

# Optical and photoinduced phenomena in chalcogenide glasses $As_2S_3$ and $As_2Se_3$ and explanation of the observed correlations

I. BANIK

*Department of Physics, Faculty of CE, Slovak University of Technology, Radlinského 11, 810 05 Bratislava, Slovak Republic*

In paper is presented an idea allowed to explain empirically found optically induced phenomena - mid-gap absorption, fatigue effect, ESR signal and mutual correlations of these phenomena. We assume that the above mentioned effects are closely related to photoluminescence. We suppose that photoluminescence creates conditions for the formation of photoinduced short-living traps in the center of the band gap, in region of photoluminescence spectrum. The starting point of our considerations is barrier-cluster-heating model.

(Received November 05, 2015; accepted April 05, 2016)

**Keywords:** Chalcogenide glass, Photoinduced changes, Mid-gap absorption, Photoluminescence spectrum, ESR signal, Barrier-cluster-heating model

## 1. Introduction

Amorphous chalcogenides, or chalcogenide glasses, have been known since the time of ancient Egypt. Discovery in 1954 by Kolomiets and Goryunova showed that these glasses possess the semiconductive properties [1]. Amorphous chalcogenides attract a lot of attention due to their unique properties. A variety of photoinduced phenomena have been discovered in chalcogenide glasses, after a comprehensive study by Ovshinsky's group [2]. Specifically, it is known, that upon illumination of sub-band-gap light, a covalent chalcogenide glass undergoes marked changes in optical, photoconductive and electrical properties [3-8]. Band gap illumination also gives some modifications in microscopic structures, which have been detected in X-ray diffraction, etc. However, real atomic changes remain speculative.

Despite today's relatively wide-spread use of non-crystalline semiconductors in technical practice, the physical processes that take place in them are still not well understood [9-20]. There is no generally accepted model of non-crystalline materials, which would be able to explain the sufficiently wide range of phenomena. Regarding optical features of chalcogenide glasses (CHG) one of the great puzzles to be explained is the origin of the exponential tails. The big problem is there to understand the nature and properties of photoluminescence in CHG. Opened remains also problems connected with mid-gap effects.

In this article we examine (study) the mid-gap optical phenomena from viewpoint of our barrier-cluster-heating (BCH) model of disordered semiconductor, which has been described in the works [21-31]. Based on that model numerous electrical and optical phenomena in chalcogenide glasses have been explained. Namely, the

optical absorption, electroabsorption, photoluminescence (PL), photoconductivity and photoluminescence excitation characteristics (PLE characteristics). Many published articles are concerned partly on mid-gap effects [3-8, 34-44].

In this article we try to explain physical essence and meaning of photoinduced mid-gap phenomena. We preassume the comprehensive view on the mid-gap phenomena.

We come out from suggestion - our hypothesis, according to which mid-gap phenomenon arises due to fact that in the field of PL spectrum, in forbidden band of CHG are at photoluminescence created shortly living photoinduced traps. During their short life, they are able to capture electrons emitted by the mid-gap radiation from the valence band. After capturing the electron in the trap relatively stable paramagnetic center occurs. Just the existence of the traps allows the absorption of photons with mid-gap energy (about  $E/2$ ,  $E$  – the optical width of the forbidden band). Mid-gap absorption can be connected also with electron transition from para-magnetic centers in to conduction band.

On the basis of listed conceptions can be possible to comprehend various properties of CHG related to mid-gap processes. Good agreement with reality is shown on justness and accuracy of initial suggestions of our accession.

## 2. Barrier-cluster-heating model of disordered semiconductors

The barrier-cluster-heating model assumes that an amorphous semiconductor consists of microscopic regions – perhaps the clusters - separated from each other by

potential barriers [21-25]. The barriers restrict the transition of low energy conduction electrons from one region to the other. The potential barriers can be depicted inside the conduction and valence bands of an amorphous material (Fig.1).

The electron levels between barriers, due to the small dimensions of the microscopic regions, exhibit a distinct discrete character. At the lower margin of the conduction band, a sub-band with carriers of low average mobility ( $\mu_1$ ) is created. The states with energy above the peaks of barriers are delocalized. They create a sub-band with a high average mobility ( $\mu_2$ ). Quite a similar situation occurs at the edge of the valence band.

The structural clusters as nano-objects can have different form: they can be opened or closed. There is every indication that in the case of chalcogenide glasses they are mainly closed clusters [33]. And that are the closed clusters that enable the best explanation of *ESR* results and X-ray structural experiments on these glasses. The non-existence of *ESR* signal in chalcogenide glasses can be only explained by the fact that these glasses consist of closed clusters, which represent systems without unoccupied bonds.

Several types of closed nanoclusters of  $\text{As}_2\text{S}_3$  were built [33]. The fairly good agreement of several characteristics, calculated from the model, with the experimental ones allows us to conclude that a model with closed clusters is very attractive and could be improved.

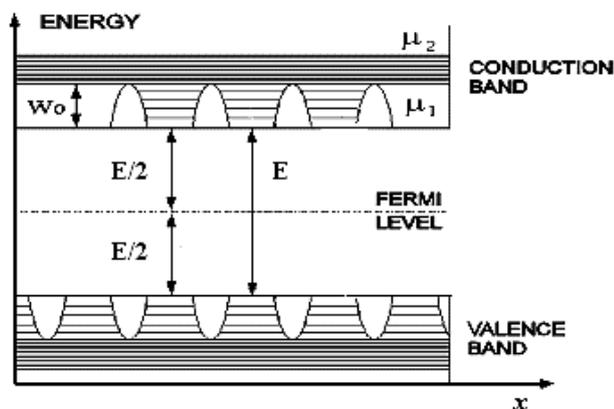


Fig. 1. The electron spectrum of an amorphous semiconductor.

