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Barrier-cluster model – the base for understanding of the optical phenomena in non-crystalline semiconductors

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The paper introduces on the first place the basic information on the barrier-cluster model of a non-crystalline semiconductor and on its possibilities to explain physical phenomena in non-crystalline semiconductors namely in chacogenide glasses. In addition, it presents the derivation of dependency of photoluminescence efficiency of primary radiation on energy of excited photons (so called PLE-characteristics). This work also brings some remarks on current open problems of non-crystalline semiconductors and sketches the new potential possibilities of this model to explain those problems.

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1. Introduction

1.1 Optical phenomena - subject of high interest

Physical phenomena in non-crystalline material are very complex and experimental research in this area is very extensive. It calls for theoretical analysis, but a generaly accepted model of non-crystalline semiconductor does not exist yet.

Chalcogenide glasses have been recognized as promising materials for infrared optical fibers and elements [1-15]. They have also found applications in xerografy, switching and memory devices, photolitography processes and in the fabrication of inexpensive solar cells, and more recently as reversible phase change optical recorders. The addition of an impurity has a pronounced effect on conduction mechanism and structure of amorphous glasses and this effect can be greatly different for various impurities.

Although the chalcogenide glasses are widely used in modern technique and technology, many physical processes in these materials remains a great mystery. Up to now generally accepted model doesn't exist which would be capable of understanding wide spectrum optical and other phenomena in these matters [16-25].

The most important phenomena observed in non-crystalline semiconductors can be explained on the base of barrier-cluster model [26-33]. The starting point of the barrier-cluster model is the assumption that there exist micro-regions in non-crystalline semiconductors which are created by closed clusters and which are separated from each other by potential barriers. The potential barriers hinder the transport of charge carriers at the margin of the conduction or valence bands. They influence significantly the optical absorption at the optical absorption edge, too.

1.2 Chalcogenide glasses

The first fundamental knowledge on non-crystalline semiconductors can be found in [16,17]. Other relevant publications on these materials are [18-23].

One of the authors of the monograph [16], N.P.Mott, was awarded the Nobel Prize in 1978 for his extraordinary contribution to the development of the physics of non-crystalline solids. He contributed substantially to the understanding of the most crucial ideas on the nature of the electronic spectrum and on the mechanism of electric charge transport in non-crystalline semiconductors. Despite this, there are still a number of crucial experimental phenomena unexplained. The structure of amorphous substances also remains an open question. It seems that a logical way leading from clarifying structure (using demanding experimental equipment, for example) to a theory based on aknown structure meets invincible obstacles already on the experimental level.

Different models are used in the creation of theoretical knowledge about amorphous materials, and the consequences of a particular model are after wards compared with reality. In this way, suitability of a particular model is verified. It is not that simple, however. No model has been suggested yet that would explain sufficiently the wide range of observed phenomena. Indeed, this may be connected to the nature of the object under discussion. Non-crystalline solids present an extremely wide variety of materials because they also include many component systems, in which the stoichiometric abundance of particular substances is not needed. Moreover, they are mostly metastable systems, and their metastable state depends on sample preparation. A little deviation in this procedure may lead to the creation of a quite different metastable state, and thus to the formation of a different non-crystalline material. A theory that would include all this complexity seems to be very demanding and complex.

1.3 Optical phenomena in non-crystalline semiconductors

The optical phenomena in non-crystalline semiconductors are of high interest. From the point of view of understanding the physical processes in non-crystalline semiconductors, it is very important to study optical properties of these materials, especially the optical absorption and luminescence (especially the photoluminescence).

In most crystalline solids, optical absorption is characterized by a sharp edge 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 out and manifest itself as a tail that extends deeply into the forbidden band [16-20, 24-31]. Its profile is exponential as a rule. The exponential tails at higher temperatures tend to fit Urbach´s formula. The slope of the tails changes with the temperature decrease. At low enough temperatures, the slope of the tail rises when the temperature decreases. However, a certain parallel shift of the curves towards lower absorption edge is observed.

The nature of the absorption edge in non-crystalline (amorphous) semiconductors has been longly discussed in literature for many years. The attempts of many authors to explain the absorption edge did not gave, up to day, satisfactory results [32-34].

From among existing theories that try to explain the Urbach's rule, none is preferred as yet. The following theories try to explain the behavior of the material:

(a) The theory of bound exciton.

It is an exciton that interacts with lattice oscillations. According to Toyozawa [16,17,35], the Gaussian shape of the exciton absorption line changes strongly if we consider the quadratic terms of mutual exciton-phonon interaction. The long-wave wing of the line changes from Gaussian to exponential. The most difficult problem to explain is why the quadratic terms exceed the linear terms.

(b) The theory of broadening the absorption margin by an electric field

This is the so-called Franc-Keldysh effect [16,17,36]. Its nature is in tunneling of the Bloch states in to the forbidden band when the energy of a photon is smaller than it would be at the bottom of the allowed band. At that, the origin of strong electric fields and, especially, the explanation of temperature dependence of the tail remain questionable.

(c) The theory of the exciton line broadening by an electric field.

Dow and Redfield [34] investigated the problem of absorption in adirect transition of exciton in a homogenous electric field. They pointed out that the tail shape is exponential. On this basis, they expressed a hypothesis that Urbach's rule can be explained by broadening of the exciton absorption line by an electric field. There remains, however, a problem of explaining the origin of internal electric fields as well as the observed temperature dependence. Mott [16] assumed that just this theory could be the most acceptable one for the non-crystalline semiconductors. However, he raised some questions at the same time. Do excitons exist at all in amorphous materials? What is the origin of internal electric fields? No one has offered a satisfactory answer yet.

In amorphous semiconductors, however, there exist some specific ways to explain the origin of the exponential tails. Questions of exponential tails and of density states at the band margins were widely discussed in the scientific community [16,17]. From this point of view, the exponential tails of optical absorption should rise as a result of optical transitions between levels belonging to the tails of density states at the margins of the valence and conduction bands. It is usually assumed that the tails of density states may have an exponential shape as well. According to Mott [16], however, such an explanation is considered to be of low probability. The main argument opposing this concept is the fact that the slope of the dependence $\ln\alpha(hf)$ has approximately the same slope on all semiconductors. It is doubtful to expect that the tails of density states should be equal, at least nearly, in all amorphous semiconductors.

To conclude this part, it should be stated, in accordance with Overhof [23], that as yet there is no plausible theory that would explains satisfactorily the origin of exponential tails in non-crystalline or even in crystalline semiconductors.

In this work, the results of the author's effort to clarify physical properties of non-crystalline semiconductors in a more comprehensive way are presented. The existence of a potential barrier among individual microscopic regions of a non-crystalline solid seems to be the most typical feature of this model. It is called the barrier-cluster model. The most important optical phenomena, observed in non-crystalline semiconductors, are then explained on the basis of this model. Before all this, physical mechanisms responsible for the rise and properties of exponential tails of optical absorption are addressed. From among further important optical phenomena explained in this study, electroabsorption, photoluminescence, photoelectric conductivity, and quantum yield should be mentioned. The barrier model enables us also to explain a series of electric transport phenomena.

