

Photoconductivity in chalcogenide glasses on the base of the barrier-cluster model

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In this article we present the new of view on the photoconductivity in chalcogenide glasses. On the base of the barrier-cluster model we attempt to explain the temperature dependence of the photoconductivity and the influence of the radiation intensity on these dependence.

(Received July 5, 2009; accepted November 12, 2009)

Keywords: Photoconductivity, Optical phenomena, Cluster, Barrier-cluster model, Chalcogenide glass, Optical absorption, Amorphous, Semiconductor, Non-crystalline semiconductor

1. Introduction

Optical properties of non-crystalline semiconductors are subject of high interest of investigators for large-scale applicability of these materials as well as for the sake to obtain important information concerning processes in such materials.

From beginning of investigation optical phenomena in chalcogenide glasses (Kolomijets) many works were published in this field mostly presented experimental results. Non-crystalline semiconductors are now applied as optical light-guide, as elements of optoelectronics (optical switches and so on), xero-materials, memory elements and others [1-15]. Situation still seems unsatisfactory if one wants to understand physical processes overshooting in these materials. 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].

In works [26-33] has been presented so-called barrier-cluster model of a non-crystalline semiconductor. On the base of the barrier-cluster model some phenomena were explained largely optical ones in non-crystalline semiconductor. Especially, here belongs the explanation of exponential tails of an optical absorption and explanation of thermal influence on it in the region of lower temperatures as well as in one of higher temperatures. On the base of the barrier-cluster model has been described quantitatively also the mechanism of electroabsorption as well as photoluminescence.

In this article basic ideas of the barrier-cluster model will be introduced as well as a total approach to explanation optical phenomena based on it. Thereafter, processes connected with photoconductivity will be described in more detail.

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

$$\ln \sigma \approx -W_{\text{photo}}/kT \quad (1)$$

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.

1.1 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 known 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.

1.1 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 indirect 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 $\ln\alpha(h\nu)$ 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 explain 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-As₂Se₃ has the form:

$$I \sim \exp(-T/T_0) \quad (2)$$

over four orders of magnitude of the intensity, where T_0 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 its 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-As₂S₃ 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-As₂Se(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].

1.2 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-As₂S₃). 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 D⁰ 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 (C₁⁻) and a three-fold coordinated, positively charged site (C₃⁺) 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 As_2S_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.

2. Barrier-cluster model and optical phenomena in chalcogenide glasses

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 [37-45]. The barrier-shave 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.

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.

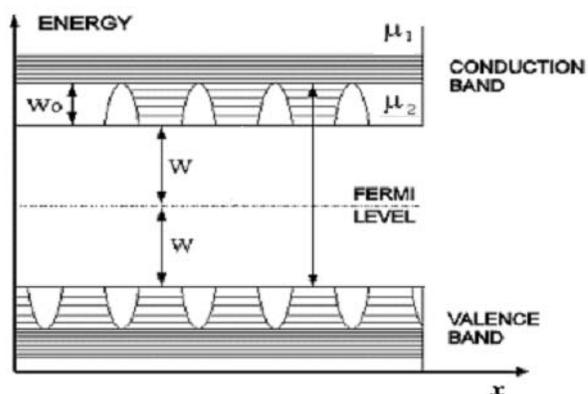


Fig. 1 The electronic spectrum of an amorphous semiconductor.

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

$$hf + W_{\text{phon}} \quad (3)$$

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.

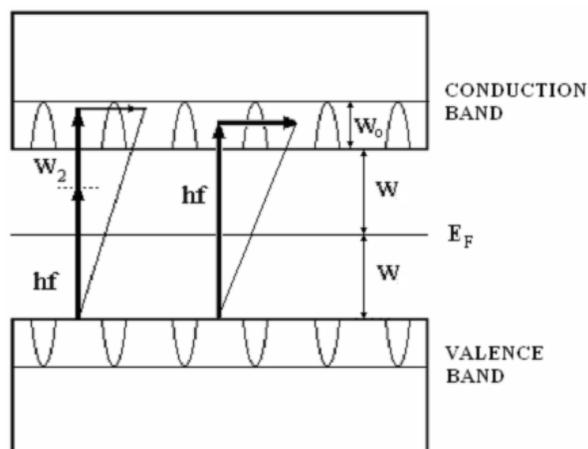


Fig. 2. Electronic spectrum of non-crystalline semiconductor and optical transition at higher (left) and at lower (right) temperature.

