. It seen that in the longwavelength range on the relatively weak optical absorption edge the sigh of the native photopleochroism coefficient is positive and its maximum value is sufficiently low relatively to the charcteristic one for the ternary II-IV-V_2 compounds [4] and does not exceed 10 – 15%. Huge increase of the amplitude of the native photopleochroism coefficient is detected in the spectral range of the grows of the optical absorption. This observation gives the base to connect the increase of the negative native photopleochroism coefficient to the high velocity of the surface recombination. Really, this process of the surface recombination should be first of all reflected on the strongly absorbed $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ excitation and as a result the excitation with $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$ gives $i^{\perp} > i^{||}$(Fig. 3).

The fact that the spectral dependencies of the native photopleochroism coefficient features do not exhibit any changes during varying the temperature in the range 77 – 300K also indicate that there are not observed any structural phase changes in this temperature range.

3. From Fig. 3 it is become evident that upon changing the Hg atoms to Cd practically all the above-considered features for the $HdGa_2S_4$ single crystals are reproduced in the case of the $CdGa_2S_4$ single crystal. At the same time in the longwavelength range of the stationary of photoconductivity spectra $i^{\perp} > i^{||}$, and at the transition from the firstly observed by us photoisotropic point ($i^{\perp} > i^{||}$) this inequality is inverted into $i^{\perp} > i^{||}$ (Fig.

2). The quantity differences are due to the strong shift to the longwavelength range of the photoisotropic point in the $CdGa_2S_4$ crystals with respect to the $HgGa_2S_4$ crystals. The position of the photoisotropic point is intermediate between the energy of the maximums of the photoconductivity for the polarizations $\boldsymbol{E}_{rad} \parallel \boldsymbol{c}$, and $\boldsymbol{E}_{rad} \perp \boldsymbol{c}$.

We find that in the $CdGa_2S_4$ crystals the native photopleochroism coefficient and its temperature dependence given in the Fig. 4 are also similar to the above-considered case of the $HgGa_2S_4$ crystals.

4. The analysis of the observed results allows to formulate that for the clarification of the reasons that cause inversion of the sign the native photopleochroism coefficient in the $CdGa_2S_4$ and $HgGa_2S_4$ compounds it is need first of all to suppress the influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. It is evident, that the one of the most effective ways to solve this problem may be creation of the photosensitive structures the $CdGa_2S_4$ and $HgGa_2S_4$ compounds.

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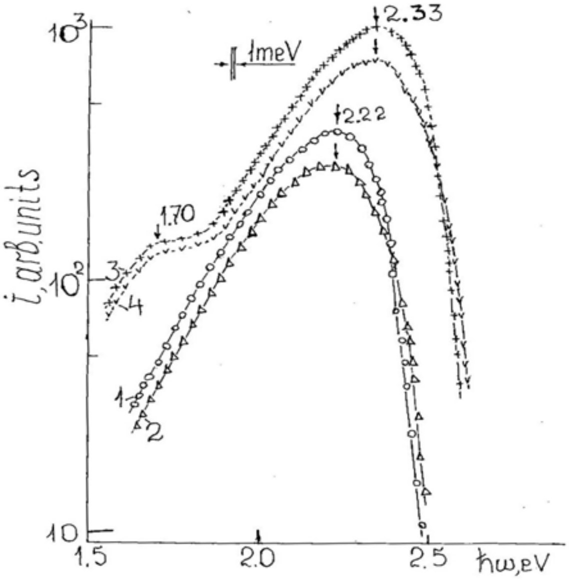

Fig. 1. Spectral dependencies of the stationary photoconductivity of the $HgGa_2S_4$ single crystals in the linearly polarized excitation; Sample No. 7; T,K: 300 – curves 1 and 2, 80 – curves 2 and 4; The incident radiation polarizations are $\boldsymbol{E} || \boldsymbol{c}$ - curves 1 and 3, and $\boldsymbol{E} \perp \boldsymbol{c}$ – curves 2 and 4). Orientation of the excitation crystallographic face is (100). The incident angle $\Theta=0^0$.

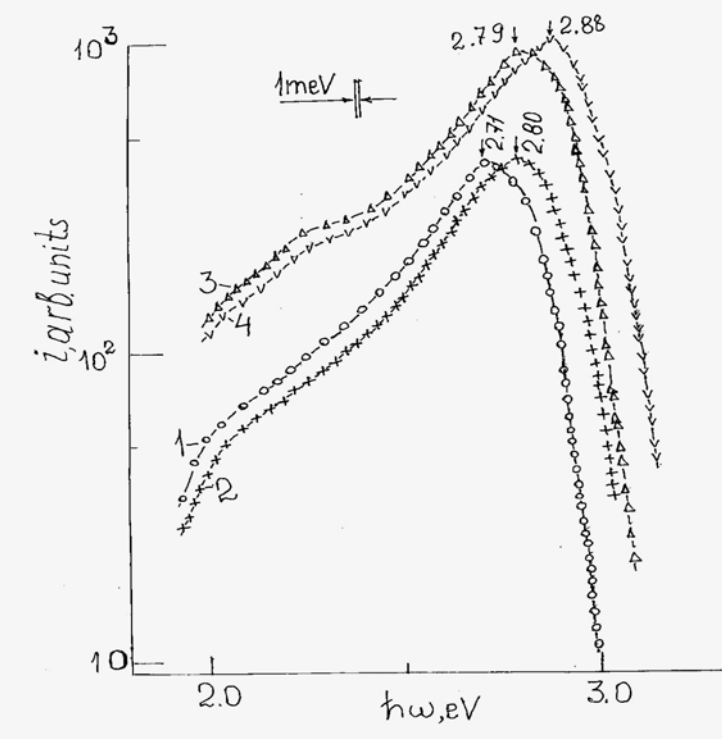

Fig. 2. Spectral dependencies of the stationary photoconductivity of the $CdGa_2S_4$ single crystals in the linearly polarized excitation; Sample No. 11; T,K: 300 – curves 1 and 2, 150 – curves 2 and 4; The incident radiation polarizations are ***E***||***c*** - curves 1 and 3, and ***E*** $\perp$***c*** – curves 2 and 4). Orientation of the excitation crystallographic face is (100). The incident angle $\Theta=0^0$.

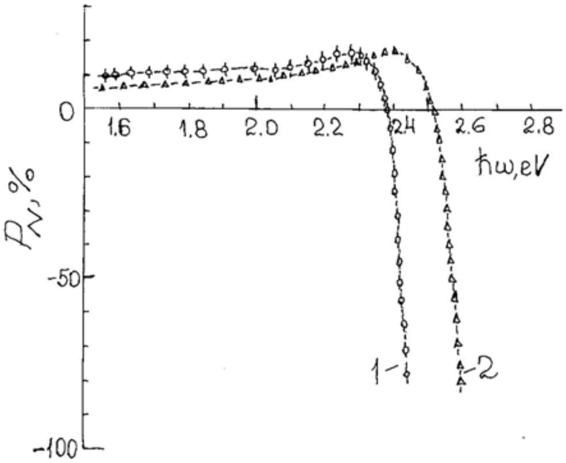

Fig. 3. Spectral dependencies of the native photopleochroism coefficient in the $HgGa_2S_4$ compounds; Sample No. 7; T,K: 300 – curve 1, 80 – curves 2.
The incident angle $\Theta=0^0$.

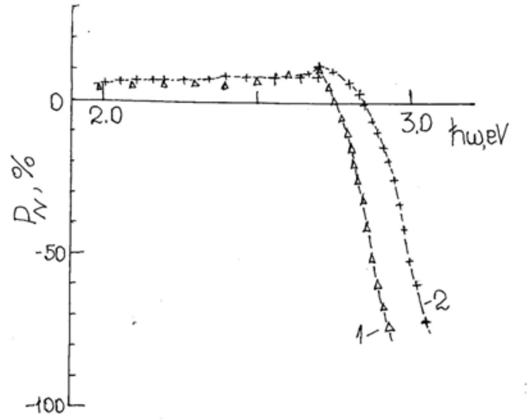

Fig. 4. Spectral dependencies of the native photopleochroism coefficient in the $CdGa_2S_4$ compounds; Sample No. 11; T,K: 300 – curve 1, 150 – curves 2.
The incident angle $\Theta=0^0$.

