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# Urbach's edge of glassy HgSe-GeSe<sub>2</sub> alloys: static disorder and temperature dependence of optical absorption

V.V. Bozhko<sup>1)</sup>, V.V. Halyan<sup>1)</sup>, O.V. Parasyuk<sup>2)</sup>

<sup>1)</sup>Department of Solid State Physics, Volyn State University, 13 prospect Voli, 43009 Lutsk, Ukraine  
E-mail: galyan@lab.univer.lutsk.ua

<sup>2)</sup>Department of Inorganic and Physical Chemistry, Volyn State University, 13 Voli av., 43009 Lutsk, Ukraine

**Abstract.** Results of investigations of spectral characteristics in the fundamental absorption range for the glass-like alloys HgSe – GeSe<sub>2</sub> are represented. To explain the phenomenon of anomaly growth of the static disorder, the model of deforming tensions is discussed. The hypothesis concerning a sharp change of physical-and-chemical properties for the transition over the double eutectic point on the stable phase diagram of the HgSe – GeSe<sub>2</sub> system with a changing glass-creating matrix is suggested.

**Keywords:** fundamental absorption, static disorder, glass-creating matrix.

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## 1. Introduction

The research of new materials is one of the basic direction in physics of amorphous semiconductors. Multicomponent chalcogenide glasses are very promising, first of all because of switching properties and the optical storage ones. Represented system of similar to glass alloys was researched for the first time. Significant factors for determination of optical, photoelectric and radiation properties of glass-like materials are the state and form of fundamental absorption range. Investigation of the optical absorption spectra in a wide range of temperatures and for large region of glass creation is a powerful tool to ascertain the electronic structure of these semiconductors and to predict physical properties of glasses.

The optical spectra of glasses of the HgSe – GeSe<sub>2</sub> system within the range of fundamental absorption are represented. Characteristic parameters of Urbach's rule are determined. Experimental data are analysed on the basis of the generalized Urbach's rule and the principle of equivalence between static and dynamic parts of a general structural disorder [3,4,5].

## 2. Materials, glass preparation and methods of investigation

The synthesis of glasses was carried out in the evacuated (0.1 Pa) silica ampoules, upper parts of which were alloys:thermostated by the asbestos tape for decreasing losses from the gas phase. The high purity elements (Ge 99.9999 wt.%, Se 99.997 wt.%) and previously synthesised HgSe (Hg 99.999 wt.%) were used for preparation of the charges. The sample was heated up to the maximal temperature 1270 K, then were kept for 10 hours. Subsequently, the ampoules were quenched in 25% solution of NaCl. Glassy phase in the alloys was controlled using X-ray diffraction (DRON-3M diffractometer) and microstructure analysis (MMU-3 microscope). The alloys (HgSe)<sub>x</sub>(GeSe<sub>2</sub>)<sub>1-x</sub> were obtained in the interval 0 ≤ x ≤ 0.4 with step x=0.1 and in the interval 0.42 ≤ x ≤ 0.6 with step x=0.02. For optical measurements the samples in the form of parallel-sided plates polished down to 0.12-0.20 mm thickness were prepared. The quality of surfaces was checked by MII-4 interferometer.

The absorption coefficient measurements were realized using the spectrometer IKS-12 with PbS