As a consequence, the dangling bonds are naturally eliminated during the glass formation and, therefore, no significant amount of charged coordination defects is necessary to explain the glass structure. On the contrary, the formation of high numbers of VAPs was predicted during illumination and in the light saturated state of the glass. A closed cluster model for the binary arsenic-chalcogenide glasses seems to be attractive for the explanation of the structural and electronic properties of non-crystalline chalcogenides. At the same time, the straight consequence of the model is the absence of coordination defects. Moreover, a bi-stable - or multi-stable - behavior of the clusters could explain the behavior of the glass under the action of various external factors - radiation, temperature,

pressure. The barrier-cluster-heating model with closed clusters for the chalcogenide glasses is able to give explanations for the general properties of these glasses.

## 2.1 Optical phenomena and barrier-cluster-heating model

The potential barriers also influence significantly the optical properties, namely the absorption at the optical absorption edge. It is caused in the first line by their inducing a strong electron-phonon interaction. These results lead in the fact that on optical transition, apart from the energy of a photon, an electron can also take over the energy of the phonons. On such a transition, the total energy taken by an electron equals the sum of the photon and phonons energies (Fig. 2). This enables to explain existence of exponential tails of an optical absorption, which reach deeply inside of a forbidden band of the semiconductor [21-23]. Another important factor - as far as influence of barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually connected with tunneling of carriers through the potential barriers. Due to this, the absorption process is influenced by barriers. These facts enable us to explain successfully not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high as well as low temperatures [21-23].

In the next part we will shortly remember some optical phenomena in CHG which are on the basis of BCH model explainable. For more detailed information the reader can find in other published articles [8-17].

## 2.2 Optical absorption

In most crystalline solids, optical absorption is characterized by a sharp edge at the margin of the absorption band. Its position corresponds to the optical width of the forbidden band. However, the situation is different in the case of non-crystalline semiconductors. The absorption band near its border is smeared (blurred) out and it creates a exponential tail that extends deep into the forbidden band. Its profile is exponential as a rule. The exponential tails at higher temperatures tends to fit empirical Urbachs formula. The slope of the tails changes with further temperature decrease. At lower temperatures, the slope of the tails does not change with further temperature decrease. However, a certain parallel shift towards lower absorption is observed. Optical phenomena in non-crystalline semiconductors represent a number of complex phenomena.

**Higher temperature range:** The starting point of the following considerations on the base of barrier-cluster-heating model is an assumption that the potential barriers in non-crystalline semiconductors proper conditions occur for a distinct absorption of light, with phonons participating in the energy exchange [21-23]. We assume that an electron in an optical transition is able to accept not only the energy  $hf$  of a photon but also the phonon (vibrational lattice) energy  $W_{\text{phon}} = W_2$  (Fig. 2). Thus, the

whole accepted energy is sum of both parts

$$hf + W_{\text{phon}} \quad (1)$$

where  $W_{\text{phon}}$  is the energy acquired from a phonon "field". The quantity  $hf$  is positively determined by the wavelength of radiation, while  $W_{\text{phon}}$  has a statistical character.

In principle, a photon (without phonon participation) can be absorbed only when the photon energy is sufficient to accomplish a transition of the electron from valence into the conduction band. It should be taken into account, however, that optical transitions on the energy levels lying just below the tops of barriers will dominate at higher temperatures. In this case, the probability of transition within a single localized region is small. The levels in adjacent clusters offer more possibilities of combination. However, they are connected with tunneling through barriers. Under these assumptions, the transitions on levels just below the barrier peaks will be more probable for two reasons. The transitions on lower levels will be restricted considerably by a small tunneling probability. The second reason rests in strong electron-phonon interaction caused by the barriers. The number of electrons that can acquire such energy from a phonon field depends on temperature and is directly proportional to

$$\exp\left(-\frac{\text{needed energy}}{2kT}\right) \quad (2)$$

whereas  $\text{needed energy} = E - hf$ , where  $E = 2W$  is the width of the forbidden band.

The number of electron transitions when irradiating material by "low energy" photons (and thus, also the coefficient of optical absorption  $\alpha$ ) is directly proportional to the value (2). The question was solved in papers [21-22]. Here we have to remark only, that for the absorption coefficient it can be written [17-27]

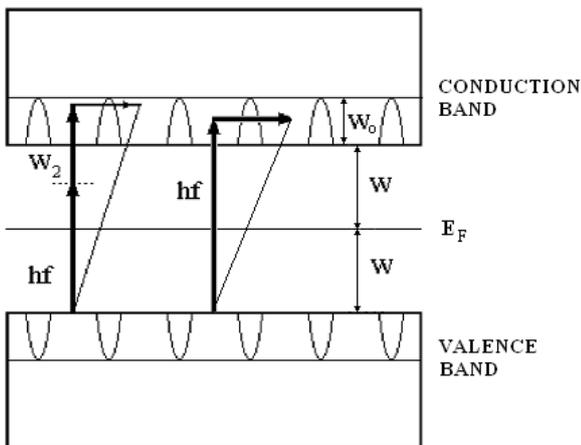


Fig. 2. Optical transition at higher (left) and at lower (right) temperature.

$$\alpha \approx \exp(hf/2kT) \quad (3)$$

or, for a particular (constant) temperature

$$\ln \alpha = hf + \text{const} \quad (4)$$

which is a mathematical expression of an exponential tail of optical absorption [21-23]. However, the slope of tails is also temperature dependent. Formula (3) is of the same kind as the empirical Urbach's formula [3,4, 11,12]. It explains the temperature dependence of the slope of exponential tails  $\ln \alpha(hf)$  at higher temperature.

