# Birefringence and Excitonic Spectra of $CdGa_2S_4$ Crystals

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***Abstract* — The spectral dependence of $\Delta n = n_o - n_e$ of $CdGa_2S_4$ crystals in short- and long- wavelength part of isotropic wavelength $\lambda_0 = 485.7$ nm (300 K) was determined. It was established what in the case when $\lambda > \lambda_0$ $\Delta n$ is positive and at $\lambda < \lambda_0$ it is negative. The wavelength $\lambda_0 = 485.7$ nm shifts in short - wavelength at decreasing of temperature. Ground and excited states of three excitonic series (A, B and C) with binding energies of 53 meV, 52 meV and 46 meV, respectively were found out at 10 K. The effective mass of electrons for k = 0 was determined form calculation of excitonic spectra ($m_c^{\parallel}$ (E||c) = $0.21m_0$ and $m_c^{\perp}$ (E⊥c) = $0.19m_0$). The holes masses are equal to $0.59m_0$, $0.71m_0$ and $0.71m_0$, respectively. The value of valence bands $V_1$ - $V_2$ splitting by crystalline field is corresponding to 24 meV and bands $V_2$ - $V_3$ splitting due to the spin-orbital interaction is equal to 130 meV.**

***Index Terms* - semiconductor compound; optical constants; birefringence; excitons.**

## I. INTRODUCTION

Thiogallate cadmium crystals $CdGa_2S_4$ belong to wide class of triple chalcogenides compounds $A^{II}B_2^{III}C_4^{VI}$. The optical properties of such compounds mainly were investigated for $CdGa_2S_4$, $CdGa_2Se_4$ and $PbGa_2S_4$ crystals [1 - 4]. The birefringence properties of cadmium thiogallate were considered in Ref. [3]. The ground states of long-wavelength excitons were found out in spectra of modulated reflection [4]. The optical properties and band structure of $CdGa_2S_4$ crystals were investigated [2 – 4]. The crystals of such group used in nonlinear devices and optical filters [3].

The results of investigation of birefringence effect, anisotropy of excitonic states and calculation of excitonic reflection spectra in $CdGa_2S_4$ crystals are represented in this work. The parameters of excitons and bands, electron and hole effective masses, values of splitting owing to crystal field ($\Delta_{cr}$) and spin-orbital interaction ($\Delta_{so}$) of upper valence bands in Brillouin zone center were determined.

## II. EXPERIMENTAL DETAILS

The bulk crystals of $CdGa_2S_4$ were grown by the Bridgman method and had sizes 1x3 cm. Crystals grown in ampoules by gas transport method exhibit plates with mirror surfaces 2.5x10 mm and thickness 3 - 4 mm. Surfaces of some plates were parallel with crystal axis c. Low temperature spectra of crystals deposed in a LTS-22 C 330 optical cryogenic system were measured on MDR-2 monochromator. Reflectivity spectra in diapason 2 – 6 eV at room temperature were measured on SPECORD-M40 and JASCO-670 spectrometers. Systems of optical measurements are computerized.

## III. RESULTS AND DISCUTIONS

The characteristic feature of cadmium thiogallate ($CdGa_2S_4$) is the refractive indexes $n_0$ and $n_e$ dispersion near absorption edge, which due to band structure. Selection rules of electron transitions describe character (allowed or forbidden) of these transitions. Values of absorption and dielectric constant in corresponding polarizations depend on these rules, and therefore a sign of birefringence. These features lead to rapid increasing of one refractive index during approaching to fundamental absorption edge. Thereby the anisotropy of interband edge absorption describes in correspond polarizations. In cadmium tiogallate crystals also the intersection of dispersion curves (isotropic point IP) in long-wavelength part from absorption edge are observed. The experimental investigation of spectral dependence of absorption coefficient in different polarization (E||c and E⊥c) really shows what near the IP $\alpha_{\parallel}$ and $\alpha_{\perp}$ ($\alpha$ – absorption coefficient) became almost equal to each other. And in polarization E⊥c the feature in form of absorption line and in polarization E||c in form of transmission line are observed [7]. Exploring the dispersion of birefringence of $CdGa_2S_4$ crystals by the interference of polarized beams in Ref. [3, 7] was established what the isotropic wavelength is $\lambda_0 = 4909$ Å. At transition over wavelength $\lambda_0 = 4909$ Å the birefringence changes a sign, i.e. from optical positive in spectral range $\lambda < \lambda_0$ the crystal become optical negative at $\lambda > \lambda_0$.