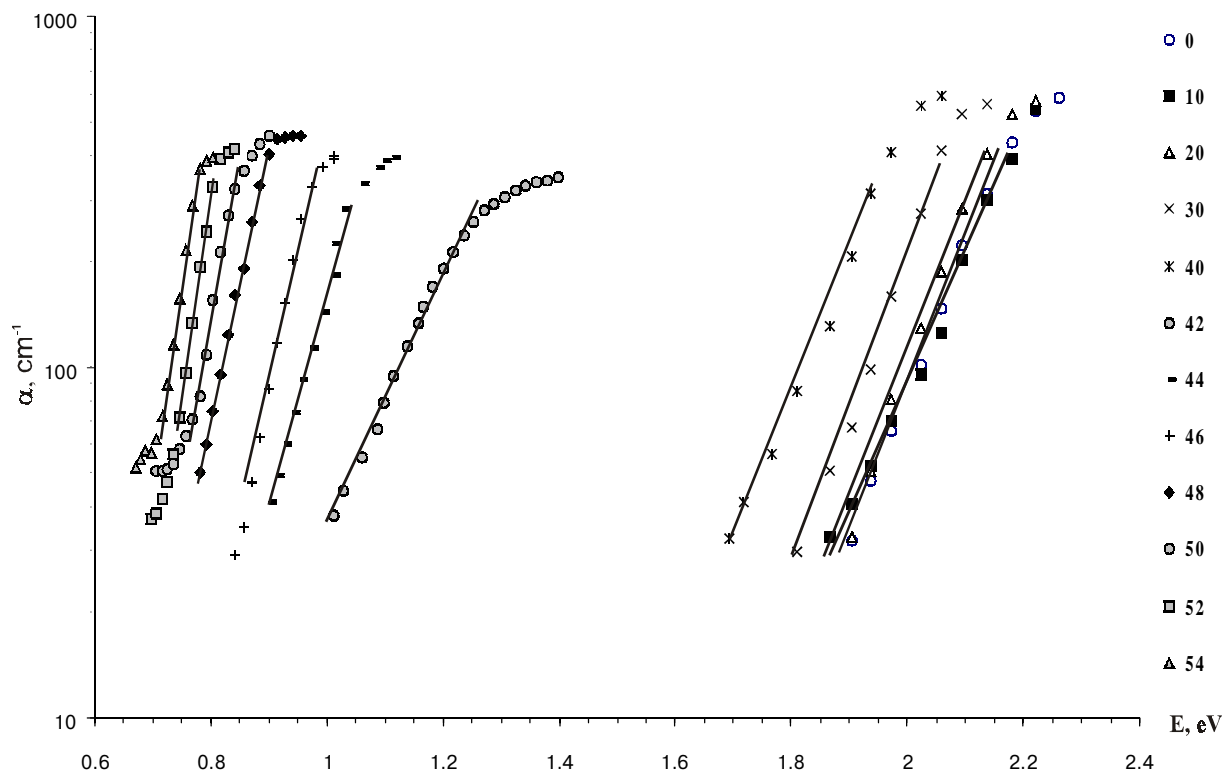


Fig. 1. Spectra of the optical absorption edge for glasses of the HgSe – GeSe<sub>2</sub> system at 290K (the numbers imply mol.% HgSe)