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 [37-45].

$$\alpha \approx \exp(hf/2kT) \quad (4)$$

or, for a particular (constant) temperature

$$\ln \alpha = hf + \text{const} \quad (5)$$

which is a mathematical expression of an exponential tail of optical absorption [16,17]. However, the slope of tails is also temperature dependent. Formula (4) 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.

2.3 The influence of temperature on the process of tunneling of electron through the potential barrier in optical absorption

The absorption of light at low temperatures and photon energy, hf , from interval $2W < hf < 2W + W_0$ is, according to the barrier-cluster model connected with tunneling of electron through the potential barrier (Fig. 2, 3). Probability, p , of tunneling depends on the energy level, on which tunneling runs. In the case of a parabolic potential barrier (Fig. 2), the dependence of potential energy $W(x)$ of electron on its position can be denoted as

$$W(x) = -ax^2 + W_0$$

where the constant, W_0 , means the height of the barrier from the bottom of the conduction band and the quantity a determines "narrowness" of the barrier. For the probability of the tunneling it can be written [26]

$$p \approx \exp\{-A \Delta W\} \quad (6)$$

where A is a constant depending on dimensions of the barrier

$$A = \left\{ \frac{\pi}{\hbar} \sqrt{\frac{2m}{a}} \right\}$$

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.

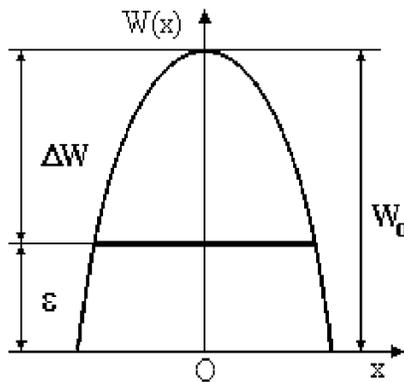


Fig. 3 The potential barrier

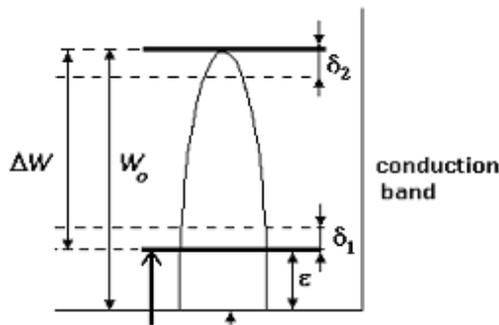


Fig. 4 The influence of temperature on the process of tunneling of electron through the potential barrier.

Should an electron take only the photon energy in absorption, we could write on the base of Fig. 2-4

$$\Delta W = 2W + W_0 - hf \quad (7)$$

The probability of tunneling is determined before all by energy of the absorbed photon, however, not only by it. It may seem at the first sight that phonons play no role in the low-temperature absorption. However, it is not the case

2.4 The influence of temperature on the optical absorption

In papers [37-39] was studied effect of temperature on electron tunneling across barriers. It was shown there, that for the quantity ΔW the relation (7) has to be replaced by the relation

$$\Delta W = 2W + W_0 - hf - CT \quad (8)$$

so that the relation (6) takes the form

$$p \approx \exp[-A(2W + W_0 - (hf + CT))] \quad (9)$$

It is assumed, that $\Delta W(T) = \Delta W(0) - \delta_1 - \delta_2$ (Fig. 4) and that the values δ_1, δ_2 are linearly dependent on temperature.

The coefficient of optical absorption of light, α , is directly proportional to probability, p [16,17], so that

$$\alpha \approx p \quad (10)$$

Based on (3,6,7), the absorption coefficient would be

$$\alpha \approx p \approx \exp[-A(2W + W_0 - (hf + CT))] \quad (11)$$

or

$$\alpha \approx \exp[A(hf + CT)] \quad (12)$$

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.

As far as the dependence $\alpha(hf)$ is concerned, it also follows from (12) that

$$\alpha \approx \exp(Ahf) \quad (13)$$

following circumstance.

