

# Urbach Rule in Solid State Physics

Ihor Studenyak<sup>1,\*</sup>, Mladen Kranjčec<sup>2</sup>, Mykhailo Kurik<sup>3</sup>

<sup>1</sup>Physics Department, Uzhhorod National University, Uzhhorod, 88000, Ukraine

<sup>2</sup>Geotechnical Department, University of Zagreb, Varazdin, 42000, Croatia

<sup>3</sup>Institute of Physics, Ukrainian National Academy of Sciences, Prospect Nauki 46, 03680 Kyiv, Ukraine

**Abstract** The paper is dedicated to the 60th anniversary of the Urbach rule. The Urbach edge behaviour, measured by optical absorption spectroscopy, is analysed for different solids. The general regularities of the Urbach rule revealed in crystalline and amorphous solids as well as the temperature behaviour of its main parameters are discussed. The main attention is paid to the studies of the possibilities of the Urbach rule parameters to be used for studying disordering processes in solids, short- and medium-range order in amorphous materials, specific features of the Urbach “bundle” in nanosystems and its variation in the vicinity of phase transitions. It is shown that the parameters obtained from the Urbach rule give an important information about dynamic properties of elementary excitations in condensed matter as well as about the interaction of electronic excitations with phonons.

**Keywords** Absorption edge, Urbach rule, Exciton (electron)-phonon interaction, Disordering

## 1. Introduction

In 1953 Franz Urbach, studying light absorption in AgBr crystals, was the first to observe experimentally an exponential increase of absorption coefficient with the photon energy while with increasing temperature the exponential parts of the absorption edge spectra formed a characteristic “bundle” [1]. Further research showed that the empirical regularity developed by Urbach for indirect-gap semiconductors [1], was later observed for direct-gap semiconductors [2] and a variety of crystalline and amorphous materials (e. g. [3–6]). The Urbach rule is revealed in layered (e.g. [7, 8]), chained (e.g. [9]) and nanodimensional (e.g. [10–12]) structures, ferroics (e.g. [9, 13–15]), and superionic conductors (e.g. [16–18]). Detailed reviews on the Urbach rule and main features of its manifestation in different materials were performed in Refs. [3, 6, 18–20]. Now the number of papers devoted to the Urbach rule is stabilized (approximately 10–15 papers annually).

Sixty years have passed from the day of the development of the universal correlation between the absorption coefficient, the energy of incident photons and temperature practically for any types of optical transitions in condensed matter. Here we do not intend to summarize the research on the Urbach rule since it is impossible in the framework of an article. The aim of this paper is to trace the main directions and trends of modern application of the Urbach rule as well

as to analyse the key problems to be solved in the future.

## 2. Main Features of Manifestation of the Urbach Rule in Crystalline Solids

In the case of the Urbach behaviour of the absorption edge, the temperature and spectral dependence of absorption coefficient is described as [1]

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp\left[\frac{\sigma(h\nu - E_0)}{kT}\right] = \alpha_0 \cdot \exp\left[\frac{h\nu - E_0}{E_U(T)}\right] \quad (1)$$

where  $E_U$  is the Urbach energy which is equal to the energy width of the absorption edge and reverse to the absorption edge slope  $E_U^{-1} = \Delta(\ln \alpha) / \Delta(h\nu)$ ,  $\sigma$  is the steepness parameter of the absorption edge,  $\alpha_0$  and  $E_0$  are the coordinates of the convergence point of the Urbach “bundle”. The exponential increase of the absorption coefficient in the range of the absorption edge is explained by transitions between the tails of density-of-states in the valence band and the conduction band, the shape and size of these tails depend on the presence of different types of disordering [4]. Figure 1 presents typical spectral dependences of absorption coefficient for different temperatures, illustrating the Urbach absorption edge in Cu<sub>7</sub>GeSe<sub>5</sub>I crystal [21]. It should be noted that Cu<sub>7</sub>GeSe<sub>5</sub>I crystal is one of the most efficient superionic conductors among copper-containing solid electrolytes [21]. A characteristic “bundle” of straight lines which meet in a point with coordinates  $\alpha_0$  and  $E_0$  is clearly revealed. Such “bundle” (Fig. 1) should be observed within the absorption coefficient variation by few orders of magnitude and in a broad temperature range, as a rule, above the Debye

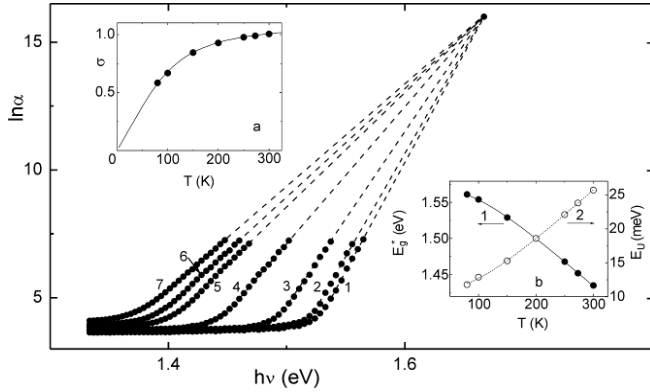
\* Corresponding author:

studenyak@dr.com (Ihor Studenyak)

Published online at <http://journal.sapub.org/optics>

Copyright © 2014 Scientific & Academic Publishing. All Rights Reserved

temperature. It should be noted that the Urbach bundle is observed as a result of Wannier-Mott exciton smearing in semiconductor and ionic crystals, as a result of Frenkel exciton smearing in molecular crystals as well as a result of smearing of interband optical transitions in non-exciton solids [3]. In some cases deviations from the Urbach behaviour occur, i.e. the shape of the optical absorption edge is still exponential, but the extrapolated linear parts do not converge in a focus with the coordinates  $\alpha_0$  and  $E_0$ .