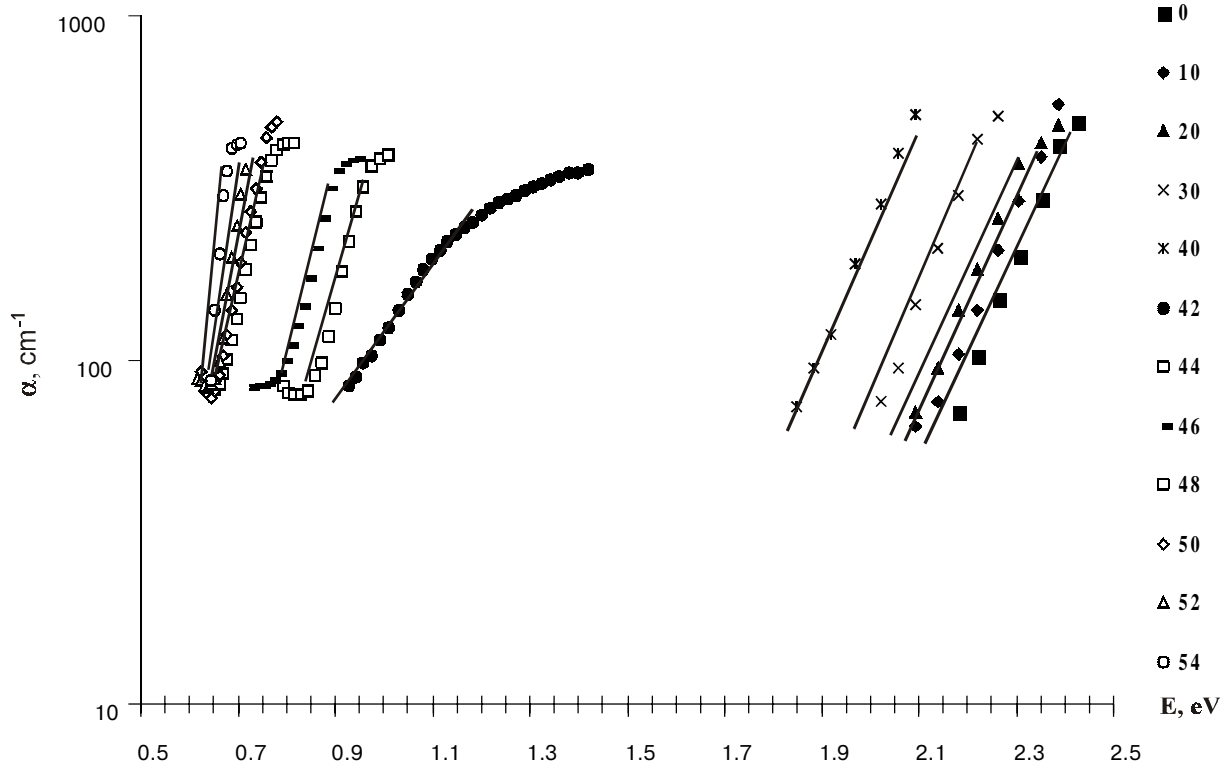


Fig. 2. Spectra of the optical absorption edge for glasses of the HgSe – GeSe<sub>2</sub> system at 77K (the numbers imply mol.% HgSe)

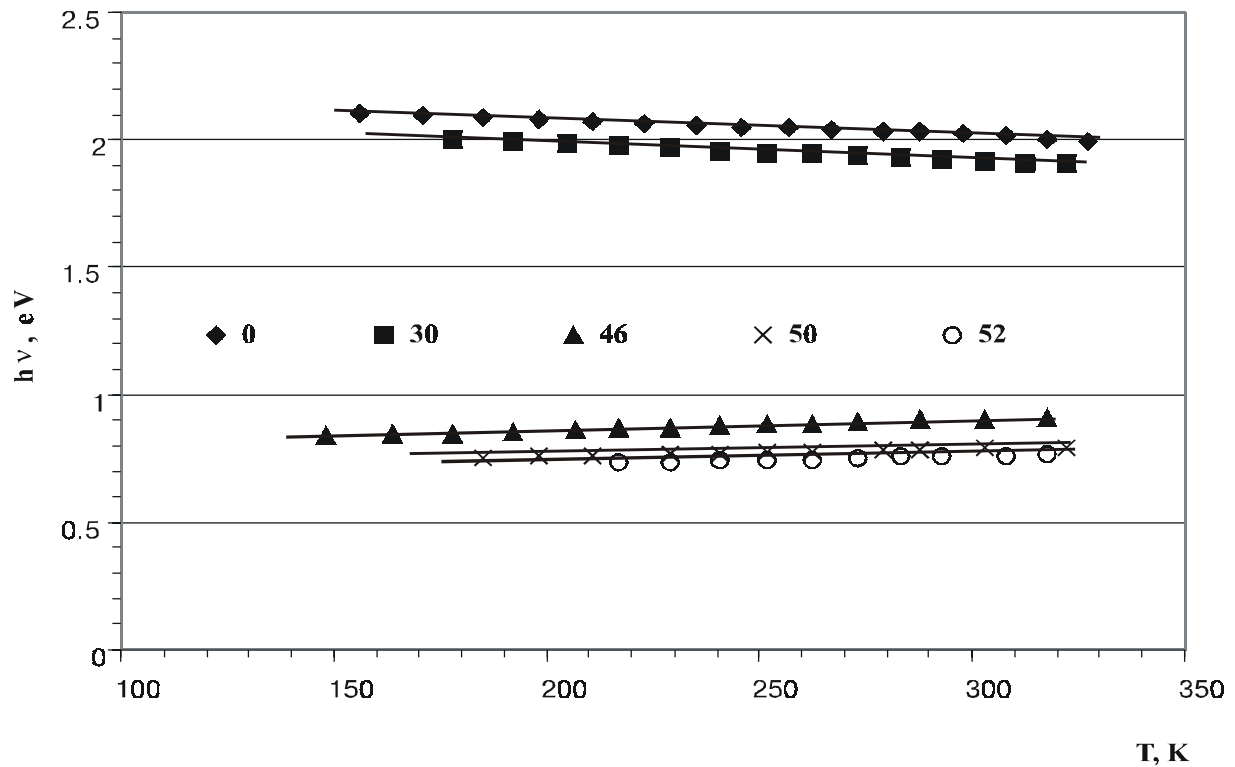


Fig. 3. Temperature dependence of the absorption edge (the numbers imply mol.% HgSe)