2.5 Photoluminescence

In works [37-45], processes of photoluminescence in chalcogenide glasses were investigated from the viewpoint of the barrier-cluster model. There was showed that in the frame of this model much regularity (relations) can be explained under the assumption that free electrons stimulate non-radiate transitions of bounded $e-h$ pairs. It is also assumed that at low temperatures free electrons are produced in process of optical absorption by manifold tunneling through potential barriers. At higher temperatures the stimulation role of non-radiate recombination of bounded $e-h$ pairs can be supplied by free thermal electrons. With increasing electron concentration the number of non-radiate transitions increases considerably and consequently photoluminescence is dimmed highly.

NOTICE: At free thermal electron concentration increase the change of recombination mechanism for photo-conduction electrons occurs which can lead to lowering photoconductivity. The photoconductivity curve will have a local maximum at given temperature. Additional increase of temperature will cause a decrease of photoconductivity.

3. Photoconductivity

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

$$p \approx \exp[-A(2W + W_0 - (hf + CT))] \quad (14)$$

$$p \sim \exp(A(hf + CT))$$

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

$$P^s \sim p^s \sim \exp[sA(hf + CT)] \quad (15)$$

The probability of the creation of a free electron is proportional to expression (15). 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

$$P^s = \exp(As(hf + CT - \beta_0)) \quad (16)$$

where $\exp(-\beta)$ represents indeed the pre-factor in that relation.

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. Generation those free electrons can be described in accord with the relation (16) by the formula

$$G = \left\{ \frac{dn}{dt} \right\}_{gen} = \exp[sA(hf + CT - \beta_1)] \quad (17)$$

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

$$R = \left\{ \frac{dn}{dt} \right\}_{RECOMB} = K \cdot n(n + n_t) \quad (18)$$

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

$$n_t = F \exp\left(-\frac{W}{kT}\right) \quad (19)$$

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

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

$$\left\{ \frac{dn}{dt} \right\} = \left\{ \frac{dn}{dt} \right\}_{GENER} - \left\{ \frac{dn}{dt} \right\}_{RECOMB} \quad (20)$$

or

$$\left\{ \frac{dn}{dt} \right\} = G - R \quad (21)$$

In an equilibrium state it holds

$$\left\{ \frac{dn}{dt} \right\} = 0 \quad (22)$$

respectively

$$\left\{ \frac{dn}{dt} \right\}_{GENER} = \left\{ \frac{dn}{dt} \right\}_{RECOMB} \quad (23)$$

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

$$n^2 + n_t n - G = 0 \quad (24a)$$

In accordance with (17) we obtain

$$n^2 + n_t n - \exp[sA(hf + CT - \beta_2)] = 0 \quad (24b)$$

The change of the constant β_1 for the β_2 in (25) in comparison with (17) is connected with existence of the constant K in (18).

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

$$n = -\frac{n_t}{2} + \sqrt{\left(\frac{n_t}{2}\right)^2 + G} \quad (25)$$

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.

In the case if $n_t \gg n$ it follows from the relations (17-19, 26) the approximate relation

$$n = \exp\left(\frac{W}{kT}\right) \exp[sA(hf + CT - \beta)] \quad (26a)$$

resp. if $n_t \ll n$

$$n = \exp[0.5 sA(hf + CT - \beta)] \quad (26b)$$

3.3 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 (25) only. Very important will be too, a distribution of the total number n of electrons into two mobility sub-bands. 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

$$n_1 = n \exp\left(-\frac{W_o}{2kT}\right) \quad (27)$$

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

$$n_2 = n \left[1 - \exp\left(-\frac{W_o}{2kT}\right)\right] \quad (28)$$

3.4 Photoelectric conductivity

The total photoconductivity will be determined as

$$\sigma \approx \mu_1 n_1 + \mu_2 n_2 \quad (29)$$

Apparently at the some time it holds $\mu_1 \gg \mu_2$.

If one substitutes the concentrations accordingly to (27, 28) into the relation (29), then one obtains

$$\sigma \approx n \left\{ \mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2 \left[1 - \exp\left(-\frac{W_o}{kT}\right)\right] \right\} \quad (30)$$

In addition, if one expresses the concentration n in accord with (25) then (30) takes the form

$$\sigma \approx \left[-\frac{n_t}{2} + \sqrt{\left(\frac{n_t}{2}\right)^2 + G} \right] \left\{ \mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2 \left[1 - \exp\left(-\frac{W_o}{kT}\right)\right] \right\} \quad (31)$$

The result we have obtained can be expressed as follows

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

where G is determined by (17) and n_t by (19). 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.