In transparent region of crystal the absorption is low and it determined by some mechanisms such as the natural optical activity or polarized local absorption bands on impurities, defects etc. The existence in crystal two types of waves (ordinary and extraordinary) with two refractive indexes $n_o$ and $n_e$ are determined by dielectric conductivity tensor of crystal $\varepsilon(\omega, \mathbf{k})$, which depends on frequency $\omega$

and wave-vector ***k***. The spatial dispersion, i.e. dependence of dielectric constant on wave-vector, calls forth an appearance of nondiagonal element $\varepsilon_{zz}$ of dielectric conductivity tensor. Thus many anisotropic crystals have refractive indexes $n_o > n_e$ in edge absorption region and $n_o < n_e$ in transparence region. The inverse dependence is possible too. Reciprocally perpendicular light wavelength with refractive indexes $n_o$ and $n_e$ can interfere in crystal.

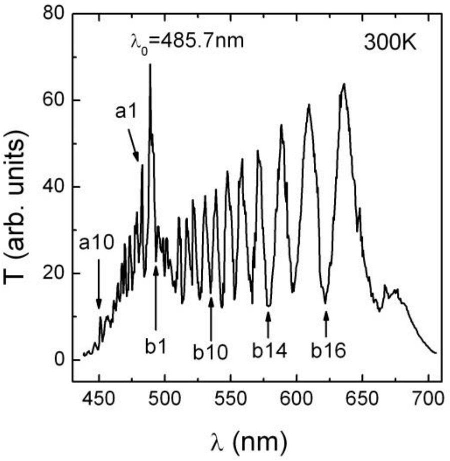

Fig. 1. The interference spectra of transmittance of $CdGa_2S_4$ crystals deposed between crossed polarizers measured at 300K.

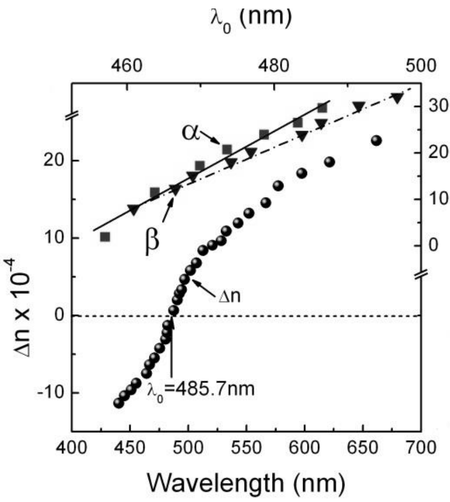

Fig. 2. The temperature dependence of line $\lambda_0$ position ($\alpha$ – results of current work and $\beta$ – results of authors Ref. [3, 7]) and the spectral dependence of $\Delta n = n_o - n_e$ calculated from interference spectrum at crystal thickness $d$ = 4.8 mm.

In transmission spectra T of crystals $CdGa_2S_4$ in parallel beam of crossed polarizators (when c axis of crystal parallel to polarization of one of polariztors) are observed a narrow transmission band localized at $\lambda_0$ = 485.7 nm (fig.1). In the case of unidirectional polarisers in the same spectral diapason a narrow absorption line is observed. The interference is observed in transmission spectra measured at 300 K of crystals $CdGa_2S_4$ deposed between crossed polarizers in convergent beams (fig. 1). The amount of side maxima can be reduced and the maximum at $\lambda_0$ wavelength can be extracted by changing of crystal thickness.

Fig. 2 shows a temperature dependence of $\lambda_0$ for crystals investigated in current work (curve - $\alpha$) and results reported in Ref. [3, 7] (curve - β). According data form Ref. [3, 7] the isotropic point was observed at 490.9 nm in $CdGa_2S_4$ crystals. Authors of article mentioned that the spectral position of IP $\lambda_0$ and rotary ability of $CdGa_2S_4$ depend on technology of crystal growth (temperature, pressure etc.). The light passed through crystal at $\lambda_0$ remains linear polarized. This means that the interaction of circular polarized waves in opposite directions takes place. These waves after passing the crystal acquire a phase difference, which determined by value of rotatory power $\rho$ of crystal. This leads to appearance of interference. The spectral dependence of $\Delta n = n_o - n_e$ were calculated for investigated crystals from interference lines a1 – a11 and b1 – b17 taking into account the sample thickness $d$ = 4.8 mm (Fig. 2).