photodetector for the samples (42-54 mol.% HgSe – (58-46 mol.%) GeSe<sub>2</sub> and DMR-4 spectrometer with silicon photodetector for the samples (0-40 mol.%) HgSe – (100-60 mol.%) GeSe<sub>2</sub>. In both above mentioned cases, the usual circuit of synchronized detection was used. The measurements were carried out at T=290 K and T=77 K using vacuum cryostat in the spectral ranges:

- 1) 550 – 2500 nm for PbS photodetector;
- 2) 450 – 1100 nm for silicon photodetector.

For glassy alloys containing 100 mol.% GeSe<sub>2</sub>, 70 mol.% GeSe<sub>2</sub>, 54 mol.% GeSe<sub>2</sub>, 50 mol.% GeSe<sub>2</sub>, 48 mol.% GeSe<sub>2</sub> the temperature dependencies of the location of optical absorption edge were evaluated (Fig. 3) using the above mentioned spectrometers and measurement procedures.

### 3. Results

The absorption factor  $\alpha$  dependencies from photon energy  $h\nu$  at 290 K and 77 K are represented in Fig. 1,2, respectively. The ordinate axis is represented in the logarithmic scale.

When the content of HgSe increases up to 54 mol.% the shift of the straight lines describing the spectral dependencies in the lower energy range is observed. According to the X-ray data the alloys from the interval (56-60) mol.% HgSe are crystalline, therefore the results of its investigation are not considered in present paper.

The alloy containing 42 mol.% HgSe is characterized by the most flatness of the approximating line. With the increasing HgSe content more than 42 mol.%, the absorption edge are still being shifted to the low-energy direction, and decreasing Urbach's exponential tail is observed. According to the results of spectral distribution the magnitude of  $E_0$  is evaluated which represents the width of exponential edge (or its steepness [2,4]).

$$E_0 = \frac{\partial h\nu}{\partial \ln \alpha}$$

For all alloys the  $E_0$  parameter value was estimated in the range  $\alpha=80-300\text{cm}^{-1}$ .

Two samples containing 100, 70 mol.% GeSe<sub>2</sub> and several samples with the considerable content of HgSe (46, 50, 52 mol.%) were selected from the alloys of the HgSe – GeSe<sub>2</sub> system. In Fig. 3 we can see the graphs of the temperature as dependencies of optical absorption edges for the above mentioned samples. The  $h\nu(T)$  function shows the linear dependence.

Non-linear sections from the low-temperature side occurring in the phosphate or silicate glasses [5] are not registered.

In consequence of the linearity of  $h\nu(T)$  the temperature coefficient for the variation of the absorption edge location can be estimated (Table 1).