**Figure 1.** Spectral dependences of the Urbach absorption edge for  $\text{Cu}_7\text{GeSe}_3\text{I}$  crystal at various temperatures  $T$ : 80 K (1), 100 K (2), 150 K (3), 200 K (4), 250 K (5), 273 K (6), 300 K (7). The insets show the temperature dependences of the steepness parameter  $\sigma$  (a), optical pseudogap  $E_g^*$  (1b) and the Urbach energy  $E_U$  (2b)

Temperature dependence of the Urbach rule parameter  $\sigma$  can be described by an equation

$$\sigma(T) = \sigma_0 \cdot \left( \frac{2kT}{\hbar\omega_p} \right) \cdot \tanh \left( \frac{\hbar\omega_p}{2kT} \right) \quad (2)$$

where  $\hbar\omega_p$  is the effective phonon energy which in most cases coincides with the energy of the phonons participating in the formation of the long-wave side of the fundamental absorption edge,  $\sigma_0$  is a parameter which describes the optical excitation in the material. For instance, in crystalline semiconductors  $\hbar\omega_p$  is the effective phonon energy in a single-oscillator model which describes exciton (electron)–phonon interaction (EPI), while  $\sigma_0$  is a parameter related to the EPI constant  $g$  as  $\sigma_0 = (2/3)g^{-1}$  [3, 22]. A typical temperature dependence of  $\sigma$  is presented as an inset in Fig. 1. It should be noted that the Urbach rule consists not only in the exponential dependence of the absorption coefficient on the photon energy at a certain temperature, but also in strict correlations between the parameters in expressions (1) and (2).

It is shown that the temperature dependences of such parameters of Urbach absorption edge (see the inset in Fig. 1) as the optical pseudogap  $E_g^*$  ( $E_g^*$  is the energy position of

the exponential absorption edge at a fixed value of absorption coefficient  $\alpha=10^3 \text{ cm}^{-1}$  [16]) and the Urbach energy  $E_U$  are well described in the framework of the Einstein model [23, 24]

$$E_g^*(T) = E_g^*(0) - S_g^* k \theta_E \left[ \frac{1}{\exp(\theta_E/T) - 1} \right], \quad (3)$$

$$E_U = (E_U)_0 + (E_U)_1 \left[ \frac{1}{\exp(\theta_E/T) - 1} \right], \quad (4)$$

where  $E_g^*(0)$  is the energy gap at 0 K,  $S_g^*$ ,  $(E_U)_0$  and  $(E_U)_1$  are the constant values,  $\theta_E$  is the Einstein temperature which corresponds to the average frequency of phonon excitations of non-interacting oscillators.

Among the most cited theoretical models which are widely used to explain the manifestations of the Urbach rule in semiconductors, are the Sumi–Toyozaava (e.g. [25]) and the Dow–Redfield models (e.g. [26, 27]). Besides, there are also other versions for the Urbach rule explanation in the literature (e.g. [28–31]). For instance, in Ref. [31] an *ab initio* theory is built to explain the temperature dependence of the Urbach absorption edge in crystalline and disordered semiconductors, which includes the effects of short-range static disordering and non-adiabatic dynamics of the interacting electron-phonon system. Within this theory, a good conformity with the experimental data was obtained for *c*-Si, *a*-Si:H, *a*-As<sub>2</sub>Se<sub>3</sub>, and *a*-As<sub>2</sub>S<sub>3</sub> [31].

### 3. Urbach Rule and Crystal Lattice Disordering

It is known that the Urbach energy  $E_U$  characterizes the degree of the absorption edge smearing due to the crystalline lattice disordering caused by structural peculiarities as well as induced by external factors. According to Ref. [32], the influence of different types of disordering on the Urbach energy  $E_U$  can be generally described as

$$E_U = k_0 \left( W_T^2 + W_X^2 + W_C^2 \right) = (E_U)_T + (E_U)_X + (E_U)_C \quad (5)$$

where  $k_0$  and  $k_g$  are constants,  $W_T^2$ ,  $W_X^2$ , and  $W_C^2$  are mean-square deviations from the electric potential of a perfectly ordered structure caused by temperature disordering, structural disordering, and compositional disordering, respectively,  $(E_U)_T$ ,  $(E_U)_X$ , and  $(E_U)_C$  are the contributions of the temperature disordering, structural disordering, and compositional disordering, respectively. The temperature disordering is mainly caused by the lattice thermal vibrations, i. e.  $(E_U)_T \equiv (E_U)_{TV}$ . The nature of the structural disordering can be intrinsic (caused by intrinsic defects of structure, e.g. vacancies or dislocations) or induced by external factors (deviation from stoichiometry, doping, ion implantation, hydrogenation, etc.).

The compositional disordering is caused by atomic substitution in mixed crystals.

As an example, consider the influence of different types of disordering on the Urbach absorption edge parameters in superionic  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals [33]. Besides the temperature disordering, caused by the lattice thermal vibrations, superionic conductors are characterized by substantial structural disordering. It is caused by non-equivalence between the number of mobile ions and positions which they can occupy, and applies only to the sublattice of mobile ions while the rigid sublattice preserves its regular structure. The structural disordering is directly related to the mechanism of ionic conductivity: the degree of the structural disordering, i.e. the amount of vacancies for the mobile ions, determines the mechanism and the efficiency of fast-ion transport. In the superionic phase, the structural disordering consists of two parts – dynamic structural disordering  $(E_U)_{X,dyn}$  and static structural disordering  $(E_U)_{X,stat}$  [16]:

$$(E_U)_X = (E_U)_{X,dyn} + (E_U)_{X,stat}. \quad (6)$$

This differentiation is rather arbitrary, since the dynamic structural disordering  $(E_U)_{X,dyn}$  can be referred to as structural (see Eq. (6)), or temperature-related

$$(E_U)_{TR} = (E_U)_{TV} + (E_U)_{X,dyn}. \quad (7)$$

Here  $(E_U)_{TV}$  corresponds to the contribution of lattice thermal vibrations. Using Eqs. (6) and (7), the Urbach energy  $E_U$  can be written in the form