**Remark:** At low temperatures the concentration of thermal photons is very small. In CHG can create also phonons of optical origin. These are created due to optical absorption, at following nonradiant recombination of  $e-h$  pairs. Phonons of optical origin can at low temperatures dominate in matter. Similarly as thermal phonons can the "optical" phonons actively participate on optical transitions. Their concentration is not determined by temperature. Exponential tails related with it have different properties as at thermal phonons. The slope of exponential tails is in this case not dependent from temperature.

**Low temperature range:** At low temperatures and at low concentration of phonons of optical origin only photons with sufficient energy can be absorbed by the material. There are not enough phonons with sufficiently high energies to realize the high-temperature mechanism of absorption. The optical transition of an electron can be virtually divided into two parts [21-23]: The first part (Fig. 2 - right) is a vertical transition onto an energy level inside its own localized region; the second part represents a horizontal tunneling transition onto a real level in an adjacent localized region. Thus, absorption of a photon in a low-temperature mechanism is connected with tunneling of the electron through a potential barrier. The barrier-cluster-heating model explains in this case the temperature parallel shift of the exponential tails, too [21-23].

### 2.3 Photoluminescence

A possible concept of physical nature of photoluminescence in chalcogenide glasses at low temperatures, from point of view of the barrier-cluster-heating model, is analyzed in works [26-28]. An electron in the course of optical transition, connected with tunneling, gets to an adjacent or a nearby region on the energy level, which is below the peak level of potential barriers. At lower temperatures, the excited electron will pass on the lowest energy levels of a given localization region. It will be free only within its own localization region. Its wave function would be localized practically in its own cluster between the neighboring barriers.

Due to Coulomb interaction and the poorly penetrable potential barrier between them, a bound state of such an  $e-h$  couple (some specific exciton) arises. As a consequence, a new energy level is formed in the forbidden band. Let us assign this level formally to that localization region where the electron rests. This level will be below the bottom of the conduction band. Levels of this kind will arise not only in the neighboring clusters, but also in the more distant regions. The height of these levels will depend on the distance from the "motherly" micro-region (for the sake of simplification, we suppose that the hole did not move, however, the holes are more inclined to

be moving in chalcogenide glasses). With increasing distance, these levels will approach the bottom of the conduction band.

At low temperatures, an optically excited electron will, with a high probability, gradually get back to the mother region of the hole. Such an approach is connected to gradual tunneling and diffusion. The approaching jumps "region-by-region", are connected to an interaction with phonons. Without phonons, such a process would not be possible. These approaching processes are in principle not radiant. An electron loses gradually a considerable part of its energy in them. In the last phase of approach, a non-radiant transition occurs to its own localization region. In this region, radiant optical recombination of the  $e-h$  pair occurs, connected with emission of a luminescence photon, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokes' shift will occur. If there were no other disturbing processes, a stationary state with a relatively high level of luminescence would establish quickly within the material. In fact, this corresponds rather well to a real situation in the first phase of irradiation. However, the state of a high luminescence begins to impair and weaken rather quickly.

#### 2.4 Free electrons as stimulators of non-radiant recombination

When irradiating a non-crystalline semiconductor by a flux of photons at low temperatures under conditions described above, free electrons are practically formed in materials substantially only by a multi-tunneling of a little part of electrons, which performed the optical transition. The slow rise of concentration of free electron is caused by the relatively low probability of multi-tunneling process. The concentration of free electrons in semiconductor stabilizes only after a long time, when dynamical equilibrium of two mutually opposing effects establishes, i.e. the process of arising of free electrons and the process of their „annihilation“ by joining holes through which, new bound  $e-h$  pairs are created. When explaining the laws of photoluminescence on the basis of the barrier-cluster-heating model, an extremely significant assumption is important in our considerations, namely that free electrons, by their effect, stimulate the non-radiant recombination of bound  $e-h$  pairs (as a kind of a catalyst), and thus, they reduce the number of radiant transitions. So, ultimately, free electrons markedly influence the luminescence process. The free electron remains free after such individual catalyst process and continues triggering non-optical transitions, acting as a catalyst.

#### 2.5 Influence of temperature and the absorbed energy quanta on photoluminescence - mechanism of free electrons origin

It was already said that a source of free electrons in a non-crystalline matter during photo-irradiation at low temperatures is a manifold tunneling of a small fraction of electrons at the process of the optical absorption connected with tunneling (Fig. 2). For this mechanism is essential

that majority of electrons execute at the optical transition a tunneling through one potential barrier. Only some electrons drive a tunnel s-time across s-barriers consecutively at the optical transition. In this manner electrons overrun a long distance from their original region (together with corresponding hole) and become free. Electron will be no longer bounded with a hole by the Coulomb force. In our model it is assumed that free electrons then activate non-radiative transitions of bounded  $e-h$  pairs. These will not contribute to the luminescence. This is why the process of stabilization of luminescence will be relative slow. In [22,26] the Street's formula

$$I \approx \exp\left(-\frac{T}{T_0}\right) \quad (5)$$

was derived the dependence of stabilised photoluminescence intensity on temperature. It is based on the concept that the photoluminescence process in a non-crystalline matter is strongly influenced by free electrons. This formula expresses the dependence of the stabilised photoluminescence upon the temperature in a low temperature range. In [26, 32] an attempt is done to describe quantitative dependence of efficiency of an excitation radiation upon the energy of stimulated photons.