CdGa2S4 crystals possess a natural opticity. For symmetry reasons the optical activity along c axis of CdGa2S4 crystal is absent and become evidence only along directions perpendicular to optical axis, there it is weaker then linear birefringence. For this reason the presence of λ0 gives a possibility to observe the gyrotropy CdGa2S4 per se. Authors of Ref. [3, 7] estimated a value of rotatory power of polarization plane at propagation light along [100] direction near λ0 = 4909 Å and it corresponded 16.87 grad/mm. At crystal thickness increasing the nearest to transmission band minima (maxima) of interference shift to each other and join into one minimum (maximum) localized at wavelength $\lambda_0$ if the thickness of sample reach $d$ ~ 10 mm as reported in Ref. [3]. The interference pattern binds with the condition, that at moving away from $\lambda_0$ the linear birefringence appears and optical activity reveals as elliptic birefringence.

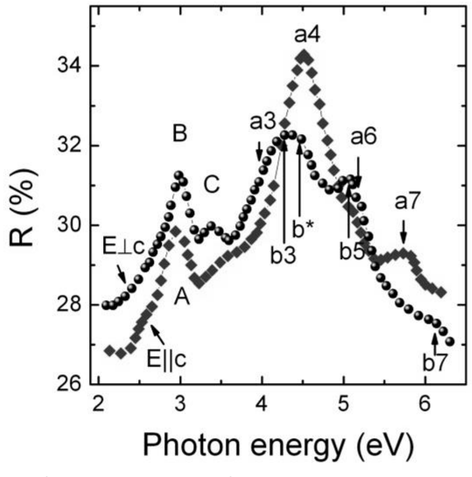

Fig. 3. Reflection spectra of $CdGa_2S_4$ crystals in E||c and E⊥c polarizations measured at temperature 300 K

Maxima at energies 3.561 eV (A) and 3.598 eV (B) in reflection spectra of $CdGa_2S_4$ crystals near the minimum of interband gap in polarized and nonpolarized light at 300 K were found out. The maximum A is revealed in E||c polarization and his contour changes in limits of 26 – 31 % at 300K. In polarization E⊥c the maximum B is observed and its contour changes in limits of 28.5 – 32.5 %. Also the weak maximum C is observed on Fig. 3. In high-energy region maxima a3 – a7 and b3 – b7 are found out in E||c and E⊥c polarizations, respectively.

Contours of reflection spectra A, B and C at temperature reduction to 10 K have a typical for excitons shape. In spectra of modulated reflection only energy positions of main states at energies 3.735 eV (A), 3.747 eV (B) and 3.81 eV (C) were found out [4]. The fig. 4 shows reflection spectra of $CdGa_2S_4$ in polarizations E||c and fig. 5 and 6 show spectra in polarization E⊥c measured at 10 K.

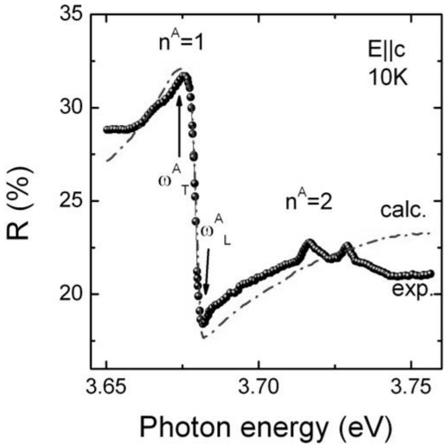

Fig. 4. Reflection spectra of $CdGa_2S_4$ in polarizations E||c measured at 10K (A – exciton).

The line at 3.676 eV and a weaker line at 3.716 eV were revealed in interband gap minimum of reflection spectra of $CdGa_2S_4$ measured at temperature 10 K. Reflection spectra in this region have a traditional for excitons shape with maximum and minimum. The maximum of reflection spectra at 3.676 eV is a ground state n = 1 and the maximum near 3.716 eV is an excited state n = 2 of long wavelength excitonic series A (marked as A). Also in reflection spectra singles out a minimum at 3.679 eV. These features cause by transversal (maxima) and longitudinal (minima) excitons. The energy of longitudinal-transversal splitting $\Delta\omega_{LT}$ of A exciton ground state was estimated as ~ 3 meV.

The intensive maximum at 3.691 eV and weaker maximum at 3.729 eV were found out in short-wavelength part from excitonic series A in reflection spectra measured in E⊥c polarization. These lines belong to ground state n =1 and excited state n = 2 of B exciton. The minimum of reflection at 3.696 eV marks out in spectra, it due to the energy of longitudinal excitton B. The longitudinal-transversal splitting of ground state of B exciton is equal to 5 meV, it is more then for A exciton (3 meV).

