

## STUDY OF OPTICAL SPECTRA OF SEMICONDUCTING COMPOUND CuInSe<sub>2</sub> IN WIDE ENERGY REGION

A.I. Kozlov, V.E. Grachev, S.G. Kozlova, \*V.V. Sobolev, and \*\*I.V. Bodnar.

*International Laboratory of Superconductivity and Solid-State Electronics (LISES),  
Academy of Sciences, Academiei str.5, Kishinev MD2028, Moldova;  
\*Udmurt State University, University str.1, Izhevsk 426034, Russia;  
\*\*Belarusian State University of Informatics and Radioelectronics,  
P.Brovka str.6, Minsk 220027, Belarus  
E-mail: kozlov@lises.asm.md*

### Abstract

The precise reflectivity spectra of copper indium diselenide are obtained in energy range 1 to 5 eV at 80 K for polarized light ( $\mathbf{E} \perp \mathbf{c}$ ,  $\mathbf{E} \parallel \mathbf{c}^*$ ). For the first time the spectra for pure polarization  $\mathbf{E} \parallel \mathbf{c}$  are evaluated. Optical functions in energy range 1- 23 eV are calculated using Kramers–Kronig transformations.

### Introduction

CuInSe<sub>2</sub> crystals belong to I-III-VI<sub>2</sub> group of semiconducting compounds and are characterized by a large reduction in the energy band gap  $E_g$  and in spin–orbit splitting  $\Delta_{so}$  as compared to their binary analog (see review [1]). These crystals reveal chalcopyrite structure (space group  $D_{2d}$ ). The different methods were used for growing of these crystals [2-4].

The optical properties of copper indium diselenide were investigated by different methodic (reflection, electroreflection, electron loss spectra) [5-10]. Electron band structure of CuInSe<sub>2</sub> was envisaged in [1,7,8]. The band structure calculations with the pseudopotential method were carried out in [11]. The value of  $E_g$  obtained experimentally is equaled to 1.0 – 1.3eV. Theory predicts the value from 0.8 to 1.6 eV [11,12]. The top of the valence band is located at  $\Gamma$  point and consists of three levels. So three exciton-like series of transitions are registered in experimental spectra. From energy positions of these three excitonic peaks parameters of spin-orbit and crystal field splitting may be evaluated.

### Reflectivity spectra

In this work the polarized reflection spectra of CuInSe<sub>2</sub> measured in the energy interval 1 to 5 eV are presented. The specimens were grown by iodine transport and had developed mirror-like surfaces of  $(10\bar{1})$ ,  $(01\bar{1})$  and  $(11\bar{2})$  types.

The reflectance spectra measurements were made at the installation built on base of DFS-12 monochromator, working in the first order of diffraction [13]. The installation was supplied with the glass cryostat with quartz window, in which the samples were cooled with liquid nitrogen through the copper bulk finger, and with a Glan-Thompson polarizing prism as a polarizer. For the measurements the more developed faces of  $(11\bar{2})$  type were used. The optical axis does not lie on the surface of any face of crystal but constitutes the angle near 35.1° with the surface of face  $(11\bar{2})$ . So the measured spectrum at polarization  $\mathbf{E} \parallel \mathbf{c}^*$  ( $\mathbf{c}^*$  is the

projection of optical axis on the reflective plane) contains admixture of spectrum related with the polarization  $\mathbf{E}\perp\mathbf{c}$ .

### Determination of “pure” polarization

The simple method [14,15], based on the recalculation of optical functions, was used for obtaining of the optical functions related with the pure polarization  $\mathbf{E}\parallel\mathbf{c}$ . For this method we do not need any additional measurements. It is based on the simple relationship [16] between the optical permittivities for extraordinary beams expanding in uniaxial absorbing crystal in different directions and parameters of tensor of complex permittivity of compound:

$$\frac{1}{\hat{\varepsilon}_\alpha} = \frac{\cos^2(\alpha)}{\hat{\varepsilon}_o} + \frac{\sin^2(\alpha)}{\hat{\varepsilon}_e}, \quad (1)$$