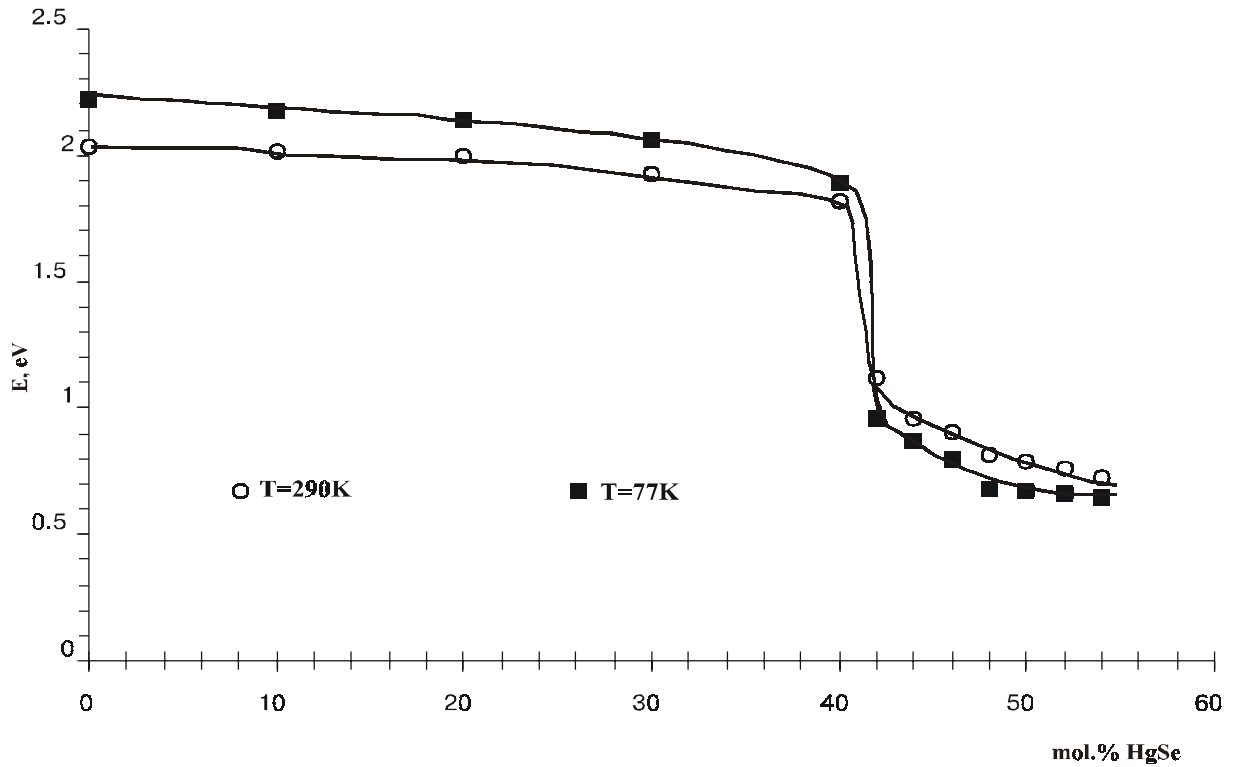


Fig. 4. The optical ionization energy determined

Table 1. Temperature coefficients of the absorption edges

Mol.%HgSe	0	30	46	50	52
$\beta \times 10^{-4} \frac{eV}{K}$	6.164	6.918	- 4.347	- 3.1	- 3.311

$$\beta = \frac{d(h\nu)}{dT}$$

According to Table 1 and Fig. 4, the temperature coefficient  $\beta$  changes the sign from “+” to “-” at the transition from the glasses with small content of HgSe to the alloys where the content of HgSe exceeds 42 mol.%.

Using the spectral distribution of the absorption factor, we can evaluate the energy gap width  $E_g$  (values  $E_g$  and  $h\nu$  were determined as energy for absorption factor  $\alpha = 100 \text{ cm}^{-1}$ ). In Fig. 4 the composition dependence of  $E_g$  for glassy alloys at T=290, 77K is given.

As we can see the decrease of the energy gap occurs for the 42 mol.% HgSe – 58 mol.% GeSe<sub>2</sub>. Here  $E_g$  for glasses containing less than 42 mol.% HgSe at T=77 K is larger than that at the room temperature. At the same time, for the alloys containing 42 and more mol.% HgSe, the energy gap is larger for the alloys examined at the liquid-nitrogen temperature. It is well agreed with the

experiment where the change of the  $\beta$  sign from “+” for the glasses having small content of HgSe to “-” for the alloys with considerable content of this component is observed.

#### 4. Theory and discussion

Obtained exponential dependencies (Fig. 1,2) would be expressed by Urbach's rule [1,4,8,9]. In general case the spectral-temperature dependence for absorption edge is evaluated from the expression

$$\alpha(h\nu, T, X) = \alpha_0 \exp \frac{(h\nu - E_g(T))}{E_0(T, X)} \quad (1)$$

where  $\alpha_0$  is a constant,  
 $h\nu$  – photon energy,

$E_g(T)$  – temperature function of the optical gap width,  
 $E_0(T, X)$  – function of the overall disorder present in system.

