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THE PHASE ANALYSIS AND OPTICAL PROPERTIES OF COMPOUNDS $InGaTe_2$, $InGaSe_2$, $TlGaSe_2$, $TlGaTe_2$

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***Abstract*—The paper presents the results of X-ray analysis, the study of surface microrelief by atomic - force microscope and optical absorption spectra of monocrystals $InGaTe_2$, $InGaSe_2$, $TlGaSe_2$, $TlGaTe_2$ obtained by the method of Bridgman - Stokbarger in the energy range of 0.5 -2,5eV. The energies of the direct and indirect transitions and band gap of these phases.**

INTRODUCTION

$A^{III}B^{VI}$ type compounds still has not lost its relevance because of their interesting physical properties and practices. It is known that compounds $A^{III}B^{VI}$ and their triple analogues $A^{III}B^{III}C^{VI}_2$ are a group of chain-layered crystal [1-4].They have a special place among the compounds, which have crystal structure with high anisotropy. Widely investigation of the properties, including optical of these compounds, opens new practical opportunities

Among the types of compounds $A^{III}B^{III}C^{VI}_2$ chain-layered monocrystalsInGaSe$_2$, InGaTe$_2$, TlGaTe$_2$ and TlGaSe$_2$ present special interest.

$TlGaTe_2$ crystallizes in the tetragonal syngony with lattice parameters of $a = 8{,}37\ \overset{0}{A}, c = 7{,}8\ \overset{0}{A}$, with spatial group $D^{18}_{4h}(I4/mcm)$, the band gap is 0.86eV and these studied with detail in works [5-11].

$TlGaSe_2$ crystallizes in monoclinic system with lattice parameters *a*=7.772 Å; *b*=10.771 Å; *c*=15.636 Å; β=100.06^0, with the number of formula units in the unit cell Z=16 and spatial group C_2, the band gap is 2,375eV.Someresults of a study of this phase described in [12-16].

Semiconductor compound $InGaSe_2$ refers to a tetragonal system, the unit cell contains two formula units the lattice parameters a=8.0511 Å, c=6.3174 Å, space group symmetry $D^{18}_{4h}(I4/mcm)$, the band gap is 1,52eV.Investigatedenergy spectrum and some properties of compounds in [17-19].

Ternary compound $InGaTe_2$ were investigated in [20-24].It was revealed that monocrystals $InGaTe_2$ have a tetragonal crystal structure with the space group symmetry $D^{18}_{4h}(I4/mcm)$ and with the lattice parameters $a = 8{,}463\ \overset{0}{A}$ и $c = 6{,}981\ \overset{0}{A}$.The band gap of the compound is 1.42eV.

In this paper carried out X-ray analysis, studied the surface micro relief and optical spectra absorption of monocrystalsInGaSe$_2$, InGaTe$_2$, TlGaTe$_2$ and TlGaSe$_2$

EXPERIMENTAL METHOD

The alloys were synthesized in vacuumed 0.0133Pa in quartz ampoule. As starting materials used Tl- 99.99 mass. %; . In- 99.99 mass %; Ga-99.99 mass. %; Se- special clean 16-5, Te-99.933mass%, S - special clean 16-5. During synthesis, used vibratory mixing. The homogenizing annealing of synthesized alloys was carried out at 860-920K for 70-90 hours. Monocrystals of compounds $TlInS_2$, $TlGaSe_2$, $InGaSe_2$ and $InGaTe_2$ grown by the method of Bridgman-Stock Barger that described in [13]. X-ray diffraction analysis was carried out in installation DRON-2 (CuK_α - radiation, $\lambda = 1.54178\ \overset{0}{A}$). The error in determining the lattice parameters was 0.005 $\overset{0}{A}$.

It is known that Scanning Force Microscopy- one of the most powerful modern methods of investigation of the morphology and local properties of a solid surface with high spatial resolution [25].

We have investigated the surface microrelief of monocrystals $TlGaSe_2$, $TlGaTe_2$, $InGaSe_2$ and $InGaTe_2$ by scanning probe microscope in an atomic-force mode.

To obtain an image by this method was carried out in a special way organized sample scanning. While scanning the probe initially moved over the sample

along a certain line and the value of the signal to the actuator is proportional to the topography of the surface, and recorded in the computer's memory. Then the probe back to the starting point and go to the next scan line, and the process was repeated again.