Up to now no satisfactory model has been proposed, in the frame of which it would be possible to explain a wider enough palette of optical and other processes in non-crystalline semiconductors. In the papers [37-45], the explanation of some optical phenomena in chalcogenide glasses on the base of a barrier- cluster model was presented. We presume that the barrier-cluster model of a non-crystalline semiconductor could be taken adequate for this aim. This model was repeatedly used for understanding some special problems of the non-crystalline solid state physics [37-45]. Naturally, one can not expect that all phenomena in non-crystalline materials can be explained by virtue of the barrier-cluster model. Nevertheless, it has allowed describing some most typical common features for a sufficiently broad class of non-crystalline materials.

The photoluminescence based on the barrier-cluster model of a non-crystalline solid was described in some previous papers by the author [37-45].

Street et al (1974) [46] discovered that the temperature dependence of the luminescence intensity in quenched a-As_2Se_3 has the form:

$$I \sim \exp(-T/T_o) \tag{1}$$

over four orders of magnitude of the intensity, where T_o is a constant. This dependence $I(T)$ was observed for instance in [47-52].

There is a serious problem how to understand the photoluminescence and especially how to explain it s temperature dependence. The luminescence is an important optical phenomenon for the theory of non-crystalline semiconductors.

The photoluminescence intensity in amorphous semiconductors decreases in time after the beginning the illumination at low temperatures. The experiments show [16, 17, 52-54] that the originally high luminescence level decreases gradually and stabilizes at a considerably lower level after a certain time. This fatigue effect is strongest in chalcogenide glasses (Cernogora et al 1973) [55] but a comparatively weak fatiguing effect has been found recently in amorphous silicon (Morigaki et al 1980) [56]. Biegelsen and Street (1980) [57], using ESR data and Shah and DiGiovanni (1981) [58, 59] using luminescence decay data concluded that fatigue in a-As_2S_3 is due to the creation of non-radiative centers by the illumination. Kirby and Davis reported the luminescence fatigue in amorphous phosphorus as early as (1980) [60]. The experimental results are presented in the papers [61-63].

Theoretical explanations of Street´s empirical law have been given by Street (1976) [64], Philips (1980) [65], Gee and Kastner (1979) [66], Highasi and Kastner (1979) [67,68].

In crystals, the temperature dependence of luminescence is usually well described by a thermally activated escape process of the trapped carrier from the luminescence center to a non-radiative center. If such a model were used for a chalcogenide glass, temperature-dependent activation energies ranging from 1 meV at low temperatures to 100 meV at high temperatures should be assumed.

Gee and Kastner (1979) and Higashi and Kastner (1979) have suggested that the Street´s formula (2) is the result of a distribution of non-radiative rates which arises, in turn, from a distribution of activation energies for the non-radiative process. It will be immediately noticed that the assumption of a single radiative rate is certainly incorrect. Indeed Highasi and Kastner (1979) showed that the time dependence (fatigue) of the photoluminescence the total light decay is determined by the very broad spectrum of radiative rates.

In present no model exists, which is able to explain sufficiently wide spectrum of physical phenomena in non-crystalline semiconductors. The existing models of luminescence in non-crystalline semiconductors were derived from the VAPs concept for these materials.

The present state of knowledge is full of many contradictions.

Recently, Tanaka has questioned the presence of the charged defects [69]. The new knowledge's above possible cluster structure of chalcogenide glasses (especially closed clusters) questioned the model based on VAPs [70-72]. In [70] we can read: "Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed… Unlike the previous theories, the new model takes into account the layered cluster structure of semiconductors."

The problem of the structure of the non-crystalline semiconductors was studied in [73-75].

1.4 Structure

In spite of tremendous efforts dedicated to chalcogenide glasses, the structure of these materials is not completely understood [76-82]. Some models have been developed with the aim to explain the first sharp diffraction peak in the diffraction pattern of various non-crystalline materials.

Many years ago it was pointed out that no ESR signal was detected in amorphous chalcogenides (a-Se, a-As_2S_3). This observation, i.e. the absence of spins in chalcogenide glasses, led Anderson [76] and Street and Mott [77] to formulate their negative effective correlation energy (negative-U) models, in terms of charged defects. The model assumes the presence of dangling bonds, but with the combination of positively and negatively charged dangling bonds, D^+ and D' having respectively no and two spin-paired electrons, being energetically favored over the neutral dangling bond D^o with one unpaired electron. The defect-based version of the negative-U model was subsequently developed by Kastner, Adler and Fritzsche [78] for the case of a-Se with singly coordinated, negatively charged selenium ($C_1{}'$) and a three-fold coordinated, positively charged site (C_3^+) emerged as the most likely equilibrium defect configurations. Thus, the valence alternation pair concept appeared. Up to day no direct experimental evidence was found for the valence alternation pair in chalcogenide glasses. Recently, Tanaka [69] has questioned the presence of the charged defects, on the basis of optical absorption measurements on highly purified $A_{S2}S_3$ samples.

The discoveries of the fullerenes led to the suggestion that other low-dimensional covalent systems, as e.g. chalcogenides could present special configurations similar to fullerenes or nanotubes. Fullerene-like objects and nanotubes with or without closed ends have been simulated in order to demonstrate that such special "objects" are possible at least in arsenic chalcogenides [70-72,74,75]. The self-organization in arsenic chalcogenides is (basically) vital for the formation of the low dimensional objects in chalcogenides.

Several types of closed nanoclusters of As_2S_3 were built (proposed). The fairly good agreement of several characteristics, calculated from the model, with the experimental ones, allows to conclude that a model with closed ends is very attractive.

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 amount of VAPs is predicted during illumination, and in the light saturated state of the glass. A closed cluster model for the binary arsenic-chalcogen glasses seems to be attractive for the explanation of the structural and electronic properties of non-crystalline chalcogenides. In the same time the direct consequence of the model is the absence of the defects of coordination.

1.5 In this article...

In this article will be introduced a short compendium of actual applications of the barrier-cluster model in explanation of optical phenomena of chalcogenide glasses. Up to now, the barrier-cluster model was used in explanation of the origin and features of the exponential tails of the optical absorption, in explanation of the electroabsorption and photoconductivity, photoluminescence and in some other optical phenomena. In this paper the consideration is then given on mathematical formulation of the photoluminescence – excitation characteristic (the *PLE* – curve) of a stimulative radiation in chalcogenide glasses based on a barrier–cluster model of a non-crystalline semiconductor.