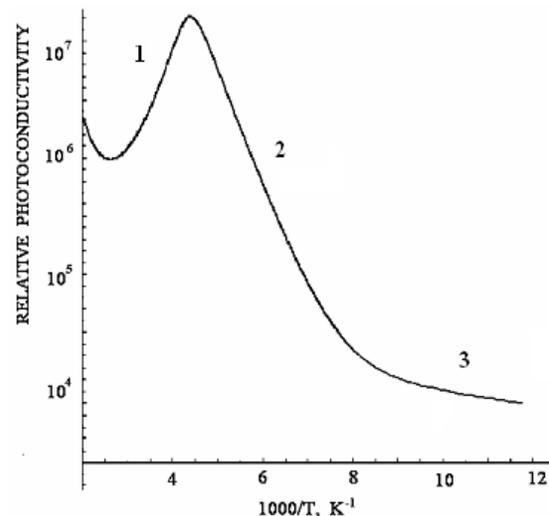


Fig 5 The photoconductivity dependency on the temperature according to the theoretical formula (32).

3.5 Computer is needed (The need for computer analysis)

Resulting relation (31, 32) determining photoconductivity is rather complex. On the first sight one can not think about the behavior of the corresponding curve. For all that, there is the need to examine this relation by using numerical methods and computer. One result we see in Fig. 5. Such investigation showed that this relation gives results in good agreement with experimental

ones. More detail arguments we shall introduce in part entitled: Discussion and confrontation.

4. Special cases

4.1 High temperatures, low intensity of optical field excitation respectively (or optical driven field)

(An interval of exponential increase of the function $\sigma(1/T)$)

In this case the condition $n_t \gg n$ is fulfilled. For R - according to (18) - approximately holds

$$R = \left\{ \frac{dn}{dt} \right\}_{RECOMB} = K \cdot n \cdot n_t \quad (33)$$

The relation (25) then takes the form

$$n_t n - \exp [sA (hf + CT - \beta_2)] = 0. \quad (34)$$

from which -with respect to (19) - it follows

$$n = \exp\left(\frac{W}{kT}\right) \exp [sA (hf + CT - \beta)] \quad (35)$$

According to (30) one can write for photoconductivity

$$\sigma \approx \exp\left(\frac{W}{kT}\right) \exp [sA (hf + CT - \beta)] \left\{ \mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2 \left[1 - \exp\left(-\frac{W_o}{kT}\right) \right] \right\} \quad (36)$$

In an interval of higher temperatures the term

$$\mu_2 \left[1 - \exp\left(-\frac{W_o}{kT}\right) \right]$$

is negligible small in comparison with the other term in last bracket. Consequently

$$\sigma \approx \exp\left(\frac{W - W_o}{kT}\right) \exp [sA (hf + CT - \beta)] \quad (37a)$$

or

$$\ln \sigma\left(\frac{1}{T}\right) \approx \frac{W - W_o}{kT} + sA (hf + CT - \beta) \quad (37b)$$

That function possesses (or at least may have) for relevant parameters local minimum. At either side of this unexpected minimum the function usually increases strongly. On the side where argument $1/T$ increases the first term dominates on the right side of the relation (37b).

The function (37b) linearly increases there (so that photoconductivity σ is the exponential function of the argument $1/T$). It holds approximately

$$\ln \sigma \approx \frac{W - W_o}{k} \left(\frac{1}{T} \right) \quad (38)$$

This function represents a straight line. Otherwise, plot of the function (38) (of independent variable $1/T$) is the straight line and the slope of this straight line is positive and equals to $+(W - W_o)/k$. At the experimental curve in Fig. 5 that straight line is depicted as the section 1.

At opposite side of the minimum of the function (37b) the term $sA (hf + CT - \beta)$ dominates. There the relation is valid approximately

$$\ln \sigma\left(\frac{1}{T}\right) \approx sA (hf + CT - \beta) = sA \left(hf + \frac{C}{\frac{1}{T}} - \beta \right) \quad (39)$$

A decrease of the value $1/T$ (increasing temperature) increases values of that function steeply (hyperbolic).

REMARK: Two extreme, but only one is observable?