In the investigated crystals, the optical absorption coefficient α (hv), depending on the energy hv radiation incident on the sample was calculated from the measured transmittance T (hv) and reflection R (hv) according to the formulas [26]:

$$T = \frac{(1-R)^2 \cdot \exp(-\alpha d)}{1-R^2 \cdot \exp(-\alpha d)} \quad (1)$$

and

$$\alpha = \frac{1}{d} \ln \left\{ \frac{(1-R)^2}{2T} + \left[R^2 + \left(\frac{1-R}{4T^2} \right)^4 \right]^{1/2} \right\} \quad (2)$$

Equation (1) is valid in the transmission coefficient T values

$$\frac{1-R}{1+R} < T < 10\%,$$

i.e. knowing the values of T and R for the same sample by the formula (2) may be with accuracy 5-7% to determine the absorption coefficient α.

The measurements of the coefficients T and R were carried out in the experimental plant with using a modulation technique and special cryostat, which allows maintaining the temperature of the sample to an accuracy of 0.1 K and a vacuum ≈0,133Pa. As the radiation source used xenon headlight DKSM-250, quartz and hydrogen lamp LP-201 (Germany). The optical part of the installation consisted of spectrometers VS2-2p monochromatic MDR-4 and Perkin-Elmer, FEU-39 were used as radiation detectors, 51, 83, narrowband amplifiers U2-6, V6-4, lock-in-Amplifier, modelh-8 , PARTM-model 124 and synchronous detector K3-2. The signals were recorded on the chart recorder of the two models Endism 620-02.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of X-ray diffraction (Figure 1), micro-relief of surfaces (Figure 2), the optical absorption spectra studies (OAS) (Fig. 3.4) in compounds $InGaSe_2$, $InGaTe_2$, $TlGaTe_2$ and $TlGaSe_2$ are given in figures 1-4.

For $TlGaSe_2$ observed exponential area in the range of the absorption coefficient α=20÷120 sm^{-1}. In the exponential slopes of p-TlGaSe2 edge of OAS respectively at different temperatures have the following values S_{100} = 34.61 eV^{-1} (T = 100 K); S_{300} = 18.94 eV^{-1} (T=300K); S_{400} = 16.07 eV^{-1} (T=400K).

Extrapolating to the high values of α absorption coefficient leads to the convergence curves α photons of energy hv. The point of convergence of the curves corresponds to the width of the forbidden zone studied object E_{g0} at T=0K.