2. Barrier-cluster model and its application to explain optical phenomena in non-crystalline semiconductors

2.1 Barrier-cluster model

The barrier-cluster model assumes that there exist potential barriers in the non-crystalline semiconductor (Fig. 1), which separate the certain microregions – clusters, and in this way, they hinder the transport of the carriers at the margin of the conduction or valence bands [27-45].

The barriers have also an influence upon the optical absorption at the optical absorption edge. The influence of the barrier is caused in the first line by their inducing a strong electron-phonon interaction. The strong electron-phonon interaction results in the fact that on optical transition, apart from the energy of a photon, an electron can also take the energy of a phonon. On such a transition, the total energy taken by an electron equals the sum of the photon and phonon energies.

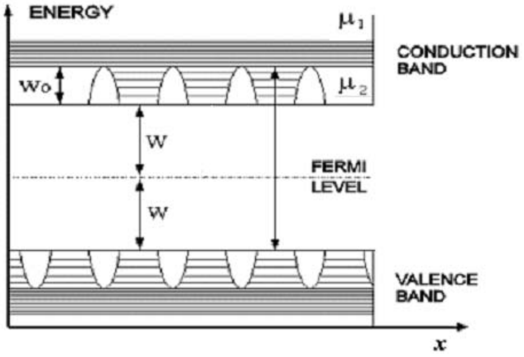

Fig. 1. The electronic spectrum of an amorphous semiconductor

Another important factor - as far as influence of the barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually accompanied with tunneling of the carriers through the potential barrier. Due to this, the absorption process is influenced by barriers. These facts enable us to explain successfully not only the creation of the exponential tails at the optical absorption edge, but also their temperature dependence at high, as well as at low, temperatures. One concept of the physical nature of photoluminescence in the chalcogenide glasses at low temperatures from point of view of a barrier-cluster model, is presented in [37-45].

2.2 Optical absorption on the base of barrier-cluster model

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 out and it creates a tail that extends deep into the forbidden band. Its profile is exponential as a rule. The exponential tails at higher temperatures tend to fit 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. One of the great puzzles to be explained is the origin of exponential tails.

Higher temperature range: The starting point of the following considerations on the base of barrier 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 [37-45]. We assume that an electron in an optical transition accepts not only the energy hf of a photon but also the phonon energy $W_{\text{phon}} = W_2$ (Fig. 2). Thus, the whole energy accepted is

$$hf + W_{\mathrm{phon}}$$

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

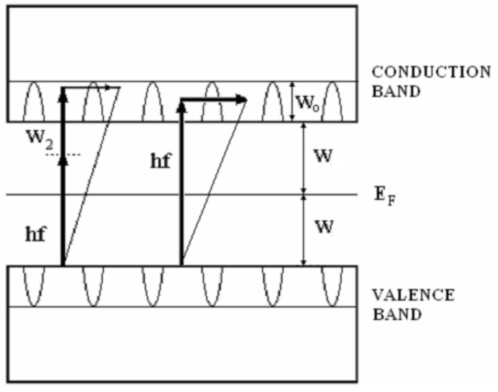

Fig. 2 Electronic spectrum of non-crystalline semiconductor and optical transition at higher (left) and at lower (right) temperature.

In principle, a photon can be absorbed only when the energy of the electron is sufficient to cause a transition of the electron 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 microregions 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. The number of electron transitions when irradiating material by "low energy" photons (and thus, also the coefficient of optical absorption α) is directly proportional to the phonon concentration corresponding to the minimal (least) energy needed for transition. For the absorption coefficient it can be written [37, 41-45].

$$\alpha \approx \exp(hf/2k\mathrm{T}) \tag{1a}$$

or, for a particular (constant) temperature

$$\mathrm{In}\ \alpha = hf + \mathrm{const} \tag{1b}$$

which is a mathematical expression of an exponential tail of optical absorption [16,17]. However, the slope of tails is also temperature dependent. Formula (1a) is of the same kind as the Urbach's formula. It explains the temperature dependence of the slope of exponential tails at higher temperature.

Low temperature range: At low temperatures practically only photons with sufficient energy, exceeding $2W$ (the width of the forbidden band), can be absorbed by material (Fig. 2).

The optical transition of electron is connected with tunneling process. The "skewed" optical transition can be virtually divided into two parts [37-45]: The first part is a vertical transition on a virtual energy level inside its own localized region (without tunneling); the following second part represents a horizontal tunneling transition on a real level in an adjacent localized region. Thus, absorption of photon in a low-temperature mechanism is connected with tunneling of electron through a potential barrier. Let us remark that at lower temperatures, absorption of light in the vicinity of optical absorption edge could principally run without tunneling process, i.e. within a single localized region. However, probability of such transitions is small due to a distinctly discrete character of the lowest levels as well as due to a small number of such levels in a single micro-region. Therefore, absorption connected with tunneling to adjacent regions is more probable.

For the probability of the tunneling it can be written [37-45]

$$p \approx \exp\ \{-A\ \Delta W\} \tag{2a}$$

where A is a constant depending on dimensions of the barrier and ΔW is the energy difference between the energy level of peaks of potential barriers and the energy level on which the tunneling is running, m – mass of electron

In papers [37-65] was studied effect of photon energy and temperature on electron tunneling across barriers. It was shown there, that

$$\Delta W = 2W + W_{\mathrm{o}} - hf - CT \tag{2b}$$

where C is constant.

The relation (2a) takes the form

$$p \approx \exp\ [-A\ (2W + W_{\mathrm{o}} - (hf + \mathrm{C}T))] \tag{3}$$

The coefficient of optical absorption of light, α, is directly proportional to probability, p [37-45], so that

$$\alpha \approx p \tag{4a}$$

Based on (2c,3a) the absorption coefficient would be

$$\alpha \approx p \approx \exp\ [-A\ (2W + W_{\mathrm{o}} - (hf + \mathrm{C}T))] \tag{4b}$$

This relation gives a true picture not only of experimentally observed exponential tails of optical absorption at low temperatures, which were already clarified in [26], but also of parallel shifting of these towards lower absorption, with decreasing temperature.

2.3 Photoconductivity

The photoelectric conductivity σ of chalcogenide glasses exhibits usually activation dependence in a relatively wide range of temperatures [16, 17]. A relation of the following type can thus express it

$$\ln \sigma \approx -W_{\mathrm{photo}}/\,\mathrm{k}T \qquad (5)$$

where W_{photo} is the relevant activating energy of photoconductivity.

At a further increase of temperature, a distinct maximum can be observed [16, 17]. The curve shape at both sides of this maximum has an exponential character.

2.3.1 Mechanism of free electrons origin – basic ideas

If we want to treat a problem of photoconductivity in chalcogenide glasses at first we have to answer the question in which way in a glass can be created free electron via optical method in a range of an exponential tail of optical absorption. Just free electrons are carriers of the photoelectric current. The photoabsorption in a range of the exponential tail is connected – as it was already said – with electron tunneling through potential barriers. Majority of electrons in this transition pass through one barrier but a certain (comparatively small) part of electrons can pass through many barriers.