Table 1.
Physical properties of the $HgGa_2S_4$ and $CdGa_2S_4$ single crystals

Compound	Space group	Lattice parameters, Å		τ	E_G, eV
		a	c	%	
$HgGa_2S_4$	S_4^2	5.50	10.23	14	2.8
$CdGa_2S_4$	S_4^2	5.577	10.08	19	3.58

Table 2.
Photoluminescence parameters of the $HgGa_2S_4$ and $CdGa_2S_4$ single crystals

Compound	300 K			77 K		
	$\hbar\omega^m$, eV	δ_S, eV	P, %	$\hbar\omega^m$, eV	δ_S, eV	P, %
$HgGa_2S_4$	2.0	0.45	30	1.8	0.4	30
$CdGa_2S_4$	2.2	0.5	35	2.0	0.45	35

Task 5

Our experimental search was devoted toward study of electrical properties and optical absorption of the $HgGa_2S_4$ single crystals, study of contact properties of these crystals with some metals with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion.

The main results are following:

1. We have used the $HgGa_2S_4$ single crystals grown in the ultralow temperature gradient by horizontal crystallization from the melts close to the stehiometric [1]. Typical dimensions of the samples used for the measurements of kinetic coefficients were 0.6 x 0.9 x 4.5 mm^3. All these samples showed n-type conductivity determined by the sign of thermoelectric power, while the samples with p-type were not obtained. Our measurements of the Hall constant on the homogeneous samples show that

concentration of the free electrons is rather small (п ≈ 10^8 –10^9 $см^{-3}$) and the specific electrical resistance ρ ≈ 10^9 – 10^{10} Ом·см.

Figure 1 show typical temperature dependence of the specific electrical resistance in the temperature range T = 77 –300 K. It is seen that exponential falling of the resistance with increasing temperature at T>77 K. Note that activation energy for the donors, keeping in mind strong compensation of the acceptors, is rather small E_D ≈ 37-40 meV. So we establish for the first time for the $HgGa_2S_4$ single crystals grown in the ultralow temperature gradient by horizontal crystallization from the melts close to the stehiometric that shallow level donors are created. Early, this fact was not known for this group of semiconductors.

2. We establish that mechanical contact of pure metal layers of (In [2], Ni, Au, Ag) with the cleaved surface of the $HgGa_2S_4$ single crystals and further with chemically polished surface of electrically homogeneous $HgGa_2S_4$ give rectifying characteristics. Fig. 2 shows typical stationary current-voltage characteristics for the one of the best surface-barrier In-п-$HgGa_2S_4$ structures (curves 1 and 1'). Rectification determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 20$ V, reaches the values $K \approx 200$, that is the record value obtained up to now for the the n-$HgGa_2S_4$ single crystals. Initial part of the current-voltage direct line (Fig. 1, curve 1) follows to the diode equation for the bias range $U<5$ V with diode strength $n \approx 10$, while with the illumination (Fig. 2, curve 2) this value falls up to the $n \approx 2$. The high values of n, reflect the influence of high simultaneous resistance that does not allow to find mechanisms of direct current flow. In the bias range $U>10$ V the current-voltage characteristics follow to the linear law

$$I_{dir} = (U - U_0) / R_0, \qquad (1)$$

Where the residual resistance without illumination of the structure $R_0 \approx$ (2-2.5) 10^7 Ω falls up to $R_0 \approx$ (6-8) 10^5 Ω. We see from Fig. 2 that direct and reverse current-voltage characteristics in the case of illumination (curves 2 and 2') shifts relatively darks in the direction of increasing direct and reverse currents. Observed reducing of the diode diode strength n of the illuminated structures at the first is induced by significant fall of R_0 under the illumination. The reverse current for In-п-$HgGa_2S_4$ barriers usually is in the range $I_{rev} \approx 10^{-9}$ A and increases with increasing the bias by a low $I_{rev} \sim U_{rev}^{\gamma}$, where $\gamma \approx 1.08$. This value indicate nonperfect periphery of the first obtained structures. The latter is limited by the limited size of available crystals and indicate the real way of further improvement of the surface-barrier structure characteristics on the base of $HgGa_2S_4$ with solving size and crystal perfection problems.

Under illumination of the surface-barrier structures on the base of n-$HgGa_2S_4$ photovoltaic effect was also observed. Photovoltage of the free motion in the surface-barrier structures on the base of n-$HgGa_2S_4$ single crystals is dominated under conditions of illumination of the structures from the side of barrier contacts. In this case the sign of the photovoltage always corresponds to the direction of the rectification in the structures and independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. These established facts on the structures obtained for the first time can be used as a base to connect rectification and photovoltaic effect with energy barrier at the contact of semiconductor with metal studied. Maximum value of the voltage photosensitivity achieved for the surface-barrier In-*n*-$HgGa_2S_4$ structures is $2 \cdot 10^3$ V/W at T=300 K.

3. Typical spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier In-*n*-$HgGa_2S_4$ structures are given in the Fig. 3. It is seen that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 0.8-3.8 eV (Fig. 3, curve 1). The spectral parameter η at $\hbar\omega$ < 2.2 eV strongly changes from structure to structure, that may be due to the differences of the crystal properties and, therefore, may be used for the diagnostic of the material perfection. Under). Under condition of illumination of firstly obtained structures from the substrate side at the photon energy range $\hbar\omega$> 2.25 eV in the η spectra appears sharp cut-off of the photosensitivity (Fig. 3, curve 2). This cut-off may indicate on increase of the optical absorption in the $HgGa_2S_4$ plate. As a result of this process, the photogeneration area more and more moves from the active area and localizes at the thin surface layer of semiconductor. It can be supposed that due to small length of a diffusion shift of the nonequilibrium charge carriers the concentration of the photogenerated carriers, which achieve the active area, with increasing the photon energy $\hbar\omega$>2.3 eV begin to fall and, therefore, the quantum efficiency of photoconversion $\eta \rightarrow 0$. It is important to note that the cut-off spectral range of η under the condition of illumination of Shottky barriers from the substrate side is in an agreement with a beginning of sharp increase of the optical absorption coefficient α (Fig. 4) exactly at photon energy $\hbar\omega \approx 2.3$ eV. This value can be used as a preliminary estimation of the absorption edge E_G of this little known semiconductor. The $\eta(\hbar\omega)$ spectra in the range of $\hbar\omega$ < 2.25 eV are practically independent on illumination geometry of the surface-barrier structures (Fig.3, curves 1 and 2) that is due to the bulk nature of the charge carrier photogeneration in the $HgGa_2S_4$ crystals. The longwavelength edge of the photosensitivity of the surface-barrier structures in the range of $\hbar\omega$ < 2.2 eV follows to the Fowler law and, therefore, is rectified in the coordinates $(\eta\hbar\omega)^{1/2}$ - $\hbar\omega$ (Fig. 5). From the extrapolation of the direct linear parts $\eta^{1/2} \rightarrow 0$ we obtain first estimation of the energy height of In-n-$HgGa_2S_4$ and Ag-n-$HgGa_2S_4$ structures $\varphi_D \approx 1.1$eV at T=300 K. Note, that for some barriers in the dependencies $(\eta\hbar\omega)^{1/2} - \hbar\omega$ revealed several direct linear parts and , correspondingly, several cut-off energies (Fig. 5). This situation may reflect complicated nature of the energy band structure of the $HgGa_2S_4$ crystals.

   The increase of the photoconductivity in the best surface-barrier structures at $\hbar\omega$ >2.3 eV under the condition of illumination of the structures from the barriers side (Fig. 3, curve 1) can be related with the fundamental absorption in the $HgGa_2S_4$ crystals, that is not possible to detect by traditional absorption spectroscopy techniques on sush a small size samples (Fig. 4). From the Fig.6 it is seen that increase of the photoconductivity in the best surface-barrier structures at the photon energy range of 2.3-2.8 eV follows the $(\eta\hbar\omega)^{1/2} - \hbar\omega$ law (curve 1). Extrapolation of this dependense $(\eta\hbar\omega)^{1/2} \rightarrow 0$ allows to estimate the energy of indirect interband optical transitions $E_G^{in} \approx 2.27$ eV for *n*-$HgGa_2S_4$ at T=300 K. More sharp increase of the photoconductivity in the surface-barrier structures at the photon energy range of $\hbar\omega$ > 2.8 eV follows to the characteristic for the direct optical transitions quadratic $(\eta\hbar\omega)^2 - \hbar\omega$ law (curve 2). Extrapolation of this dependense $(\eta\hbar\omega)^2 \rightarrow 0$ allows to estimate the energy of direct interband optical transitions $E_G^{dir} \approx 2.86$ eV for *n*-$HgGa_2S_4$ at T=300 K. This value is in a good agreement with results of Ref. [3].