At lower energies of the exciting photons in the region of exponential absorption tail the photoluminescence intensity increases with the increase of the photon energy  $hf$ , in line with the absorption  $\alpha$  growth. Thus, photoluminescence in this region copies the course of absorption  $\alpha$ . (We can speak about good correlation). Strictly speaking, in this range of photon energies relative high number of generated  $e-h$  couples recombine radiatively. At higher energies of the exciting photons in the region of exponential tail, absorption will continue to increase exponentially but luminescence passes through the maximum and it will decrease with further increase of photons energy.

This experimental fact is - as we believe - due to the fact that at higher photon energies the tunneling of electrons through barriers will be in progress on higher energy levels. That increases probability of simple tunneling. The probability of s-multiple tunneling of electrons overriding long distances will rise much faster. Thereby, with energy increase of exciting (activating) photons free electron production will increase in a substance essentially and thus also the number of non-radiate  $e-h$  pair recombination. The radiation transition number as well as the photo-luminescence "niveau" will no longer be proportional to the number of absorbed photons. With increasing photon energy the luminescence increases first slows down, and then stops and finally luminescence begins to sink.

## 2.6 Photoconductivity

Explanation of photoconductivity from the point of view of the barrier-cluster-heating model was published in works [21-31].

## 3. Photoinduced phenomena in chalcogenide glasses

The glass is known to exhibit a variety of radiative effects. The most famous may be the defect formation and radiation compaction in silica glasses [3,4], which is now commercially utilized for producing Bragg-grating fibers [3]. However, since the oxide glass has a wide bandgap of 4-9 eV and the structure comparative rigid, intense pulsed lasers or ultraviolet source are needed for inducing these phenomena. On the other hand, the chalcogenide glass has a bandgap of 1-3 eV and flexible structures and accordingly, it exhibits many kinds of prominent photoinduced phenomena [4]. These phenomena have been extensively studied during the last decades because of their potential applications, especially in optics and optoelectronics.

Chalcogenide glasses show several photoinduced changes in structure and properties, including volume, amorphization, devitrification, mechanical (e.g. plasticity), rheological (e.g. viscosity), optical (e.g. darkening), birefringence, luminescence, electrical (e.g. conductivity, dielectric constant), or the chemical (e.g. etching, dissolution). Shimakawa et al [3] have reviewed such phenomena which can be permanent, metastable or temporary with regard to light exposure. Numerous interesting applications have been conceived and designed based on these properties of chalcogenide glasses, especially in amorphous thin film form.

Most of the existing models interpret the photoinduced effects through the production of electron-hole pairs as the result of photoexcitation of chalcogenide lone pairs. The most spectacular photoinduced effect is probably the photoinduced fluidity, or "photofluidity". Photofluidity is considered as a keystone to understand various photoinduced phenomena. The giant photoexpansion has evoked vivid interest in the mechanism and application. Light-induced changes in chalcogenide glasses optical properties are either scalar (shift of the absorption edge toward lower energies) or vector (emergence of macroscopic polarization dichroism and birefringence).

An usual trend to explain photoinduced properties of chalcogenides and their compounds is considering specific bistable defects, which were called the valence alternation pairs (VAPs) [34-39]. Origination of VAPs is associated with the structure of the outer shells of atoms forming the compound. All possible VAP types in chalcogenides and also in compounds with tetrahedral coordination of atoms were analysed in detail in [34-39]. A critical viewpoint of models proposed to explain photoinduced effects in

chalcogenide glasses was presented by Fritzsche [18], one of the founders of the science of photo-induced transformations in chalcogenide glasses. He believes that there are two kinds of effects inducing changes in chalcogenide glass optical properties. Effect of the first type is related to reconstruction of bistable centers, whereas the second type is associated with reconstruction of the entire glass structure.

In spite of tremendous effort dedicated to chalcogenide glasses, the structure and properties of these materials have not been completely understood yet [3,6,9]. It was pointed out many years ago that no ESR signal was detected in amorphous chalcogenides (a-Se, a-As<sub>2</sub>S<sub>3</sub>). This observation, viz the absence of spins in chalcogenide glasses, led Anderson [36] and Street and Mott [37] to formulate their negative effective correlation energy (negative-U) models, in terms of charge defects. But, Tanaka [13, 38] has questioned the presence of the charged defects on the basis of optical absorption measurements on highly purified As<sub>2</sub>S<sub>3</sub> samples.

### 3.1 Mid-gap absorption and photoinduced PL

Forbidden gap of CHG without optical excitation is (from point of view of the barrier-cluster-heating model) clear. Glass is transparent in the mid-gap region. The existence of the photoinduced mid-gap absorption is experimental fact. In which way our BCH model is able to explain this? Mid-gap absorption is determined by creation of energetic levels in the area of the middle of the forbidden band. These levels are created by the influence of primary excitation of radiation with energy of photons corresponding approximately to the width of the forbidden band [3, 5].

On the beginning of our reasoning we pronounce a hypothesis, on the basis of which we will in further part explain the essence (substance) of photoinduced mid-gap effects. As a starting point for the understanding of photoinduced mid-gap effects we consider photoluminescence spectrum of CHG. It is strange, but everything indicates, that photoinduced states – traps are created just in this band of energies, which belongs to the PL spectrum of given CHG. We assume also, that the density of the created short living traps corresponds to profile of PL curve. These mentioned assumptions represent of course the hypothesis only. Nevertheless the consequences, which imply from this hypothesis indicate, that this hypothesis – represents concerning reality quite good.