The source of free electrons in a non-crystalline matter during photo-irradiation at low temperatures is a multiple tunneling of a small electron fraction at the process of the optical absorption connected with tunneling. For this mechanism, it is essential that the majority of electrons execute a tunneling through one potential barrier at the optical transition. Some electrons drive a tunnel s - times across s barriers consecutively at the optical transition. In this manner, electrons overcome a long distance from their original region (together with a corresponding hole) and become free. An electron will no longer be bounded with a hole by the Coulomb force.

According to [37-45], the probability, p, of a single tunneling of such a particle is proportional to the expression (3b)

$$p \sim \exp\,(A\,(hf + CT)) \qquad (6)$$

For the probability p^s of the multiple-tunneling of the electron through s barriers, we can write

$$P^s \sim \mathrm{p}^s \sim \exp[sA\,(hf + CT)] \qquad (7a)$$

The probability of the creation of a free electron is proportional to expression (6). Since the probability is small, the number of free electrons will slowly increase after the beginning of the illumination of the glass.

The probability of a free electron appearance at the mechanism of multiple tunneling during absorption at the temperature T and energy of activating photon hf is given as follows

$$P^s = \exp(\mathrm{As}.(hf + CT - \delta)) \qquad (7b)$$

where exp(-β) represents indeed the pre-factor in that relation.

2.3.2 Processes affecting free electron concentration

In our consideration we come out from an assumption that for photoconductivity are responsible free electrons created in a process of optical absorption by the mechanism of multiple electron tunneling through potential barriers (which are situated) occurred at lower margin of the conduction band.

As will be shown later free electrons significantly affect photoluminescence, which is not clear at first sight.

Generation free electrons can be described in accord with the relation (7) by the formula

$$G = \left\{\frac{dn}{dt}\right\}_{gen} = C_{01}\exp\left[sA\left(hf + CT - \delta\right)\right] \qquad (8)$$

where a generation factor G determines the number of free electrons created in a unit time.

That number is of course proportional to the probability P^s of multiple tunneling of an electron at optical absorption.

A reversal process to the electron generation is a recombination action which can be in general described by the relation

$$R = \left\{\frac{dn}{dt}\right\}_{RECOMB} = K.\,n(n + n_t) \qquad (9)$$

where R is the recombination factor. It represents the number of annihilated free electrons per unit time. Symbol n_T denotes concentration of hole (or free electrons) of thermal origin. Process of recombination is affected in general (at higher temperatures) also by holes created by means of thermal mechanism. It holds

$$n_t = K_0 \exp(-\frac{W}{kT}) \qquad (10)$$

where W is the width (broadness) of forbidden gap of a non-crystalline semiconductor (chalcogenide glass) and K_0 is a constant.

The change of free electron concentration with time is given by the relation.

$$\left\{\frac{dn}{dt}\right\} = \left\{\frac{dn}{dt}\right\}_{GENER} - \left\{\frac{dn}{dt}\right\}_{RECOMB} \qquad (11)$$

or

$$\left\{\frac{dn}{dt}\right\} = G - R \qquad (12)$$

In an equilibrium state it holds

$$\left\{\frac{dn}{dt}\right\} = 0 \tag{13}$$

respectively

$$\left\{\frac{dn}{dt}\right\}_{GENER} = \left\{\frac{dn}{dt}\right\}_{RECOMB} \tag{14}$$

In a steady state $G = R$, so that $n(n + n_t) = G$, from which it follows

$$n^2 + n_t n - G = 0 \tag{15}$$

In accordance with (8) we obtain

$$n^2 + n_t n - C_{01} \exp\left[sA\left(hf + CT - \delta\right)\right] = 0 \tag{16}$$

The solution of this equation in an interval of positive values of n is

$$n = -\frac{n_t}{2} + \sqrt{\left(\frac{n_t}{2}\right)^2 + G} \tag{17}$$

This relation also automatically includes character of a recombination mechanism which one changes from one type to other one with increasing temperature. The change of the recombination mechanism type in significant manner influences the shape of a photoconductivity curve and it is a dominant reason (source) for existence of maximum that curve.

2.3.3 Photoconductivity – the basic relation

At first sight appears that a way to express photoconductivity will lead by means of well known formula

$$\sigma = e\mu\ n \tag{18}$$

where μ is the mobility of free electrons and e the electron charge. In non-crystalline materials the things are more complex. In conduction band there exist (in the simplest case) two mobility sub-bands: first one of high mobility over the peak level of potential barriers and the second one of low mobility under level mentioned above. This matter of fact must be taken further into account.

2.3.4 Two mobility sub-bands of free electrons

Next we want to point out one important feature: a level of photoconductivity is not determined by concentration n given by (17) only. Very important will be too, a distribution of the total number n of electrons into two mobility sub-bands (Fig. 1). This distribution split is caused by the temperature. One fraction of concentration n_1 in a steady state will be in sub-band of high mobility μ_1 therefore, at energy levels above the peaks of potential barriers. The second fraction of concentration n_2 will be distributed in sub-band of low mobility μ_2 at energy levels below the peaks of potential barriers. The number n_1 of free photo-electrons in the sub-band of high mobility can be expressed as

$$n_1 = n(t)\exp\left(-\frac{W_O}{2kT}\right) \tag{19a}$$

Whereas, the number of free electrons in the sub-band of low mobility (with energy width W_o) will be determined by the difference $n - n_1 = n_2$, where

$$n_2 = n(t)\left[1 - \exp\left(-\frac{W_O}{2kT}\right)\right] \tag{19b}$$

Whereas, the number of free electrons in the sub-band of low mobility (with energy width W_o) will be determined by the difference $n - n_1 = n_2$, where

2.3.5 The photoconductivity in stationare regime

The total photoconductivity will be determined as

$$\sigma(t) \approx \mu_1 n_1 + \mu_2 n_2 \tag{20}$$

Apparently at the some time it holds $\mu_1 > \mu_2$. From relations (17, 19a,b, 20b) we obtain

$$\ln\sigma\left(\frac{1}{T}\right) \approx \ln\left(\left[-\frac{n_t}{2} + \sqrt{\left(\frac{n_t}{2}\right)^2 + G}\right]\left\{\mu_1 \exp\left(-\frac{W_O}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_O}{kT}\right)\right]\right\}\right) \tag{21}$$

