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Excitonic Polaritons and Electronic Band Structure of $CdAl_2S_4$ Single Crystals

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Abstract

Reflection and wavelength modulated reflection spectra were investigated at temperature 10 K in $CdAl_2S_4$ crystals. Ground and excited states of three excitonic series (A, B and C) were found out. Contours of excitonic reflection spectra were calculated and main parameters of excitons and bands in k = 0 were determined. The effective mass of electrons m_c is equal to $0.30m_0$ and holes masses m_{v1}, m_{v2} and m_{v3} are equal to $1.55m_0$, $0.90m_0$ and $2.07m_0$, respectively in Γ point of Brillouin zone. Valence bands V_1 - V_2 splitting due to crystal field (141 meV) and bands V_2 - V_3 splitting by spin-orbital interaction (152 meV) were estimated. Spectral dependences of optical functions (n, k, ε_1 and ε_2) were determined by Kramers-Kronig analysis of reflection spectra measured at energies 3 - 6 eV and in E⊥c and E∥c polarizations. Energies of direct electron transitions were determined and identified in the actual points of Brillouin zone in the framework of actual band structure theoretical calculations of $CdAl_2S_4$.

1. Introduction

The $CdAl_2S_4$ crystals belong to the class of triple chalcogenide $A^{II}B_2^{III}C_4^{VI}$ compounds [1]. Compounds of this class are formed to crystalline lattice of different space groups. Compounds $CdGa_2S_4$ and $CdAl_2S_4$ are the most wide-gap crystals of the abovementioned group [1]. Changing of Ga cation on Al one leads to the gap increasing from 3.7 eV to 4.5 eV, but crystal lattice symmetry (S_4^2) does not change. The substitution of the Gacation by In one leads to the changing not only the band gap but also to the crystal symmetry change. The $CdIn_2S_4$ compound crystallized as a spinel with band gap (E_g) 2.24 eV [1].

Optical properties and an energy band structure of $CdAl_2S_4$ crystals in the region of edge absorption were investigated by authors of Refs. [2, 3]. A dynamic of crystal lattice was examined in detail in Ref. [4 - 7]. The phonon-polaritons investigation was discussed in Ref. [8], and the influence of pressure on Raman spectra was investigated in Ref. [9]. Especially interesting results were received at the birefringence and gyration investigation of a cadmium thiogallate [10, 11]. The main states of long-wavelengths excitons in wavelength modulated reflection spectra were found out [12]. Crystals of this group were usually used as optical filters [10, 11] and different devices in nonlinear optics [13-15].

This work dedicates to investigations of optical spectra anisotropy in excitonic region and in the absorption depth of CdAl$_2$S$_4$ crystals. Calculations of excitonic reflection spectra contours were effectuated. Parameters of excitons and bands i.e. effective masses of electrons and holes, values of splitting dye to crystal field (Δ_{cr}) and spin-orbital interaction (Δ_{so}) of the top valence bands in Brillouin zone center were determined. Optical functions (n, k, ε_1 and ε_2) for energies 3 - 6 eV were calculated. Features of abovementioned optical functions were discussed in frameworks of the theoretically calculated band structure of thiogallate group crystals.

2. Experimental Methods

The CdAl$_2$S$_4$ crystals were grown from the gas phase in a pumped closed ampoule. Temperature in a source zone exceeds on 100 -150 K the temperature in a deposition zone (600 K). Crystals were the plates with mirrored surfaces (2.5x10 mm) and thickness 3 - 4 mm. Surfaces of plates were parallel to c axis. A composition and crystal quality were controlled by x-ray microscopy.

Low-temperature spectra of crystals deposed in the closed helium LTS-22 C 330 optical cryogenic system were measured on a MDR-2 spectrometer and on a double high-aperture SDL-1 spectrometer with a linear dispersion of 7 Å/mm and an aperture ration of 1:2. The optical system is allowed to register spectra with a spectral width of

spectrometer slit of 0.02 Å (±0.01 meV). Reflection spectra were registered with accuracy of ±0.2 meV and wavelength modulated reflection spectra with accuracy ±0.5 meV. Reflection spectra for energies 2 - 6 eV were measured on Specord-M40 spectrometer with accuracy ±0.5 meV. All measurement systems are computerized.

3. Experimental Results and Discussions

3.1. Excitons in CdAl$_2$S$_4$

A characteristic peculiarity of A^{II}B$_2^{III}$C$_4^{VI}$ crystals is refractive indices n$_o$ and n$_e$ dispersion near the absorption edge, which is due to features of band structure. Selection rules of electron transitions determine their character (allowed or forbidden). Values of absorption and dielectric constant in respective polarizations depend on these rules and thus the sign of birefringence depends too. These features lead to the quick growth of one of refractive indices at approaching to the edge of intrinsic absorption. The anisotropy of fundamental absorption edge of the crystal in corresponded polarizations was determined by this fact. For example the intersection of dispersion curves (isotropic point - IP) in CdGa$_2$S$_4$ crystals was observed at long-wavelengths from absorption edge.
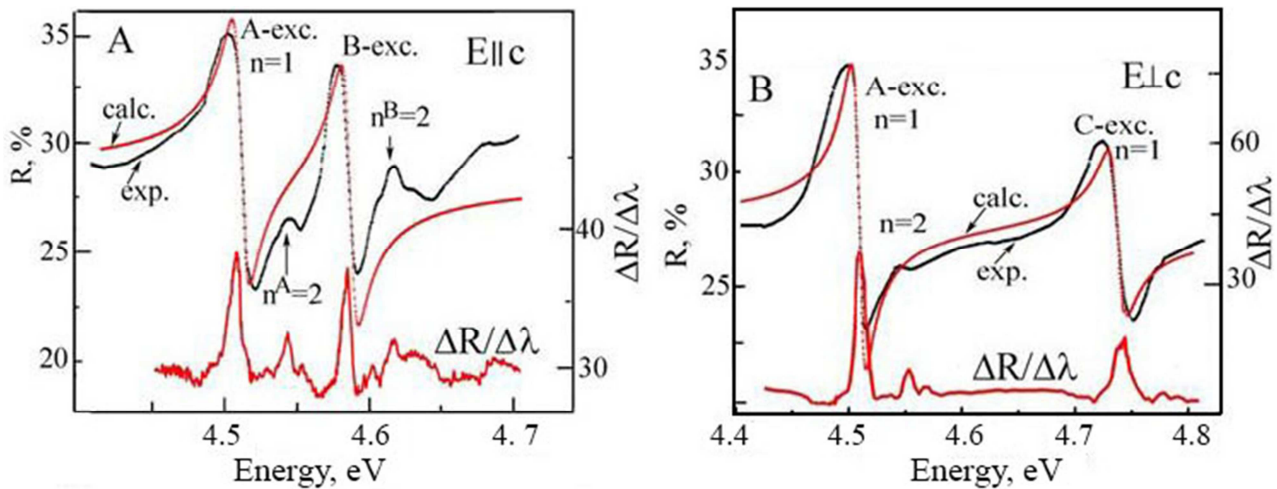
Figure 1. *Experimental (exp.) and calculated (calc.) reflection spectra and wavelength modulated reflection spectra in E∥c (A) and E⊥c (B) polarizations measured at temperature 10 K.*