PL spectrum of majority of CHG is situated in the centre of forbidden band. By low energies of photons the absorption of mid-gap radiation practically doesn't occur, because the band of induced states lies too high above the valence band. By some higher energies of photons excited electrons can be caught on lower situated traps, created on the energetical levels in lower area of PL spectra.

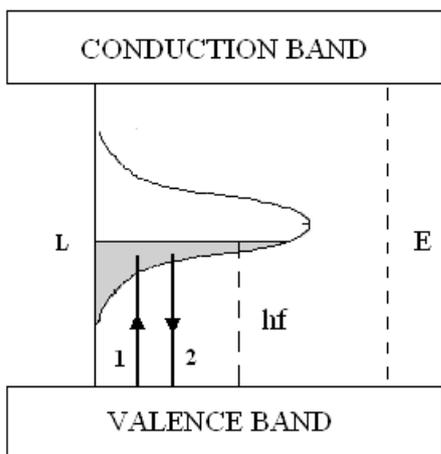


Fig. 3. Mid-gap phenomena at low photon energies of mid-gap radiation, 1- absorption, 2- PL amplification.

The transitions of electrons to the higher levels cannot pass off. With growing photon energy of the mid-gap radiation electron will successively occupy also traps created on the higher and higher energetical levels. Finally electrons will occupy practically whole energetical area belonging to PL spectrum. The higher is the photons' energy of mid-gap radiation, the larger area, belonging to PL spectrum is occupied with electrons by mid-gap absorption (Fig. 3). As consequence is there consecutive growth of absorption.

Mid-gap absorption is growing however nonlinearly with energy  $hf$  –very slowly on beginning, then swiftly and in the last phase slowly again. In such a way it responds to the growth of „occupying area“. Simplifying we can assume, that given „activated“ area is uniformly occupied with excited electrons. At the photons, which energy lies in upper part of PL curve the absorption shows now a feature of the saturation.

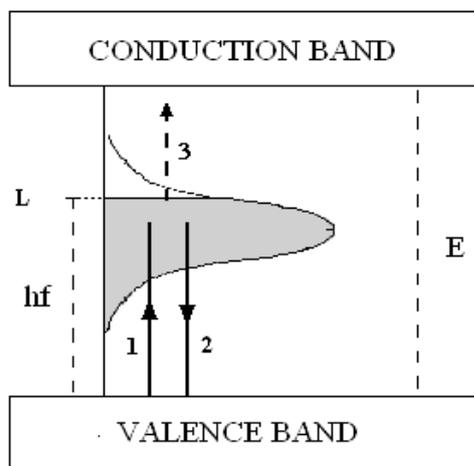


Fig. 4. Electron processes at high photon energies of mid-gap radiation, 1- absorption, 2- PL amplification, 3-absorption.

Except of described mechanism of absorption of the mid-gap radiation it is needed to mention also the existence of other mechanism, which is responsible for another component of mid-gap absorption (which markedly influences PL). This pass off on the „higher floor“ of electron spectra. It relates with the transitions of electrons from area occupied photoinductive traps (as paramagnetic centers) to the conduction band of semiconductor (Fig. 4 - transition 3).

### 3.2 Amplification of the luminescence

The traps originated in the area of photoluminescence spectrum are – as we were ascertaining – capable to catch electrons excited by mid-gap radiation from the valence band (Fig. 3 - transition 1). Caught electron though after a life-time reverts spontaneously into the valence band, during which time photon often radiates (Fig. 3 - transition 2). In this way it causes the amplification of PL of glass. Mid-gap absorption and amplification of PL are closely connected. At low photon energy  $hf$  the PL increases analogically as mid-gap absorption. For the higher energy of photons is it more complicated.

At the higher photon energy (which surpasses  $E/2$ ) the situation will be different. The PL curve begins to decrease inspite of reality that photoabsorption (PA) is not decreased (Fig. 5). Physical reason of this consists on the creation of free electrons by the mechanism illustrated on the Fig. 4 - transition 3. BCH model presupposes, that free electrons in CHG with their catalytic effect evokes nonradiative recombination of coupled electron-hole ( $e-h$ ) pairs. In other case they can recombine in a radiative way. Just this effect is responsible for the corresponding weakening of PL. Concisely it can be said, that the runnings of mid-gap PL in area of energy lower than half width of forbidden gap ( $E/2$ ) are analogous as the running of the mid-gap photoabsorption. Whilst in the area above  $E/2$  are both runnings different.

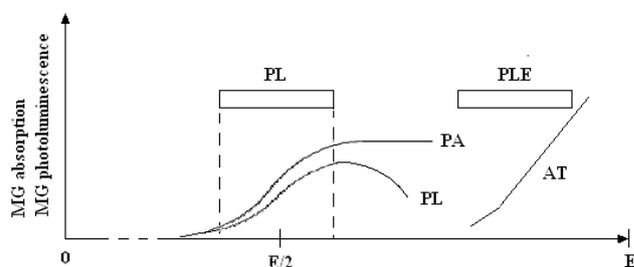


Fig. 5. Dependence of mid-gap photoabsorption PA and photoinduced photoluminescence PL on photon energy at low and at high  $hf$  energies.