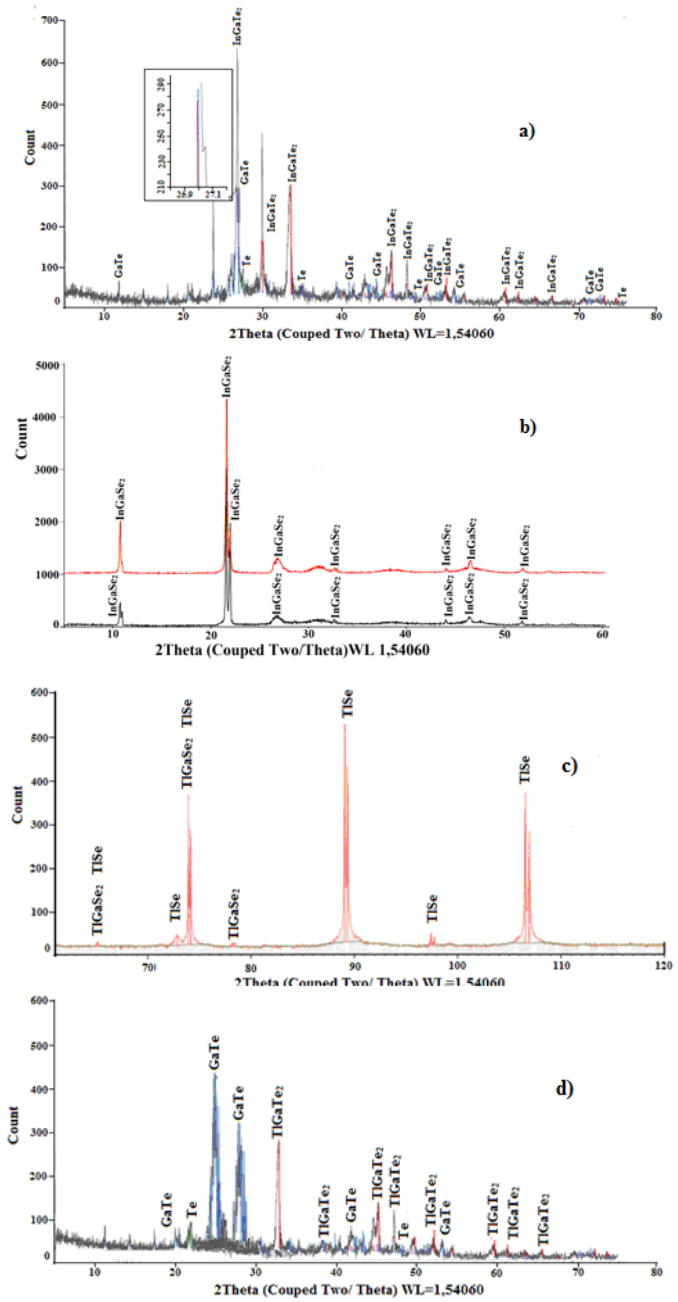

Fig. 1. XRD patterns of compounds a) $InGaTe_2$ b) $InGaSe_2$ c) $TlGaSe_2$ d) $TlGaTe_2$

The value of p-$TlGaSe_2$ E_{g0}=2.375 eV and $\alpha_0 = 7.5 \cdot 10^3$ sm^{-1}. In the temperature offset edge OAS p-$TlGaSe_2$ found especially at temperatures of 101 K; 106 K; 108 K; 117.2 K; 135- 150 K; 253 K and 340 K, related, appear to structural changes in the compound (Figure 3). As seen in Figure 3, in the area of structural transitions iso-absorption curves have some kinks that in some way makes it difficult to extrapolate the curves. However, given the small fractures temperature dependence data iso-absorption can be extrapolated to zero value of temperature.

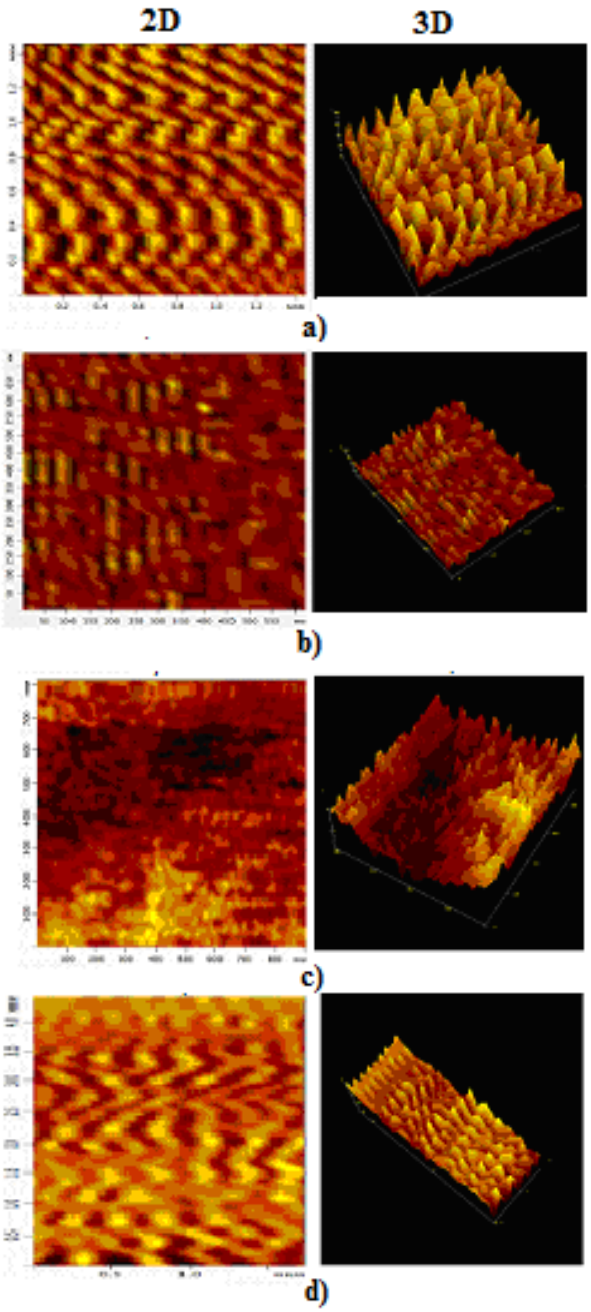

Fig.2 The Microrelief of the surfaces of compounds a) $InGaTe_2$ b) $InGaSe_2$ c) $TlGaSe_2$ d) $TlGaTe_2$ in 2D and 3D scale.