4. So, in this work for the first time, the problem of creation of the photosensitive structure on the base of *n*-$HgGa_2S_4$ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of *n*-$HgGa_2S_4$ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

Referencies

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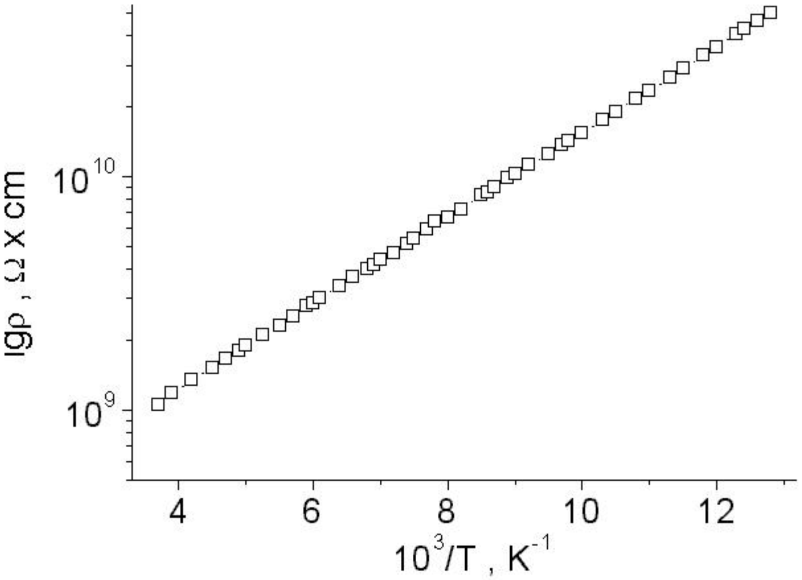

Fig. 1. Temperature dependencies of the specific resistance stationary photoconductivity of the $HgGa_2S_4$ single crystals; Sample No. 7n.

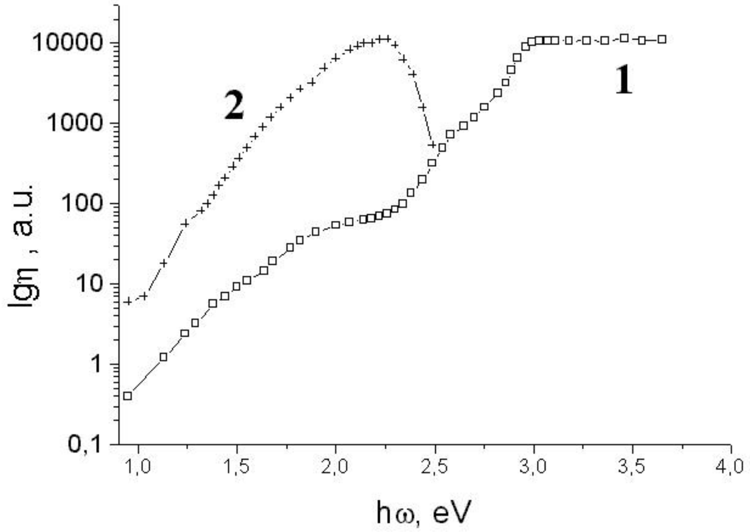

Fig. 2. Stationary (curves 1 and 1’) and light (curves 2 and 2’) current-voltage characteristics of In-*n*-$HgGa_2S_4$ at *T*=300 K (Sample 17n. Transmission direction is realized at the external positive bias at the barrier contact. Power density of illumination lamp *L*≈1mW/cm^2. Curves 1’ and 2’ are reverse branches of current-voltage characteristics).

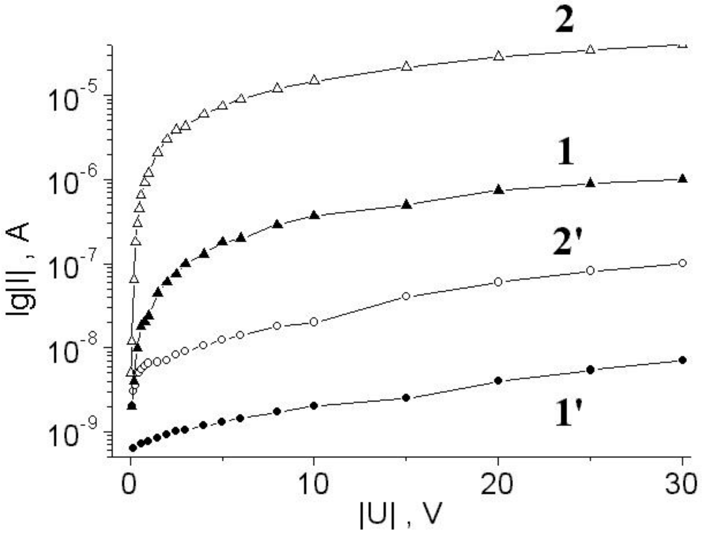

Fig. 3. Spectral dependencies of the relative quantum efficiency photoconversion of the surface-barrier In-*n*-$HgGa_2S_4$ structures in the coordinates $\eta^{1/2}$ - $\hbar\omega$ at *T*=300 K in the unpolarized radiation (Sample 17-3n). Illumination from the barrier contact side –curve 1 and from the substrate side – curve 2. Spectral resolution better than 1 meV.

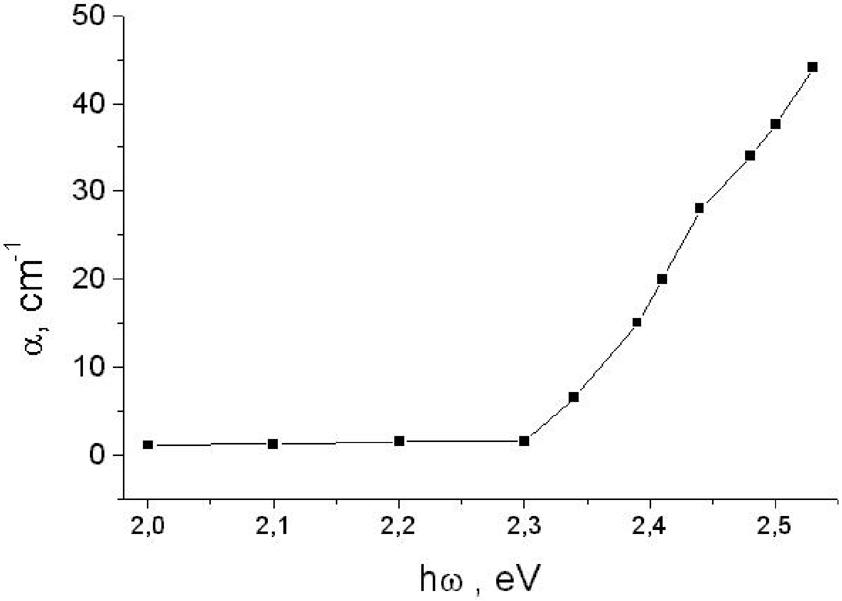

Fig. 4. Spectral dependencies of the optical absorption coefficient *n*-$HgGa_2S_4$ single crystal at *T*=300 K (Sample 17-3n. Sample size 0.6 x 2.1 x 4.3 mm^3).

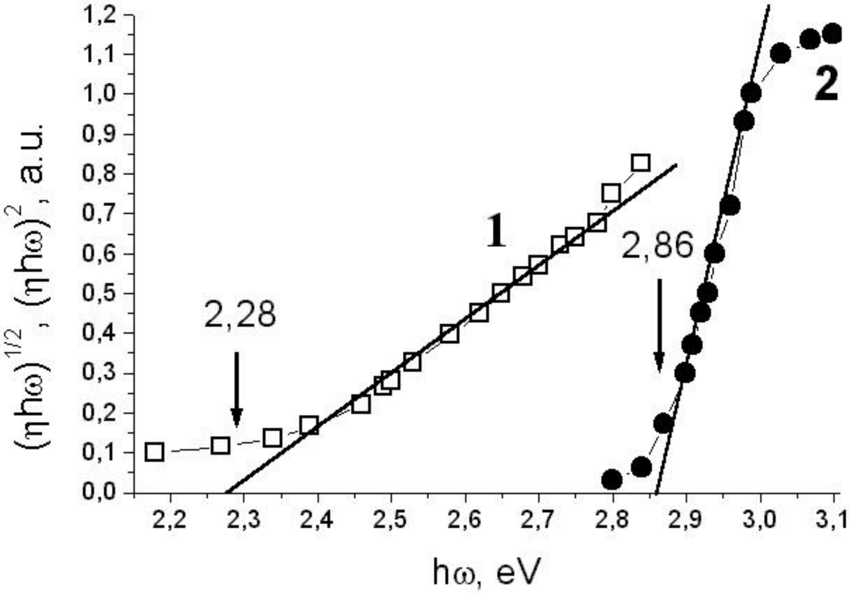

Fig. 5. Spectral dependencies of the relative quantum efficiency of the photoconversion for the surface-barrier In-*n*-$HgGa_2S_4$ structures in the coordinates $(\eta\hbar\omega)^{1/2}$ - $\hbar\omega$ at *T*=300 K (Sample 15-n). Illumination of the structure by nonpolarized radiation from the energy barrier contact side. Arrows indicate the values of cut-off energy.