Intensive lines at energies of 4.503 eV and 4.565 eV ascribing to the ground states of A and B excitonic series were discovered in reflection spectra of CdAl$_2$S$_4$ crystals at 10 K in E∥c polarization (see Figure 1). Weaker lines at energies of 4.540 eV and 4.604 eV are the excited states (n = 2) of the same excitons. Maxima at energies 4.504 eV and 4.736 eV were observed in reflection spectra in E⊥c polarization. The shape of these lines has a traditional excitonic form with maxima and minima. Weaker features at 4.740 eV and 4.976 eV are observed in short-wavelength region. The maximum of reflectivity at 4.504 eV is a ground

state n = 1 and maximum at 4.540 eV is an excited state n = 2 of long-wavelength excitonic series (for convenience indicated as A). Maxima 4.736 eV and 4.776 eV are the ground and excited states of C excitonic series, respectively. Reflectivity spectra have a well produced maxima and minima. These features are caused by presence of transversal (maxima) and longitudinal (minima) excitons. On the base of these data the energies of longitudinal-transversal splitting of A, B and C excitons ground states (ω_{LT}) were estimated (they change in limits 3.7 - 4.6 meV, see Table 1).

The longitudinal-transversal splitting of A exciton ground

state is more than its for B exciton, and it is equal to 4.1 meV in comparison to 3.7 meV. It should be noted that the excitonic series A is observed in both polarizations E‖c and E⊥c (Figure 1). Maxima at energies of 4.736 eV and 4.776 eV are observed at short-wavelengths and can be attributed to ground and excited states of C excitonic series. These maxima become apparent only in E⊥c polarization. The value of longitudinal-transversal splitting for C exciton is equal to 4.6 meV. For more precise determination of energies of ground and excited excitonic states the wavelength modulated reflection spectra (ΔR/Δλ) were measured (Figure 1).

Taking into account an energy position of lines n = 1 and 2 in reflection and wavelength modulated reflection spectra of $CdAl_2S_4$ crystals measured in E‖c polarization the Rydberg constant (R) of A and B free excitons (48 - 49 meV) was determined. A convergence limit of Aexcitonic series is E_g = 4.552 eV. Based on observed in E‖c polarization maxima at 4.765 eV (n = 1) and 4.804 eV (n = 2) the binding energy of B exciton (48 meV) and band gap E_g (4.615 eV) were calculated. The continuum energy of C exciton is equal to 4.790 eV.

Contours of excitonic reflection spectra were calculated according well-know dispersion relations described in Ref. [16, 17]. Reflectivity of crystal in the case of normal light incidence on the border crystal-vacuum can be calculated by:

$$R = \left| \frac{\left(\frac{1-n_0}{1+n_0}\right) + \left(\frac{n_0 - n^*}{n_0 + n^*}\right) e^{i2kn_0 t}}{1 + \left(\frac{1-n_0}{1+n_0}\right) \times \left(\frac{n_0 - n^*}{n_0 + n^*}\right) e^{i2kn_0 t}} \right|^2 \qquad (1)$$

where $n^* = (n_1 n_2 + \varepsilon_b)/(n_1 + n_2)$, n_1 and n_2 are refractive indices of transversal waves in dependence on damping factor γ. In the case $\gamma \neq 0$:

$$(n_1 \times n_2)^2 = \varepsilon_b \left(1 - \frac{\omega^2}{\omega_0^2} - i\frac{\gamma\omega}{\omega_0^2}\right) \frac{Mc^2\omega_0}{\hbar\omega^2} - \frac{2\omega_{LT}\varepsilon_b Mc^2}{\hbar\omega^2} \qquad (2)$$

$$(n_1 + n_2)^2 = \varepsilon_b - \left(1 - \frac{\omega^2}{\omega_0^2} - i\frac{\gamma\omega}{\omega_0^2}\right) \frac{Mc^2\omega_0}{\hbar\omega^2} + 2\left[-\varepsilon_b\left(1 - \frac{\omega^2}{\omega_0^2} - i\frac{\gamma\omega}{\omega_0^2}\right)\frac{Mc^2\omega_0}{\hbar\omega^2} - \frac{2\omega_{LT}\varepsilon_b Mc^2}{\hbar\omega^2}\right]^{1/2} \qquad (3)$$

where t is a depth of dead layer, k is a wave vector, $n_0 = \sqrt{\varepsilon_b}$. A reduced effective mass $\mu^* = \varepsilon_b^2 R/R_H$, where R_H is a Rydberg energy of hydrogen atom (13.6 eV). Values of background dielectric constant ε_b near the excitonic resonances A, B and C equaled to 8.8 (8.5), 8.6 and 8.4, respectively, were used for calculations of excitonic spectra contours. Taking into account abovementioned background dielectric constants the reduce effective masses for A, B and C excitonic series corresponded to $0.28m_0$, $0.26m_0$ and $0.28m_0$ (see Table 1). Calculation parameters were fit to the best coincidence of experimental and calculated contours of reflection spectra. The translation mass of exciton M, electron mass and hole mass were estimated from the calculation of reflection spectra contours.