The obtained value of the energy gap at T=0 K E_{g0}=2.380 eV satisfactorily coincides with the value E_{g0}=2.375eV, calculated from the spectral dependence of the absorption coefficient measured at different temperatures. Average coefficient of thermal displacement in this area of the absorption coefficient α (α=10^2 см$^{-1}$) $(dE_g/dT)_p$= -3.42·10^{-4} eV/K.

As seen from Figures 3 a, b, c, d for all the compounds studied in the curve of the energy of the incident photons is first observed a smooth, then a sharp increase in the absorption coefficient. It is known that a sharp increase in the absorption coefficient characteristic for direct optical transitions.

Therefore, the area of the weak growth of the absorption coefficient can be related to indirect optical transitions, and a sharp rise in area - with direct transitions. Figure 3. shows the dependence $\alpha^2 = f(h\nu)$ and $\alpha^{1/2} = f(h\nu)$ for the direct optical transitions, respectively. Extrapolation of linear plots to zero value $(\alpha h\nu)^{1/2} \to 0$ and $(\alpha h\nu) \to 0$ defined energy of direct and indirect transitions for compounds $InGaSe_2$ $InGaTe_2$, $TlGaTe_2$ and $TlGaSe_2$ at room temperature. The obtained values are given in the table.

Table.

Compounds	***Energy absorption on the boundary (eV)***	***Energies direct transitions (eV)***	***Energies indirect transitions (eV)***
$InGaSe_2$	1,28	1	0,72
$TlGaSe_2$	2,155	2,20	2,125
$InGaTe_2$	0,78	0,9	0,8
$TlGaTe_2$	0,72	0,93	0,68

At higher values of the absorption coefficient α in the p-$TlGaSe_2$, observed the area of direct and indirect "allowed" optical transitions. Analysis of the spectral dependence of the α from photon energy hv showed that the bandgap $TlGaSe_2$ for direct - E_{gd} and indirect - Egi optical transitions was, respectively, equal to (at T = 300 K): E_{gd} = 2.154 eV and E_{gi} = 2.125 eV for p -$TlGaSe_2$.

Exponential optical absorption edge. Urbach rule.

The question of the physical basis of the empirical Urbach rule was considered in many studies [27-28]. Most of the works devoted to the subject, explain the exponential edges of the objects OAS interaction of electrons (excitons) with vibrations of the crystal lattices. There are a number of works in which analyzed the weak and strong exciton - phonon interaction. The most reliable in explaining Urbach "tail" of the absorption in polar crystals, including in ferroelectric materials, which include some of the compounds type $A^{III}B^{III}C^{VI}_2$ (eg, $TlGaSe_2$, $InGaSe_2$, $InGaTe_2$ and $TlGaTe_2$), is the theory of Mahan [29] get the right approach Urbach for electrons in the conduction band parabolic interacting with longitudinal optical phonons.

Furthermore, as random electrical fields associated with the thermal fluctuations of volume density of free charge carriers, and thermal fluctuations of the electrical polarization of a significant effect on the shape of the edge of OAS ferroelectrics [30]. Both of these mechanisms cause local deformation of the valence band and the conduction band, which leads to an exponential form OAS edges of the objects.

Thus, this suggests that the exponential shape of the edge of OAS is characteristic of polar crystals, including those for test compounds AIIIBIIICVI2, and most likely regularity describing the shape and temperature behavior of OAS edge is rule Urbach.