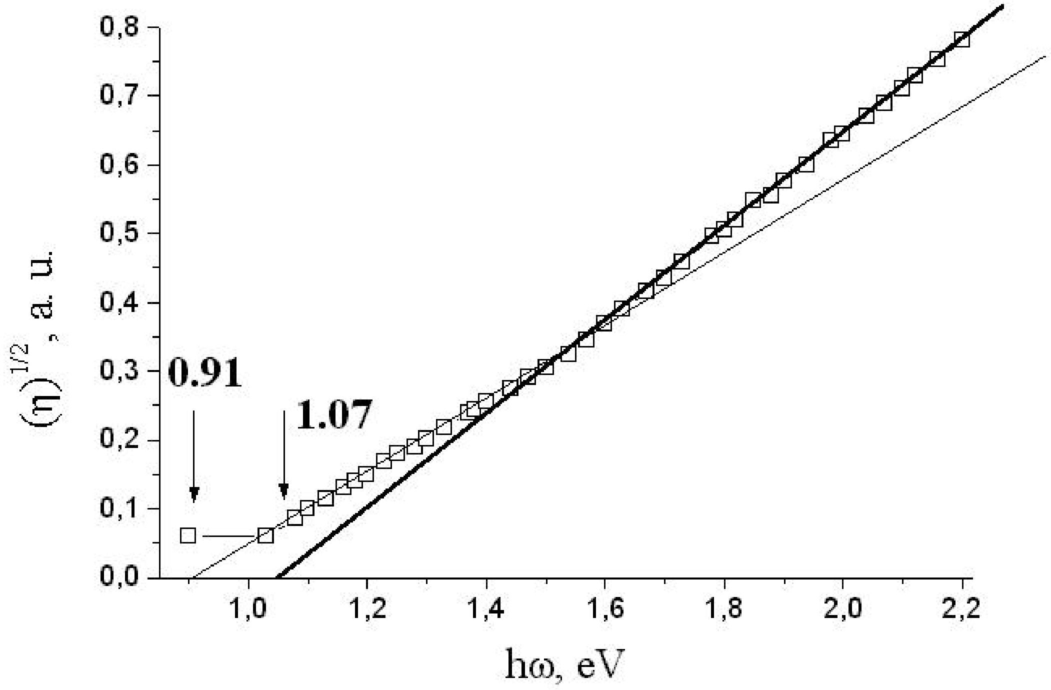

Fig. 6. Spectral dependencies of the relative quantum efficiency of the photoconversion for the surface-barrier In-*n*-$HgGa_2S_4$ structures in the coordinates $(\eta\hbar\omega)^{1/2}$ - $\hbar\omega$ - curve 1 and $(\eta\hbar\omega)^{1/2}$ - $\hbar\omega$ - curve 2 for the nonpolarized radiation at T=300 K . Illumination of the structure from the energy barrier contact side. Arrows at curves 1 and 2 indicate the values of cut-off energy.

- compliance with tasks and milestones as described in the work plan

  All works are in compliance with tasks and milestones.

- achievements of the past year

  Our polarization dependent measurements of the photoconductivity spectra on the $CdGa_2S_4$ and $HgGa_2S_4$ crystals, for the first time, allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The observed dependencies are rather complicated and may depend on the nature of the lattice defects and also on presence of close lying energies of the optical transitions that have different selections rules

  Our study of the azimuthal dependencies of photoconductivity i_φ of the $CdGa_2S_4$ and $HgGa_2S_4$ single crystals allow to establish that the positive the native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane.

The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axisies [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the $HgGa_2S_4$ $CdGa_2S_4$ single crystals.

The analysis of the observed results allows to formulate that for the clarification of the reasons that cause inversion of the sign the native photopleochroism coefficient in the $CdGa_2S_4$ and $HgGa_2S_4$ compounds it is need first of all to suppress the influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. It is evident, that the one of the most effective ways to solve this problem may be creation of the photosensitive structures the $CdGa_2S_4$ and $HgGa_2S_4$ compounds.

The problem of creation of the photosensitive structure on the base of n-$HgGa_2S_4$ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of n-$HgGa_2S_4$ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

9. Current technical status
   - on schedule, behind, ahead

     All works are on schedule.
   - refining next year schedule if necessary
   - recommendation for changes of the work plan, if necessary

10. Cooperation with foreign collaborators
    - exchange of scientific material (information, computer codes and data, samples)

      We present 2nd year annual report.
    - signature of protocols (with short description)
    - research carried out jointly
    - trips to/from foreign collaborators
    - workshops, topical meetings organized by the project team
    - joint attendance to international conferences

11. Problems encountered and suggestions to remedy

12. Perspectives of future developments of the research/technology developed

Our study with development of different optical and electrical research techniques show a new perspectives and opens up new approaches for better understanding the band structure of chalcopyrite crystals and structures on their base.

Attachment 1:	Illustrations attached to the main text
Attachment 2:	Other Information, supplements to the main text
Attachment 3:	Abstracts of papers and reports published during the year of reference
Attachment 4:	Information on patents and property rights.

III. ATTACHMENTS

III. Summary of personnel commitments for the 2d year

Category I – 245 days and Category II – 325 days.

IV. Equipment acquired during the year.

No equipment was acquired.

7. Technical progress during the 3d year

According to the Work Plan we have conducted the Task 5:

Polarized photosensitivity measurements (in a temperature range from 77 to 300K) of surface barriers on In/$CdGa_2S_4$ and In/$HgGa_2S_4$.

We have performed investigations of the contact phenomena of photosensitive surface-barrier structures on the base of the $CdGa_2S_4$ single crystals with n-type conductivity We study the stationary and light current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion in dependence of the geometry of excitation with a unpolarized irradiation.

The main efforts of our experimental search was devoted toward study of electrical properties and optical absorption of the $CdGa_2S_4$ single crystals, study of contact properties of these crystals with some metals such as In, Au, Cu, Ni, and Ag with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion. We have observed photovoltaic effect of the surface-barrier structures studied stationary and current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion.

Our main results are following:

1. For our study we have used the $CdGa_2S_4$ single crystals grown without preliminary doping by different impurities using two different techniques:

    I) by horizontal crystallization from the melts close to the stochiometric for ternary compounds,
    II) by gasphase transport reactions.

    From the measurements of the kinetic coefficients we established that without doping both techniques allows to obtain samples that showed n-type conductivity with very high specific electrical resistance $\rho \approx 10^9 - 10^{10}\ \Omega\cdot\mathrm{cm}$ at $T = 300\mathrm{K}$. The most high-ohmic samples are obtained by the gasphase crystallization technique. Estimations on the base of our measurements give the following values for the concentration $n \approx 10^8$ - 10^9 cm^{-3} and mobility $\mu_n \approx$ 1-10 см^2/(В с) at T=300 K. At the temperatures lower than the room temperature rapid increase of ρ does not allow to carry out temperature dependent measurements of $\rho(T)$ and $n\ (T)$.

2. Figure 1 shows spectrum of optical absorption $(\alpha\hbar\omega)$ for one of the n-$CdGa_2S_4$, on which was performed experiments on creation of the photosensitive structures. The beginning of an increase of the optical absorption at $\hbar\omega > 2.8$ эВ can be used for estimation of the energy band gap of the n-$CdGa_2S_4$ single crystals. As seen in the Fig. 2, in the coordinates of $(\alpha\hbar\omega)^{1/2} - \hbar\omega$ the $\alpha(\hbar\omega)$ the spectrum exhibits linear behavior, which by taking into account the theory of the interband optical transitions in semiconductors [1] can be interpreted as the indirect interband optical transitions in the n-$CdGa_2S_4$ single crystals grown by the both crystallization techniques used.