Table 1. *The exciton and the free carrier mass parameters deduced from the fits of Eq. (1) to the reflectivity spectra for $CdAl_2S_4$ crystal.*

		A, E‖c	B, E‖c	A, E⊥c	C, E⊥c	Δ_{cf}, meV	Δ_{so}, meV
	n = 1, eV	4.503	4.565	4.504	4.736		
Exciton state	n = 2, eV	4.540	4.604	4.540	4.776	141	152
	ω_{LT}, meV	4.1	3.7	4.0	4.6		
R, eV		0.049	0.048	0.048	0.054		
E_g (n=∞), eV		4.552	4.615	4.552	4.790	137	163
ε_b		8.8	8.6	8.5	8.4		
μ^*, m_0		0.28	0.26	0.28	0.28		
M, m_0		1.9	2.2	1.9	2.4		
m_c^*, m_0		0.30	0.30	0.30	0.30		
m_{v1}^*, m_0		1.55		1.55			
m_{v2}^*, m_0			1.90				
m_{v3}^*, m_0					2.07		

It is well known, that excitonic mass M is the sum of hole and electron masses $m_v^* + m_c^*$ and reduced effective mass $1/\mu^* = (1/m_v^*) + (1/m_c^*)$. Effective masses of electrons in conduction band m_{c1}^* and holes in valence band m_{v1}^* were determined from calculated M and μ^* masses. It was received the magnitude of translation mass M = $1.9m_0$ for A excitonic series in E‖c, k⊥c polarization. Masses of electrons (m_c^* = $0.30m_0$) and holes (m_{v1}^* = $1.55m_0$) were estimated for this polarization taking into account the magnitude of reduced effective mass (μ^* = $0.28m_0$).

Figure 1 shows that the excitonic series A is observed in both polarizations E‖c and E⊥c and energies of longitudinal and transversal excitons for different polarizations agree in the limits of experimental errors (±0.5 meV). Calculated parameters ε_b and M for A exciton almost the same for polarizations E‖c and E⊥c. The translation mass of B exciton were estimated as $2.2m_0$ by calculations of contours of reflection spectra in E‖c polarization. Taking into account the value of reduced effective mass of this polarization (μ^* = 0.26m0) the electron ($0.30m_0$) and hole (m_{v2}^* = $1.90m_0$) masses were determined in k = 0.

Calculations of reflection spectra of C exciton ground state in E⊥c, k⊥c polarization were carried out by abovementioned dispersion relations. The calculations give the good agreement experimental and theoretical results at the next parameters: ε_b = 8.4, ω_0 = 4.836 eV, ω_{LT} = 4.6 meV, γ = 0.6 meV, M = $2.4m_0$ and t = 10 Å. The excited state n = 2 of C exciton situated at energy 4.976 eV. At these parameters the binding energy R = 54 meV and band gap E_g = 4.790 eV. The effective mass of holes m_{v3}^* ($2.07m_0$) were calculated on a base of parameters of C excitonic series (M = $2.4m_0$ and μ^* = $0.28m_0$), table 1. These values are in good agreement with

data reported in Ref. [18] (m$^{\parallel}_c$ = 0.214m$_0$, m$^{\perp}_c$ = 0.198m$_0$ and m$^{\parallel}_h$ = 0.381m$_0$, m$^{\perp}_h$ = 0.77m$_0$).

Ground and excited states of three excitonic series A, B and C with binding energies 53 meV, 51 meV and 46 meV, respectively [19] were observed in CdGa$_2$S$_4$ crystals at 10 K. The effective mass of electrons in k = 0 (m$_c$$^{\parallel}$(E$\parallel$c) = 0.21m$_0$

and m$_c$$^{\perp}$(E$\perp$c) = 0.19m$_0$) was determined from exciton spectra calculations. Holes masses m$_{v1}$, m$_{v2}$ and m$_{v3}$ are equal to 0.59m$_0$, 0.71m$_0$ and 0.71m$_0$, respectively. Values of splitting of valence bands V$_1$ - V$_2$ due to crystal field equal to 24 meV and bands V$_2$ - V$_3$ splitting due to spin orbital interaction equal to 130 meV.
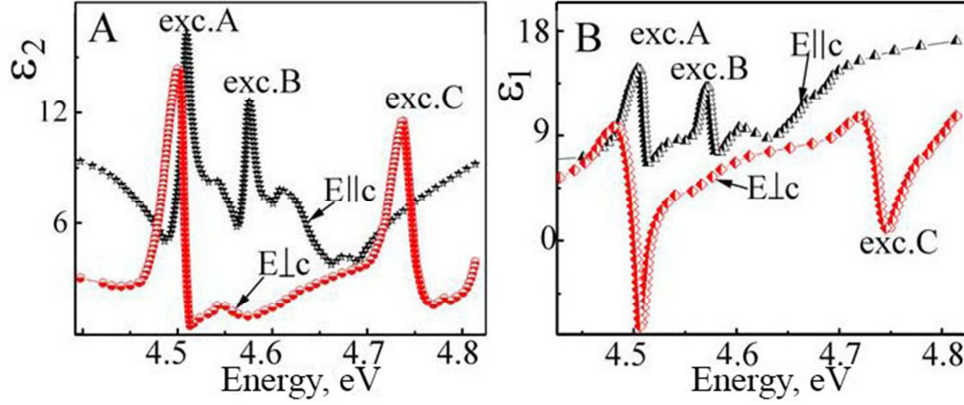
Figure 2. *Spectral dependences of imaginary (ε$_2$) and real (ε$_1$) parts of complex dielectric constant in CdAl$_2$S$_4$ crystals measured at temperature 10 K in E∥c and E⊥c polarizations for excitonic region.*