Generally speaking: At lower photon energies mid-gap radiation does not contribute to creation of free electrons. Electrons at small photon energies of mid-gap radiation cannot transit into conduction band. At higher energies

exceeding half width of forbidden gap  $E/2$  to absorption of mid-gap radiation also electron transitions from photoinduced band contribute into conduction band (Fig. 4). Just this mechanism give rise to additional creation of free electrons, which than contribute to suppression of PL.

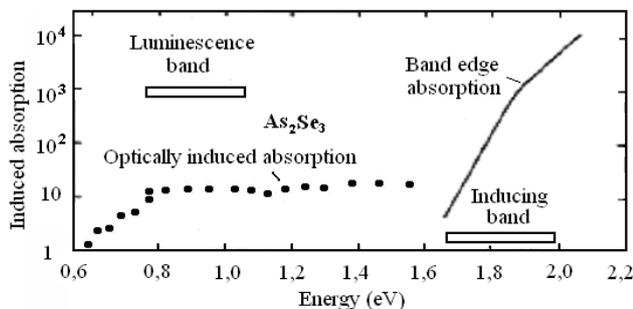


Fig. 6. Dependence of the photoinduced mid-gap absorption in  $As_2Se_3$  on photon energy of mid-gap radiation [7]. [Bishop]

Experimental results of this type as it is illustrated on Fig. 6, are in agreement with our model. Our suggestions support also experimentally observed saturation as well as overall course of absorption curve. We comment that in the case of Fig. 6 on the vertical axis dependence  $\ln \alpha(hf)$  is depicted. Definite shifts of both actual courses toward idealised case which we see at Fig. 5 can be connected with simplifying of reality at our calculation.

Upper described mechanism of photoinduced mid-gap absorption (and connected PL with it) represents the idealized view on reality. On the mid-gap absorption - besides photons - also phonons can participate. Energy absorbed by an electron at transition into photoinduced band can have two members  $hf + W_{phon}$ , where  $W_{phon}$  represents energy gained by the electron from lattice. At very low temperatures there are phonons of optical origin, which are created at non-radiate recombination of  $e-h$  pairs.

Experiments verify also dependence of PL at energies of photons of mid-gap radiation exceeding  $E/2$  (Bishop [7]).

The catching of electrons on the traps causes in CHG creation of paramagnetic centers. ESR signal of CHG is proportional to concentration of ESR centers. These centers have relatively good stability. By increasing of temperature these centers are disintegrated.

Radiating transition of electrons from ESR centres to valence band is accompanied with by PL signal. The higher is the concentration of ESR centres, the higher is the mid-gap PL. This is the cause of observable correlations of mid-gap effects - mid-gap PL and ESR signal.

### 3.3 Traps occupation by free electrons

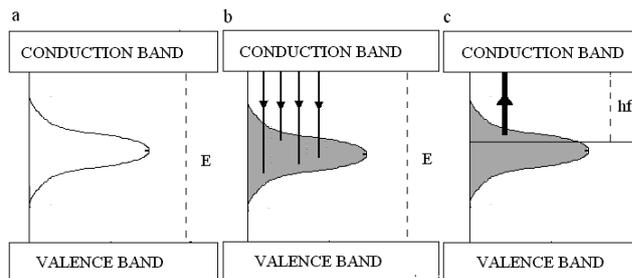


Fig. 7. PL spectrum (a), trap occupation by free electrons (b) and mid-gap absorption (c).

Traps generated by photoluminescence can also be occupied with electrons from the "top" (Fig. 7b) – with electrons from the conduction band. This cause the increase of ESR signal, which is the result of increasing number of the paramagnetic centers. That is the essence of photoinduced ESR signal in CHG, discovered by Bishop [7].

Traps are getting filled as the concentration of ESR centers will be at some equilibrium level, determined by equilibrium between filling of traps and decay of produced paramagnetic centres. It can be possible to suggest that filled traps restrict the optical transitions top-down. This process is therefore associated with gradually fading luminescence. The luminescence of fatigue is observed.

Lets think about the fact what will happen if in equilibrium state created after long term acting excitation radiation (without acting of mid-gap radiation) we will turn off the excitation radiation at low temperatures. ESR centres will stay frozen. ESR signal will be stable. At higher temperatures paramagnetic centres will begin to decay, ESR signal will gradually decrease. Optical transitions of electron from ESR centres in to valence band will cause the PL. Its intensity will be proportional to the concentration of the ESR centres and also to the "level" of ESR signal. Correlation of listed two mid-gap phenomena will be observed.

If a substance, in the above described relaxation process, is simultaneously irradiated by the mid-gap radiation, (by the disabled excitational radiation) mid-gap absorption is observed. It is enabled by optical transitions shown in Fig. 7c. We talk about electron transition from paramagnetic centers into the conduction band. "Active area" for optical transitions (Fig. 7 - the area above the horizontal line) depends upon the energy of mid-gap radiation photons. By the energy -  $hf$  - increasing, active surface area increases as well. The dependence of the absorption upon the energy of mid-gap photons, is in this case, analogous to the case of PA curve in Fig. 5.

Mid-gap absorption of type Fig 6c will have at lower intensities of mid-gap radiation similar course as course of ESR signal and course of photoinduced PL. It will act as correlation of both mid-gap effects. Let's list that also at this relaxation none electron transitions from valence band does run into the photoinduced band, because at turn off excitation radiation no traps are created.