In general the curve (36) has two extreme, one maximum and one minimum. The maximum appertains to maximum of photoconductivity which is well observable in experiment. The other extreme - minimum - wasn't observed (as far as we known) in experiment. It is possible that this interval of sufficiently high temperatures is outside of validity our model. This can be connected among others with the highness of potential barriers (W_o) which in a case of chalcogenide glasses reaches about a few of $10^{-1} eV$. It is possible that this yet hidden section of the curve will emerge at lower incident photon energies. Such observation should support the barrier cluster model.

The relation (36) can be written down as

$$\sigma \approx \exp\left(\frac{W}{kT}\right) G \left\{ \mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2 \left[1 - \exp\left(-\frac{W_o}{kT}\right) \right] \right\} \quad (40)$$

accordingly, in this region it holds $\sigma \approx G$. The photoconductivity increases in this case proportional to the intensity of illumination (irradiation). In different parts of the photoconductivity curve it will be otherwise.

4.2 Intermediate temperatures (high intensity of optical exciting)

(The region of exponential decrease of the function $\sigma(1/T)$).

In the special case, when $n_t \ll n$, regarding (18) it is possible for coefficient R write

$$R = \left\{ \frac{dn}{dt} \right\}_{RECOMB} = K \cdot n(n + n_t) = K n^2 \quad (41)$$

Instead of (24) one obtains

$$n^2 - G = 0 \quad (42)$$

Problem solution gives

$$n = \exp [0.5 sA (hf + CT - \beta)] \quad (43)$$

The photoconductivity in this case will be expressed (taking into account (24)) as follows.

$$\sigma \approx \left[\exp [0.5 sA (hf + CT - \beta)] \left\{ \mu_1 \exp \left(-\frac{W_0}{kT} \right) + \mu_2 \left[1 - \exp \left(-\frac{W_0}{kT} \right) \right] \right\} \right] \quad (44)$$

The relation (44) with respect to (17) takes the form

$$\sigma \approx \sqrt{G} \cdot \left\{ \mu_1 \exp \left(-\frac{W_0}{kT} \right) + \mu_2 \left[1 - \exp \left(-\frac{W_0}{kT} \right) \right] \right\} \quad (45)$$

In this region thus it holds

$$\sigma \approx \sqrt{G} \quad (46)$$

The photoconductivity increases with increasing illumination proportional to the second root of intensity illumination. This is in agreement with experiment [16, 17].

The relation (45) in a region of intermediate temperatures when inequality

$$\mu_2 \left[1 - \exp \left(-\frac{W_0}{kT} \right) \right] \ll \mu_1 \exp \left(-\frac{W_0}{kT} \right) \quad (47)$$

is valid can be written as

$$\ln \sigma \left(\frac{1}{T} \right) = -\frac{W_0}{k} \frac{1}{T} + \text{const.} \quad (48)$$

This dependency $\ln \sigma(1/T)$ represents the straight line with negative slope $(-W_0/2k)$. At the experimental curve in Fig. 5, that straight line is depicted as the section 2.

Just, this section represents most typical behavior of the photoconductivity in chalcogenide glasses. That character of dependency manifests (expresses) oneself in a broad extent (a few orders) of photoconductivity. The slope of (48) enables us to determine (at least evaluate) energy width W_0 of a low mobility sub-band and so the height of potential barriers.

4.3 Low temperatures and very low levels of photoconductivity

(A region of stabilizing $\sigma(1/T)$ -function at a low level)

At very low temperatures in the relation (17), consequently in the formula

$$\sigma \approx \left[\exp [0.5 sA (hf + CT - \beta)] \left\{ \mu_1 \exp \left(-\frac{W_0}{kT} \right) + \mu_2 \left[1 - \exp \left(-\frac{W_0}{kT} \right) \right] \right\} \right] \quad (49)$$

the term (in the curl bracket) will have the value μ_2 .

Then that relation can be approximate as

$$\sigma \approx \mu_2 \left[\exp [0.5 sA (hf + CT - \beta)] \right] \quad (50)$$

The steep exponential regress of photoconductivity at lowering temperature almost stops in this region (Fig. 5, section 3). The function

$$\ln \sigma \left(\frac{1}{T} \right) \approx \ln \mu_2 + 0.5 sA (hf + CT - \beta) \quad (51)$$

at $T \rightarrow 0$ approaches the value

$$\ln \sigma \left(\frac{1}{T} \right) \approx \ln \mu_2 + 0.5 sA (hf - \beta) \quad (52)$$

That predicts our model. But in our consideration a simplifying assumption was used: the mobility of a low mobility sub-band was allowed to be a constant independent on the temperature. That's not the case. In reality, decreasing the temperature in a certain range mobility μ_2 decreases slowly.