The effective mass of electrons (m$_c$) is equal to 0.14m$_0$ and effective masses of holes (m$_{v2}$ and m$_{v3}$) are estimated at 0.76m$_0$ and 0.94m$_0$, respectively, in Γ point of Brillouin zone of CdGa$_2$Se$_4$ crystals. The hole mass m$_{v1}$ depends on wave-vector direction and it is equal to 1.15m$_0$ in E∥c, k∥a polarization and it is 0.48m$_0$ for E∥c, k∥b polarization. Valence bands in Brillouin zone center are split by crystal field (Δ$_{cr}$ = 49 meV) and by spin-orbital interaction (Δ$_{so}$ = 351 meV). Effective masses of electrons are decreased when these masses compare in the series of crystals CdAl$_2$S$_4$ - CdGa$_2$S$_4$ - CdGa$_2$Se$_4$. Effective masses of holes diminish at the passage from CdAl$_2$S$_4$ to CdGa$_2$S$_4$ but they increase at transition from CdGa$_2$S$_4$ to CdGa$_2$Se$_4$.

Optical functions for excitonic region in E∥c, k⊥c and E⊥c, k⊥c polarizations were calculated on the base of Kramers-Kronig relations. Spectral dependencies of real (ε$_1$) and imaginary (ε$_2$) parts of permittivity have maxima and minima in a region of longitudinal and transversal excitons (Figure 2). Pronounced maxima in region of transversal excitons were appeared in the permittivity imaginary part (ε$_2$) spectrum for A excitonic series in E∥c and E⊥c polarizations. Maxima in E∥c and E⊥c polarizations are shifted on a value around 1.0 - 1.3 meV, this shift is due to the exchange interaction of excitons. The splitting of minima of transversal excitons has almost the same magnitude. Bohr radius (α$_B$) of s-state of B$_{2u}$ exciton is equal to 0.3x10^{-5} cm and for B$_{3u}$exciton α$_B$ = 0.2x10^{-6} cm.
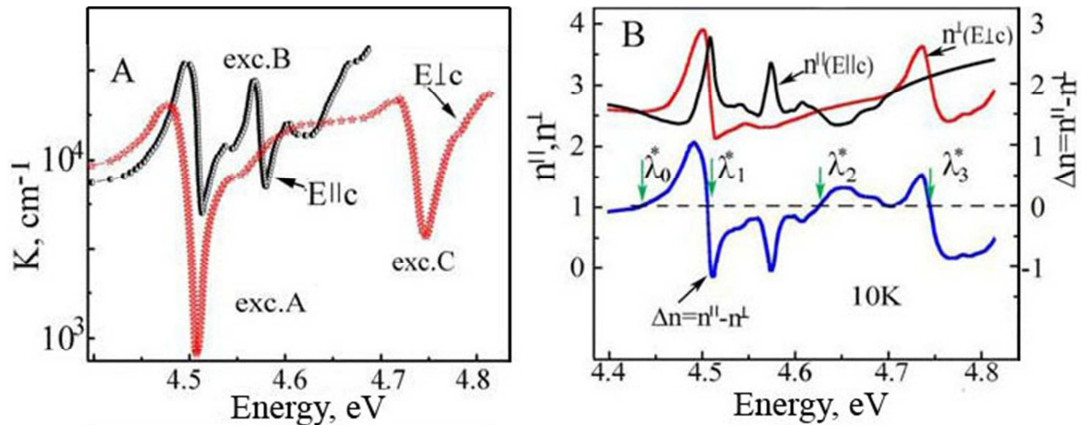
Figure 3. *Spectral dependencies of absorption coefficient (K), refractive indices (n$^{\perp}$ and n$^{\parallel}$) and its difference (Δn) at temperature 10 K in E∥c and E⊥c polarizations in the excitonic region.*

Spectral dependencies of refractive indices in E∥c, k⊥c and E⊥c, k⊥c polarizations have almost the same polarization dependencies as reflection spectra. Curves n$^{\parallel}$(E∥c) and n$^{\perp}$(E⊥c) intersect in a few points (see Figure 3). The refractive index in A exciton region has a maximal value at

energies of transversal exciton. Positions of A exciton maxima in refractive indices spectra in the case of E∥c, k⊥c and E⊥c, k⊥c polarizations do not coincide on a value of exchange interaction of A exciton.

3.2. Electron Transitions in Intrinsic Absorption Region of CdAl₂S₄ Crystals

It is well known that electron transitions are possible when photon energy is equal to the energy interval $E_c - E_v$. This is a first necessary condition (a selection rule) for a realization of electron transitions. Direct electron transitions happen at the equality of wave-vectors in the initial and final states ($k_v = k_c$). These transitions become apparent as maxima of reflection spectra in the intrinsic energy region. The analysis of electron transitions in the intrinsic energy region is realized by comparison of theoretically calculated spectral dependency of imaginary part of permittivity ($\varepsilon_2(\omega)$) with a spectrum calculated from experimentally measured reflection spectra. The imaginary part of complex permittivity is determined by

$$\varepsilon_2(\omega) = \frac{2\hbar\omega}{E_0^2 \omega \varepsilon_0} W_{CV} \qquad (4)$$

where W_{CV} is a optical transitions probability,

$$W_{CV} = \frac{4\pi}{\hbar} \frac{e^2}{m^2} \frac{A_0^2}{(2\pi)^3} \int |\Pi_{CV}^e|^2 \delta(E_C - E_V - \hbar\omega) d^3k \qquad (5)$$

where A is a vector potential,

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = A_0 \vec{e} \omega_0 \sin(\vec{k}\vec{r} - \omega t) \qquad (6)$$

This means that, the imaginary part of complex dielectric constant is equal to:

$$\varepsilon_2(\omega) = \frac{e^2}{m^2 \omega^2 \pi^2 \varepsilon_0} \int_{\Omega} |\Pi_{CV}^e|^2 \delta(E_{CV} - \hbar\omega) d^3\vec{k} \qquad (7)$$

where δ function in this equation defines a implementation of energy conservation law. In addition $\varepsilon_2(\omega)$ depends on matrix element $|\Pi_{CV}^e|^2$, whose magnitude is determined by wave functions in initial and finite states of a transition. These relations should be taking into account for every polarization separately in the case of anisotropic crystals. In allowed polarization the absorption coefficient and the imaginary part of permittivity ($\varepsilon_2(\omega)^{allow}$) exceed these values in forbidden polarization ($\varepsilon_2(\omega)^{allow} >> \varepsilon_2(\omega)^{forbid}$).

