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Chalcogenide glasses in the frame of the barrier-cluster and local heating model

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In physics of non crystalline materials there are many challenging problems. This article offers the explanation of the some phenomena in the disordered semiconductors, first of all in chalcogenide glasses on the fundamentyals of the barrier-cluster-heating model. This model assumes that an amorphous semiconductor consists of nanoregions (clusters), separated from each other by potential barriers. Barrier-cluster-heating model allows to explain many phenomena observed in chalcogenide glasses. In this article the mechanism of the appearance weak absorption tail (second exponential tails) of optical absorption in chalcogenide glasses is explained.

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1. Introduction

Chalcogenide glasses represent from the point of view of applications one important group of non-crystalline materials. They are glasses containing one (or more) of the elements S, Se, Te. To the well-known chalcogenide glasses belong the As_2S_3 and As_2Se_3.

The physical principle of optical phenomena in non-crystalline semiconductors are not fully understood yet. There is hitherto not a model, which would be able to clarify a wider range of optical phenomena in these solids. And at that, technical applications of these solids constantly grow. An enormous number of experimental papers were published. However, the theory seriously remains behind [1-11].

To the relevant problems – as regards to the optical properties of chalcogenide glasses - belong the explanation of origin of the exponential tails of optical absorption (misunderstand up to now). The experiments show, that in adition to normal exponential tail there exists the weak (second) absorption tail, which may be observed in very low absorption region (misunderstand up to now).

It appears that our barrier-cluster-heating model (BCH model) of a non-crystalline semiconductor is able to explain several significant phenomena in non-crystalline semiconductors, especially in chalcogenide glasses [12-16]. In this paper the weak absorption tail will be explained in a frame of barrier-cluster-heating model.

Barrier-cluster-heating model originated as synthesis of two various independently created models - barrier-cluster (BC) model and local-heating (LH) model. Synthesis of both mentioned insights brought also synergic effect, enabling the deeper understanding of physical processes in amorphous semiconductors.

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

2.1 Barrier-cluster (BC) model

The barrier-cluster model comes out from the assumption that there exist potential barriers in a non-crystalline semiconductor, which separate certain nanoregions – clusters and in this way, they hinder the transport of the carriers at the margin of the conduction or valence bands [12-16]. The barriers also influence significantly the optical absorption at the optical absorption edge. It is caused in the first line by their inducing a strong electron-phonon interaction, which 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 and thus, on such a transition, the total of energy taken by an electron equals the sum of the photon and phonon energies. Another important factor - as far as influence of barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually connected with tunneling of carriers through the potential barrier. Due to this, the absorption process is influenced by barriers. These facts enable us to explain successfully not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high as well as low temperatures. The nanoregions in chalcogenide glasses are created in chalcogenide glasses by closed clusters. That enables us to understand the spin properties of CHG too.

2.2 Physical nature of photoluminescence

A possible concept of physical nature of photoluminescence in chalcogenide glasses at low temperatures, from point of view of a barrier-cluster model, is depicted in Fig. 1. 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 nanoregion 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 nanoregion (cluster), but also in the more distant regions. The height of these levels will depend on the distance electron from the "motherly" nanoregion (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.

In Fig. 1, several levels are depicted on both sides of the hole (in one-dimensional model). These levels create a kind of "funnel" of levels. A new energy level will appear not only in adjacent nanoregions but also in the original mother nanoregion in which the hole rests. The electron level in the mother region is the lowest one from among all levels of the funnel.

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. These levels are not shown in the diagram.

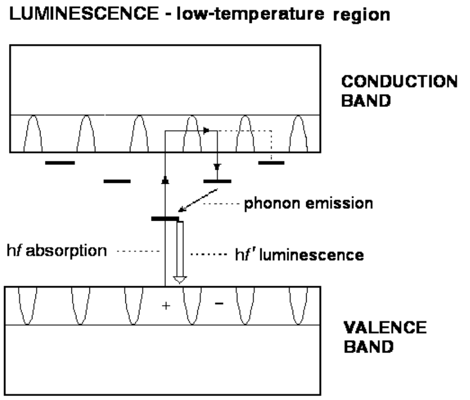

Fig. 1 The processes connected with photoluminescence

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 by 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 the emission of a luminescence photon, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokes shift will occur.