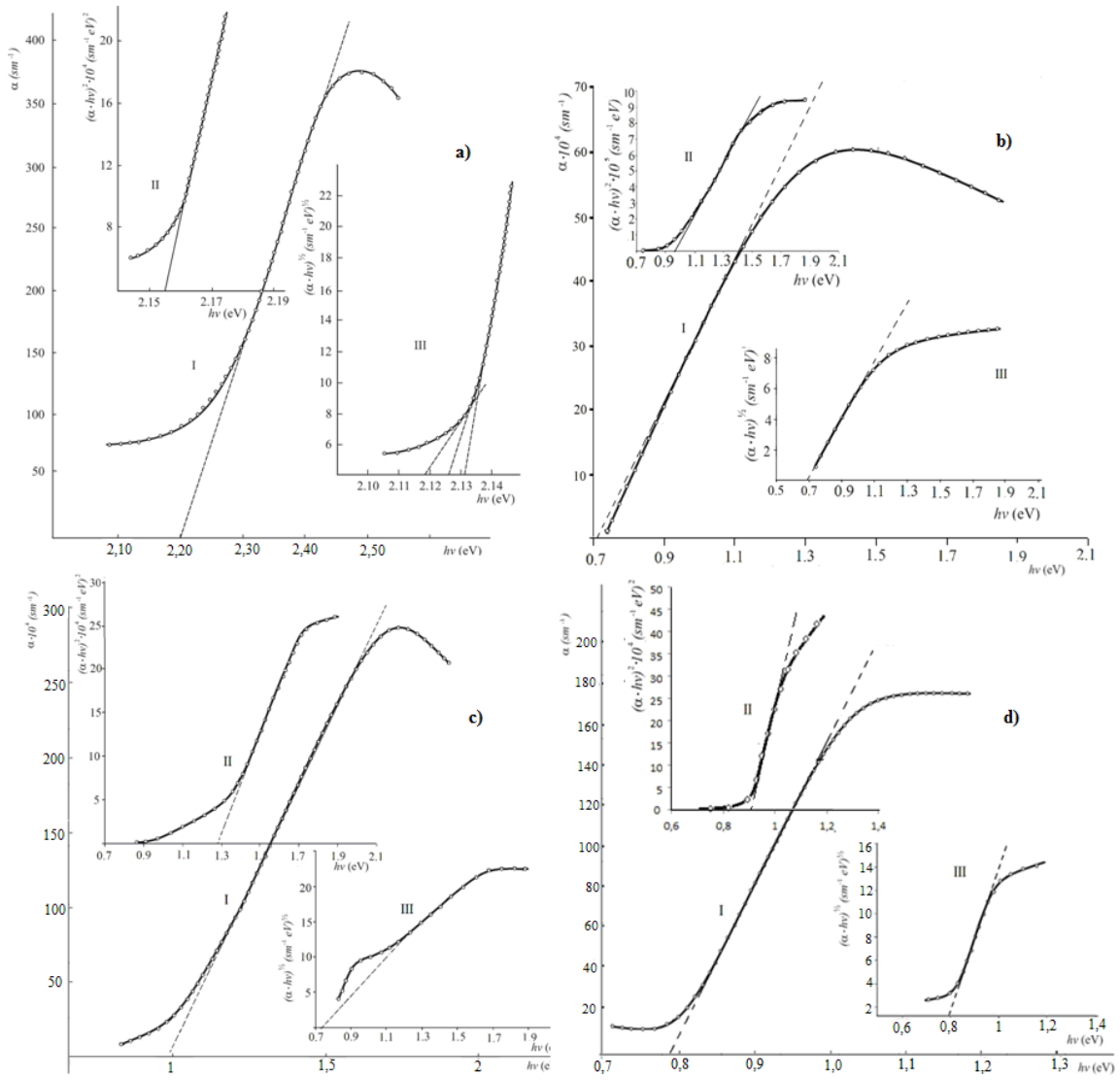

Figure 3. The spectral dependence of the optical absorption monocrystals $TlGaSe_2$ (a), $TlGaTe_2$ (b), $InGaSe_2$ (c), and $InGaTe_2$ (d) on the border of the absorption at 300 K (I) in the area of direct transition (II) and in indirect (III) transition.

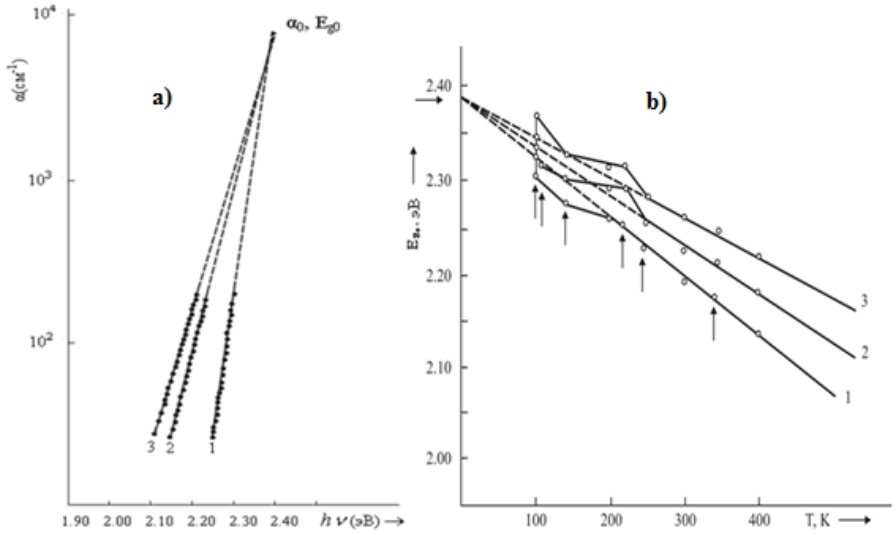

Figure 4. The spectral dependence of the exponential section optical absorption edge of the crystal $TlGaSe_2$ at temperatures of 1-77K, 2-300K and 3-400K. α_0- E_{g0} and values of the absorption coefficient and the band gap corresponding to the temperature 0, K (a); iso-absorption curves $TlGaSe_2$ screened at temperatures 1-77K, 2-300K

3-400K and (b).