The structure of CdAl₂S₄ crystals is analogous with crystal lattices of CdGa₂S₄ and CdGa₂Se₄. These crystals have S_4^2 space group. Band structure calculations for CdGa₂S₄ crystals show that extrema of valence and conduction bands, which determining the minimal width of band gap, lay in Γ point of Brillouin zone [19, 20]. The bands in minimum of interband gap in CdGa₂S₄ crystals are defined by wave functions of gallium and sulfur atoms.

It is known, that the amplitude of reflectivity (R) links with phase (φ) of reflected beam up by equation:

$$r = \sqrt{R} e^{-i\varphi} \qquad (8)$$

Spectral dependences of reflectivity (R) and of optical functions (n, k, φ, ε_1 and ε_2) interrelate by relations

$$\begin{cases} r = \frac{N-1}{N+1} = \frac{n+ik-1}{n+ik+1} \\ r = \sqrt{R} e^{-i\varphi} = \sqrt{R}(\cos\varphi - i\sin\varphi) \end{cases} \Longrightarrow \begin{cases} n = \frac{1-R}{1-2\sqrt{R}\cos\varphi + R} \\ k = \frac{2\sqrt{R}\sin\varphi}{1-2\sqrt{R}\cos\varphi + R} \end{cases} \qquad (9)$$

The magnitude of reflectivity simultaneously with its phase should be calculated for each wavelength, i.e. $R = R(\omega)$ and $\varphi = \varphi(\omega)$. The phase of reflected light relates with reflectivity magnitude by Kramers-Kronig integral:

$$\varphi(\omega_0) = \frac{\omega_0}{\pi} \int_0^{\infty} \frac{\ln R(\omega)}{\omega_0^2 - \omega^2} d\omega \qquad (10)$$

It is necessary to measure the reflectivity in the infinite frequency diapason for the reflected beam phase determination (see equation 10). But experimental measurements of reflection spectra are possible only in the frequency interval ($\omega_a - \omega_b$), in our case 2 - 6 eV. It was used well known method for calculation, when φ magnitude in high-energies (where the reflection coefficient was not measured) was made the extrapolation of the spectral dependence of reflection coefficient by certain function (a slop function of reflection). The function $R(\omega) = c\omega^{-p}$ was used for $b \le \omega \le \infty$ in the calculations, where c and p are constant and the approach $R(\omega) = R(a)$ were used for $0 \le \omega \le a$. The influence on reflection spectra by lattice vibration was neglected due to the insufficient contribution in to the value φ. The calculated value of φ and experimentally determined value of R allow determining the optical functions (n, k, ε_1 and ε_2).

Maxima at energies 3.501 eV (A- exciton) and 3.548 eV (B -exciton) were discovered in reflectivity spectra of CdAl₂S₄ crystals in polarized and no-polarized light at temperature 300 K in the region of interband minimum (see Figure 1). The maximum A, whose contour changing in the range of 26 -31% at 300K, was appeared in E∥c polarization. The maximum B, its contour changing from 28.5 to 32.5%, and a weak maxima C was observed in E c polarization (Figure 1, A). Maxima a3 - a7 and e3 - e7 were revealed at high energies in E∥c and E⊥c polarizations.

Figure 4 shows the spectral dependences of reflection and wavelength modulated reflection of CdAl₂S₄ crystals in E∥c and E⊥c polarizations measured at temperature 80 K. Three groups of maxima are observed in the intrinsic region of reflection spectra. The most long-wavelength group is formed by excitonic transitions (A, B and C). The second group is situated at energies 3.9 - 5.2 eV and the last group - near 5.2 - 6.5 eV.
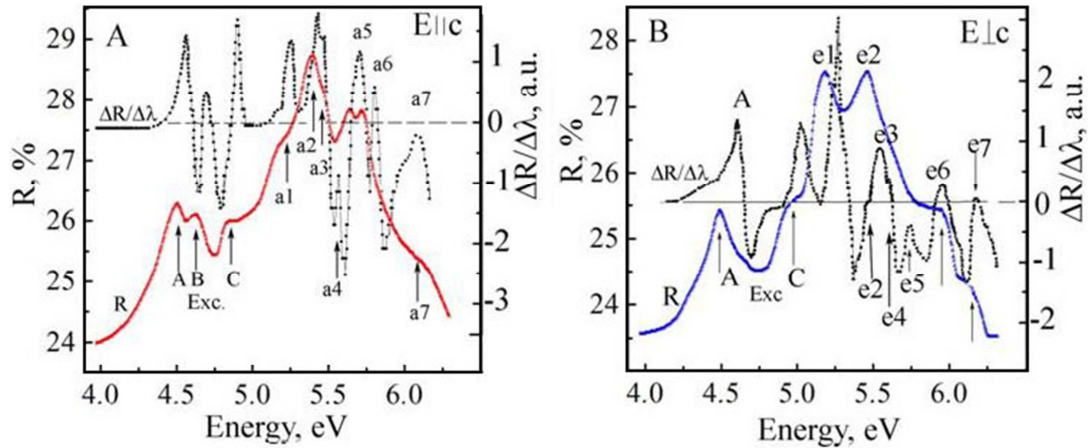
Figure 4. *Reflection (R) and wavelength modulated reflection (ΔR/Δλ) spectra of CdAl₂S₄ crystals in E∥c (A) and E⊥c (B) polarizations measured at temperature 80 K.*