If there is no other disturbing processes, a stationary state with a relatively high level of photoluminescence 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 photoluminescence begins to impair and weaken rather quickly.

When explaining the laws of photoluminescence on the basis of the barrier-cluster-heating model, an extremely significant assumption is important in our considerations, namely that free electrons, by their effect, stimulate the non-radiant recombination of bound *e-h* pairs (as a kind of a catalyst), and thus, they reduce the number of radiant transitions. So, ultimately, free elrctrons markedly influence the photoluminescence process. The creation of freeelectrons occurs at low temperatures via the mechanism of multi-tunneling of a carrier through potential barriers (here, only tunneling of electrons is assumed) [12-16].

The model enables to explain not only the Stokes-like rule, fatigue effect and Street relation, but, also, the photo-excitation characteristic (PLE characteristic), too [12-16]. Barrier-cluster model gives a new look at the density of states within the forbidden band and allows for the explanation not only of important electrical and optical features of chalcogenide glasses, but also the results of X-ray structure experiments and ESR-measurements.

3. Local heating (LH) model

3.1 The structure of the glass and anomal low-temperature phenomena

The structure of glasses run everytime many polemics in the circles of experts. Malinovský et al [1-2] presumes, that the typical feature of the glasses is the existence of inhomogeneities at the nanometrical scale. An indirect evidence of this is provided according to [1], by known low-temperature anomalies.

Authors state that the experimental data testifying to the existence of nano-regions in glasses are somewhat indirect. These arguments include [1]:

a) pre-peak in the radial distribution function obtained from X-ray structural data

b) excess heat capacity $C(T)$ and the “plateau” in the temperature dependence of thermal conductivity $\lambda(T)$ in the interval $T = 10\text{-}20$ K, which are observed in all glasses and amorphous materials.

c) low-frequency peak (boson peak) found in Raman scattering spectra of light in all amorphous materials.

Several important facts confirm the accuracy of the assumptions of described model of the local heating. These include the following observations:

The maximum frequency of the boson peak allows determining the correlation radius of the structure. It was demonstrated, that the boson peak has universal shape for a large number of glasses with different chemical compositions and corresponds approximately to one value R = 1 nm. If the characteristic size of nanoregions is somewhat different in different glasses, then these differences have to be simultaneously observed in experiments with structural factor measurements and in estimations based on the low-frequency Raman scattering of light. Indeed, it was shown, that the estimations based on the structural factor and on the Raman scattering are the same with good precision. Moreover, if one can simultaneously change the boson peak position and the width of the pre-peak in structural measurement. Experiments performed with vitreous SiO_2 modified by high pressure confirmed this rigorous correspondence. Further arguments in favour of local heating model can be found in many papers.

3.2 Local heating model and photo-induced changes

In the framework of the local heating model, photo-induced effects in chalcogenide glasses are caused by heating of the nanoregion during energy quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixed the photo-induced transformation. It is shown in [1] that in the case of chalcogenide glasses the reasonable estimations indeed lead to such heating.

It seems that the nanometer structure of chalcogenide glasses is a reminiscence of its crystalline analogues, implying the polarization dichroism for nanoregions. In the frame of the local-heating model, photoinduced vector changes occur because of selective absorption predominantly in those nanoregions whose maximum absorption axis coincides with the direction of polarization in the light wave. The model of the local heating explains the existence of photo-induced vector effects even after long-time irradiation of the chalcogenide sample.

3.3 Relaxation of electronic excitation

The energy relaxation of the electronic state in a material inhomogeneous on the nanoscale should appreciably differ from that in the homogeneous medium (for example, in crystals). In materials with spatial dispersion, the excitation energy should be localized on the inhomogeneities with sizes of athe order of the correlation radius of the structure [1].