where  $\hat{\varepsilon}_\alpha = n_\alpha^2 - k_\alpha^2 - 2in_\alpha k_\alpha$  is equivalent complex permittivity,  $n_\alpha$  is refractive index and  $k_\alpha$  is extinction index, relating to the beam of light expanding in absorbing uniaxial crystal in direction forming angle  $\alpha$  with the optical axis;  $\hat{\varepsilon}_o = n_o^2 - k_o^2 - 2in_o k_o$  is parameter of tensor of complex permittivity of compound for  $\mathbf{E}\perp\mathbf{c}$  (ordinary beams of light);  $\hat{\varepsilon}_e = n_e^2 - k_e^2 - 2in_e k_e$  is parameter of tensor of complex permittivity of compound for  $\mathbf{E}\parallel\mathbf{c}$  (extraordinary beams of light). So for obtaining of data related with optical properties of compound for the polarization  $\mathbf{E}\parallel\mathbf{c}$  we need only to calculate optical functions, relating to polarizations  $\mathbf{E}\parallel\mathbf{c}^*$  and  $\mathbf{E}\perp\mathbf{c}$ , and to calculate all that we desire using relationship (1). The FORTRAN program for the calculating of optical functions of uniaxial crystals with the optical axis, forming finite angle  $\alpha$  with the surface under investigation, using the Kramers-Kronig transformations, was developed.

### Optical functions in wide energy interval

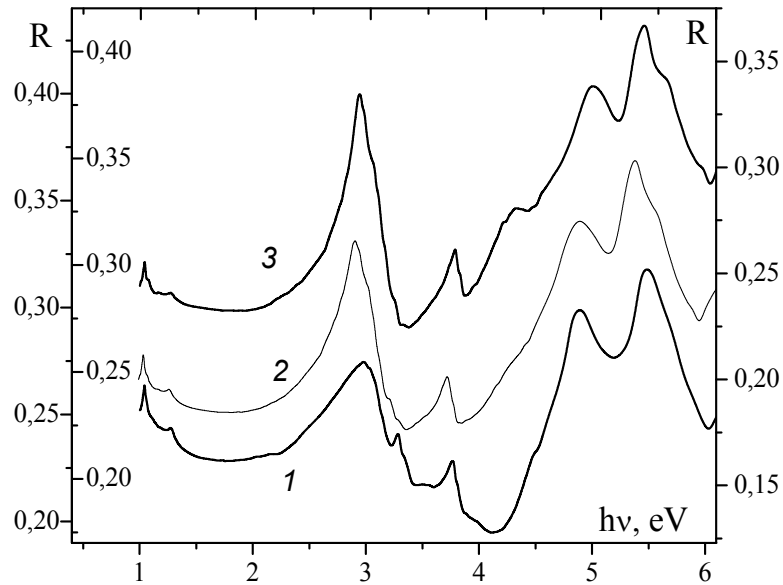
For the calculating of optical functions of  $\text{CuInSe}_2$  on the base of our experimental data in region 1 to 5 eV we used the data of other authors in the range 4–23 eV [5,6]. The full complex  $(R, \varepsilon_1, \varepsilon_2, n, k, \mu, \varepsilon_2 E^2, n_{ef}, \varepsilon_{ef}, \text{Im}(\varepsilon^{-1}), \text{Im}(1+\varepsilon)^{-1}, \alpha, \beta, \theta)$  of optical functions has been calculated for polarizations  $\mathbf{E}\perp\mathbf{c}$ ,  $\mathbf{E}\parallel\mathbf{c}^*$  and  $\mathbf{E}\parallel\mathbf{c}$  at 80K. The technique of calculations is described in [13,17,18].

The optical functions in the investigated region exhibit strong anisotropy (Fig.1 to 4). At the low energy edge of fundamental absorption band near 1eV one can find the doublet exciton-like structure in polarization  $\mathbf{E}\perp\mathbf{c}$ , which in polarizations  $\mathbf{E}\parallel\mathbf{c}^*$  and  $\mathbf{E}\parallel\mathbf{c}$  becomes the triplet. These peculiarities are connected with direct transitions excited between top of valence band triply splitted by noncubic crystalline field and spin-orbit interaction and the lowest state at a bottom of conduction band. Exciton spectra have been investigated earlier in [19-21].