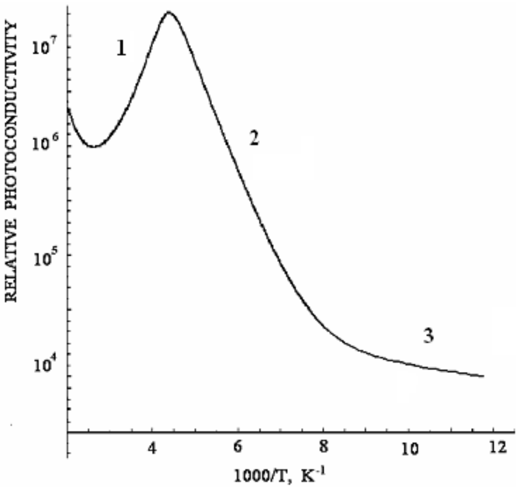

Fig. 3 Illustration: Photoconductivity dependence upon the temperature according to the theoretical formula (21)

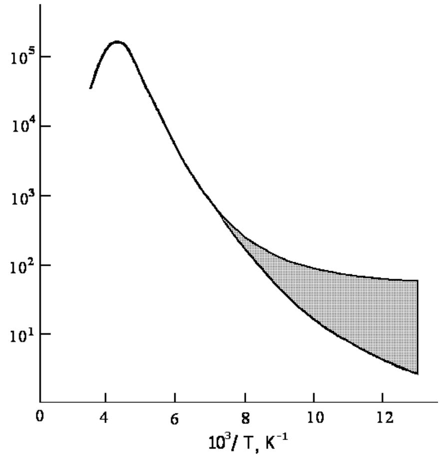

Fig 4. The experimental dependence of photoconductivity upon the temperature according to [16]. The grey area corresponds to different samples made from the same material.

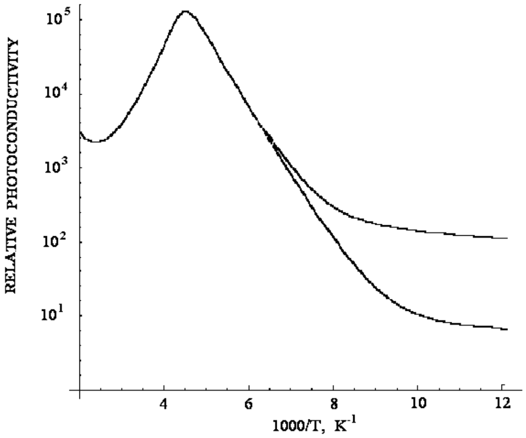

Fig 5. Photoconductivity dependence upon the temperature according to the theoretical formula (21) for different mobility values μ_2 of curriers in a sub-band of low mobility

2.3.5 Photoelectric conductivity in non-stationare regime

The total photoconductivity will be determined as

$$\sigma(t) \approx \mu_1 n_1(t) + \mu_2 n_2(t) \qquad (22)$$

2.3.6 Photoelectric conductivity after switch on an exposition

Free electron concentration changes after activation of an optical exposition

We are interested in the time dependence of the transitive conductivity $\sigma(t)$ for $t \geq 0$, if the optical exposition of a glass began at the time $t = 0$. At this time the free electron concentration is equal to $n = n_o = 0$

The solution of the differential equation

$$\frac{dn}{dt} = \exp\left[sA\left(hf + CT - \delta\right)\right] - K.n^2 \qquad (23)$$

obeying initial condition $n_o = 0$ is the function

$$n(t) = \sqrt{\frac{G}{K}}\tanh\left(\sqrt{KG}\,t\right) \qquad (24)$$

which can be written, respecting relations (8), as

$$n(t) = \sqrt{\frac{\exp\left[sA\left(hf + CT - \delta\right)\right]}{K}}\tanh\left(\sqrt{K\exp\left[sA\left(hf + CT - \delta\right)\right]}\,t\right) \qquad (25)$$

This relation for free electron concentration will be used later in determining photoconductivity dependence on the time.

The time dependence of photoconductivity

With respect to the relations (19a,b, 22,24) one can write down

$$\sigma(t) \approx \sqrt{\frac{G}{K}}\tanh\left[\sqrt{KG}\,t\right]\left\{\mu_1\exp\left(-\frac{W_O}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_O}{kT}\right)\right]\right\} \qquad (26)$$

2.3.7 Photoconductivity after break of exposition

An initial state after the break of an optical exposition of a sample will be a steady state in which the initial free electron concentration is n_o. The steady state results from the fact, that for $t < 0$ is G = const. $\neq 0$. (On the contrary, for $t \geq 0$ the relation $G = 0$ will be valid.)

The behavior of the electron concentration $n(t)$ for $t \geq 0$ under these conditions also determines the differential eq. (12), accounting that now $G = 0$. At the solution of the differential eq. obtained in this way

$$\frac{dn}{dt} = -K.n^2 \qquad (27)$$

one can not refer to the solution of the more general eq. (12), which includes also our peculiar case in which $G = 0$. One can solve eq. (27) directly by the separation of variables. The solution obeying initial condition $n(t = 0) = n_o \neq 0$ is given as

$$n(t) = \frac{1}{\frac{1}{n_0} + Kt} \qquad (28)$$

considering $\tanh(\infty) = 1$.

$$\sigma(t) \approx \frac{1}{\frac{1}{n_0} + Kt}\left\{\mu_1\exp\left(-\frac{W_O}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_O}{kT}\right)\right]\right\} \qquad (29)$$

where G is determined by (8) and n_t by (10). Just in this form (that is, in a form of a graph of the type log $\sigma(1/T)$ usually were published measured graphical dependences.

2.4 Photoluminescence

2.4.1 Photoluminescence and barrier-cluster model

A possible concept of physical nature of photoluminescence in chalcogenide glasses at low temperatures, from point of view of a barrier-cluster model, is analyzed in works [16, 17, 21, 22]. An electron in the course of optical transition, connected with tunneling, gets to an adjacent or a nearly region on an energy level, which is below the peak level of potential barriers. At lower temperatures, the excited electron after an optical transition, 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 microregion 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 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 microregion (cluster), but also in the more distant regions. The height of these levels will depend on the distance from the "motherly" microregion (for the sake of simplification, we suppose that the hole did not move). With increasing distance, these levels will approach the bottom of the conduction band.

However, discrete levels of excited states in a given region also belong to each level of the funnel, as the lowest energy level of the given localization region. 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. At that, the approaching jumps "region-by-region", are connected to an interaction with phonons. Without phonons, such an approaching 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 Stokesian 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.

2.4.2 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 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.

2.4.3 Influence of temperature

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 electron fraction at the process of the optical absorption connected with tunneling**.** For this mechanism is essential that majority of electrons execute at the optical transition a tunneling through one potential barrier. 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-radiate transitions of bounded pairs *e-h*. These pairs will not contribute to the luminescence. This is why the process of stabilization of luminescence will be relative slow. In [16, 17], the Street's formula

$$I \approx \exp\left(-T/T_0\right) \tag{30}$$

was derived to give the dependence of photoluminescence on temperature. It is based on the concept that the photoluminescence process in a non-crystalline matter is strongly influenced by free electrons.

2.4.4 Influence of the absorbed energy quanta

In [41] the first attempt is done to describe quantitatively dependence of efficiency of an excitation radiation upon the energy of stimulated photons in region of exponential tails.