In this situation, the excitation energy is transferred in two stages: at the first stage, the high-frequency phonons are generated in the region limited by the correlation radius of the structure R and, only after a lapse of time, the energy is transferred to long-wavelength vibrations. During this time, the localized phonons appear to be locked inside the correlation region of the structure and exhibit a specific spectrum depending on the characteristic size.

Therefore, the localized energy can bring about an interesting phenomenon - local rearrangements in the nanoregion, in which a energy quantum is absorbed. Such structural transformations in actual fact were observed most clearly in chalcogenide glasses [1] and, to some extent, in glasses of other compositions and various amorphous materials.

4. Barrier-cluster-heating model (BCH model)

4.1 BCH model - as synthesis of two models

BCH model originated as synthesis of two various models of chalcogenide glasses - barrier-cluster (BC) model and local-heating (LH) model. These were created and developed independently one from the other. It was shown, that these two models are mutually compatible, and that they are mutually complemented and enriched. The compability of both mentioned insights enables us to create extended barrier-cluster-heating model (BCH = BC + L). But BCH model is not a mechanical connection of the two models. Synthesis brought deeper understanding of physical processes in amorphous semiconductors (BCH > BC + LH). In the lastpart of this article are analysed the problem of “weak absorption tail” in chalcogenide glasses, which enables the synthesis of both models.

BCH model is based on the supposition that glasses at nano-meter scales are inhomogeneous, consisting of nano-regions - clusters. Between clusters there are potential barriers affecting not only the electrical transport, but optical absorption as well. BCH model is capable to explain the number of important electrical, optical effect in chalcogenide glasses - the conductivity (Meyer-Neldel rule), optical absorption, Urbach’s rule, electroabsorption, photoluminiscence, relation between MNR and Urbach’s rule. The closed-cluster structure can explain the results of X-ray structure measurements and the absence of an ESR signal in the case of chalcogenide glasses. The model provides a new explanation for the density of states within the forbidden band and explains, why the attempts at identification of gap-states (the charged-defect and valence-alternation pairs) by various optical and other methods fail [17-18]. Energy released by non-radiative recombination of electron-hole pair localized in one nanoregion is absorbed by the respective clusters. It causes the increase of temperature of the cluster. The photoinduced structural effects in chalcogenide glasses are caused by heating of the nanoregion during energy quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixed the photoinduced transformation. BCH model is capable to explain various photoinduced changes, and relations, such as the relation between photoluminescence and photoexpansion. It is able to explain the weak absorption tail and some further mid-gap effects, too. We assume, that the barrier-cluster-heating model can be expected stimulate a development of new interpretations of physical phenomena in chalcogenide glasses.

4.2 Monoenergetical phonons

For the explanation of Meyer-Neldel rule [16] based on the barrier-cluster model we used concept that a non-radiate recombination transition of an electron from a conduction band to a valence band in a non-crystalline semiconductor is connected with production of series monoenergetical phonons. Further we shall speculate about that how these monoenergetical phonons influence an optical absorption of the non-crystalline substance. Our next consideration shall lead to explanation of a mechanism of origin exponential tails of optical absorption that is to explanation of the Urbach empirical rule. We show that there is a connection between Meyer–Neldel rule and Urbach rule [12].

It is known, that exponential tails of the optical absorption reach deep in a forbidden band of the width 2W. If $hf < 2W$, energy of a photon alone is not sufficient for an optical transition of an electron to the conduction band. The missing energy $2W – hf$ phonons can offer to electron not only thermal ones (controlled by Maxwell-Boltzmann distribution function) as it was described upper, but also monoenergetical ones. The energy ΔE of one monoenergetical phonon is small, usually much smaller than is deficit of energy $2W – hf$ ($\Delta E << 2W – hf$). An optical transition demand the electron has accept needed energy $N\Delta E$ from more (N) monoenergetical phonons.

In the following we use the concept of monoenergetical phonons also by explanation of the formation of exponential tails of optical absorption. In some situation play the dominant role just monoenergetical phonons and the influence of thermal phonons is relatively small.