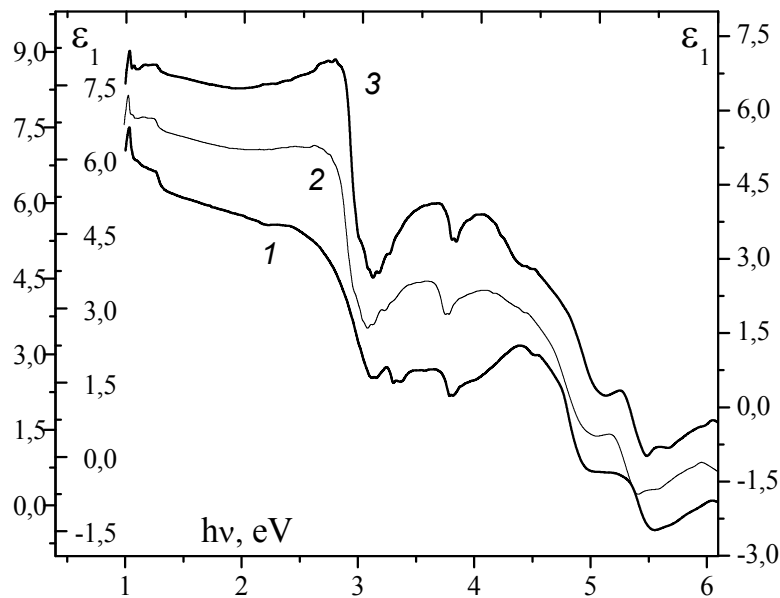
Three polarized maxima in  $R$  spectra in the energy range 2 to 4 eV may be connected with excitons from Cu 3d subband, which is included in chemical interaction in the copper based compounds [9].

At energies higher than 4 eV the strong broad band of absorption with complicated polarization dependence is found. All spectra exhibit the pronounced polarization dependence. Some maxima in  $R$  at  $\mathbf{E}\perp\mathbf{c}$  have notable shift or absent in comparison with  $\mathbf{E}\parallel\mathbf{c}$  (Fig.1). Energies of prominent reflectance features of  $\text{CuInSe}_2$  between 2 and 6 eV are following: 2.94, 3.24, 3.72, 4.80 and 5.40 eV ( $\mathbf{E}\perp\mathbf{c}$ ), 2.91, 3.72, 4.89, 5.4 eV ( $\mathbf{E}\parallel\mathbf{c}^*$ ), 2.91,

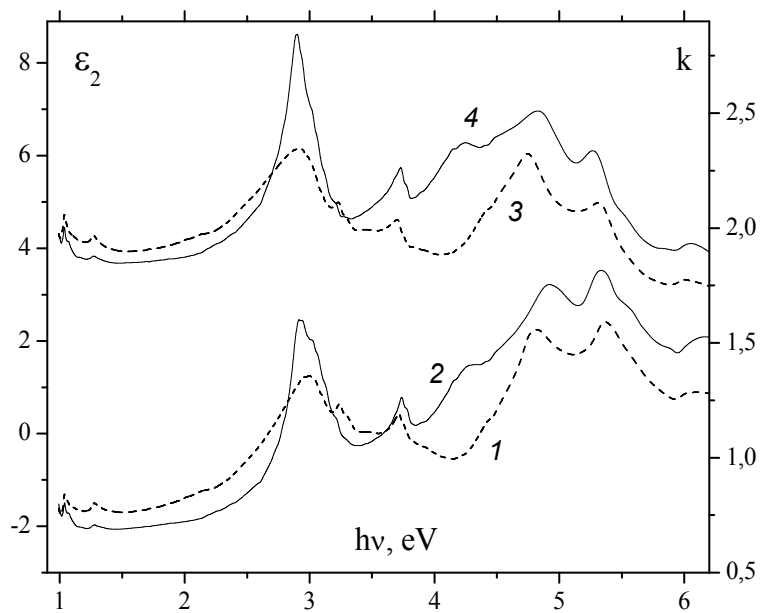
3.74, 4.27, 4.95, 5.39 eV ( $\mathbf{E}\parallel\mathbf{c}$ ). The authors of article [5] have published other data: 2.92, 3.24, 3.72, 4.85, 5.43 (5.38) eV. These results are obtained due to a contribution of about 35% of  $\mathbf{E}\perp\mathbf{c}$  to the spectrum with nominal  $\mathbf{E}\parallel\mathbf{c}^*$ .



