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BIREFRINGENCE AND EXCITON SPECTRA OF CuAlSe_2 AND CuAlS_2 CRYSTALS

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Abstract. The excitonic reflection spectra of CuAlS_2 and CuAlSe_2 crystals were measured at the temperature of 10 K for polarizations $E||c$ and $E\perp c$. Ground and excited states of the excitons were found out in the investigated spectra. Symmetries of the observed excitons were determined. The shapes of ground states lines of Γ_4 and Γ_5 excitons were calculated by means of the Kramers-Kronig relations. Exciton parameters and values of energetic gaps ($\Gamma_7-\Gamma_6$, $\Gamma_6-\Gamma_6$, and $\Gamma_7-\Gamma_6$) were determined. Optical reflection spectra in the depth of absorption band ($E_g - 6$ eV) were measured at 80 K for $E||c$ and $E\perp c$ polarizations. Optical constants were calculated from measured reflection spectra by Kramers-Kronig analysis. The phase in the excitonic region was determined. Transmission spectra of CuAlSe_2 single crystals deposit in crossed polarizers demonstrate a birefractive effect. In the case of parallel polarizers interference due to birefractance was observed. The isotropic point was determined.

Keywords: absorption and reflection spectra, excitons, polaritons, birefringence.

1. Introduction

CuAlSe_2 and CuAlS_2 compounds, as well as their solid solutions belonging to the III-VI₂ materials crystallize in the chalcopyrite structure with the $I42d - D_{2d}^{12}$ space group. Stimulated emission and second harmonic generation at 10.6 μm as well as generation of infrared (IR) radiation in the region of 4.6 and 12 μm was realized in these compounds [1-4]. Biexcitons [5], interference of additional waves [6], resonance Raman scattering [7-9] and intense emission due to exciton polaritons and bound excitons [10-12] have been observed in these crystals. Optoelectronic devices and solar cells are developed on the basis of these materials [13-18]. The photoluminescence properties of CuAlSe_2 crystals doped with Er^{3+} ions [15] as well as the photoelectrical properties of surface barrier structures on the basis of CuAlSe_2 have been studied [17, 18]. These materials possess a strong anisotropy of optical properties in the visible and infrared spectral ranges which is very important for the development of polarized optoelectronic devices.

The goal of this paper is to investigate the main exciton parameters as well as the energy gaps at the center of the Brillouin zone as a function of composition of $\text{CuAl}_{1-x}\text{Ga}_x\text{Se}_2$ solid solutions. The energy position of $n=1$ and 2 lines of the $\Gamma_4(\text{A})$, $\Gamma_5(\text{B})$ and $\Gamma_5(\text{C})$ exciton series, as well as the $\Gamma_7(\text{V}_1) - \Gamma_6(\text{C}_1)$, $\Gamma_6(\text{V}_2) - \Gamma_6(\text{C}_1)$, $\Gamma_7(\text{V}_3) - \Gamma_6(\text{C}_1)$ energy intervals, are determined from wavelength modulated optical reflectivity spectra. The

effective electron mass (m_{c1}^*), and hole masses (m_{v1}^* , m_{v2}^* , m_{v3}^*), are estimated from the analysis of exciton reflectivity spectra according to a single-oscillator model of dispersion relations. The asymmetry parameters of reflectivity spectra are determined.

2. Experimental details

CuAlSe₂ and CuAlS₂ crystals in the form of platelets with 2.5 × 1.0 cm² mirror-like surfaces and thicknesses of 300–400 μm were grown by chemical vapor transport [16]. The surface plane of the platelets contains the C -axis. The optical reflectivity and wavelength modulated spectra were measured using a MDR-2 (LOMO, Russia) spectrometer. For low-temperature measurements, the samples were mounted on the cold station of a LTS-22 C 330 optical cryogenic system.

3. Experimental results and discussion

3.1. Excitonic spectra of CuAlS₂ crystals

According to theoretical calculations of the band structure [3 – 6], the minimum of interband gap is formed by direct electronic transitions at the center of Brillouin zone for CuAlS₂ crystals. The lower conduction band possesses Γ_6 symmetry and the upper valence bands V_1 , V_2 , V_3 possess Γ_7 , Γ_6 and Γ_7 symmetries, respectively. The interaction of electrons from the conduction band Γ_6 with holes from Γ_7 is determined by the product of irreducible representations $\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5$. As a result of this interaction, the Γ_4 exciton allowed in E||c polarization, Γ_5 exciton allowed in E⊥c polarization and Γ_3 exciton forbidden in both polarizations are formed in the long-wavelength part of the spectrum. The interaction of electrons from the conduction band C_1 of Γ_6 symmetry with holes from the valence band V_2 with Γ_6 symmetry leads to the appearance of three excitonic series Γ_1 , Γ_2 , and Γ_5 . According to the selection rules, Γ_5 excitons are allowed, while Γ_1 and Γ_2 excitons are forbidden for E⊥c polarization.