3. We have established that mechanical contact of pure metal layers of (In, Ag and Cu) with the cleaved surface of the $CdGa_2S_4$ single crystals as well as with freshly cleaved surface of the electrically homogeneous $CdGa_2S_4$ independently of the growth techniques used, show sharp rectifying characteristics (Fig. 3). The maximum value of the rectification was obtained when In as a barrier contact was used. The maximum value of the rectification coefficient determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 10$ - 20 V, reaches the values $K \approx 15$ at $T = 300$ K.

   In the bias range $U > 10$ - 15 V the current-voltage characteristics follow to the linear law

   $$I_{dir} = (U - U_0) / R_0, \qquad (1)$$

   Where the residual resistance without illumination of the structure $R_0 \approx (3\text{-}5)\ 10^8\ \Omega$ at $T = 300$K. The falls up to $R_0 \approx (6\text{-}8)\ 10^5\ \Omega$. The reverse current at the bias $U \approx 5$ V $I_{rev} \sim U_{rev}^{\gamma}$, where $\gamma \approx 1.1$ in the range $U_{rev} < 10$ V and increases with increasing of the reverse bias. This value indicate influences of the nonperfect periphery of the first structures and solving the problems of their doping may allow further essential improvement of the surface-barrier structure characteristics on the base of n-$CdGa_2S_4$.

4. Under illumination of the surface-barrier structures on the base of n-$CdGa_2S_4$ the observed photovoltaic effect is connected with formation at the interface of the metal/semiconductor of potential barrier that cause the separation of the was also observed. The sign of photovoltage of the free motion in the surface-barrier structures on the base of n-$CdGa_2S_4$ single crystals always corresponded to the negative potential on the semiconductor. In this case, the sign of the photovoltage is independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. Therefore, the photosensitivity the structures developed is determined by the photovoltaic processes in the single energy barrier connected with the contact of semiconductor and metal studied. Maximum value of the voltage photosensitivity achieved for the surface-barrier In-n-$CdGa_2S_4$ structures is 100 V/W at T=300 K. Some of the typical spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier n-$CdGa_2S_4$ structures are given in the Fig. 4 and Fig. 5. It is well seen that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 1 – 4 eV. The spectra $\eta(\hbar\omega)$ are located in the short wavelength range $\hbar\omega > 2.2$ eV only in the case if as the substrate for the barriers used the n-$CdGa_2S_4$ crystals grown from the melt (Fig. 4 and Fig. 5). The latter can be induced by the higher value of defect concentration and, consequently, by absorption in the crystals obtained fro the gas phase. The spectral dependencies $\eta(\hbar\omega)$ of the surface barrier structures are very complicated (Fig. 4 and

Fig. 5). They contain many broad structures, maximum energy position of which and the values of the photoconversion strongly changes from structure to structure at $\hbar\omega < 2.7$ eV. For the many structures obtained on the base of the $CdGa_2S_4$ crystals grown from the melt close to the stekhiometric at the photon energy range $\hbar\omega > 2.8$ eV there exist sharp maximum at $\hbar\omega = 3.67$ eV that coincides with the energy of the direct interband transitions in this compound [3-5]. Note that some of these structures in the spectra $\eta(\hbar\omega)$ of the surface-barrier In-*n*-$CdGa_2S_4$ structures were observed in the studies of the energy spectra of local sates in this semiconductor by other authors [6-8]. The nature of these levels is not understood yet. Clarification of the situation requires detail analyze and revealing connections between these structures in the $\eta(\hbar\omega)$ spectra and growth conditions of growth as well as thermal treatments of the $CdGa_2S_4$ crystals. Observed different features in the $\eta(\hbar\omega)$ spectra of the investigated structures give base to consider application of the photoactive absorption spectroscopy for study energy spectra of local states, and, consequently, of crystal perfection of $CdGa_2S_4$.

5. So, for example, as seen from Fig. 5 in the surface-barrier structures obtained on the base of gasphase $CdGa_2S_4$ crystals using the same technology conditions at the photon energy range $\hbar\omega > 2.8$ eV in the η spectra always appears sharp cut-off of the photosensitivity that does not allow to study photosensitivity in the range of the direct optical transitions in this semiconductor. At the same time, from the Fig. 5 one may conclude that the contribution to the photoactive absorption in the impurity range for the sample grown by gasphase is higher than for the same type of surface-barrier structures for the samples obtained from the melt close to the Stochiometric.

   Our analyze shows that the long wavelength edge of the $\eta\hbar\omega$ spectra of the surface-barrier structures follows to the Fowler law that allows to connect it with photoemission of electrons into the semiconductor. From the extrapolation of the long wavelength part $\eta^{1/2}\to 0$ allows to obtain the energy height of In-n-$CdGa_2S_4$ structures $\varphi_B \approx 1.2$eV at T=300 K. Similar values of φ_B were obtained for the surface-barrier structures with Au and Cu layers.

   5. So, in our work, the problem of creation of the photosensitive structures on the base of *n*-$CdGa_2S_4$ crystals is solved and for the first time investigations of the photoelectrical properties have been performed. Our experimental results on the firstly obtained structures allow determining the main photoelectrical parameters of the structures as well as properties of new ternary $CdGa_2S_4$ semiconductor compound. It is established that the surface-barrier structures on the base of *n*-$CdGa_2S_4$ single crystals allow photogeneration in the wide spectral range of 1- 4 eV due to such a different on the nature processes as photoemission of nonequilibrium current carriers, optical transitions with participation of local states and interband indirect and direct optical transitions. As a result, it is also shown that the surface-barrier structures on the base of $CdGa_2S_4$ single crystals are interesting for different device applications for the short wavelength photoelectronics.

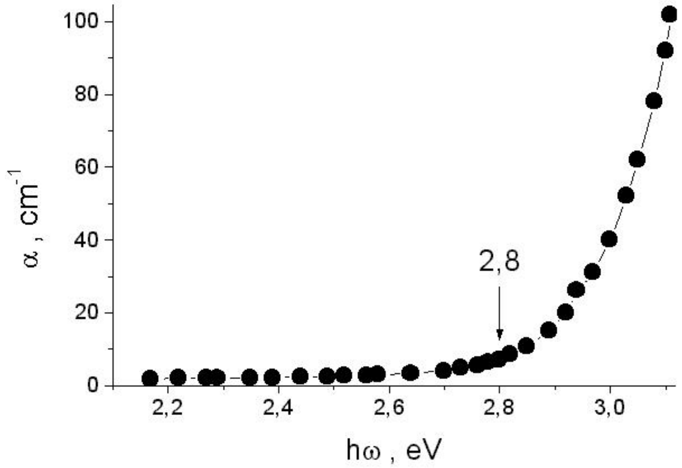

Fig. 1. Spectral dependence of the optical absorption coefficient for the $CdGa_2S_4$ single crystal at *T*=300 K in nonpolarized light (Sample No.11K grown from the melt. Thickness of the plate d≈0.5 mm).

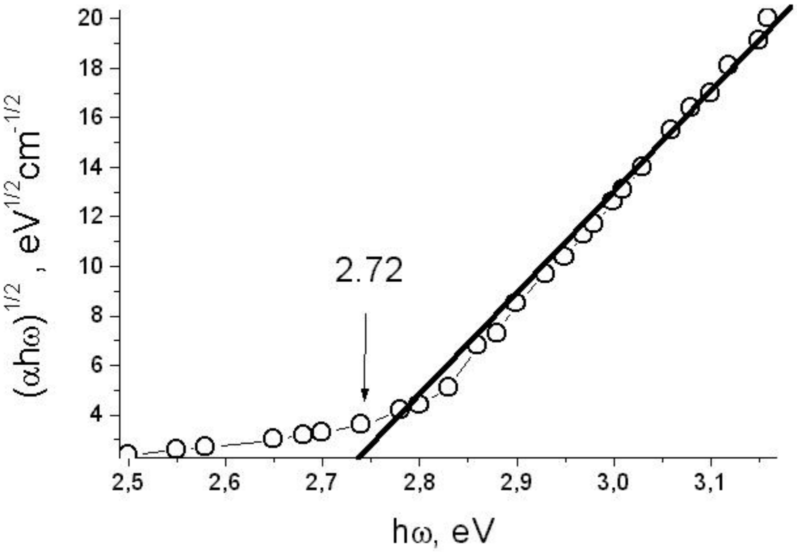

Fig. 2. Spectral dependence of the optical absorption coefficient in the coordinates of $(\alpha\hbar\omega)^{1/2} - \hbar\omega$ for the $CdGa_2S_4$ single crystal at *T*=300 K. (Sample No.11K Vertical arrow indicate the extrapolated value of photon energy).