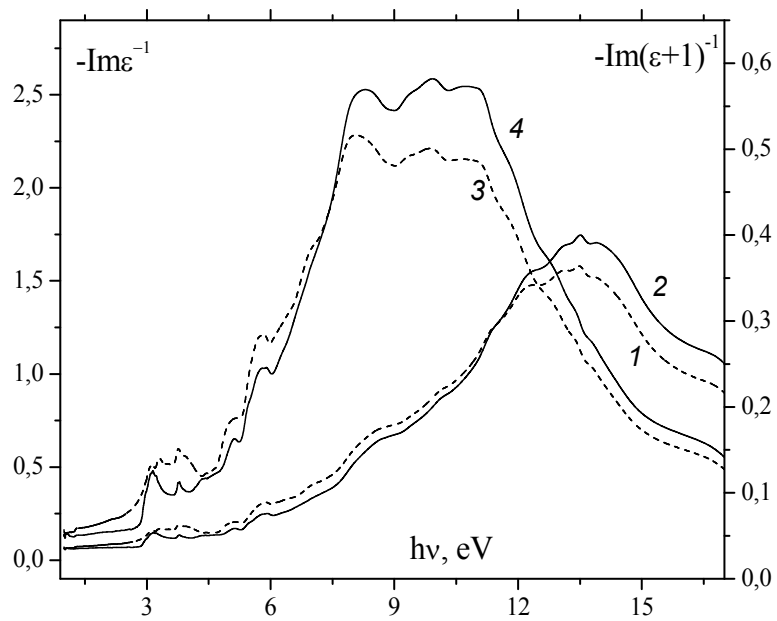
**Fig.1.** Reflectivity spectra  $R$  of  $\text{CuInSe}_2$  at temperature 80K for polarizations  $\mathbf{E}\perp\mathbf{c}$  (1),  $\mathbf{E}\parallel\mathbf{c}^*$  (2) and  $\mathbf{E}\parallel\mathbf{c}$  (3).



**Fig.2.** Real part of dielectric function  $\epsilon_1$  of  $\text{CuInSe}_2$  at temperature 80K for polarizations  $\mathbf{E}\perp\mathbf{c}$  (1),  $\mathbf{E}\parallel\mathbf{c}^*$  (2),  $\mathbf{E}\parallel\mathbf{c}$  (3).



**Fig.3.** Optical functions  $k$  (1,2) and  $\epsilon_2$  (3,4) of  $\text{CuInSe}_2$  at 80K and polarizations  $\mathbf{E} \perp \mathbf{c}$  (1,3) and  $\mathbf{E} \parallel \mathbf{c}$  (2,4).



**Fig.4.** Optical functions  $-\text{Im}\epsilon^{-1}$  (1,2) and  $-\text{Im}(\epsilon+1)^{-1}$  (3,4) of  $\text{CuInSe}_2$  at 80K and polarizations  $\mathbf{E} \perp \mathbf{c}$  (1,3)  $\mathbf{E} \parallel \mathbf{c}$  (2,4).

The functions  $\varepsilon_1$  (see Fig.2),  $\varepsilon_2$ ,  $k$ ,  $Im(\varepsilon^{-1})$ ,  $Im(1+\varepsilon)^{-1}$  (see Fig.3,4) exhibit different behavior in polarizations  $\mathbf{E}\perp\mathbf{c}$  and  $\mathbf{E}\parallel\mathbf{c}$ . The spectra  $k$ ,  $\varepsilon_2$  are looking like spectrum  $R$ , especially in case of  $\mathbf{E}\perp\mathbf{c}$ . The form of spectra  $\varepsilon_1$  differs significantly from those of  $R$ . The absorption index  $\mu$  at energy 6 eV reaches  $0.8\cdot 10^{-6}\text{sm}^{-1}$  ( $\mathbf{E}\perp\mathbf{c}$ ),  $0.9\cdot 10^{-6}\text{sm}^{-1}$  ( $\mathbf{E}\parallel\mathbf{c}$ ). The functions of surface and bulk plasmons have noticeable structures at energies 8-11 eV and 13-14 eV. The function  $\varepsilon_{ef}$  reaches saturation at 9 eV, but  $n_{ef}$  doesn't reach saturation at 21 eV.

*The results obtained give the most total information about band structure of CuInSe<sub>2</sub> and the reliable basis for the more precise determination of band structure of this compound.*

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