Spectral dependencies of refractive index (n), imaginary part of permittivity (ε_2) and its differences (Δn and $\Delta\varepsilon_2$) were calculated by Kramers-Kronig method from measured reflection spectra (Figure 5). Also spectral dependencies `of extinction coefficients ($k^\perp$ and $k^\parallel$), its difference ($\Delta k = k^\perp - k^\parallel$), phases ($\varphi^\parallel$ and $\varphi^\perp$) and a phases difference ($\Delta\varphi = \varphi^\perp - \varphi^\parallel$) were calculated for E∥c and E⊥c polarizations at temperature 80 K (see Figure 6).
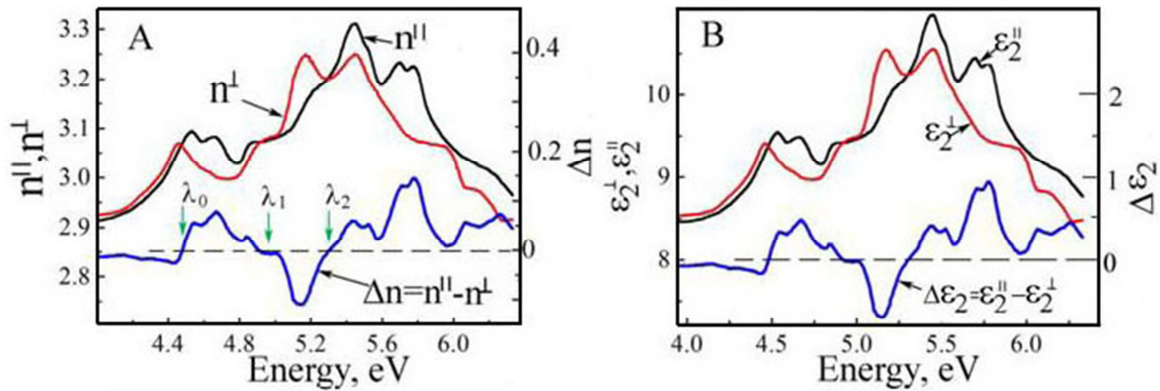
Figure 5. *A - spectral dependencies of refractive indices ($n^\parallel$ and $n^\perp$) and its difference ($\Delta n = n^\parallel - n^\perp$); B - spectra of permittivity imaginary parts ($\varepsilon_2^\parallel$ and $\varepsilon_2^\perp$) and theirs difference ($\Delta\varepsilon_2 = \varepsilon_2^\parallel - \varepsilon_2^\perp$) for E∥c and E⊥c polarizations in CdAl₂S₄ crystals.*

Features for all calculated optical functions have a good correlation with features observed in measured reflection spectra of CdAl₂S₄ crystals (see Figures 1 - 4 and Table 2). Spectral dependencies of refractive indices $n^\parallel$ and $n^\perp$ intersect in three energies: 4.474 eV, 4.924 eV and 5.303 eV (marked as λ_0, λ_1 and λ_2). The difference $\Delta n = n^\parallel - n^\perp$ crosses the zero axis at the same energies (wavelength), Figure 5, A. Spectral dependencies of imaginary parts of permittivity in E∥c and E⊥c polarizations ($\varepsilon_2^\parallel$ and $\varepsilon_2^\perp$) and its difference ($\Delta\varepsilon_2 = \varepsilon_2^\parallel - \varepsilon_2^\perp$) have the same features at the same wavelengths, Figure 5, B. The intersection of spectral dependencies of refractive indices indicates that the crystal has isotropic and does not recognize the light polarization at these wavelengths. Such regularities show optical activity and take place in a lot of crystals including $A^{II}B_2^{III}C_4^{VI}$ compounds [21].

Table 2. *Direct transitions determined from analysis of maxima in reflection (R), wavelength modulated reflection (ΔR/Δλ) and permittivity imaginary part (ε_2) spectra and electron transitions responsible for these features in CdAl₂S₄ crystals.*

| Index	Result [6], eV	R, 80 K (ΔR/Δλ), eV	Index	Result [6], eV	R, 80 K(ΔR/Δλ), eV	Transitions
a1		5.170 (5.205)	e1	4.116	5.176 (5.196)	$N(V_1) \to N(C_1)$ $N(V_2) \to N(C_1)$
a2		5.405 (5.421)	e2	4.216	5.460 (5.487)	
a3		5.473 (5.485)	e3		(5.540)	$N(V_1) \to N(C_2)$
a4		5.578 (5.584)	e4		(5.566)	$P(V_1) \to P(C_1)$
a5	5.355	5.646 (5.664)	e5	5.306	5.7 (6.172)	$P(V_1) \to P(C_2)$
a6	5.591	5.745 (5.765)	e6		5.95 (5.95)	$P(V_2) \to P(C_2)$
a7	5.913	6.128 (6.136)	e7		6.25 (6.35)	$H(V_1) \to H(C_1)$