$E_0$  is a quantitative characteristic of disorder for glassy alloys and represents contributions of the dynamic (thermal) and static disorder components [3]:

$$E_0(T, X) = K(u^2_T + u^2_X) \quad (2)$$

$\langle u^2 \rangle_T$  – root-mean-square thermal shifting of atoms;

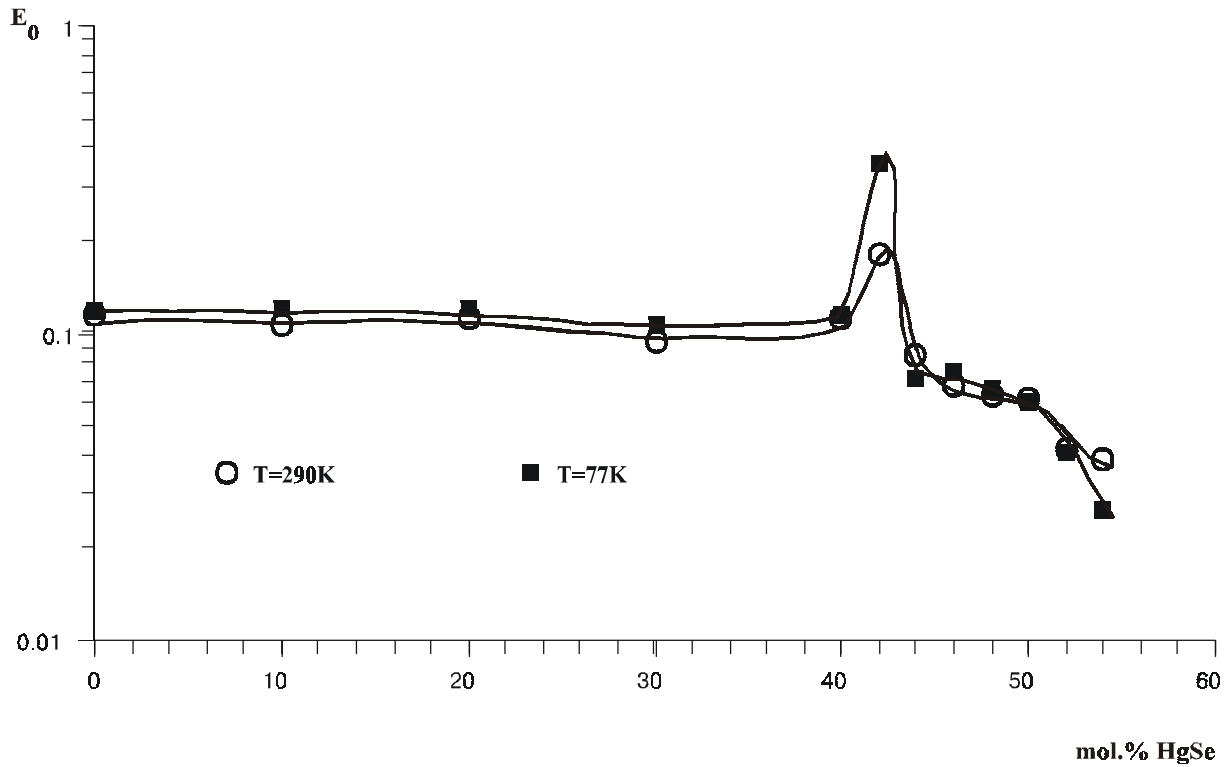


Fig. 5. Dependence of static disorder on the HgSe content

$\langle u^2 \rangle_x$  – root-mean-square static shifting of atoms caused;  
 $K$  – deformation potential constant.

Actually, in amorphous structures the dynamic and static components of overall structural disorder occur. But regarding the particular systems one of these components is dominant. For glassy materials, the base of structural disordering is static disorder (possible exception is SiO<sub>2</sub> [4]):

$$\langle u^2 \rangle_x \gg \langle u^2 \rangle_T$$

Then the function

$$E_0(T, X) = E_0(X) = K \langle u^2 \rangle_x \equiv E_0 \quad (3)$$

does not depend on temperature now.