4.3 The origin of weak absorption exponential tails from the point of view BCH model

Following consideration is related to the origin of exponential tails of optical absorption, which is connected with the participation of monoenergetical phonons on optical transition. The conclusions can be used for the explanation of the formation of both types of exponential tails – normal-standard (with steeper slope – for the region of higher absorption) and weak absorption tails (WAT) with lesser slope (steep) – for the region of lower absorption. Different properties of both types of tails will result then from the different values of the probability of subsidiary absorption of phonons in two different situations. This will we make clear later.

4.4 The mechanism of creation of exponential tails (not only WAT)

We assume, that on the matter acts monochromatical radiation with deficit energy hf deficient for usual optical transition from the valence band to conduction band, so $hf < 2W$, where $2W$ is width of the forbidden band. If this transition should be realized, electron - except for photon´s energy - has to accept needed energy $2W – hf$ from N monoenergetical phonons. We asume, that in compliance with publication [12-16] it deals with monoenergetical phonons originated by non-radiant recombination of bearer. Minimal number N obtained monoenergetical phonons energie ΔE needed for transition, then will be

$$N = (2W - hf)/ \Delta E \tag{1}$$

Let w_1 denotes probability that an electron accepts one monoenergetical phonon of energy ΔE. Probability of absorption N monoenergetical phonons then will be $w_N = w_1^N$. We shall write down w_1 as

$$w_1 = \exp(- s) \tag{2}$$

where $s > 0$ (because $w_1 < 1$). Then

$$w_N = w_1^N = \exp(-sN) \tag{3}$$

From (1-3) one gets:

$$w_N = \exp\left(-s\,\frac{2W - hf}{\Delta E}\right) = \exp\left[-b\,(2W - hf)\right] = \exp\left[b\left(hf - 2W\right)\right] \tag{4}$$

where

$$b = s/\Delta E = -ln w_1/\Delta E \tag{5}$$

At the last arrangement we use the relation (2).

The probability w_N will determine level of an optical absorption related to monoenergetical phonons ($w_N \sim \alpha$). This component of absorption will be (4)

$$\alpha \sim \exp(b(hf - 2W) \tag{6}$$

from which follow

$$\ln \alpha(hf) = b\,(hf - 2W) + \text{const} \tag{7}$$

We can see, that steepness of the exponential tail ln $\alpha(hf)$ determines the value of the parameter b. This is however on the basis of formulae (5) dependent indirectly proportional from the probability w_1. We obtain

$$\ln \alpha(hf) = (-ln w_1 /\Delta E)\, hf - 2bW + \text{const}$$

The slope of exponential tail determine the value of the expresion "$-ln w_1/\Delta E$", which at condition $w_1 < 1$ decreases with increasing of probability w_1. Just the different value of this probability for two different cases causes the various slope of the standard exponentional tail and weak absorption tail – WAT.

4.5 Two cases of participation of phonons in the optical absorption

The previous reasoning enables us in the principle to explain the origin of exponential tails of optical absorption in case of both known types of exponential tails. It is important to realize two possible cases of participation of the phonons to the optical absorption.

1. By the standard tails on the absorption participate diffused monoenergetical phonons – phonons diffused through the whole volume of the sample.
2. In case of weak absorption tail on the absorption participate the localized monoenergetical phonons – phonons localized in certain cluster, which was created after non-radiative recombination of *e-h* pair inside this cluster.

The participation of phonons on optical absorption cause the creation of the exponential tails in both introduced cases. The slopes of both tails will be, however, considerably different.

4.6 Weak absorption tail

Next, we are going to describe the mechanism of creation of the weak absorption tail (WAT) of optical absorption from point of view of the barrier-cluster-heating model. In case of WAT have photons of absorved light relatively small energy. Their energy alone doesn´t be sufficient for the optical transition of electron from the valence band to the conduction band. Electron however can also in case of WAT utilize for the optical transition except for the energy of photon also vibrational energy of grid, therefore energy of phonons. Similar mechanism enabled us to explain also the origin of normal-standard exponential tails in the region of higher absorption. It is here however one significant distinct. Just this will be responsible for the fact, that WAT have less slope as standard exponential tails.