Spectral dependencies of extinction coefficients ($k^\parallel$, $k^\perp$ and Δk) and phases ($\varphi^\parallel$, $\varphi^\perp$ and $\Delta\varphi$) happen at shorter wavelengths (Figure 6). These features are due to electron transitions from valence to conduction bands and in full they

are determined by selection rules of interband transitions. Calculations of excitonic spectra measured at 10 K show that refractive indices $n^{\|}$ and $n^{\perp}$ intersect four times at different energies: 4.632 eV (λ^{*}_0), 4.705 eV (λ^{*}_1), 4.825 eV (λ^{*}_2) and 4.945 (λ^{*}_3), Figure 3, B. Excitonic states are formed in

nearby of three valence bands V_1, V_2 and V_3 near conduction band C_1. Excitonic states at 10 K appear according selection rules for excitonic transitions and play essential role in the optical activity of crystal in the region of these transitions.
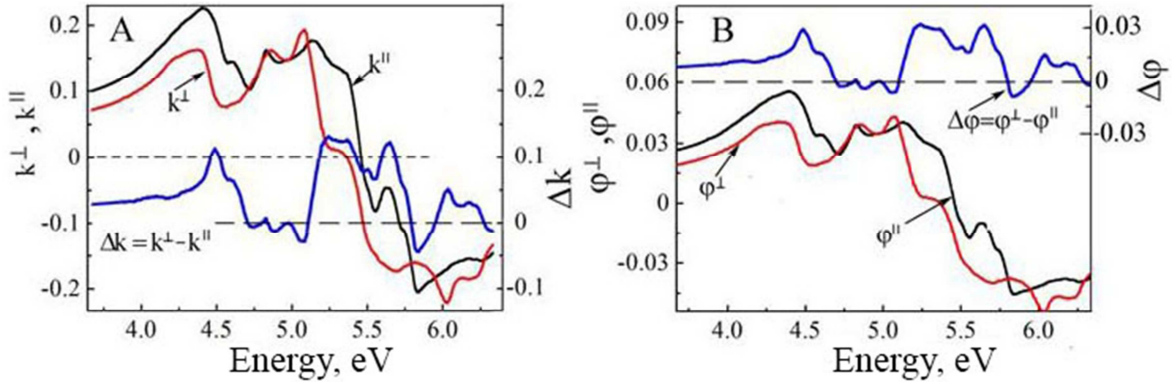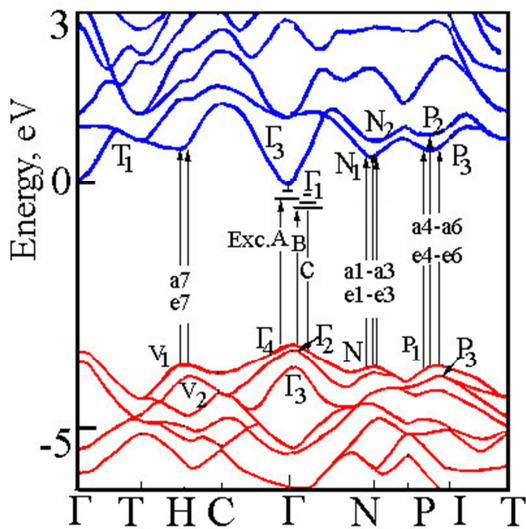

Figure 6. *Spectral dependencies of extinction coefficient k (A), phase φ (B) in E||c and E⊥c polarizations and its differences Δk = k⊥ - k|| (A) and Δφ = φ⊥ - φ|| (B) for CdAl₂S₄ crystals at temperature 80 K.*

The first theoretical calculation of $A^{II}B_2^{III}C_4^{VI}$ crystal's band structure was carried out in four actual point of Brillouinzone (Γ, T, N and P) [22, 23]. The later calculation of these crystals band structure was effectuated in Γ, T, H, C, N, P and I points of Brillouin zone [24]. Revealed features of reflection and permittivity spectra of $CdAl_2S_4$ crystals were analyzed based on the latest band diagram [24]. Figure 7 shows the enlarged proportionally fragment of band structure calculated by authors Ref. [24].

Theoretical calculations of energy band structure in all abovementioned points of Brillouin zone were carried out without taking into account spin-orbital interaction and crystal field. Valence bands in these points according approaches are degenerated. The lattice symmetry reducing from chalcopyrite to S_4^2 structure leads to the bands splitting by crystal field. Spin-orbital interaction results in the band splitting too. As a result the degenerated bands are split on elementary bands as shown in Figure 7.

Figure 7. *Energy band structure of CdAl₂S₄ crystals.*

The intensive maxima of reflection spectra in E||c and E⊥c polarizations due to excitonic states A, B and C are observed in the region of interband minimum of $CdAl_2S_4$ crystals. Energy intervals between bands V_1, V_2 and V_3 are determined from the difference in continuum energies of excitonic series A, B and C. The energy band structure has maxima of valence bands in actual points Γ, N, H and neighborhood P - I of Brillouin zone (see Figure 7). Based on the fact that only direct allowed transitions are observed in reflection spectra, these maxima are identified as direct transitions in such points of Brillouin zone where maxima of valence band and minima of conduction band have the same value of wave vector. As mentioned above, minimal energy intervals are due to by exciton states localized in Brillouin zone center. According the theoretical calculations [24] the next high-energy interval is observed in N point. Thus, maxima a1 (e1), a2 (e2) and a3 (e3) is caused by transitions in N point from V_1, V_2 to C_1, C_2 bands. The top valence band in N and Γ points is split due to spin-orbital interaction and crystal field.

According theoretical calculations the energy intervals V_1 - C_1 near P point (direction I) are more than ones in N point and less than intervals V_1 - C_1 in another points of Brillouin zone, for example H point. Therefore maxima a4 (e4), a5 (e5) and a6 (e6) are more probably due to the electron transitions in P point (direction I) of Brillouin zone from valence band V_1 to conduction bands C_1 and C_2 (see Figure 7).

4. Conclusions

Ground and excited states of three excitonic series A, B and C were discovered in $CdAl_2S_4$ crystals at temperature 10 K. Reflection spectra excitonic contours were calculated by dispersion equations and the main parameters of excitons and bands in k = 0 were determined. The effective mass of electrons m_c^* was $0.30m_0$ and effective masses of holes m_{v1}^*,

m_{v2}^{*} and $m^{v3^{*}}$ were equal to $1.55m_0$, $0.90m_0$ and $2.07m_0$, respectively. The splitting of bands V_1 - V_2 due to crystal field (141 meV) and bands V_2-V_3 by spin-orbital interaction (152 meV) were estimated.

Optical constants (n, k, ε_1 and ε_2) for polarizations E∥c and E⊥c were calculated at energies 3 - 6 eV from reflection spectra by using Kramers-Kronig analysis. Discovered direct transitions were discussed and identified in actual points of Brillouin zone according new theoretical calculations of CdAl$_2$S$_4$ energy band structure.