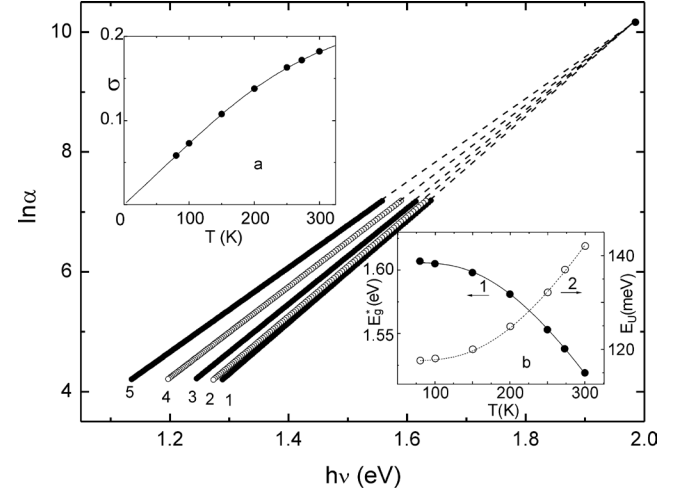
$$E_U = (E_U)_{TR} + (E_U)_{X,stat} + (E_U)_C. \quad (8)$$

It should be noted that the static structural disordering in superionic conductors, caused by structural imperfections, leads to appearance of local non-uniform electric fields which in turn result in an additional smearing of the energy bands. The dynamic structural disordering, which appears in the superionic phase, is related to the hopping motion of mobile copper ions participating in ionic transport and providing high ionic conductivity.

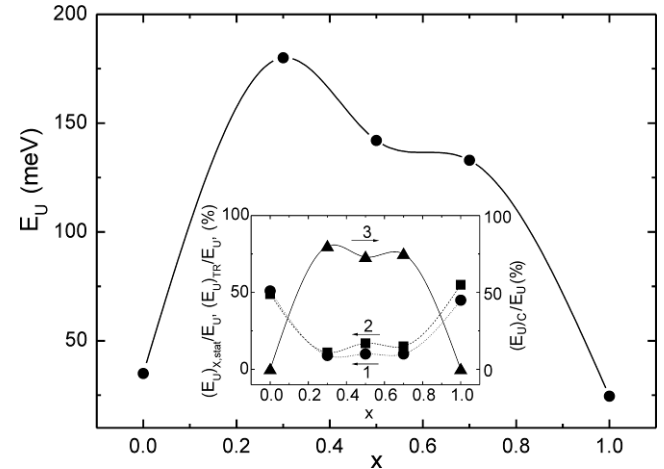
The Urbach absorption edge, typical for  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals, is presented for  $\text{Cu}_7\text{Ge}(\text{S}_{0.5}\text{Se}_{0.5})_5\text{I}$  in Fig.2 whereas the temperature dependences of the steepness parameter  $\sigma$ , optical pseudogap  $E_g^*$  and the Urbach energy  $E_U$  are illustrated as the insets in Fig.2.

The compositional dependence of  $E_U$  (Fig.3) can be used to study the influence of different types of disordering on the Urbach absorption edge parameters. With the account of the equivalence, independence and additivity of the contributions of different types of disordering in  $E_U$  in Eq. (8), one can separate the contributions of the static structural disordering, temperature-related disordering and compositional disordering according to the procedure developed in [18]. In pure crystals, only the static structural disordering  $(E_U)_{X,stat}$  and the temperature-related

disordering  $(E_U)_{TR}$  contribute to  $E_U$ . Hence, in  $\text{Cu}_7\text{GeS}_5\text{I}$  crystal the relative contribution of the above mentioned types of disordering in  $E_U$  at 300 K is nearly equal, whereas in  $\text{Cu}_7\text{GeSe}_5\text{I}$  crystal the contribution of  $(E_U)_{TR}$  exceeds the contribution of  $(E_U)_{X,stat}$ .



**Figure 2.** Spectral dependences of the Urbach absorption edge for  $\text{Cu}_7\text{Ge}(\text{S}_{0.5}\text{Se}_{0.5})_5\text{I}$  mixed crystal at various temperatures  $T$ : 80 K (1), 150 K (2), 200 K (3), 250 K (4), 300 K (5). The insets show the temperature dependences of the steepness parameter  $\sigma$  (a), optical pseudogap  $E_g^*$  (1b) and the Urbach energy  $E_U$  (2b)



**Figure 3.** Compositional dependence of the Urbach energy  $E_U$  for  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals. The inset shows the compositional dependences of relative contributions of the static structural disordering (1), temperature-related disordering (2), and compositional disordering (3) to the Urbach energy  $E_U$

In  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals with the increasing selenium content a maximum is revealed in the compositional dependence of  $E_U$  which indicates the influence of the compositional disordering (Fig.3). The contributions of the above mentioned type of disordering in  $E_U$  were evaluated using the  $(E_U)_0$ ,  $(E_U)_1$ , and  $\theta_E$  parameters (see Eq.(4)). The obtained compositional dependences of the  $(E_U)_{X,stat}$ ,  $(E_U)_{TR}$ , and  $(E_U)_C$  contributions into  $E_U$

for  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals are shown as the inset in Fig. 3. With increasing selenium content, the contributions of  $(E_U)_{X,stat}$  and  $(E_U)_{TR}$  linearly decrease at  $x < 0.5$  and increase at  $x > 0.5$ , whereas the contribution of  $(E_U)_C$  increases at  $x < 0.5$  and decreases at  $x > 0.5$ .