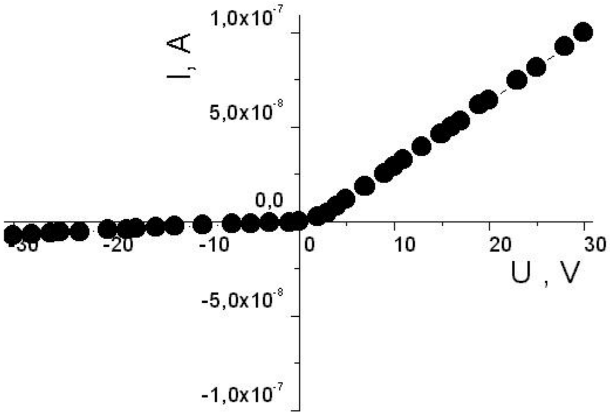

Fig. 3. Stationary current-voltage characteristic of In-*n*-$CdGa_2S_4$ surface-barrier structure at *T*=300 K (Sample 17K grown from the melt. Transmission direction is realized at the external positive bias at the barrier contact.).

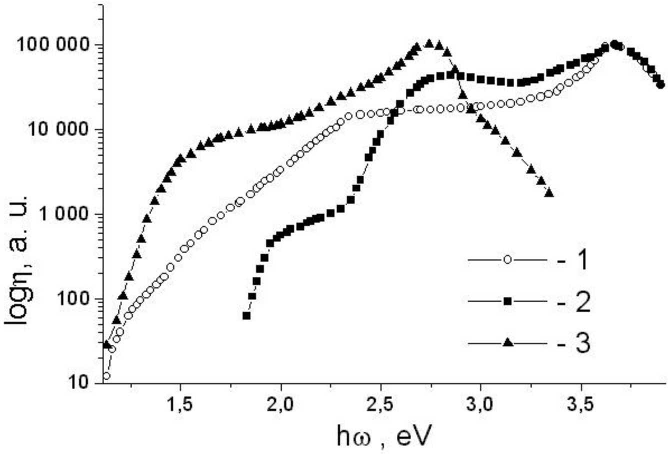

Fig. 4. Spectral dependencies of the relative quantum efficiency of photoconversion for the surface-barrier In-*n*-$CdGa_2S_4$ structures at *T* = 300 K in the nonpolarized radiation (Sample No.17K – curve 1, Sample No.19B – curve 2, Sample No.34SP – curve 3. The crystal is grown from the gasphase).

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According to the Work Plan we have conducted the Task 5:

Polarized photosensitivity measurements (in a temperature range from 77 to 300K) of surface barriers on In/$CdGa_2S_4$ and In/$HgGa_2S_4$.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ in the temperature range 77-300K.

C) Milestones Completed

The main efforts of our early experimental search was devoted toward the study of polarized photoluminescence (task 3) and stationary photosensitivity of homogeneous n-$CdGa_2S_4$ and n-$HgGa_2S_4$ single crystals. These pioneer investigations has allowed for the first time to analyze the anisotropy of the optoelectronic processes in such materials. However these experiments due to the influence of the surface recombination of photogenerated pairs and not sufficient perfection of these semiconductors do not allowed to observe the anisotropy of the photoactive absorption in the range of fundamental optical transitions of the $CdGa_2S_4$ and n-$HgGa_2S_4$ single crystals. Keeping in mind this aim we have obtained wideband-photosensitive structures of $CdGa_2S_4$ and $HgGa_2S_4$ (Task 5, Q9 and 10), that opened new possibilities for the first time to study photopleokhroism [1] in crystals with ordered vacancy.

The main results of the first investigations of the polarized measurements of the photosensitivity of surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ are following:

1. Our study of the photosensitivity of the surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ created on the oriented surfaces (100) and (001) on $CdGa_2S_4$ and $HgGa_2S_4$ wafers, has revealed the observation of the laws, characteristic for the anisotropic semiconductors in dependencies of the shortage current on the orientation of the vector of the electric field of the light wave relative to the tetragonal axes ***c*** of the preliminarly undoped $CdGa_2S_4$ and $HgGa_2S_4$ ternary compounds. Under conditions of illuminating such a structures by the linearly polarized radiation along the normal to the acceptance surface (001), the shortage photocurrent, as a rule, does not dependended on the space orientation of ***E.*** If one shines the structures from the acceptance surface (001), the photocurrent revealed the periodic dependence on the azimutal angle between ***E*** and ***c***, which known as the Malluse law [1]. These dependencies allow to make important conclusion that anisotropic semiconductor compounds $CdGa_2S_4$ and $HgGa_2S_4$ with ordered stochiometric vacancy show the phenomenon of the native photopleohroism, and azimutal dependencies for the surface-barrier structures correspond to the symmetry of unit cell of these compounds.
2. We have obtained the spectral dependencies of the relative quantum efficiency of photoconversion η(hw) of the oriented surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$.Under conditions of illumination of of surface-barrier structures In-n-$CdGa_2S_4$ from the side of semitransparent barrier layer in (d=0.1 mm) along the normal to the (001) surface $CdGa_2S_4$, the longwavelength edge of the relative quantum efficiency of photoconversion η(hw) in the range of indirect interband transitions exhibit the same polarization dependence as the coefficient of the optical absorption of the $CdGa_2S_4$. The dependence in the temperature range 80-300 K is connected with shift of the long wavelength part of the spectra η(hw) to the short wavelength part of the spectra with the transition from the polarization **Ec** to **E $\perp$ c,** why the inequality $\eta > \eta^{\perp}$ Is satisfied. Such an inequality is achieved for the In-n-$CdGa_2S_4$ structures, that fulfill the correspondence between the processes of optical absorption and photo conversion in the range of high absorption. Polarization splitting of the η(hw) spectra is ≈ 70 – 80 meV and may be due

to the lifting of the degeneracy in the free zone due to the high natural tetragonal distortion of the $CdGa_2S_4$ crystallic lattice.

In the range of indirect interband transitions in the $CdGa_2S_4$ the coefficient of natural photopleohroism P_N is positive and reach the maximum ≈50% near the photon energy hw ≈ 2.75 that is close to the energy of the interband transitions of the $CdGa_2S_4$ crystals (Fig. 1).

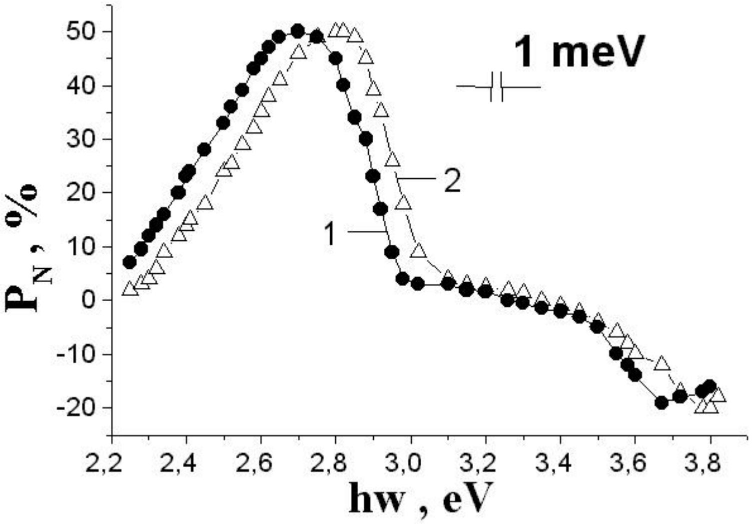

Fig. 1. The coefficient of natural photopleohroism in the range of indirect interband transitions of the surface-barrier structures In-n-$CdGa_2S_4$ at room temperature (1) and 80 K (2). The illumination of the structure is from the side of the barrier contact. The illumination surface of the $CdGa_2S_4$ is (100).

With increase of the photon energy in the range hw > 2.9 eV the coefficient of natural photopleohroism in the temperature range 80-300 K is fall dawn and is kept rather law ($P_N \approx$ 2-5%) until 3.4 eV that may be the result of concurrence between optical transitions with other side selection rules. And only with approaching to the energy of direct interband transitions $E_G^{dir} \approx$ 3.7 eV (T=300 K) is became an increase of the amplitude of the negative photopleohroism coefficient up to ≈20%. This experimental fact means that the direct interband transitions in the $CdGa_2S_4$ single crystals mainly are allowed in the $\mathbf{E} \perp \mathbf{c}$ polarization. Because there is not detailed theoretical calculations of the band structures $CdGa_2S_4$ single crystals it is impossible to perform a comparison.