Maxima at 3.814 eV and 3.864 eV observed in short wavelength belong to ground n = 1 and excited n = 2 states of C excitonic series. Taking into account energy position of lines n = 1 and 2 in reflection spectra for E||c polarization was determined Rydberg constant (R) of free A exciton (53 meV). The convergence limit of A excitonic series Eg = 3.729 eV. In E⊥c polarization on the base of discovered maxima 3.691 eV ($n^B$ = 1), 3.729 eV ($n^B$ = 2) the binding energy R of excitons equal to 51 meV and band gap equal to 3.742 eV were determined. In the case of C exciton we have next values binding energy 46 meV and continuum energy 3.860 eV

The fitting of excitonic reflection spectra was executed on the base of well know dispersion equations of exciton-polaritons detailed expounded in Ref. [5].

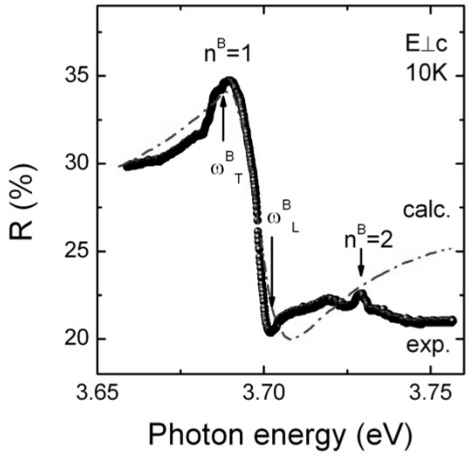

Fig. 5. Reflection spectra of $CdGa_2S_4$ in polarizations E⊥c measured at 10K (B – exciton).

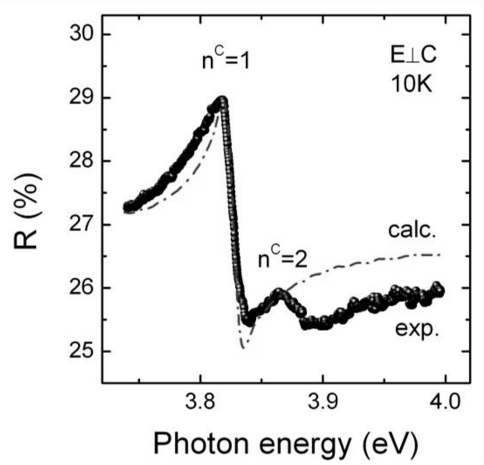

Fig. 6. Reflection spectra of $CdGa_2S_4$ in polarization E⊥c measured at 10K (C - exciton).

The reduced effective mass was calculated according formula: $\mu = \varepsilon_b^2 R/R_H$, where $R_H$ - Rydberg energy of hydrogen atom (13.6 eV). At calculation of contours of excitonic reflection spectra were used a value of background dielectric constant $\varepsilon_b$ near the excitonic resonances A, B and C equals to 6.0, 5.9 and 5.8, respectively. At such values of $\varepsilon_b$ the reduced effective mass μ was equal to $0.14m_0$, $0.13m_0$ and $0.11m_0$ for A, B and C excitons, respectively (see. Table 1).

Calculated parameters were fitted by the best coincidence of experimental and calculated curves of reflection spectra. Fig. 7 shows a calculation of reflection spectra contours for excitonic series A and B measured in nonpolarized light and calculated according two-oscillator model. The received data were corrected by one-oscillator model calculation for E||c and E⊥c polarizations (see fig. 4, fig. 5. and fig. 6). The exciton translation mass and electron and hole masses were estimated form reflection spectra calculations. The received results are represented in Table 1.

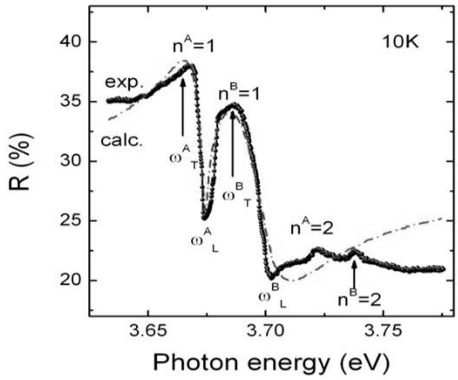

Fig. 7. The reflection spectra of $CdGa_2S_4$ crystals in nonpolarized light measured at 10 K. exp. is a measured and calc. is a calculated by dispersion equations spectra.