#### 4. Urbach Rule in Amorphous Materials

The optical absorption edge in amorphous materials is characterized by the presence of a smeared exponential tail, the temperature and spectral behaviour of which is described by the Urbach rule in a broad temperature range (e.g. [34–36]), or is described by the Urbach rule in a limited temperature range (e.g. [37]), or does not obey the Urbach rule at all (e.g. [35]). In the first case, for amorphous semiconductors, contrary to crystals, the absorption edge is smeared more away and the temperature dependence of the absorption edge slope (see Eq. (2)) is less pronounced [3, 6]. Besides,  $\sigma_0 < 1$ , that is the evidence for electron self-localization due to the structural disordering. In the two latter cases the slope of the spectral dependences of the optical absorption edge remains unchanged with temperature in a limited temperature range or in the whole temperature range under investigation and a parallel red shift with temperature is observed. An attempt to describe the above mentioned specific behaviour by a modified (so-called “glassy”) Urbach rule was undertaken [35]:

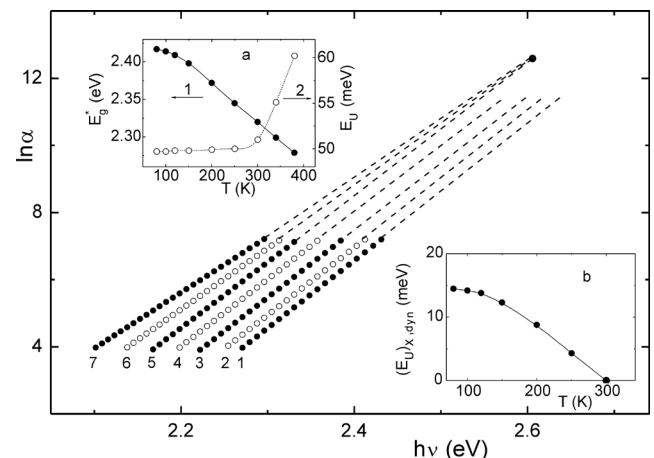
$$\alpha(h\nu, T) = \alpha_{nc} \cdot \exp\left[\frac{h\nu}{E_{nc}} - \frac{T}{T_0}\right] \quad (9)$$

where  $\alpha_{nc}$  is a constant,  $T_0$  is a characteristic temperature, determined from the experiment and having no clear physical sense,  $1/E_{nc}$  is a temperature-independent logarithmic slope of the absorption coefficient spectral dependence,  $E_{nc} \equiv E_U$ . The main disadvantage of Eq. (9) is its inapplicability for the description of temperature behaviour of the exponential absorption edge at low temperatures [35].

Based on the equivalence of static and dynamic components of structural disordering in amorphous systems, it was shown [35] that Eq. (1) and Eq. (9) are the limiting cases of the general exponential dependence of absorption coefficient in the range of the optical absorption edge. Earlier [37], using the formalism of separation of contributions of the static and dynamic components of structural disordering, we explained the Urbach behaviour of the absorption edge in  $\text{As}_2\text{S}_3$  glass, based on the presence of short- and medium-range order.

Studies of the optical absorption edge of glassy  $\text{As}_2\text{S}_3$  show the presence of two temperature ranges [37]: (i) the range of a parallel red shift of the edge in the temperature interval of  $80 \text{ K} \leq T < 300 \text{ K}$ , and (ii) the range of the Urbach behaviour of the absorption edge at  $T \geq 300 \text{ K}$  (Fig. 4). The parallel red shift of the optical absorption edge in  $\text{As}_2\text{S}_3$  and, accordingly, the temperature invariance of the Urbach

energy  $E_U$  (see the inset in Fig. 4) are related to the absence of the medium-range order in the atomic arrangement. Like in partially disordered superionic conductors, in completely disordered glasses the structural disordering can be presented as a sum of static structural disordering  $(E_U)_{X,stat}$  and dynamic structural disordering  $(E_U)_{X,dyn}$ . It should be noted that the contribution of the temperature-independent static structural disordering  $(E_U)_{X,stat}$  is caused by the absence of the long-range order and the presence of solely the short-range order in the atomic arrangement, and the contribution of the temperature-dependent dynamic structural disordering  $(E_U)_{X,dyn}$  is related to the absence of the medium-range order. At low temperatures in glassy  $\text{As}_2\text{S}_3$  semiconductor only the short-range order is present in the atomic arrangement; with increasing temperature the contribution of  $(E_U)_{X,dyn}$  decreases, resulting in a gradual formation of the medium-range order. A decrease of the contribution of the dynamic structural disordering  $(E_U)_{X,dyn}$  along with the increasing contribution of the temperature disordering  $(E_U)_{TV}$  at the invariable contribution of  $(E_U)_{X,stat}$  leads to the temperature invariance of  $(E_U)_{TR}$  and the Urbach energy  $E_U$ , respectively, as well as to the parallel red shift of the absorption edge. At  $T \geq 300 \text{ K}$   $(E_U)_{X,dyn} = 0$ , and the increase of the Urbach energy  $E_U$  is determined by the increasing contribution of the temperature disordering [37].



**Figure 4.** Spectral dependences of the absorption coefficient logarithm for  $\text{As}_2\text{S}_3$  glassy semiconductor at various temperatures  $T$ : 80 K (1), 150 K (2), 200 K (3), 250 K (4), 300 K (5), 340 K (6), 380 K (7). The insets show the temperature dependences of the optical pseudogap  $E_g^*$  (1a), the Urbach energy  $E_U$  (2a) and the contribution of  $(E_U)_{X,dyn}$  (b)

Thus, in amorphous materials, for which the Urbach behaviour of the optical absorption edge is observed in the whole temperature range under investigation, in this temperature range both medium-range order and short-range

order are present. Simultaneously, the non-Urbach behaviour in the whole temperature range reflects the presence of solely the short-range order at the total absence of the medium-range order.