For those structures the so-called glassy modification of Urbach's rule is realised (1)

$$\alpha(h\nu, T) = \alpha_g \exp\left(\frac{h\nu}{E_0} + \frac{T}{T_0}\right); T_0 = \frac{E_0}{\beta} \quad (4)$$

In [4] the equality (3) is easily evaluated analytically from (1) using linear dependence  $E_g(T)$  [10,11]

$$E_g(T) = E_g(0) - \beta T \quad (5)$$

Where  $E_g(0)$  – gap energy at zero temperature;

$$\beta = \frac{dE_g}{dT} \text{ – thermal coefficient of gap energy.}$$

The proportion (2) is equivalence of static and dynamic types of disorder. If the edge shift occurs without variation of the slope angle (strictly speaking, this case is realised for most of the HgSe – GeSe<sub>2</sub> glasses) then the temperature dependence  $h\nu(T)$  completely coincides with the temperature variations of  $E_g(T)$  (Fig.3).

$$h\nu(0) - h\nu(T) = E_g(0) - E_g(T) = \beta T \quad (6)$$

It has to be noted that the equations (4), (5), (6) is correct only for the temperature range where the functional dependence of the absorption edge  $h\nu(T)$  is linear. In glassy systems below the some fictitious temperature  $T < T'$  and above the glass-transition temperature  $T > T_g$  the non-linear temperature dependence of the absorption edge is observed. For  $T > T_g$  the irreversible structural transitions of the glass-creating matrix occur [12,13]. At  $T < T'$  for the description of  $E_g(T)$  or  $h\nu(T)$  we should consider the phonon contribution [14,15] been prevalent in the low-temperature range. Discussion about the  $h\nu(T)$  behaviour at  $T_g < T < T'$  oversteps the limits of the present paper and will not be considered in the further analysis of the experimental data for the HgSe – GeSe<sub>2</sub> glasses.

The glassy modification (4) of the generalized Urbach's rule is characteristic of the HgSe – GeSe<sub>2</sub> alloys (see Fig. 5). It follows from (3) as far as  $E_0$  is not dependent on temperature function yet.

The exceptions are the 42 mol.% HgSe and 54 mol.% HgSe glasses. In the last case  $E_0$  decreases when temperature puts down. The same regularity is exhibited in some silicate glasses [4] and also for As<sub>2</sub>Te<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub> [1]. But the most typical it is for the crystal media whose absorption edge is expressed by (1). In such materials static lattice disturbance is small comparing with the amplitude of atom heat oscillations, then

$$\langle u^2 \rangle_T \gg \langle u^2 \rangle_X$$

In the framework of the one-phonon approximation [16], the mean square shifting of atoms is proportional to  $kT$ .

$$E_0(T, X) = E_0(T) = K \langle u^2 \rangle_T = K\gamma kT \quad (7)$$

$\gamma$  has the dimensionality inverted to  $K$ ,  $[\gamma] = \text{Å}^2/\text{eV}$ .

From the equation (1) using (5), (7) we can obtain "crystalline" modification of Urbach's rule

$$\alpha(h\nu) = \alpha_{kr} \exp \left\{ \frac{1}{K\gamma} \left( \frac{h\nu - E_g(0)}{kT} \right) \right\} \quad (8)$$

Where  $\alpha_{kr} = \alpha_0 \exp \frac{\beta}{K\gamma k}$ .

In the HgSe – GeSe<sub>2</sub> alloys the "crystalline" modification of Urbach's rule appears only in the "boundary" sample where the glassy state is existed. As it has been shown previously, the alloys containing more than 54 mol.% HgSe are the crystalline ones. If we follow for the  $E_0$  variation with increasing of the HgSe content (Fig. 5), we should note that in the interval (0-40) mol.% HgSe the value of  $E_0$  is nearly constant. But for the ranges (44-54) mol.% HgSe the  $E_0$  downtrend is seen evidently. This means that the structure ordering of glassy alloys gradually carries out with the next transition of the "glassy" for crystalline Urbach's rule. As a consequence, the crystallization of medium occurs (56 – 60 mol% HgSe). On the assumption of the above mentioned we can do the conclusion that the alloy is as if "prepares" for the crystallization.