Table 1. The exciton and the free carrier mass band parameters deduced from the fits of the reflectivity spectra for $CdGa_2S_4$ crystal.

| | | A (eV), E\|\|c | B (eV), E⊥c | C (eV), E\|\|c | $\Delta_{cf}$ (meV) | $\Delta_{so}$ (meV) |
|---|---|---|---|---|---|---|
| Exciton state | $n = 1$<br>$n = 2$<br>$\omega_{LT}$ | 3.676<br>3.716<br>1.6 | 3.691<br>3.729<br>2.8 | 3.814<br>3.864<br>2.5 | 24 | 130 |
| $R$ | | 0.053 | 0.051 | 0.046 | | |
| $Eg\ (n = \infty)$ | | 3.729 | 3.742 | 3.860 | 21 | 123 |
| $\varepsilon_b$ | | 6.3 | 6.3 | 6.6 | | |
| $\mu^*, m_0$ | | 0.15 | 0.14 | 0.14 | | |
| $M, m_0$ | | 0.8 | 0.9 | 0.9 | | |
| $m_c^*, m_0$ | | 0.21 | 0.19 | 0.19 | | |
| $m_{v1}^*, m_0$ | | 0.59 | | | | |
| $m_{v2}^*, m_0$ | | | 0.71 | | | |
| $m_{v3}^*, m_0$ | | | | 0.60 | | |

The value of translation mass M = $0.8m_0$ for A exciton was received from calculation of reflection spectra in E||c polarization. Effective masses of electrons ($m_{c1} = 0.21m_0$) and holes ($m_{v1} = 0.59m_0$) were determined also for k = 0 taking into account received background dielectric constant and binding energy in given polarization. For polarization E⊥c the translation mass of B exciton was equaled to $0.9m_0$. In consideration what binding energy equals to 51 meV and background dielectric constant equivalent to 6.3 effective masses of electrons ($0.19m_0$) and holes ($0.71m_0$) were determined. These values have a good correspondence with values from Ref. [6] ($m^{||}_c = 0.214m_0$, $m^{\perp}_c = 0.198m_0$ и $m^{||}_h = 0.381m_0$ $m^{\perp}_h = 0.77m_0$). The temperature shift $\beta = \Delta E/\Delta T$ of bands $V_1$ - $C_1$ is equal to $3.97\text{x}10^{-4}$ eV/K and for bands $V_2$ - $C_1$ it correspond to $3.21\text{x}10^{-4}$ eV/K. According data of Ref. [6] = $2.44\ \text{x}10^{-4}$ eV/K for couple of bands $V_1$ - $C_1$. Temperature shifts of bands $V_1$ - $C_1$ и $V_2$ - $C_1$ were determined due to the fact what excitonic maxima in reflection spectra were found at low and room temperatures out. The pronounced anisotropy of optical spectra both in excitonic region and in region of lattice dynamics was discovered in lead thiogallate crystals. In lead thiogallate crystals excitonic maxima at room temperature have a bigger binding energy (291 meV) in comparison with cadmium thiogallat and due to Frenkel excitons.

## CONCLUSION

The series of interference lines near wavelength $\lambda_0$ = 485.7 nm (300K) in transmission spectra of $CdGa_2S_4$ crystals deposed between crossed polarizers was found out. It shifts to short wavelength at temperature decreasing. The spectral dependence $\Delta n = n_o - n_e$ was determined and it was ascertained what in the case then $\lambda > \lambda_0$ $\Delta n$ positive and at $\lambda < \lambda_0$ $\Delta n$ negative. The narrow-band filters and gradient filters can be produced on the base of $CdGa_2S_4$ crystals.

Ground and excited states of three excitonic series A, B and C were found out in $CdGa_2S_4$ crystals at 10 K. Contours of excitonic reflection spectra were fitted and main parameters of excitons and bands for k = 0 were calculated by dispersion equations. In Γ point of Brillouin zone effective mass of electrons $m_c$ is equals to $0.15m_0$, and holes masses $m_{v1}$, $m_{v2}$, $m_{v3}$ are equal to $0.59m_0$, $0.71m_0$ and $0.71m_0$, respectively. The band splitting by crystal field of valence bands $V_1$ - $V_2$ and by spin-orbital interaction of bands $V_2$ - $V_3$ were determined and equal to 24 meV and 130 meV, respectively.

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