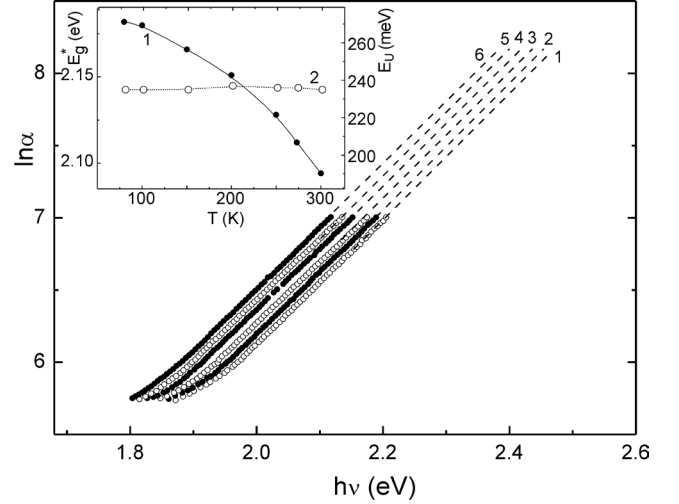
## 5. Urbach Rule in Nanosystems

Smearing of the optical absorption edge in nanocrystals can result not only from the static structural disordering caused by the presence of impurity atoms in separate nanocrystals, but also from topological disordering caused by their chaotic distribution as well as by differences in their average size. If the average radius of the nanocrystals exceeds the Bohr exciton radius (i.e. in the absence of confinement), the similar tails in the absorption edge spectra are formed as for bulk crystals [11]. In the opposite case (in the presence of a strong confinement effect) the density - of-states tails are formed by averaging over the nanocrystal size distribution.

A transition from bulk  $\text{CdS}_x\text{Se}_{1-x}$  crystals to glass - embedded nanocrystals leads to the energy gap increase and a blue shift of the absorption edge [11]. At low temperatures, a parallel blue shift of the absorption edge is observed, caused by the presence of the dynamic structural disordering. At  $T \geq 300$  K a characteristic Urbach "bundle" is revealed, described by Eq. (1), and the steepness parameter of the absorption edge is described by Eq. (2). Thus, the absorption edge smearing in  $\text{CdS}_x\text{Se}_{1-x}$  nanocrystals is caused not only by the presence of high concentration of charged impurities, but also by confinement of both phonons and excitons [11].

Consider the case of  $\text{As}_2\text{S}_3\text{-Cu}_6\text{PS}_5\text{I}$  nanocomposite prepared by incorporation of nanocrystals of  $\text{Cu}_6\text{PS}_5\text{I}$  superionic conductor in an  $\text{As}_2\text{S}_3$  glass matrix [38]. Temperature studies of the absorption edge showed that in the temperature interval  $100 \text{ K} \leq T \leq 300 \text{ K}$  a red shift of the absorption edge is observed with the temperature increase, the absorption edge slope remaining unchanged (Fig.5). The non-Urbach behaviour of the optical absorption edge in the temperature interval  $100 \text{ K} \leq T \leq 300 \text{ K}$  can be explained using the formalism of separation of the contributions from the static structural disordering and the dynamical structural disordering. In Eq. (8),  $(E_U)_{TR}$  is the contribution of the temperature-related disordering which results from the thermal vibrations of atoms and structural elements  $(E_U)_{TV}$ , leading to the absorption edge smearing due to the EPI, and dynamic structural disordering  $(E_U)_{X,dyn}$  results from the absence of the medium-range order in  $\text{As}_2\text{S}_3$  glass matrix. Note that the contribution of the temperature-independent static structural disordering  $(E_U)_{X,stat}$  results from (i) the absence of the long-range order and the presence of solely the short-range order in the atomic arrangement in  $\text{As}_2\text{S}_3$  glass matrix, (ii) the topological disordering caused by the differences in size and shape of  $\text{Cu}_6\text{PS}_5\text{I}$  nanocrystals as well as their chaotic

distribution in the  $\text{As}_2\text{S}_3$  glass matrix, (iii) confinement of both phonons and excitons in  $\text{Cu}_6\text{PS}_5\text{I}$  nanocrystals. The explanation of the temperature independence of the Urbach energy  $E_U$  and the parallel red shift of the absorption edge in the  $\text{As}_2\text{S}_3\text{-Cu}_6\text{PS}_5\text{I}$  nanocomposite is similar to the one mentioned above for  $\text{As}_2\text{S}_3$  glassy semiconductor [38].



**Figure 5.** Spectral dependences of the absorption coefficient logarithm for  $\text{As}_2\text{S}_3\text{-Cu}_6\text{PS}_5\text{I}$  nanocomposite at various temperatures  $T$ : 77 K (1), 150 K (2), 200 K (3), 250 K (4), 273 K (5), 300 K (6). The inset shows the temperature dependences of the optical pseudogap  $E_g^*$  (1) and the Urbach energy  $E_U$  (2)

## 6. Urbach Rule and Phase Transitions

Phenomenological analysis of the Urbach absorption edge behaviour at phase transitions (PT) was carried out in Ref. [39]. It is known that the EPI change at a PT causes the energy gap  $E_g$  variation which can be expanded in a series over the order parameter  $\eta$  of the PT