This is connected with lowering of mean level at which transport of electrons through barriers is in progress. For all that a soft lowering of photoconductivity at a temperature decrease apparently overshoots too in this region due to the decrease of μ_2 at a cooling.

The relation (49) can be written as

$$\sigma \approx \sqrt{G} \left\{ \mu_1 \exp \left(-\frac{W_0}{kT} \right) + \mu_2 \left[1 - \exp \left(-\frac{W_0}{kT} \right) \right] \right\} \quad (53)$$

so that it holds

$$\sigma \approx \sqrt{G} \quad (54)$$

The better approximation in the region of low temperatures

The better approximation in the region of the very low temperatures we obtain if the band of low mobility split in a more sub-region with different mobilities.

The situation in the simplest case of two sub-regions shows the Fig. 6b. In these case the electrons can have three values of mobilitie μ_1, μ_2, μ_3 .

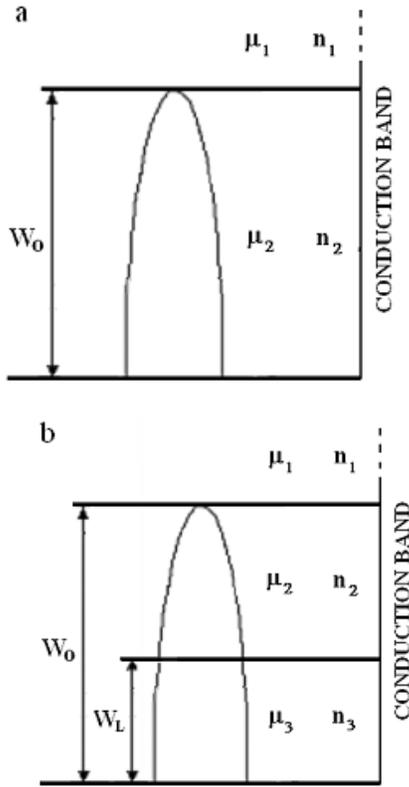


Fig. 6 The simplified look on mobility of electrons in conductin band. High mobility band is situated above level of the peaks of the barrier. Below is the low mobility band. a) - one band of the low mobility μ_2 , b) - two bands of the low mobilities μ_2, μ_3 .

In accordance with Fig. 6 it is possible for concentration of electron in separate sub-regions of conduction band to write

$$\begin{aligned} n_1 &= n \exp\left(-\frac{W_0}{kT}\right), \\ n_2 &= n \left[\exp\left(-\frac{W_L}{kT}\right) - \exp\left(-\frac{W_0}{kT}\right) \right], \\ n_3 &= n \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \end{aligned} \quad (55)$$

For photoconductivity then is valid

$$\sigma \approx n \left\{ \begin{aligned} &\mu_1 \exp\left(-\frac{W_0}{kT}\right) + \mu_2 \left[\exp\left(-\frac{W_L}{kT}\right) - \exp\left(-\frac{W_0}{kT}\right) \right] + \\ &+ \mu_3 \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \end{aligned} \right\} \quad (56)$$

$$\ln \sigma \left(\frac{1}{T} \right) \approx \ln (n \left\{ \begin{aligned} &\mu_1 \exp\left(-\frac{W_0}{kT}\right) + \mu_2 \left[\exp\left(-\frac{W_L}{kT}\right) - \exp\left(-\frac{W_0}{kT}\right) \right] + \\ &+ \mu_3 \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \end{aligned} \right\}) \quad (57)$$

$$\sigma \approx \left[-\frac{n_i}{2} + \sqrt{\left(\frac{n_i}{2}\right)^2 + G} \right] \left\{ \begin{aligned} &\mu_1 \exp\left(-\frac{W_0}{kT}\right) + \mu_1 \left(\exp\left(-\frac{W_L}{kT}\right) - \right. \\ &\left. - \exp\left(-\frac{W_0}{kT}\right) \right) + \mu_3 \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \end{aligned} \right\} \quad (58)$$