In another sample with 42 mol.% HgSe, the functional temperature dependence of  $E_0$  is also observed (Fig 5). It is emerged an interesting question: is it also the consequence of the dominant influence of the dynamic disordering? Is it necessary to use the "crystalline" modification of Urbach's rule (8) used for the 54 mol.% HgSe sample? As we can see from Fig. 5, the magnitude of the  $E_0$  parameter at 77 K much exceeds the magnitude at 290 K. It follows from this that the condition (7) can not be applied.

$$E_0(T, X) \neq K\gamma kT$$

Actually, it is an evident fact that the mean-square shifting  $\langle u^2 \rangle_T$  at the low temperature can not exceed the heat shifting of atoms at high temperature.

The anomalous  $E_0$  increasing can be explained on the basis of the next model. Under the influence of photons, electrons from valence band occupy the energy levels in the tail of conduction band. In this connection the overflow of the energy levels occurs so at the transition to the next energy level electron does not occupy the higher energy state  $E_{n+1}$  ( $E_{n+1} > E_n$ ) but jumps for the same level  $E_n$ . From the energy viewpoint, these transitions are unprofitable in local scope. But in the range of the whole glassy medium it is quite admissible. The overflow of the energy levels results in the existence of large deformation tension and pressure on atoms by glass-creating network. As a consequence, the quite large disordering of atoms is observed for the 24 mol.% HgSe alloy (see Fig. 5). At high temperatures, due to the heat energy  $kT$  the considerable part of the charges moves from the localized states to the delocalized ones above the transition point  $E_c$  [1]. Besides, the charges located in the condition band over  $E_c$  (for electrons) can form Debye screening [19]. These factors promote decreasing of the tensions in amorphous medium. Therefore, the  $E_0$  decreasing occurs at 290 K comparing with the liquid-nitrogen temperature.

The oneness of the 42 mol.% HgSe alloy was confirmed in [20]. In the glassy GeSe<sub>2</sub> there must be the same polyhedrons (the  $[\text{GeSe}_4]^{-4}$  tetrahedral) as in crystalline GeSe<sub>2</sub>. But in the glassy alloy the tetrahedrons form the continuous structure network disordered in space. When we deal with the complex glass the new basic structures exist (BS). According to the HgSe – GeSe<sub>2</sub> phase diagram [21] the composition of 42 mol.% HgSe – 58 mol.% GeSe<sub>2</sub> corresponds to the binary eutectic point. In aftereutectic alloys the GeSe<sub>2</sub> BS are primary formed, in eutectic alloys the GeSe<sub>2</sub> and Hg<sub>2</sub>GeSe<sub>4</sub> BS are formed simultaneously, and for the undereutectic ones the primary Hg<sub>2</sub>GeSe<sub>4</sub> and secondary GeSe<sub>2</sub> BS are formed.

The represented experimental data show the change of physical properties for the transition from glass with small content HgSe to samples with large content of this component. For transitions though point of binary eutectic the band gap (Fig. 4) is changed. Thermal coefficient  $\beta$  changes its sign, too. In aftereutectic alloys in comparison to undereutectic ones the value of static disorder  $E_0$  is decreased (Fig. 5). The hypothesis of possible cause of its phenomena is discussed. According to one of the basic cause of structural change, the similar to glass alloys have structural-phase transition in the point of binary eutectic, by another words, the change of germanium glass creating matrix (BS – GeSe<sub>2</sub>) by the mercury-germanium one (BS – Hg<sub>2</sub>GeSe<sub>4</sub>).

## 5. Conclusions

The optical distributions of the absorption factor of the alloys in the system HgSe – GeSe<sub>2</sub> were researched. Absorption boundary for these glasses is explained according to Urbach's rule. Difference between similar to glass and crystal modifications of Urbach's rule is shown and represented for the researched system of alloys. Crystal modification is realized only in the sample with 54 mol% HgSe, which find of border the creation of glass, though its structure is not crystalline. The change of physical properties of these alloys for transition over the point of double eutectic (42 mol% HgSe) is fixed. It corroborates the results [16,17] where the change structural unit formation order in under-eutectic and after-eutectic alloys was observed, too. The hypothesis about changing the glass-creating matrixes in the point of double eutectic is discussed. Anomaly growth of the static disorder  $E_0$  is explained using the model of deformation tensions.

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