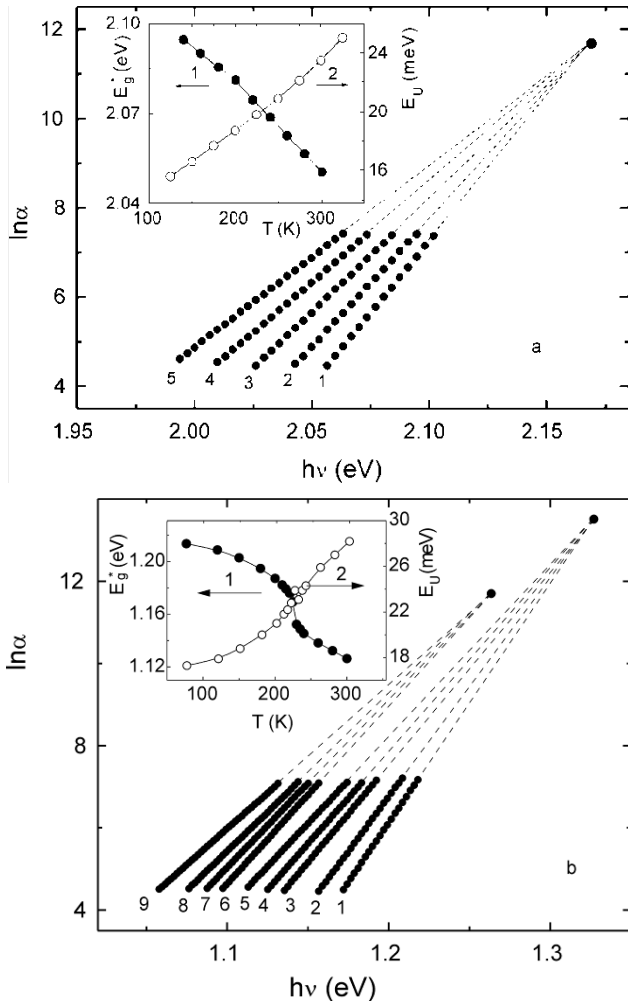
$$\Delta E_g = B\eta^2 + C\eta^4 + D\eta^6 + \dots \quad (10)$$

where  $B, C, D, \dots$  are the expansion coefficients. In the case of the Urbach behaviour of the absorption edge one can use the  $E_g^\alpha$  value determined at a fixed absorption level:

$$E_g^\alpha(T) = E_0 - \frac{kT}{\sigma(T)} \ln \left( \frac{\alpha_0}{\alpha} \right). \quad (11)$$

Being restricted to the first term of the expansion in Eq. (10), the variation of the absorption edge in the PT range can be written as  $\Delta E_g^\alpha = \phi\eta^2$  where  $\phi$  is a constant which generally does not coincide with  $B$ . Therefore, the energy position of the absorption edge  $E_g^\alpha$  taking into account the anomalies at the PT will be determined from the equation

$$E_g^\alpha(T) = E_0 - \frac{kT}{\sigma(T)} \ln \left( \frac{\alpha_0}{\alpha} \right) + \phi\eta^2. \quad (12)$$



**Figure 6.** Spectral dependences of the absorption coefficient logarithm for  $\text{Cu}_6\text{P}(\text{S}_{0.9}\text{Se}_{0.1})_5\text{I}$  (a) and  $\text{Cu}_6\text{P}(\text{S}_{0.1}\text{Se}_{0.9})_5\text{I}$  (b) crystals at various temperatures  $T$ : (a) 140 K (1), 180 K (2), 220 K (3), 260 K (4), 300 K (5); (b) 77 K (1), 150 K (2), 200 K (3), 215 K (4), 225 K (5), 230 K (6), 240 K (7), 260 K (8), 300 K (9). The insets show the temperature dependences of the optical pseudogap  $E_g^*$  (1) and the Urbach energy  $E_U$  (2)

It was suggested [39] that at a PT all three parameters of the Urbach rule are changed, hence three limiting cases are possible: (i) at the PT only the  $\sigma$  value changes whereas  $\alpha_0$  and  $E_0$  parameters remain the same, (ii) at the PT only the  $E_0$  value changes whereas  $\alpha_0$  and  $\sigma$  parameters stay invariable; for a first-order PT two convergence points of the Urbach absorption edge are observed, the energy difference between them being  $\Delta E_0 = \beta\eta^2$ . At a second-order PT, as a result of the continuous variation of the order parameter  $\eta$ , only one of the convergence points is revealed; (iii) at the PT the  $\alpha_0$  value is the only one that changes while the  $E_0$  and  $\sigma$  parameters are constant. The change of the  $E_0$  parameter, apparently, is directly related to the energy gap variation. The anomaly of the  $\sigma$  parameter can be related to the EPI change ( $\sigma_0$ ) as well as to

a change of the energy  $\hbar\omega_p$  of the effective phonon which interacts with the exciton (electron) in the vicinity of the PT. It is difficult to give any physical explanation to the change of the  $\alpha_0$  parameter [39].

In general case (iv) all the mentioned anomalies of the absorption edge behaviour can be observed simultaneously, i. e. the change of  $E_g^*(T)$  at the PT is determined by the anomalies in the temperature behaviour of Urbach absorption edge parameters  $\alpha_0$ ,  $E_0$ , and  $\sigma$ .

A great number of papers was devoted to the study of anomalous temperature behaviour of the Urbach rule parameters in the PT range in various crystalline solids (e.g. [9, 13–18]). Different versions of the experimental manifestation of the Urbach rule parameter anomalies at first-order and second-order PTs can be presented using an example of mixed superionic  $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  crystals [17].

In  $\text{Cu}_6\text{P}(\text{S}_{0.9}\text{Se}_{0.1})_5\text{I}$  mixed crystal in the range of the second-order PT only a variation of the  $\sigma$  parameter is observed, while the  $\alpha_0$  and  $E_0$  parameters remain unchanged (Fig. 6a), corresponding to the case (i). On the contrary, in the range of the first-order PT in  $\text{Cu}_6\text{P}(\text{S}_{0.1}\text{Se}_{0.9})_5\text{I}$  variation of all parameters ( $\alpha_0$ ,  $E_0$ , and  $\sigma$ ) is observed (Fig. 6b), corresponding to the case (iv). The insets in Fig.6 present the temperature dependences of such parameters of the Urbach “bundle” as the optical pseudogap  $E_g^*$  and the Urbach energy  $E_U$ . It should be noted that in  $\text{Cu}_6\text{P}(\text{S}_{0.9}\text{Se}_{0.1})_5\text{I}$  in the range of the second-order PT a change of slope is revealed in the temperature dependence of  $E_g^*$ , while in the range of the first-order PT a stepwise change of  $E_g^*$  is observed (Fig.6). The corresponding characteristic changes are revealed in the temperature dependences of  $E_U$  (Fig.6).