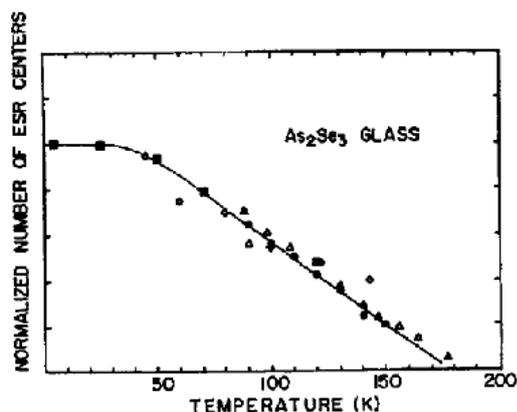


Fig. 8 Experimental results confirm correlations by thermal dependence of three mid-gap phenomena in  $As_2Se_3$  – ESR signal, photoinduced mid-gap absorption and photoluminescence (details in [7]).

Saturated state of ESR centres is created of course also at long lasting occurring of both radiations – excitation radiation and mid-gap radiation.

Let's ask a question: What will happen if after such a steady saturated condition at a sufficiently low temperature of both radiations (excitation and mid-gap) will be simultaneously switched off. Paramagnetic centers remain frozen at low temperatures. ESR signal will remain preserved. If in such a situation the sample will get suitably tempered (annealed), paramagnetic centers will gradually disintegrate. The released electrons move into the valence band. This is associated with fading luminescence. In the case of mid-gap irradiation will mid-gap absorption (mechanism in Fig. 7c) gradually decline (the number of occupied centers decreases). This fact is confirmed by Bishop's experiments (1977).

The dissolving (decaying) of paramagnetic centers at low temperatures can cause also infrared radiation from the area of luminescence curve. In other case it can be turned off (cancelled) only excitation radiation and mid-gap radiation still occurs. Also in this case becomes evident synchronous decrease of ESR signal, photoluminescence and mid-gap absorption.

Experimental results of Bishop (Fig. 8) confirm correlations by thermal dependence of three mid-gap phenomena in  $As_2Se_3$  – ESR signal, photoinduced mid-gap absorption and photoluminescence (detail information in [7]).

#### 4. Discussion

In coherence with presented view on mid-gap phenomena stay stands more questions opened. For example:

Which is microscopic mechanism of creating of catching traps and paramagnetic centres? Can be things explained by the suggestion that structural clusters have the character of multi-stable object? Can be profile and location of PL spectrum in the middle of forbidden band to explain in a way that radiated recombinations are predominantly two photons, at which two photons are emitted (sent)

simultaneously. Their overall energy equals to the width of forbidden band? In spite of opened questions we think that indicated way of explaining of mid-gap phenomena is prospective.

**Remark:** Basic idea about “two photons emission” in CHG was by author described in the article [29]. It is suggested that probability of this emission is equal to the product  $p_1 p_2$ , where  $p_1$  is probability of sending of first photon,  $p_2$  is probability of sending of second photon. Single probabilities are dependent upon the energy of competent photon and these have Gaussian profile.

#### 5. Conclusion

In this article we present possible explanation of experimentally observed photoinduced mid-gap effects – photoinduced mid-gap absorption, amplification of photoluminescence (at mid-gap absorption) and photoinduced ESR emergence signal in chalcogenide glasses. We are also interested in mutual correlations between these phenomena. The observed effects we can explain based on the barrier-cluster-heating model. Photoinduced effects are the consequence of traps creation in the forbidden band of semiconductor. At the same time we presuppose, that the photoinduced traps are created in energetical region belonging to the photoluminescence spectra. Further we presuppose that the probability of the creation of traps corresponds to the profile of the spectra.

Created traps are filled at mid-gap radiation by electrons from valence band. The occupying of the traps with electrons is connected with creation of paramagnetic centres and the increasing of the ESR signal. Traps can be filled also by electrons from conduction band. This process passes off also without impact of mid-gap radiation. It triggers the creation of optically induced ESR signal by the photoluminescence. By sufficiently high energy of photons of mid-gap radiation this radiation will be absorbed also as a consequence of optical transitions of electrons from paramagnetic centers into conduction band.

Barrier-cluster-heating model explains also photoluminescence amplifying by mid-gap absorption and relaxation above mentioned mid-gap processes in CHG after switch off excitation radiation and mid-gap radiation. From mentioned imaginations (as hypothesis) results whole row of implications which good correspondent with experimental facts. Closed-cluster structure can explain the absence of an ESR signal in the case of chalcogenide glasses. BCH model is capable to explain the number of important electrical, optical and photoinduced effect in chalcogenide glasses. This provides new view on the density of states within the forbidden band of the semiconductor and explains, why the attempts at identification of gap-states by various optical and other methods fail. It can also explain the results of X-ray-structural measurements. We assume, that the barrier-cluster-heating model can be expected to stimulate a development of new interpretations of physical phenomena in non-crystalline semiconductors, and specifically in chalcogenide glasses.

### Acknowledgement

The corresponding research has been supported by grant VEGA 1/0184/14, Slovakia.