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 α growth. Thus, photoluminescence *I* in this region copies the course of absorption α. We can speak of a good correlation). Strictly speaking, in this range of photon energies practically all generated *e-h* couples recombine radiantly. There is negligibly small number of free electrons in the solid and therefore the non-radiant recombinations practically do not occur. At higher energies of the exciting photons in the region of exponential tail, absorption will continue to increase exponentially but photoluminescence passes through the maximum and it will decrease with further increase of photons energy.

This experimental fact is - as we believe - due - from point of view of barrier-cluster model - to the fact that at higher photon energies tunneling of electrons through barriers runs on higher energy levels, which strongly increases the probability of *s*-fold tunneling of some electrons to larger distances. In this way the production of free electrons increases considerably with the increase of energy of exciting photons and consequently, also the amount of non-radiant recombination. The number of radiant transitions decrease, and thus also of the photoluminescence level.

At higher photon energies a tunneling of electrons trough barriers will be in progress on higher energy levels. That increases a probability of (a simple) tunneling. The probability of an s-multiple tunneling of electrons overriding long distances will rise much faster. Thereby, with energy increase of activating photons a free electron production will increase in a substance essentially and thus also a number of non-radiate *e-h* pair recombination. The radiate transition number as well as the luminescence “niveau” will no longer be proportional to the number of absorbed photons consequently to the number of generated *e-h* pairs. With increasing photon energy the luminescence increase first slows down, and then stops and finally luminescence begins to sink.

2.4.5 Time development of the photoluminescence

The level of luminescence of a non-crystalline semiconductor will depend on the concentration, *N*, of the bound pairs *e-h*. This value depends on the concentration, *n*, of free electrons in the material. The time dependence of the concentrations mentioned above can be described [16,17] by the following system of two differential equations:

$$\frac{dN}{dt} = C_{01}\exp(A(hf + CT - \delta)) - C_2N - C_3C_{01}\exp(sA(hf + CT - \delta)) - C_4Nn + C_5n^2 \tag{31a}$$

$$\frac{dn}{dt} = C_3C_{01}\exp(sA(hf + CT - \delta)) - C_5n^2 \tag{31b}$$

where d*N*/d*t* is the change of the concentration of the bound *e-h* pairs per time unit, the d*n*/d*t* is the change of the concentration of the free electrons per time unit. The first term, C_1, at the right hand side of the equation (31a) represents the number of pairs produced by incident photons per time unit. The term C_2N means the number of radiant recombination of bound *e-h* couples per time unit. The term $C_3C_{01}.\exp(sA(hf + CT + \delta))$ is, according to (7,8), the number of multi-tunneling electrons through s-barriers, and simultaneously the number of newly created free electrons. The term C_4Nn means the number a non-radiant recombination of bound pairs having passed through a non-radiant transition under the catalyst influence of free electrons. The term C_5n^2 is the number of free electrons captured by a free hole and creating a new bound *e-h* couple with it.

The number of radiate recombination and so the photoluminescence intensity *I* [41,45] will be proportional to the number *N* of coupled *e-h* pairs so that

$$I \approx N \tag{32}$$

2.5 Elektroabsorption

Under electroabsorption, influence of absorption of a non-crystalline solid by external electric field is understood [16, 17]. Kolomiec with co-workers observed electro-absorption in amorphous semiconductor As_2S_3 and in several other chalcogenide materials. As experiments show, an increase of optical absorption in non-crystalline semiconductors is observed in strong electric field. The influence of the field is relatively small and is proportional to the square of intensity of the field. At that, the change of absorption coefficient $\Delta\alpha$, influenced by the field depends also on energy of absorbed photon. In article [39,40] the phenomena of the electroabsorption in chalcogenide glasses is explained on the base of the barrier model. For relative change of the absorption coefficient under influence of an electric field *E* the relation

$$\frac{\Delta\alpha}{\alpha} = -C_1 hf + C_2\,, \quad \frac{\Delta\alpha}{\alpha} = const.E^2 \tag{33}$$

are derived. This is in agreement with experiment. In paper [40] the problem of influence of temperature on the optical absorption and electroabsorption in chalcogenide glasses in region of exponential tails is analyzed. There is derived the relation

$$\frac{\Delta\alpha}{\alpha} = -C_1(hf + CT) + C_2 \tag{34}$$

which is in agreement with experiments.

2.6 Bell-bottomed profile of a photoluminescence radiation

In article [44] physical idea was published enabling to make clear, on the base of the barrier-cluster model, possible (thinkable) mechanism of origin a bell-bottomed profile of a luminescence spectrum in chalcogenide glasses.

2.7 Amplifying photoluminescence effect of a low energy radiation

It is known from experiment that photoluminescence efficiency of a radiation with energies from a region exponential tail of optical absorption can increase (amplify) supplementary (additive) radiation, which by itself doesn't activate (evoke) photoluminescence. Feasible explanation of that effect on basis of the barrier cluster model realizes the work [44]. Subsistence of possible mechanism is energy attendance of phonons originated from „optical mechanism". Phonons originate in non-radiate energy transitions excited e-h pairs onto lower levels. Energy can gain an electron from phonons at simultaneous absorption of a low energy photon of the supplementary radiation

Electron at absorption of a low energy photon admits simultaneously besides that insufficient light energy also energy of a phonon, which is sufficient for transition onto higher enough energy levels. Without energy participation of a phonon an optical energy quantum alone of the supplementary radiation to such transition would be insufficient. An increase of the transition number "upwards" expresses oneself as an increase of photoluminescence. If there wasn't a phonon production by originate radiation then absorption of the supplementary radiation would be impossible. Low energy radiation alone would not be able to evoke photoluminescence. More detail information concerning that process a reader can find in the work [44].

2.8 The second exponential tail of the optical absorption

Possible explanation of essence of the second exponential tail origin of the optical absorption (in a region very low absorption) is introduced in the work [44]. The explanation of that phenomenon presumes too a role of phonons produced in an optical process.

3. General mathematical formulation of a PLE-characteristics of a chalcogenide glass

3.1 PLE-charakteristic

In Fig. 6 are depicted three dependences known from experiment representing optical properties some particular chalcogenide glass. The curve 1 represents a bell-bottomed profile of a photoluminescence spectrum a particular glass. The curve 2 (PLE characteristics) represents typical dependency of the photoluminescence efficiency primary excited radiation on photon energy in a region exponential tail of an optical absorption. A true (proper, intrinsic) tail of the optical absorption of a glass represents graph 3. The graphs shown in the Fig. 3 are representative for many chalcogenide glasses. They represent standard (peculiar) optical properties of broad class non-crystalline substances. In this paper we try to express by means of mathematics dependency represented by the curve 2.It is searching for mathematical formula which properly expresses dependence of an integral photoluminescence level upon photon energy of primary excited radiation in an energy region belonging to the tail of optical absorption. The curve 2 is usually called as PLE characteristics (which comes from Photo Luminescence Excitation).