The lines $n = 1$ ($\omega_t = 3.543$ eV, $\omega_l = 3.546$ eV) and $n = 2$ (3.565 eV) of the hydrogen-like Γ_4 exciton series were revealed in the reflection spectra of CuAlS₂ crystals measured at 10 K in E||c polarization [7]. The reflection spectra in the $n = 1$ region has a typical form with a 3.543 eV maximum and a 3.546 eV minimum. These peculiarities are explained by the presence of transversal and longitudinal excitons. The longitudinal-transverse splitting energy of Γ_4 excitons estimated on the basis of these data equals 3 meV. A Rydberg constant of 32 meV is determined for Γ_4 excitonic series from the energetic position of $n = 1$ and $n = 2$ lines (fig. 1). The continuum energy (E_g , $n = \infty$) is 3.575 eV. The energy values discussed above for the ground ($n = 1$) and excited ($n = 2$) excitonic states are satisfactorily correlating with the 3.534 eV and 3.665 eV values previously obtained at 77 K [8].

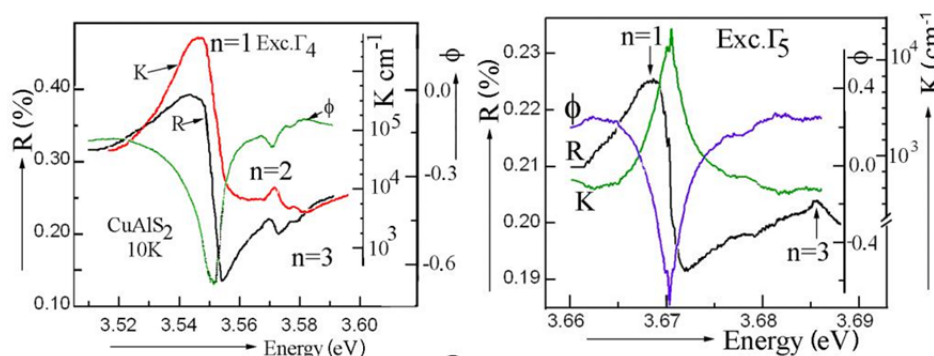


Figure 1. Spectral dependence of absorption coefficient (K) and of phase (Φ) of the reflected beam calculated from the measured reflection spectra (R) in CuAlS₂ crystals.

A maximum at 3.668 eV (transversal exciton) and a minimum at 3.670 eV (longitudinal exciton) related to Γ_5 excitonic series are revealed in $E \perp c$ polarization (Fig. 1). The transverse-longitudinal splitting of Γ_5 exciton equals 2.0 meV. An excited state $n = 2$ is revealed at 3.687 eV. The exciton binding energy of Γ_5 excitons is 25 meV, and the convergence limit of the series is 3.693 eV. The C exciton is revealed at 3.813 eV ($n=1$) in the same polarization [7]. The reflection coefficient for the B-excitonic series is 21% at 3.6 eV, and the dielectric constant ϵ_b is 7.2. A value of the effective mass μ equal to $0.09m_0$ is derived for a binding energy of 25 meV.

The phase φ of the reflected beam and the magnitude of the absorption coefficient K in the resonance region of Γ_4 and Γ_5 excitons are obtained from the calculations of reflection spectra by means of Kramers-Kronig relations (Fig. 1). It is known that the amplitude of the reflection coefficient R is related to the phase φ of the reflected beam according to the following expression:

$$r = \sqrt{R}e^{-i\varphi} \quad (1)$$

The optical functions n , k , R , φ , ϵ_1 , ϵ_2 are related to each other by the following correlations:

$$\left\{ \begin{array}{l} r = \frac{N-1}{N+1} = \frac{n+ik-1}{n+ik+1} \\ r = \sqrt{R}e^{-i\varphi} = \sqrt{R}(\cos\varphi - i\sin\varphi) \end{array} \right. \quad (2) \quad \left\{ \begin{array}{l} n = \frac{1-R}{1-2\sqrt{R}\cos\varphi+R} \\ k = \frac{2\sqrt{R}\sin\varphi}{1-2\sqrt{R}\cos\varphi+R} \end{array} \right. \quad (3)$$

The phase $\varphi \approx \varphi(\omega)$ is calculated for each wavelength value by using the Kramers Kronig integrals on the basis of experimentally measured amplitude values of the reflection coefficient $R \approx R(\omega)$. The phase of the reflected beam is related to the amplitude according to the following expression:

$$\varphi(\omega_0) = \frac{\omega_0}{\pi} \int_0^{\infty} \frac{\ln R(\omega)}{\omega_0^2 - \omega^2} d\omega \quad (4)$$

The spectral dependences of the phase of the reflected beam and the absorption magnitudes in the region of excitonic resonances Γ_4 and Γ_5 are also shown in Fig. 1. It is evident from the calculated results that the phase of the reflected beam changes in the same way for both excitonic resonances, reaching the lowest values at frequencies near ω^L . A difference is observed in the contours of the absorption spectra for Γ_4 and Γ_5 excitons. For the Γ_4 excitons, the absorption maximum nearly corresponds to the transversal exciton frequency ω^T , while for Γ_5 excitons it is shifted towards the frequency of longitudinal exciton ω^L .