## 7. Conclusions

The paper deals with the characteristic features of Urbach rule manifestation in the crystalline, non-crystalline compounds, and nanosystems as well as with the effect of disordering processes and phase transitions on the parameters of Urbach absorption edge. It is shown that by using the Urbach rule it is possible to obtain the important information about the dynamics of electronic excitations of the condensed state, when the contribution of different lattice vibrations is considerable in the absorption processes. The Urbach rule allows one to find rather easily the degree of localization of states in the lattice and to determine the effect of lattice disordering on the localization of electronic excitations.

Today it can be said that in 1953 F. Urbach established an

important instrument for studying optical absorption in various non-metallic materials, differing in structural features, aggregate state, dimensionality of the crystal lattice, phase transition types and other physical properties. Its advantages are the simplicity and universality for various materials and systems. It is likely that in future the Urbach rule will be successfully applied in medicine and biology in the study of soft matter, including nanobiosystems.

## REFERENCES

- [1] F. Urbach, "The long-wavelength edge of photographic sensitivity and electronic absorption of solids", *APS Journals, Phys. Rev.*, vol.92, pp.1324-1326, 1953.
- [2] H.W. Martienssen, "Über die excitonenbanden der alkahalogenidkristalle", *Elsevier, J. Phys. Chem. Solids*, vol.2, pp.257-267, 1957.
- [3] M.V. Kurik, "Urbach rule (Review)", *Wiley-VCH, Phys. Stat. Sol. (a)*, vol.8, pp.9-30, 1971.
- [4] G.D. Cody, "Urbach edge of crystalline and amorphous silicon: a personal review", *Elsevier, J. Non-Cryst. Solids*, vol.141, pp.3-15, 1992.
- [5] M.E. Kassem, A.A. Higazy, R.R. Zahran, and A.Y. Kandeil, "Optical properties of  $\gamma$ -irradiated low-density polyethylene", *Elsevier, Mat. Lett.*, vol.16, pp.236-242, 1993.
- [6] M.V. Kurik, "Urbach rule in optics of condensed matter", *Nauka, Ukr. Fiz. Zhurnal*, vol.39, pp.1058-1062, 1994.
- [7] M. Kranjčec, I.D. Desnica, I.P. Studenyak, Gy.Sh. Kovacs, M.V. Potory, Yu.V. Voroshilov, and V.Yu. Gebesh, "Preparation and fundamental optical absorption edge in  $\text{In}_4(\text{P}_2\text{Se}_6)_3$  single crystals", *Elsevier, Mat. Res. Bull.*, vol.34, pp.2297-2307, 1999.
- [8] B. Abay, H.S. Guder, H. Efeoglu, and Y.K. Yorgurcu, "Temperature dependence of the optical energy gap and Urbach-Martienssen's tail in the absorption spectra of the layered semiconductor  $\text{Tl}_2\text{GaInSe}_4$ ", *Elsevier, J. Phys. Chem. Solids*, vol.62, pp.747-752, 2001.
- [9] K. Zickus, A. Audzjonis, J. Batarunas, and A. Sileika, "The fundamental absorption edge tail of ferroelectric  $\text{SbSI}$ ", *Wiley-VCH, Phys. Stat. Sol. (b)*, vol.125, pp.645-651, 1984.
- [10] Q. Shen, and T. Toyoda, "Photoacoustic studies of annealed  $\text{CdS}_x\text{Se}_{1-x}$  ( $x=0.26$ ) nanocrystals in glass matrix", *PSJ, Japan J. Appl. Phys.*, vol.38, pp.3163-3167, 1999.
- [11] V.P. Kunets, N.R. Kulish, Vas.P. Kunets, and M.P. Lisitsa, "Urbach's rule peculiarities in structures with  $\text{CdS}_x\text{Se}_{1-x}$  nanocrystals", *ISP, Semiconductor Physics, Quantum Electronics and Optoelectronics*, vol.5, pp.9-15, 2002.
- [12] B.I. Turko, V.B. Kapustyanyk, V.P. Rudyk, M.V. Partika, M.V. Kvasnytsya, and A.P. Vas'kiv, "Manifestation of size effect in behavior of the intrinsic absorption edge of nanostructured polycrystalline zinc oxide thin films", *Springer, J. Appl. Spectroscopy*, vol.74, pp.310-312, 2007.
- [13] P.P. Guranich, E.I. Gerzanich, A.G. Slivka, V.S. Shusta, and V.A. Bobela, "Phase p,T,x-diagram and peculiarities of physical properties of  $(\text{Pb}_x\text{Sn}_{1-x})_2\text{P}_2\text{Se}_6$  crystals with an incommensurate phase", *Taylor & Francis, Ferroelectrics*, vol. 132, pp.173-183, 1992.
- [14] K. Noba, and Y. Kayanuma, "Urbach tail for ferroelectric materials with an order-disorder-type phase transition", *APS Journals, Phys. Rev. B*, vol.60, pp.4418-4421, 1999.
- [15] I.P. Studenyak, O.A. Mykajlo, Yu.M. Vysochanskii, and V.B. Cajipe, "Optical absorption studies of phase transitions in  $\text{CuCrP}_2\text{S}_6$  layered antiferroelectrics", *IOP Publishing, J. Phys.: Condens. Matter.*, vol.15, pp.6773-6779, 2003.
- [16] I.P. Studenyak, M. Kranjčec, Gy.Sh. Kovacs, V.V. Panko, D.I. Desnica, A.G. Slivka, and P.P. Guranich, "The effect of temperature and pressure on the optical absorption edge in  $\text{Cu}_6\text{PS}_5\text{X}$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) crystals", *Elsevier, J. Phys. Chem. Solids*, vol.60, pp.1897-1904, 1999.
- [17] I.P. Studenyak, M. Kranjčec, Gy.Sh. Kovacs, I.D. Desnica, V.V. Panko, and V.Yu. Slivka, "Influence of compositional disorder on optical absorption processes in  $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  crystals", *MRS, J. Mat. Res.*, vol.16, pp.1600-1608, 2001.
- [18] I.P. Studenyak, M. Kranjčec, and M.V. Kurik, "Urbach rule and disordering processes in  $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{Br}_{1-y}\text{I}_y$  superionic conductors", *Elsevier, J. Phys. Chem. Solids*, vol.67, pp.807-817, 2006.
- [19] M.V. Kurik, and L.I. Tsikora, "Exciton-phonon interaction in crystals of linear polyacenes", *Wiley-VCH, Phys. Stat. Sol. (b)*, vol.66, pp.695-702, 1974.
- [20] H. Sumi, and A. Sumi, "The Urbach-Martienssen rule revisited", *PSJ, J. Phys. Soc. Japan*, vol. 56, pp.2211-2220, 1987.
- [21] I.P. Studenyak, M. Kranjčec, V.V. Bilanchuk, O.P. Kokhan, A.F. Orliukas, E. Kazakevicius, A. Kezionis, and T. Salkus, "Temperature variation of electrical conductivity and absorption edge in  $\text{Cu}_7\text{GeSe}_5\text{I}$  advanced superionic conductors", *Elsevier, J. Phys. Chem. Solids*, vol.70, pp.1478-1481, 2009.
- [22] M.V. Kurik, "Experimental evaluation of exciton-phonon interaction constant", *Maik, Fiz. Tverd. Tela*, vol.33, pp.615-618, 1991.
- [23] M. Beaudoin, A.J.G. DeVries, S.R. Johnson, H. Laman, and T. Tiedje, "Optical absorption edge of semi-insulating GaAs and InP at high temperatures", *APS Journals, Appl. Phys. Lett.*, vol.70, pp.3540-3542, 1997.
- [24] Z. Yang, K.P. Homewood, M.S. Finney, M.A. Harry, and K.J. Reeson, "Optical absorption study of ion beam synthesized polycrystalline semiconducting  $\text{FeSi}_2$ ", *AIP, J. Appl. Phys.*, vol.78, pp.1958-1963, 1995.
- [25] H. Sumi, and Y. Toyozawa, "Urbach-Martienssen rule and exciton trapped momentarily by lattice vibration", *PSJ, J. Phys. Soc. Japan*, vol. 31, pp.342-357, 1971.
- [26] D. Redfield, "Effect of defect fields on the optical absorption edge", *APS Journals, Phys. Rev.*, vol.130, pp.916-918, 1963.
- [27] .D. Dow, and D. Redfield, "Toward a unified theory of Urbach's rule and exponential absorption edge", *APS Journals, Phys. Rev. B*, vol.5, pp.594-610, 1972.
- [28] T. Skettrup, "Urbach's rule derived from thermal fluctuations