It is important to note, that reduction of the temperature in the range from 300 to 80 K the spectral shape of the photopleohroism coefficient does not exhibit any changes, but only a shifts to the short wavelength range with a speed of $\approx 4 \cdot 10^{-4}$ eV/K that is typical value for tmemperature shift of the band gap for diamond like semiconductors [5].

The absence of the notable changes in th P_N(hw) spectrum and of the values of the P_N allows to conclude about the absence of a phase transitions in the $CdGa_2S_4$ in the temperature range 80-300 K.

3. We have obtained η(hw) spectra of the In-n-$HgGa_2S_4$, structures on oriented n-$HgGa_2S_4$ single crystals. Increasing of the photon energy up to hw≈2.3 эВ of the (100) oriented surface-barrier structures In-n-$CdGa_2S_4$ and In-n-$HgGa_2S_4$ leads to $\eta > \eta^{\perp}$ and to positive sign of $\Delta \eta = \eta - \eta^{\perp}$. And further, at the definite value of the photon energies the

Δ η crosses 0 and (photoisotropic point) and then in the range 2.4 – 3.8 eV is negative. This situation is the same for all obtained our In-n-$HgGa_2S_4$ structures.

Our analyze of η(hw) for linearly polarized radiation has shown that charcteristic for the indirect optical transitions dependencies $(\eta'^{\perp}\ hw)^{1/2}$ = f (hw) are less sensitive to the polarization and their extrapolation to the 0 gives equal for both polarizations the value of $E_G^{in} \approx 2.28$ eV (T=300 К), which is obtained from the analyze of the photosensitivity spectra for the unpolarized radiation. Transition from the polarization **E** ⊥ to **Ec** practically causes parallel shift of the η(hw) spectra to the short wavelength range of ≈80 meV. The analyze of these dependencies $(\eta'^{\perp}\ hw)^2$ = f (hw) has allowed to determine direct band gap $E_G^{nir} \approx 2.87$ eV (T=300 К) for **E** ⊥ **c** polarization and E_G^{nir} ≈2.95 ev for polarization **E c** . The reduction of the temperature in the range from 300 to 80 К the the grows of these parameters take plays with a speed of ≈ 4 · 10^{-4} eV/K for the both polarizations of the incident radiation.

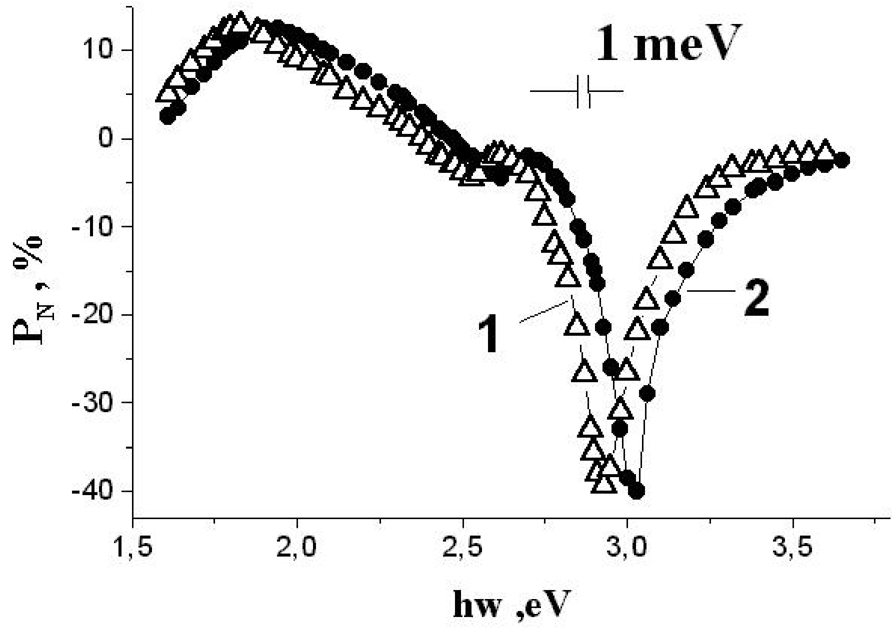

Fig. 2. The coefficient of natural photopleohroism in the range of indirect interband transitions of the surface-barrier structures In-n-$HgGa_2S_4$ at room temperature (1) and 80 K (2). The illumination of the structure is from the side of the barrier contact. The illumination surface of the $HgGa_2S_4$ is (100)

Fig. 2 shows the coefficient of natural photopleohroism in the range of indirect interband transitions of the surface-barrier structures In-n-$HgGa_2S_4$ at room temperature and 80 K. It is seen that reduction of the temperature practically does not influence to the shape of P_N(hw) spectra, but causes their shift to the short wavelength range with the same speed that was determined for the direct interband optical transitions. The sign of the P_N is positive only in the range of the nonintrinsic absorption of the n-$HgGa_2S_4$ crystals at hw <2.3 eV, while its inversion is observed with transition to to the short wavelength range hw>2.5 eV. The maximum of the negative coefficient of natural photopleohroism P_N is reached as in the case of the $CdGa_2S_4$ crystals at energies close to the energy of the E_G^{nir}. The same was early observed for the psevdodirect ternary $A^{II}B^{IV}C^{V}_2$ compounds with the chalcopyrite structure [1,6].

4. In conclusion, for the first time for the surface-barrier structures created on oriented single crystals of ternary compounds with ordered stochiometric vacancy $CdGa_2S_4$ and $HgGa_2S_4$ we have obtained spectra of the relative quantum efficiency of photoconversion for the linearly polarized radiation in the temperature range 77-300K.

$\eta(hw)$ in the range of indirect interband transitions exhibit the same polarization dependence as the coefficient of the optical absorption of the $CdGa_2S_4$. The dependence in the temperature range 80-300 K is connected with shift of the long wavelength part of the spectra $\eta(hw)$ to the short wavelength part of the spectra with the transition from the polarization **Ec** to **E ⊥ c,** why the inequality $\eta > \eta^{\perp}$ Is satisfied.

In conclusion, development of the polarized photoelectrical spectroscopy allowed for the first time to obtain photactive absorption in the range of direct interband transitions, to determine the energy and temperature coefficients for this transitions, as well as to observe the phenomenon of the natural photopleochroism. Our study revealed the possibility of application of the $CdGa_2S_4$ and $HgGa_2S_4$ in the polarized photoelectronics for the highly desired shortwavelength spectral range and demonstrated the further need for development of technological investigations on improvement structural perfection and sizes of these single crystal compounds.

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According to the Work Plan we have conducted the Task 6:

Temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of $CdGeAs_2$ *for determination mobility, concentration, activation energy of impurity level, and degree of compensation.*

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of $CdGeAs_2$ grown by low temperature crystallization.

The main efforts of our early experimental search were devoted toward the study of polarized photoluminescence and stationary photosensitivity of homogeneous n-$CdGa_2S_4$ and n-$HgGa_2S_4$ oriented single crystals. These investigations have allowed for the first time to analyze the anisotropy of the optoelectronic processes in such materials.

High values of résistance and low values of free carriers that are realized by using modern growth technologies do not allow performing detailed temperature dependent measurements of the kinetic coefficients – electroconductivity σ and Hall coefficient R. Therefore, for study temperature dependencies of the above kinetic coefficients we have measured another ternary anaisotropic compound - $CdGeAs_2$ with the chalcopyrite that is very close to the structure of n-$CdGa_2S_4$ and n-$HgGa_2S_4$ crystals with the structure of ordered stochiometric vacancy. And for this $CdGeAs_2$ crystal we have measured temperature dependencies $\sigma(T)$ and $R(T)$.

For our measurements $CdGeAs_2$ crystals were grown by low-temperature crystallization from solutions-solvents. All $CdGeAs_2$ crystals, grown by this technique, had well-developed shapes, characteristic for chalcopyrite compounds (space group D_{2d}^{12} [1]). Our x-ray diffraction measurements have shown that within the accuracy of the measurements the lattice parameters are close to $CdGeAs_2$, grown at the crystallization temperature close to the stochiometric ternary compound $CdGeAs_2$ melt [1,2].
Measurements of kinetic parameters are performed on the samples with dimensions of ~ 0.1 x 0.3 x 5 mm^3 in the low constant electric and magnetic fields ($E \leq 1$ V/cm, $H \leq 5$ ke). Current contacts to such a small samples were prepared by welding of pure indium and potential contacts were created by electric discharge with 50 μm diameter platinum wires near the mechanically and chemically polished surfaces of the $CdGeAs_2$ crystal surfaces. Connections of the wires were made without destroying surface quality of the crystal. The quality of such contacts were sufficiently high and withstand thermal cycling at the temperature range 300-77 K. Measurements of the potentials were performed by compensating technique.