According to the rule Urbach [27-29], the exponential dependence of α absorption coefficient by photon energy hv follows the law of

$$\alpha = \alpha_0 \exp\left[\sigma\left(h\nu - E_{g0}\right)/kT\right], \quad (3)$$

where hv-energy of the photon which involved in the absorption, E_{g0}-the band gap of the crystal at T = 0 K, *κ*–is the Bolsman constant, σ-parameter which generally depends on the temperature, and in the case of electron-phonon interaction.

$$\sigma = \sigma_0 \frac{2kT}{\hbar\omega_{ph}} th\left(\frac{\hbar\omega_{ph}}{2kT}\right), \quad (4)$$

and $\hbar\omega_{ph}$ - optical phonon energy, and σ_0-parameter defined from a comparison with the experience.

Experimental results on the study edges of OAS monocrystals$TlGaSe_2$, $InGaSe_2$, $InGaTe_2$ and $TlGaTe_2$ are shown in Figures 3 and 4. It is seen that the steepness (slope) edge of OAS in these crystals is rather small. This fact is one of the reasons the assumption of strong violation of OAS edge in the studied sites. From Figure 4 shows that the absorption curves depicted in semi-logarithmic scale, provide converging "node" absorption coefficient obeys the formula (3) and a point of convergence which has coordinates α0 and $E_{g0} = hv_0$.

The temperature range for this behavior α is usually above the Debye temperature of the substance. The validity of the formula (3) may also be elucidated using iso-absorption curve. For p-TlGaSe2 this dependence is shown in Figure 4, which shows that the values of α_0 and E_{g0} close to the analogous values obtained from the temperature dependence of α.

Existing kinks on the curves of iso-absorbing crystals p-TlGaSe2 (Figure 2 section 2) relate structural changes, including with incommensurate phases in these crystals. These data are confirmed for the p-$TlGaSe_2$, $InGaSe_2$, $InGaTe_2$ and $TlGaTe_2$ as noted above, the existing structural changes in these compounds more difficult to extrapolate to zero values of temperature. The most reasonable explanation for the formula (3) in the investigated objects, is the mechanism of occurrence of sufficiently large internal fields generated polar modes of vibration of the crystal lattice [27, 28.]. However, the small value of the slope edge OAS points to a certain influence of the lattice defects type dislocations in the interlayer exponential edge OAS compounds.

The stacking faults and interlayer lattice dislocations in AIIIBIIICVI2 compounds play an essential role in shaping their edges OAS, and many of their kinetic properties are explained in terms of the influence of these defects. In [28], the average value of the internal random field, forming an exponential edge OAS, and a Gaussian distribution of its intensity E_{vn} - it can be determined based on data of the steepness of the edges of OAS and the effective mass of the charge carriers - m *

As a rough approximation, taking for m * = m_0, where m_0 - mass of the electron, and knowing the value of S = 18.94 eV^{-1} (300 K) for p-of $TlGaSe_2$, certain value E_{vn} turned out to be 5 · 10^7 V / m, lying in a reasonably theory acceptable limits.

Types of optical transitions. In all of the studied spectral dependence of the alpha crystals, when α≥10^2 cm^{-1} does not fit into the framework, we have examined above exponential OAS edge.

Optical transitions in the edges of OAS studied objects are transitions indirect type and confirmed by calculations of band structure [5,11,15,19].

CONCLUSIONS

Studied the optical properties of the compounds TlGaSe2, InGaSe2, InGaTe2 TlGaTe2 in a wide range of photon energies and temperatures. The edge of the optical absorption of these compounds consists of three types of optical transitions: exponential, direct and indirect "allowed" optical transitions. The values of the inside crystal fields and phonons participating in indirect optical transitions, and an exponential optical absorption edge and band gap for direct and indirect optical transitions. The experimental results are compared with theoretical calculations of the band structure calculated for the extreme components of the investigated solid solutions.

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