The localised phonons are phonons released by the conclusive non-radiant recombination such *e-h* pair, those both components (electron and hole) are, after previous consecutive approach on the levels of funnel´s walls, in this same nanoregion. The produced phonons are for the same time localized in actual nanoregion [1]. Electron of concerning cluster has in such case to disposal the backing of whole set of localized phonons for the optical transition in its respektive nanoregion. For the origin of WAT are in some meaning responsible just nanoregions, therefore nano-inhomegenities. They are here typical feature of glasses in general. Just they bear, according our opinion, responsibility not only for the anomal low temperature phenomena in the glasses, but also responsibility for the origin of WAT.

In the framework of the barrier-cluster-heating model, photo-induced structural effects in chalcogenide glasses are caused by heating of the nanoregion during the energy quantum absorption above the glass transition temperature. In general it haven´t deal about the melting of nanoregion. It can deal only with the local increasing of temperature of nanoregion without its melting. In the nanoregion after the non-radiant recombination *e-h* pair is created high density of phonons localized for some time in this region [1]. This increases the probability of the presence of phonons on the optical transition. Electrons of given nanoregion will have therefore markedly higher probability of gaining energy from the phonon´s field. The probability w_1 in (2) of the absorption of one phonon on the optical absorption is in this situation markedly higher, as by the formation of standard exponential tails, when it deals about the absorption of the set of independent in volume of sample diffused phonons.

Thanks to the greater value of probability w_1 and according (2) to subsequently also lower value of the parameter *s*, will the parameter *b* have according the formula (5) markedly lower value, as by the standard absorption of diffused phonons. Just this causes (according to the formula (7, or 8)) less steepness of WAT. For the origin of WAT is therefore responsible the higher probability w_1 of cooperative participation of phonons on the optical absorption in case of localized monoenergetical phonons produced in concerning localized region by the recombination of *e-h* pair in this.

Number of nanoregions, in which *e-h* pair recombines in non-radiative way, is everywhere in the matter, usually relative small. Therefore small absorption will be conditioned by the localized phonons (in clusters) produced in such way. Under an usual condition predominate optical transitions of electrons from the valence band to the conduction band in nano-regions without the presence of *e-h* pairs by the active attendance of non-localized (diffused) phonons. This explains the dominance of standard absorption – absorption with steeper slope of exponential tails in region of higher absorption. WAT will be revealed on the experimental graphs of dependance ln $\alpha(hf)$ there only, where is fundamental absorption lower, lower as the absorption connected with optical transitions conditioned with localized phonons. Only in this region of small values *hf* will have dependance ln $\alpha(hf)$ small steepness. By sufficient increasing of energy *hf* absorbed fotons become to the transition from the small steepness of graph to the large steepness, because by higher values of photons´ energy will predominate the fundamental absorption.

Remark: The weak absorption tail can be considered – from the point of view of BCH model – as new indirect proof of existence of nanoregions (clusters) in glasses (despite of this, that in this case doesn´t deal explicitly with the low-thermal phenomenon). The indirect proof of existence of nano-inhomogeneities provide, therefore, not only known low-temperature anomalies.

Remark: BCH model enables to explain futher photo-induced effects, too. In [19] there are the "*e-h-e*" centers described, which enables to explain photo-induced mid-gap absorption.

In general, the theory of barrtier-cluster model is useful for the interpretation of the properties of chalcogenide films with relevance in solar cell devices based on these materials [20-25].

5. Conclusions

Barrier–cluster-heating model of the non-crystalline semiconductors, is based on the assumption that in non-crystalline semiconductors, there exist nanoregions separated from each other by potential barriers. We suppose that these nanoregions in chalcogenide glasses are created by closed clusters. This model allows explanation not only of a number of important electrical and optical 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. In the framework of the BCH model, photo-induced effects in chalcogenide glasses are caused by heating of the nanoregion during energy quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixed the photo-induced transformation. In the article the mechanism of originating from the weak absorption exponential tails of optical absorption is explained.

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