The accuracy of measurements of the kinetic coefficients – electroconductivity σ and Hall coefficient R nor exceeded 3 and 5%, respectively.

Our measurements have shown that used growth technique of the $CdGeAs_2$ crystals allows to obtain electrically uniform samples with n-type conductivity without preliminary doping.

Table 1 demostrate the size of electrically homogeneous samples and measured values of electroconductivity σ and Hall coefficient R nor exceeded 3 and 5%, respectively at $T =$ 300 and 77 K. The spread of the values of the potential at the zounds were not exceeded 3%.

Table 1.

Electrical properties of n-$CdGeAs_2$ crystals at $T =$ 300 and 77 K.

No	Dimensions	300 K		77 K	
	Mm	σ $\Omega^{-1} \cdot cm^{-1}$	R cm^3/Q	σ $\Omega^{-1} \cdot cm^{-1}$	R cm^3/Q
1п	0.12x0.25x4.5	2950	3.85	5000	6.83
3п	0.20x0.40x5.0	2830	3.53	5120	6.60
4п	0.23x0.35x5.5	2760	3.61	5100	6.51
5п	0.15x0.32x4.2	2870	3.35	5200	6.35
7п	0.17x0.30x3.0	2580	3.88	4900	6.53
10п	0.11x0.25x4.1	2820	3.55	4980	7.03

Note, that samples grown by the generally used technique of direct crystallization close to the stochiometric ternary compound $CdGeAs_2$ melt show only p-type conductivity and high electric inhomogeneity [3]. As a result at the nitrogen temperatures measurements of the Hall coefficients became impossible due to the coexistence of areas with n- and p-type conductivity. The high electrical conductivity iindicated also by a very low magnetoresistense (less then 0.01 % at magnetic fields up to 15 кe).

Therefore, by extrapolating obtained results to the $A^{II} B^{III}_2 C^{VI}_4$ compounds it is possible to conclude that such properties as

i) low concentration of free carriers,
ii) low mobility of charge carriers,
iii) noncontrolled type of conductivity, and
iv) existence of deep levels,

need to connect with the fact that currently used technique does not allow to solve needed in such cases problem of control the deviations from the stochiometry that is the main reason of observed fixed level of semiconductor parameters of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals.

One of the most actual technology directions of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals is to find new ways of considerable reduction of a crystallization temperature of these ternary chalcogenids that will allow to decrease concentration of the lattice defects of nonstochiometric nature.

Typical temperature dependences R(T) and $\sigma(T)$ for one of the sample is shown in Fig.1.

Figure 2 shows typical experimental temperature dependence for Hall mobility $\mu_n(T)$ and in Fig. 3 we present comparison of experimental data with calculated results $\mu_n(T)$ for different scattering mechanisms.

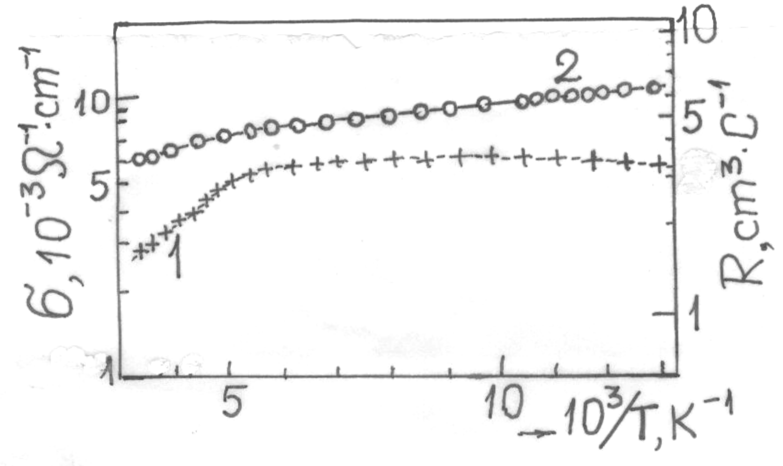

Fig.1. Temperature dependences for specific conductivity (curve 1) and hall coefficients (curve 2) for n-$CdGeAs_2$ single crystal sample grown by low temperature crystallization (Sample 10n).

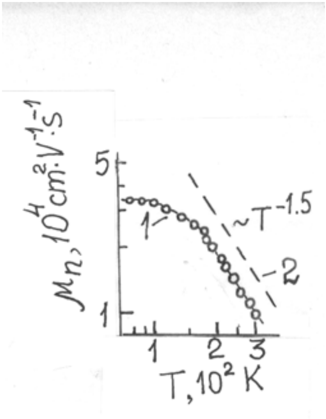

Fig.3. Experimental Temperature dependences for for Hall mobility μ_n(T) (curve 1) for n-$CdGeAs_2$ single crystal sample grown by low temperature crystallization (Sample 10n). Theoretical data μ_n(T) (curve 2) calculated for the case of the scattering by lattice vibrations.

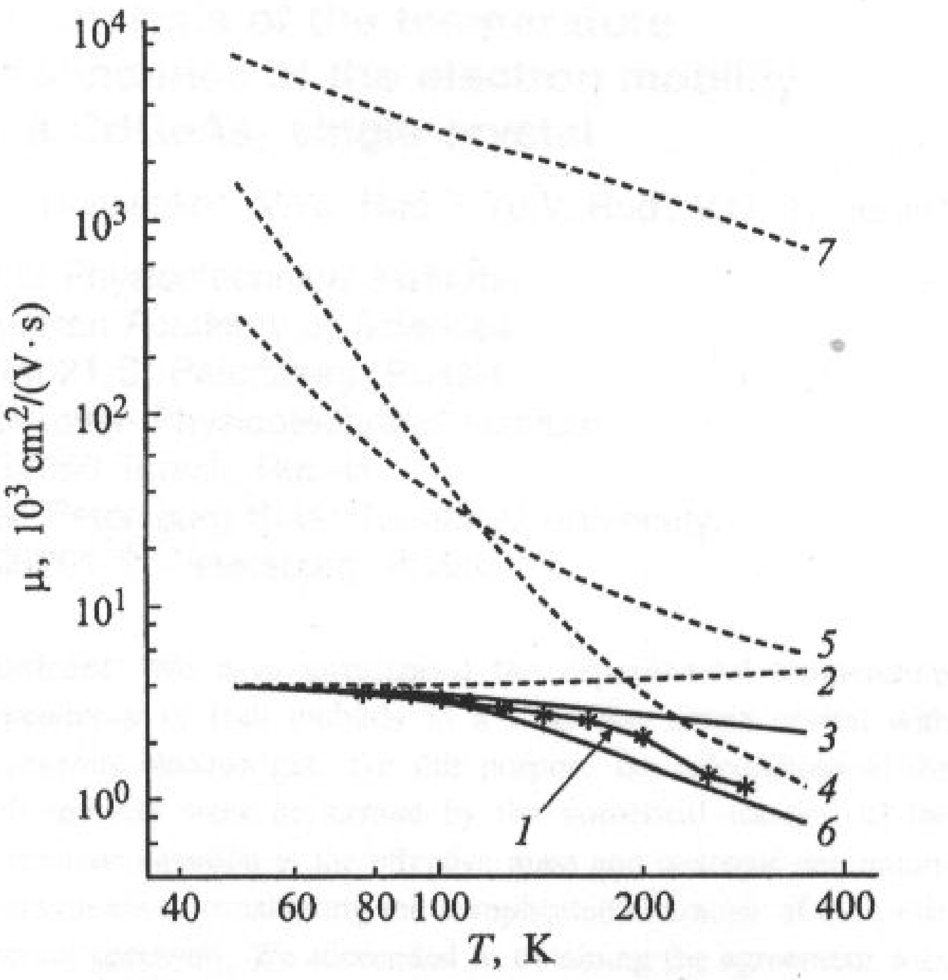

Fig.3. Experimental (curve 1) and calculated dependences $\mu_n(T)$ for n-$CdGeAs_2$ single crystal sample calculated for the case of the scattering: on impurity ions (curve 2), ions and polar optical phonons (curve 3), plasma vibrations (curve 4), polar optical phonons (curve 5), ions, polar optical phonons and plasma vibrations (curve 6), and acoustic vibrations (curve 7).

III. ATTACHMENTS

V. Summary of personnel commitments for the 3d year

Category I – 212 days and Category II – 303 days.

VI. Equipment acquired during the year.

No equipment was acquired.

IV. SIGNATURES

Deputy Director

Ioffe Physico-Technical Institute V. A. Dergachev

Project Manager Yu. V. Rud'

08/31/04