References

[1] Ju. O. Derid, S. I. Radautsan, I. M. Tiginyanu, Multicomponent chalcogenides A^{II}B$_2^{III}$C$_4^{VI}$, Kishinev, Stiinta, (1990) 4.

[2] S. I. Radautzan, N. N. Syrbu, I. I. Nebola, V. G. Tyrziu, D. M. Berca, Energy band structure and two-phonon absorption in crystals CdGa$_2$S$_4$ and CdGa$_2$Se$_4$, Semiconductors, 11 (1977) 69-74.

[3] H. Neuman, W. Horig, G. Nooke, N. N. Syrbu, The fundamental absorption edge of PbGa$_2$S$_4$, Solid State Communications, 65 (2) (1988) 155.

[4] H. Neuman, H. Sobotta, N. N. Syrbu, S. I. Radautsan, V. Riede, Vibrational properties of CdGa$_2$S$_4$, Crystal Res. &Technol. , 19 (5) (1984) 709-714.

[5] R. Bacewiezt, P. P. Lottici, R. Razetti, Solid State Physics, 12 (1979) 3603.

[6] N. N. Syrbu, V. E. Tezlevan, V. I. Perchekli, Effect of ordered vacancies on vibrational Raman spectra of CdGa$_2$S$_4$ crystals, Optics and Spectroscopy, 75 (2) (1993) 355-359.

[7] N. N. Syrbu, V. T. Tezlevan, Energetic band-structure and optical spectra of CdGa$_2$Se$_4$, CdGa$_2$S$_4$ and CdAl$_2$S$_4$ crystals, Physica B Condensed matter, 210 (1) (1995) 43-48.

[8] N. N. Syrbu, L. L. Nemerenco, V. Z. Cebotari, Vibrational and polariton spectra of CdGa$_2$S$_4$ and CdAl$_2$S$_4$ crystals, Crystal Res. &Technol. , 37 (1) (2002) 101-110.

[9] D. Erandonea, R. S. Kumar, F. J. Manjon, V. V. Ursaki, I. M. Tiginyanu, High-pressure x-ray diffraction study on the structure and phase transitions of the defect-stannite ZnGa$_2$Se$_4$ and defect-chalcopyrite CdGa$_2$S$_4$, Journal of Applied Physics, 104 (6) (2008) 063524.

[10] L. M. Suslicov, Z. P. Gol'dmasi, I. F. Kopinet, V. Ju. Slivka, Optics and Spectroscopy, 51 (1981) 307.

[11] Ju. V. Vorosilov, V. Ju. Slivka, Anoxidic materials for electronics, L'vov, Visshaia Shkola, (1989) 123.

[12] A. N. Georgobiani, Yu. V. Ozerov, S. I. Radautsan, I. M. Tiginyanu, Investigation of fundamental optical transitions in CdGa$_2$S$_4$ by methods of modulation spectroscopy, Sov. Phys. − Solid State (USA), 23 (1981) 1221-1226.

[13] M. E. Doroshenko, T. T. Basiev, V. V. Osiko, V. V. Badikov, D. V. Badikov, H. Jelinkova, P. Koranda, J. Sulc, Oscillation properties of dysprosium-doped lead thiogallate crystal, Optic Letters, 34 (5) (2009) 590-592.

[14] Yu. V. Orlovskii, T. T. Basiev, L. N. Dmitruk, V. V. Osiko, D. V Badikov, V. V. Badikov, S. B. Mirov, Mid- IR Laser Transitions in Nd^{3+} Doped CaGa$_2$S$_4$, PbGa$_2$S$_4$, and PbCl$_2$ Laser Crystals, CLEO/QELS, Baltimore, Maryland, USA, 2, (2005) 877.

[15] E. L. Ivcenco, A. V. Selikin, JETF, 76 (1979) 1837.

[16] K. Suresh, N. V. Poornachandra Rao, K. V. R. Murthy, UV-Visible Excitable Luminescent Properties of CaAl$_2$S$_4$: Eu^{2+} Phosphor, International Journal of Luminescence and Applications, 5 (1) (2015) 149-153.

[17] N. N. Syrbu, V. V. Ursaki, Exciton Polariton Dispersion in Multinary Compounds, in Exciton Quasiparticles: Theory, Dynamics and Applications, Randy M. Bergin (Editor), Nova Science Publishers Inc. , 2010 USA.

[18] T. G. Kerimova, S. C. Mamadov, I. A. Mamedov, Deformation potentials of band extrema Γ (000) in CdGa$_2$S$_4$, Semiconductors, 32 (2) (1998) 148-150.

[19] N. N. Syrbu, V. Z. Cebotari, Davydov multiplets in vibrational spectra of PbGa$_2$S$_4$ and MgGa$_2$S$_4$ crystals, Journal of physics. Condensed matter, 10 (15) (1998) 3467-3477.

[20] N. N. Syrbu, V. E. L'vin, I. B. Zadnipru, V. M. Golovei, Raman and infrared vibration spectra of PbGa$_2$S$_4$ crystals, Semiconductors, 25 (10) (1991) 1721-1730.

[21] N. N. Syrbu, V. I. Parvan, V. V. Ursaki, Optical Materials, 34 (2012) 691.

[22] V. L. Panaiutin, B. E. Ponedelnikov, A. E. Rozenson, V. I. Chijikov, Band structure of semiconductors with cadmium thiogallate lattice, Izv. Vuzov SSSR, Fizika, 8 (1979) 57-64. (in Russian).

[23] V. L. Panaiutin, B. E. Ponedelnikov, A. E. Rozenson, V. I. Chijikov, Band structure of zinc thiogallate and selengallate, Semiconductors, 15 (2) (1981) 311-315.

[24] X. Jiang, W. R. L. Lambrecht, Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II−III$_2$−VI$_4$, Physical Review B, 69 (3) (2004) 0352011.