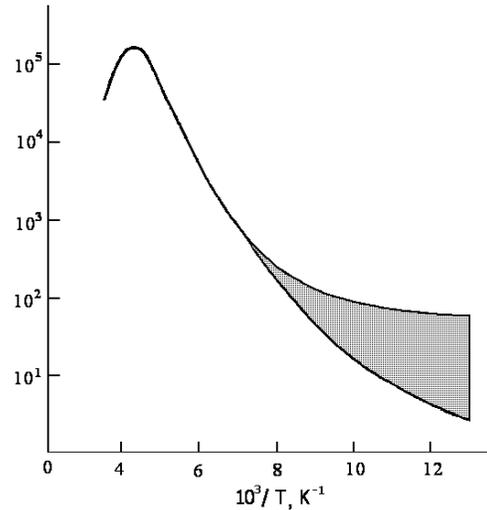


Fig. 7. The experimental dependence of photoconductivity upon the temperature according to [16]. The grey area corresponds to different samples made from the same material.

In a special cases we can instead of relation (40), resp. (44, 49) write

$$\sigma \approx \exp\left(\frac{W}{kT}\right) \exp[sA(hf + CT - \beta)] \left\{ \mu_1 \exp\left(-\frac{W_0}{kT}\right) + \mu_2 \left[\exp\left(-\frac{W_L}{kT}\right) - \exp\left(-\frac{W_0}{kT}\right) \right] + \mu_3 \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \right\} \quad (59)$$

$$\sigma \approx \left[\exp[0.5 sA(hf + CT - \beta)] \right] \left\{ \mu_1 \exp\left(-\frac{W_0}{kT}\right) + \mu_2 \left[\exp\left(-\frac{W_L}{kT}\right) - \exp\left(-\frac{W_0}{kT}\right) \right] + \mu_3 \left[1 - \exp\left(-\frac{W_L}{kT}\right) \right] \right\} \quad (60)$$

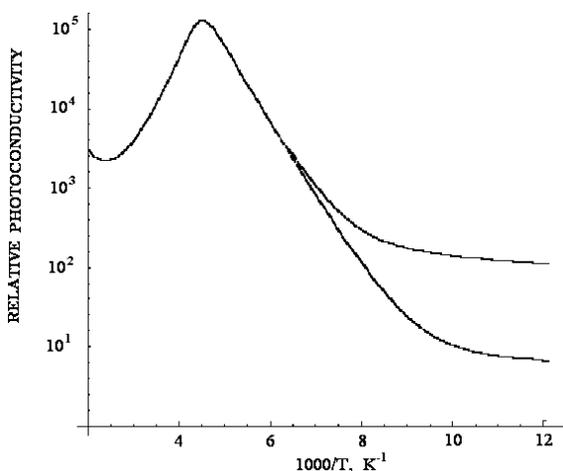


Fig. 8. Photoconductivity dependence upon the temperature according to the theoretical formula (32) for different mobility values μ_2 of carriers in a sub-band of low mobility

5. Discussion

Typical dependence of photoconductivity obtained from experiment for a special chalcogenide glasses is depicted in Fig. 7. If compare that result with theoretical one (see Fig. 8, one can conclude that quantitative agreement is relatively good. The relation (31, or 32) enables to investigate dependence of photoconductivity on intensity of an incident irradiation.

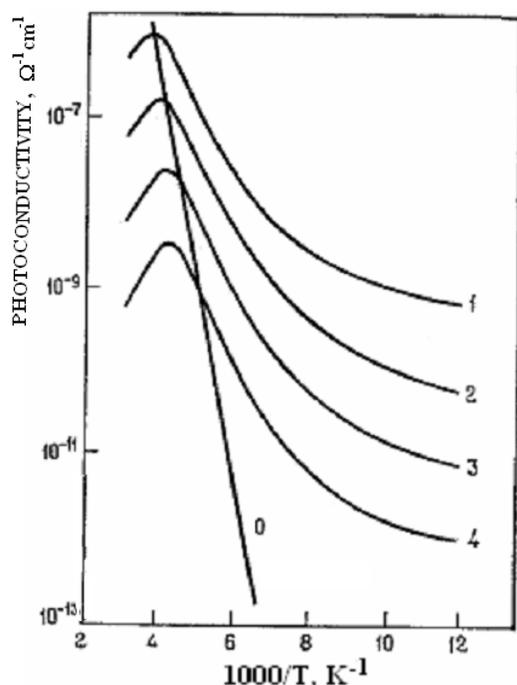


Fig. 9 The experimental temperature dependences of the photoconductivity in a chalcogenide glass for various intensities of the activated irradiation [17].