- in the band-gap energy”, APS Journals, Phys. Rev. B, vol.18, pp.2622-2631, 1978.
- [29] J. Szczyrbowski, “The exponential shape of the optical absorption edge tail”, Wiley-VCH, Phys. Stat. Sol. (b), vol.105, pp.515-524, 1981.
- [30] J.G. Liebler, S. Schmitt-Rink, and H. Haug, “Theory of the absorption tail of Wannier excitons in polar semiconductor”, Elsevier, J. Luminesc., vol.34, pp.1-7, 1985.
- [31] C.H. Grein, and S. John, “Temperature dependence of the Urbach optical absorption edge: A theory of multiple phonon absorption and emission sidebands”, APS Journals, Phys. Rev. B, vol.39, pp.1140-1151, 1989.
- [32] A. Skumanich, A. Frova, and N.M. Amer, “Urbach tail and gap states in hydrogenated a-SiC and a-SiGe alloys”, Elsevier, Solid State Commun., vol.54, pp.597-601, 1985.
- [33] I.P. Studenyak, M. Kranjčec, V.V. Bilanchuk, O.P. Kokhan, A.F. Orliukas, A. Kezionis, E. Kazakevicius, and T. Salkus, “Temperature and compositional behaviour of electrical conductivity and optical absorption edge in  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed superionic crystals”, Elsevier, Solid State Ionics, vol.181, pp.1596-1600, 2010.
- [34] I.T. Godmanis, A.N. Trukhin, and K. Huebner, “Exciton-phonon interaction in crystalline and vitreous  $\text{SiO}_2$ ”, Wiley-VCH, Phys. Stat. Sol. (b), vol.116, pp.279-287, 1983.
- [35] I.A. Weinstein, and A.F. Zatsepin, “Modified Urbach’s rule and frozen phonons in glasses”, Wiley-VCH, Phys. Stat. Sol. (c), vol.1, pp.2916-2919, 2004.
- [36] D.I. Bletskan, V.N. Kabacij, I.P. Studenyak, and V.V. Frolova, “Edge absorption spectra of crystalline and glassy  $\text{PbGeS}_3$ ”, Maik, Optics and Spectroscopy, vol.103, pp.772-776, 2007.
- [37] M. Kranjčec, I.P. Studenyak, and M.V. Kurik, “On the Urbach rule in non-crystalline solids”, Elsevier, J. Non-Cryst. Solids, vol.355, pp.54-57, 2009.
- [38] I.P. Studenyak, R.Yu. Buchuk, M. Kranjčec, I.I. Makauz, I.M. Voynarovych, L. Daroczi, I. Charnovich, and S. Kökényesi, “Structural, electrical and optical properties of  $\text{As}_2\text{S}_3\text{-Cu}_6\text{PS}_5\text{I}$  nanocomposites”, Elsevier, J. Non-Cryst. Solids, vol.357, pp.96-99, 2011.
- [39] V.I. Zametin, M.A. Yakubovskii, L.M. Rabkin, “Anomalies of absorption edge at phase transitions”, Maik, Fiz. Tverd. Tela, vol.21, pp.491-498, 1979.