### References

- [1] N. A. Goryunova, B. T. Kolomiets, *Izv. Akad. Nauk., Ser. Fiz.* **20**, 1496 (1956), or *Zh. Tekhn. Fiz.* **25**, 984 (1955).
- [2] J. P. de Neufville, S. C. Moss, S. R. Ovshinsky, *J. Non-Cryst. Solids*, **13**, 191, (1974).
- [3] K. Tanaka, K. Shimakawa, *Amorphous chalcogenide Semiconductors and Related Materials*, Chap. 6, Springer, New York, 2011.
- [4] A. V. Kolobov, K. Tanaka, *Photoinduced phenomena in amorphous chalcogenides: from phenomenology to nanoscale*, Chap. 2, *Handbook of Advanced Electronic and Photonic Materials and Devices*, edited by H.S. Nalva, Vol. 5: Chalcogenide glasses and Sol-Gel Materials, ISBN 0-12-513755-9, (2001).
- [5] T. Tada, T. Ninomiya, *Journ. of Non-cryst. Solids*, **114**(1), 88 (1989).
- [6] V. K. Malinovski, N. F. Surovtsev, *Chalcogenide Letters*, **9**(2), 79 (2012).
- [7] S. G. Bishop, U. Strom, P. C. Taylor, *Phys. Rev.* **B15**, 2278 (1977).
- [8] M. Popescu, *Photoinduced Phenomenon and elements for integrated Optics based on Non-crystalline chalcogenide semiconductors*, Ed. Chisinau, 2003.
- [9] K. Tanaka, *J. Optoelectron. Adv. M.*, **15**(11-12), 1165 (2013).
- [10] H. Overhof, *J. Non-Cryst. Sol.*, **227-230**, part I, 15 (1998).
- [11] I.P. Studenyak, M. Kranjčec, M.V. Kurik, *Int. Journ. of Optics and Applic.*, **4**(3), 76-83,(2014).
- [12] M.H. Brodsky, *Amorphous semiconductors*, Springer Verlag Berlin, Heidelberg, New York, 1979. (*Amorfnyje poluprovodniki*, Mir, Moskva, 1982).
- [13] K. Tanaka, *J. Optoelectron. Adv. M.* **3**(2), 189 (2001).
- [14] M. Popescu, *Non-crystalline chalcogenides*, *Solid state science and technology Library*, Vol.8, Kluwer academic publishers, Dordrecht/Boston/London (2000).
- [15] M. Popescu, *Non-Crystalline Chalcogenides*, Chap. 3, Kluwer Academic Publisher, Dordrecht, (2000).
- [16] M. Popescu. *J. Optoelectron. Adv. M.*, **7**(4), 2189 (2005).
- [17] M. Popescu, *J. Optoelectron. Adv. M.* **8**(6), 2164 (2006).
- [18] H. Fritzsche, *Phys Stat. Solidi B.* **246**, 1768 (2009).
- [19] A. M. Andriesh, M. S. Iovu, *Moldavian journal of physical science*, **2**(3-4), 246, (2003).
- [20] A. M. Andriesh, M. S. Iovu, S. D. Shutov, *J. Optoelectron. Adv. M.*, **4**(3), 631 (2002).
- [21] I. Banik, *Journ. of Non-Crystalline Solids* **353**, 1920 (2007).
- [22] I. Banik, *J. Optoelectron. Adv. M.*, **11**(12), 1915 (2009).
- [23] I. Banik, *Central European Journal of Physics* **3**(2), 270 (2005).
- [24] I. Banik, *J. Optoelectron. Adv. M.* **11**(12), 1931 (2009).
- [25] I. Banik, *Acta Electro-technica et Informatika*, **10**(3), 52 (2010).
- [26] I. Banik, *Journal Non-Oxide and Photonic Glasses*, **1**( 1), 6 (2009).
- [27] I. Banik, *J. Optoelectron. Adv. M.* **14**(9-10), 711 (2012).
- [28] I. Banik, M. Popescu, *J. Optoelectron. Adv. M.*, **15**(11-12), 1179 (2013).
- [29] I. Banik, *Proc. ADEPT 2015, High Tatras, Štrbské Pleso 1-4*. Ed. D. Pubiš, I. Letrichova, J. Kováč, p. 164-168, University of Žilina, ISBN 978-80-554-1033-3, (2015).
- [30] I. Banik, G. Pavlendová, *Advanced Materials Research*, **1126** (2015).
- [31] I. Banik, *Proc. Thermophysics, Podkylava 2013*, ed. O. Zmeškal, p. 32, 2013.
- [32] I. Banik, *J. Optoelectron. Adv. M.*, **11**(12), 1915 (2009).
- [33] M. Popescu, *J. Optoelectron. Adv. M.* **6**(4), 1147 (2004).
- [34] R. A. Street, T. M. Searle, I. G. Austin, *Journ. Phys. C*, **6**, 1830 (1973).
- [35] R. A. Street, T. M. Searle, I. G. Austin, *Amorphous and Liquid Semiconductors*, eds. J. Stuke, W. Brening, Taylor and Francis, London, 1974, (1974).
- [36] P. W. Anderson, *Phys. Rev. Lett.* **34**, 953 (1975).
- [37] R. A. Street, N. F. Mott *Phys. Rev. Lett.* **35**, 1293 (1975).
- [38] K. Tanaka, *J. Optoelectron. Adv. M.*, **9**(10), 3171 (2007).
- [39] M. A. Kastner, D. A. Adler, H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
- [40] S. G. Bishop, U. Strom, P. C. Taylor, *Phys. Rev.* **B152278** (1977).
- [41] S. G. Bishop, U. Strom, P. C. Taylor, *Phys. Rev. Lett.* **34**, 1346 (1975).
- [42] S. G. Bishop, N. J. Shevchik, *Phys. Rev. B* **12**, 1567 (1975).
- [43] S. G. Bishop, U. Strom, P. C. Taylor, *Solid State Commun.* **18**, 573 (1976).
- [44] S. G. Bishop, U. Strom, P. C. Taylor, *Phys. Rev. Lett.* **36**, 543 (1976).

\*Corresponding author: ivan.banik@stuba.sk