The experimental dependences of the photoconductivity for various intensities of the irradiation we can see in Fig. 9. The theoretical dependences according to (32) we see in Fig. 10. The experimental data relevant for photoconductivity activated by irradiation in a region of the exponential tail can be explained in the frame of the barrier-cluster model.

As it was shown above, in low temperature region and high intensity of irradiation the level of photoconductivity is proportional to the root of irradiation intensity (hence $\sigma \approx \sqrt{G}$) whereas in a region of high temperatures and low intensities the photoconductivity is proportional to the level of irradiation (hence $\sigma \approx G$). It is in accordance with experimental results.

Here presented model of photoconductivity of chalcogenide glasses enables to explain characteristic dependency of photoconductivity on temperature in relatively wide temperature interval. It explains why the photoconductivity in a wide interval of temperatures decreases and why this decrease at certain low values of the photoconductivity practically stops, or at least rapidly slows down. The reason rests in small values of the electron mobility in the region of low mobility sub-band (under the level of barrier's peaks)

At sufficiently high temperatures relevant concentration of free electron of a thermal origin exists. Mechanism of recombination in that region of temperatures is by now different from that in the region of low electron concentration of thermal origin. It results in an increase of photo-carriers recombination and consequently to the decrease of photoconductivity at an increase of the temperature.

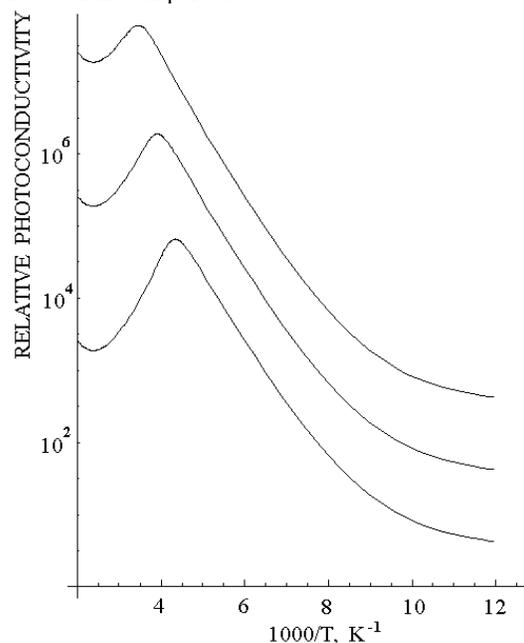


Fig. 10 The theoretical temperature dependences of the photoluminescence in a chalcogenide glass for various intensities of an activated irradiation (according to (32)).

Acquired theoretical expression of the photoconductivity curve represents behavior of the real experimental curve in the wide interval of temperatures at either side of the curve maximum. The theoretical behavior of the curve in a region of very high temperatures provides however a new strong increase of photoconductivity by increasing temperature. That fact is not experimentally confirmed up to now because experiments on the photoconductivity in that region of the temperatures are missing. One can not exclude, that in this temperature region the conditions for applicability of our model are no longer fulfilled. Maybe, it is due to the fact that the energy width W_0 of the low mobility sub-band is rather small (at about $10^{-1}eV$). Therefore, it is possible that in this region the relation (17) for expression of the generation factor G is no longer applicable.

6. Conclusion

It is shown in this article, that several experimental data relevant for photoconductivity activated by irradiation in a region of the exponential tail can be explained in the frame of the barrier-cluster model. When the temperature and energy of activating photons increases, the probability of the multiple tunneling also increases which implies an increase of an optical production of free electrons. This leads to the increase of photoconductivity.

Study of the optical properties of chalcogenide glasses is very important for the determination of the electronic band structure as well as other optical parameters, such as optical energy gap and refractive index.

Note: A further literature about the optical phenomena in chalcogenide glasses can be found in [83 - 95].

Acknowledgement

At the end, I want to thank Prof. Viktor Bezák from the Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava and Prof. František Čulík from the FCE, Slovak University of Technology in Bratislava for valuable discussions on this topic.

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