3.2. Birefringence in crystals and interference of CuAlSe₂ single crystals

When the light waves pass through a thin crystal with plane parallel surfaces, the waves reflected from the first and second surfaces interfere. The condition of interference is the following:

$$2\pi nd\lambda^{-1} = N\pi + \pi/2 \quad (5)$$

From the spectral position of two neighboring maxima (minima) λ_a , λ_b of the transmission or reflection spectra one can determine the refractive index, if the thickness d of the sample is known. The transmission or reflection spectra are measured separately for the $E \parallel c$ and $E \perp c$ polarizations, and the refractive indices n_{\parallel} and n_{\perp} are determined, respectively:

$$n_{||} = 1/2d(\lambda_{a||}^{-1} - \lambda_{b||}^{-1}) \text{ for the } E||c \text{ polarization,}$$

$$n_{\perp} = 1/2d(\lambda_{a\perp}^{-1} - \lambda_{b\perp}^{-1}) \text{ for the } E\perp c \text{ polarization,}$$

where n is the refractive index, d is crystal thickness, and λ_a and λ_b are the wave length of maxima in the transmission spectrum.

The difference of the refractive indices can be determined from measurements with cross-oriented (or parallel-oriented) polarizers. In a crystal situated between the two polarizers the light waves with polarizations $E||c$ and $E\perp c$ gain a difference of phases and interfere, producing a series of bands. The difference in phase is acquired due to different light velocities for the waves with different polarizations, i.e. due to different values of $n_{||}$ and n_{\perp} . As shown in the lower part of figure 2, a narrow transmission band with very weak side bands is observed at the wavelength λ_0 in the spectrum of a thick sample ($d= 570 \mu\text{m}$) placed between two cross-oriented polarizers (band-pass mode) [19]. A narrow absorption band is observed for the crystal with this thickness placed between two parallel-oriented polarizers (not shown in this figure). For a thinner crystal ($d= 15 \mu\text{m}$) placed between two parallel-oriented polarizers, a series of bands 1–10 are produced on the short-wavelength side of the isotropic point, while the bands a1–a7 are produced on the long-wavelength side of λ_0 (upper part of figure 2). The emergence of these side bands is due to the small thickness of the sample. The number of bands is determined by the thickness of the sample and the difference $\Delta n = n_o - n_e$. The value of Δn is determined from the position of interference bands and the thickness of the crystal. The method with two polarizers for measuring the birefringence is more sensitive and efficient compared to the method using separate polarizers for the determination of n_o and n_e refractive indices: $\Delta n = N_{\perp} \lambda / d$, where $N_{\perp} = 0, \pm 1, \pm 2, \dots$

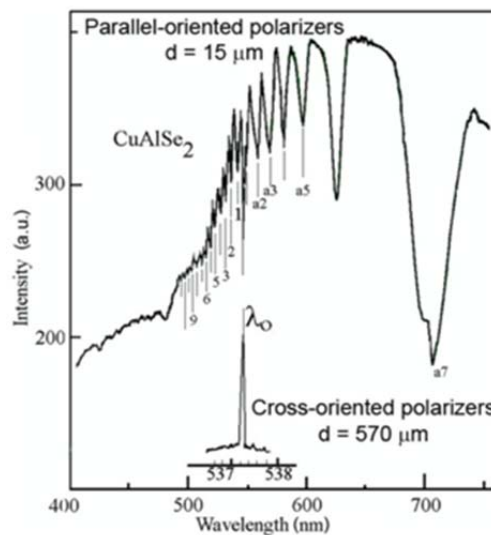


Figure 2. Transmission spectrum of CuAlSe_2 crystals measured with cross-oriented and parallel-oriented polarizers.

4. Conclusions

The results of this study demonstrate that CuAlSe_2 crystals possess a strong anisotropy of optical properties in the region of excitonic transitions. The parameters of Γ_4 and Γ_5 excitons were determined by Kramers-Kronig calculations of the reflection spectra, and the energy interval between the $\Gamma_7-\Gamma_6$, $\Gamma_6-\Gamma_6$ and $\Gamma_7-\Gamma_6$ bands were found to be of 3.575, 3.693, and 3.963 eV, respectively.

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