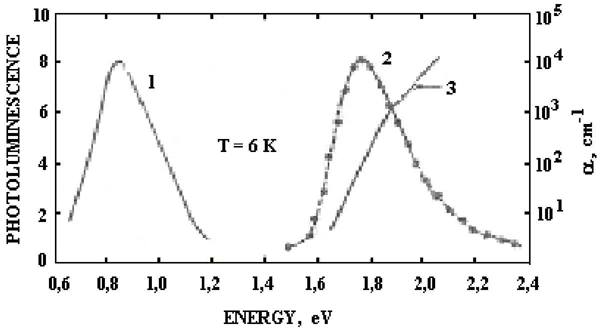

Fig. 6. Some optical properties of the As_2Se_3. 1- photoluminescence-belt spectrum, 2 – PLE-characteristics, 3- exponential tail of optical absorption α

The *PLE*-curve represents the luminescence efficiency of a primary activated radiation which energies belong to a region of an exponential tail of an optical absorption.

This paper is devoted to study of a photoluminescence efficiency of a primary excited radiation which energies fall into a region of an optical absorption exponential tail. The efficiency is expressed by a curve $I(hf)$ representing a dependence of an excited integral photoluminescence intensity I on (upon) the exciting photon energy hf of the primary radiation.

3.2 The time changes of two concentrations

As a starting point for derivation of the curve mentioned above, and denoted as PLE characteristics (Photo Luminescence Efficiency), is system of two coupled differential eqs. which ones express the time changes of two concentrations:

1) $n(t)$ - the concentration of photoconductive electrons, and

2) $N(t)$ - the concentration of coupled *e*-*h* pairs (excitons).

The two differential eqs. like these ones were introduced in the former paper (formulae (31a,b)) in actual paper). In that paper the eqs. were valid only for the case that in a substance the free electron concentration n_t of a thermal origin is negigible small in comparission with that one n of an optical origin. Further on, these special relations (31a,b) will be modified by taking into account also the influence of free thermal electrons. Those electrons affect the photoluminescence in two ways: they affect the photocarrier concentration (it is connected with additional possibility of their mutual recombination) and they also stimulate additional non-radiate recombonation of coupled *e-h* pairs.

3.3 Generalized differential equations

The generalized differential eqs. will be of the form

$$\frac{dN}{dt} = C_{01}\exp(A(hf + CT - \delta)) - C_2N - C_3C_{01}\exp(sA(hf + CT - \delta)) - C_4N(n+n_t) + C_5n(n+n_t) \quad (35)$$

$$\frac{dn}{dt} = C_3C_{01}\exp(sA(hf + CT - \delta)) - C_5n(n+n_t) \quad (36)$$

The term $C_4N(n+n_t)$ appearing at the right side in the first eq. reads that non - radiate recombination of coupled *e-h* pairs stimulate besides photoelectrons (of the concentration n) thermal free electrons too (of the concentration n_t). The term $C_5n(n+n_t)$ accounts a recombination mechanism of photoconductive electrons when thermal free electrons (and holes) in a substance are present.

In presented paper we restrict ourselves by stationary problems only, when it holds

$$dn/dt = dN/dt = 0$$

The outlet (basis) of our next treatment (consideration) therefore (consequently) will be the system of two following eqs.

$$0 = C_{01}\exp(A(hf + CT - \delta)) - C_2N - C_3C_{01}\exp(sA(hf + CT - \delta)) - C_4N(n+n_t) + C_5n(n+n_t) \quad (37)$$

$$0 = C_3C_{01}\exp(sA(hf + CT - \delta)) - C_5n(n+n_t) \quad (38)$$

which can be rewritten as

$$0 = C_{01}\exp(A(hf + CT - \delta)) - C_2N - C_4N(n+n_t) \quad (39)$$

$$0 = C_3C_{01}\exp(sA(hf + CT - \delta)) - C_5n(n+n_t) \quad (40)$$

If one solves the first eq. for the concentration N, one obtains

$$N \sim \frac{C_{01}\exp(A(hf + CT - \delta)}{C_2 + C_4(n + n_t)} \quad (41)$$

Because the intensity I of photoluminescence is proportional to the concentration N of coupled pairs ($I \approx N$) the relation

$$I \sim \frac{C_{01}\exp(A(hf + CT - \delta)}{C_2 + C_4(n + n_t)} \quad (42)$$

will be valid. This relation represents properties of the PLE characteristics in a concentrated form. The additional relations (43-45)

$$n = -\frac{n_t}{2} + \sqrt{\left(\frac{n_t}{2}\right)^2 + G} \quad (43)$$

$$n_t = K_0 \exp(-\frac{W}{kT}) \quad (44)$$

$$G = C_{01}\exp\left[sA\left(hf + CT - \delta\right)\right] \quad (45)$$

also hold.

The equation (42) along with the triplet equations (43-45) express photoluminescence efficiency $I(hf)$ of the excited radiation in dependency on photon energy. The temperature emerges as a parameter that characteristics $I(hf)$.

The relation (43) shows, that the concentration n photoconductive electrons is influenced by the concentration n_t of thermal electrons too.

In upper mentioned relations as the dependent variables emerges I – the integral intensity of excited photoluminescence radiation and as the independent variable hf – the photon energy of the primary excited radiation. The role of the parameter plays the temperature T. G – is the generation factor of the free photo-electrons (accruing from s-multiple tunneling through potential barriers). The quantity W is the activation energy of a glass and k – the Boltzmann constant. Moreover, in the relations introduced above emerge constants A, C, C_{01}, C_2, C_4, δ, s, K_0.

3.4. Special cases of the PLE-characteristics

We shall discuss below following three special cases.

1) If the concentration of free electrons of the thermal origin is negligible small i. e. condition $n >> n_t$ is fulfilled then it follows from (15)

$$n = \sqrt{G =} \sqrt{C_{01}}\exp\left[0.5\, sA\left(hf + CT - \delta\right)\right] \quad (46)$$

The relation (42) takes the form

$$I \sim \frac{C_{01}\exp(A(hf + CT - \delta)}{C_2 + C_4\sqrt{C_{01}}\left[\exp(0.5sA(hf + CT - \delta\right]} \quad (47)$$

That relation represents the PLE – characteristics if the concentration of free electrons of the thermal origin is negligible small. The relation is identical with (47).

2) If besides the condition $n >> n_t$, in denominator of (47) the first term C_2 doninates (the second one can be neglected) then one can write

$$I \sim \frac{C_{01}\exp(A(hf + CT - \delta)}{C_2} = \frac{1}{C_2}\alpha(hf) \quad (48)$$

In that case, as seen - photoluminescence simulates (imitates) behaviour of absorption $\alpha(hf)$ and so behaviour of an exponential tail. It is known from experiment, just so in lower part of an exponential tail.

On the contrary, if the term C_2 in (47) is negligible small in comparison with the second one, the PLE characteristics acquires the form

$$I \sim \frac{C_{01}\exp(A(hf+CT-\delta)}{C_4\sqrt{C_{01}}\left[\exp\left(0.5sA\left(hf+CT-\delta\right)\right)\right]} \tag{49}$$

or

$$I \sim \frac{\sqrt{C_{01}}}{C_4}\exp\left[-\left(0.5s-1\right)A(hf+CT-\delta)\right] \tag{50}$$

$$I \sim \exp(-\frac{T}{T_0}) \tag{51}$$

$$I \sim \exp(-\frac{hf}{H_0}) \tag{52}$$

or also

$$I \sim \exp(-\frac{T}{T_0})\exp(-\frac{hf}{H_0}) \tag{53}$$

The relation (51) coincides whith known Street`s empirical law [16,17]. That one has been derived on the base of barrier- cluster model in work [41?]. The relation (53) can be called generalized Street`s law. That generalized Street`s law has been derived in work [41].

The generalized PLE characteristic (42-45) yields the same results under the special conditions as these ones which have been obtained (acquired) before [85]. The PLE curve (42-45) represents behaviour of that experimental curve in wider interval of photon energies from the region optical absorption of an exponential tail.

3) When in a substance during a stationary optical exposition dominates concentration of free thermal electrons i.e. when $n \ll n_t$ and at the same time the term C_2 in (42) is negligible small in compare with the next term in denominator, the relation (42) takes the form

$$I \sim \frac{C_{01}\exp(A(hf+CT-\delta)}{C_4 n_t} \tag{54}$$

Respecting (10) it can be written as

$$I \sim \frac{C_{01}}{C_4}\exp\left(\frac{W}{kT}\right)\exp(A(hf+CT-\delta) \tag{55}$$

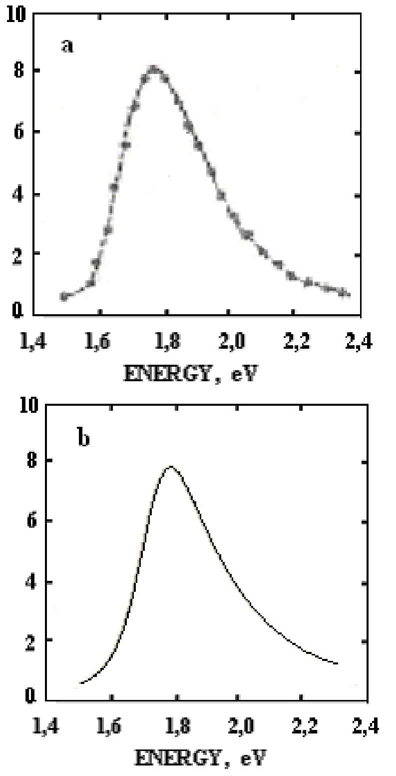

Fig. 7. Illustration - depencence of the relative photoluminescence effectivity on the photon energy, a) experiment – As_2Se_3, b) theory.

At suitable conditions it can be approximately valid

$$I \approx \exp(\frac{W}{kT}) \tag{56}$$

In the given case with increasing value of $1/T$ intensity of photoluminescence exponentially increases.

4. Discusion - confrontation with experiments

We introduce now for the illustration two graphs (Fig. 7)). The first (Fig. 7a) of them demontrates the experimentaly determined (typical) dependence of the photoluminescence effectivity of primary exciting radiation in chalcogenide glass As_2Se_3 on the photon energy [16,17]. The second graph (Fig. 7b) represents the curve determined on the base barrier-cluster model (relation (42)). From (Fig. 7) it is evident on first sight, that the character of both dependences is analogical. Barrier-cluster model can explain, way the photoluminescence in upper part of exponential tail of the optical absorption (in this case over 1,8 eV) decreases with increasing of the photon energy (althoug the absorption increases in this region). The introduced comparision represents one serious argument for the support of the barrier-cluster model. Another very important argument for support of the barrier-cluster model published in the last time is the explanation of the mechanismus of the photoconductivity [83]. A computer analysis shows that the relation (42) represents well behavior of experimental *PLE*-characteristics of chalcogenide glasses.

The relations (18, 42) enables to explain the experimental fact, that between photoconductivity and photoluminescence intensitty *I* exists the inverse relation. These processes are connected so, that when the photoconductivity increase, than the photoluminescence intensity I decrease.

From relation (18) it follows that photoconductivity σ is directly proportional to the concentration n of the free electrons. From relation (42) we see, that at low temperatures (when $n_t << n$), if C_2 in denominátor is negligable, the luminescence intensity I is indirectly proportional to the concentration n.($I \approx 1/n$). The result is $I \approx 1/\sigma$. It is in agreement with experiments.

Note: A further literature about the optical phenomena in chalcogenide glasess can be found in [87 - 110].

5. Conclusion

Non-crystalline solids (substances) represent a very broad and varied family of substances. In general, it is going on substances of a non-stechiometric structure occurring very often in a metastabil state, which markedly depends on the development (preparation) process.

In physics of non-crystalline materials still exists much open fundamental problems. Barrier-cluster model allows to explain not only of a number of important optical and electrical features of chalcogenide glasses, but also the results of X-ray structure measurements and ESR experiments. This concept gives a new look at the density of states within the forbidden band and at the exponential tails of the optical absorption. Article gives also arguments in favor of a supplementary hypothesis according to which free electrons in a non-crystalline solid are capable of the stimulating non-radiant recombinations of bound electron-hole pairs. Based on such concept, absorption, photoluminescence and photoconductivity processes as well as their mutual interdependence can be understood.

Title of this paper recalls our belief that the barrier cluster model may become a starting point (basis) for understanding some important processes in non-crystalline materials. We believe that the barrier cluster model to a certain extent can inspire (influence) an approach of physicists to this kind of substances. Together, we are aware an immense (measureless) expansiveness (largeness) of problems in this field as well as (namely) that many questions this model is unable (incapable) to answer. Especially, it is going on important effects connected with structural changes under the influence of radiation which are relevant from viewpoint of technical applications. Such effects are interesting e.g. from viewpoint of memory reading and so on. Effect of radiation is connected with cluster rebuilding (reconstruction) as structural elements of these substances. Cluster conversion implies (causes) too a change of barrier structure. This effect a static barrier-cluster model is unable to reconsider.

It is clear, if one wants to understand more complex phenomena, then one should first make oneself clear fundamentals of simpler phenomena. To this end, we think, the barrier cluster model obliges. It seems to us that in this paper introduced matter respecting the barrier cluster model offers a reader sufficiency of arguments to become more disposed for new ideas eventually one attempts to bring further arguments in favour of the barrier-cluster model.

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