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An explanation of optical phenomena in non-crystalline semiconductors

Ivan Banik*

Department of Physics, Faculty of Civil Engineering,
Slovak University of Technology,
Radlinského 11, 813 68 Bratislava, Slovak Republic

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Abstract: Barrier model of a non-crystalline semiconductor is described in this article. The most important optical phenomena, which are typical for this group of materials, are explained on the base of this model. The model assumes that in non-crystalline semiconductors the potential barriers exist, which separate certain microscopic areas from each other, assuming barriers possess a parabolic profile. This conception explains the rise of exponential tails of optical absorption at the end of optical edge as well as electro-absorption, photoelectric conductivity, photoluminescence, and others. Using this model, many electric transport properties of non-crystalline semiconductors can be explained successfully.
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1 Introduction

The physical properties of non-crystalline materials are much more complex than those of crystals. The wide-range research in this area is very extensive. The quantitative increase of new experimental data in this research calls for theoretical analysis. At present, there is no uniform theory that would clarify the vast variety of observed phenomena.

The present state of physics of non-crystalline semiconductors seems to be incredibly complex. The Nobel Prize winner N. Mott, in the introduction to the second edition of his work [1] (edited in the Russian language in 1982 [2]) characterized this state in these words: "There were never so many discrepancies as there are now in the physics of

* E-mail: ivan.banik@stuba.sk

non-crystalline solids". If he lived, he would probably observe again: "This state is no better now, but rather worse".

H. Overhof, in his lecture at the remembrance of N. Mott's anniversary [3] has not only praised Mott's great contribution to the physics of non-crystalline solids, but he also introduced a very important idea at the end of his performance: "It seems to me, as far as the theory of non-crystalline semiconductors is concerned, that one of the fundamental pillars of the pedestal, on which such a theory should rest, is still unknown to us." This is to some extent quite crude, however true.

In the monograph [1], the most fundamental knowledge on non-crystalline materials can be found. One of the authors of this monograph, 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. The work [4] has become another important publication in the field. 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 a 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 afterwards 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.

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 at the edges of fundamental optical absorption [1,4]. A correct explanation of this effect will probably help to understand other electron processes in amorphous materials.

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. It is usually denoted as an exponential tail of optical absorption at the margin of optical absorption edge.

Exponential tails of optical absorption on crystalline semiconductors (CdS, Se) [1] were also observed in some rare cases. They were a few eV wide. They can be described by the following empirical formula:

$$\alpha \approx \exp\left[\frac{\gamma\,(hf - E_o)}{kT}\right] \tag{1}$$

where γ *and* E_o are constants [1]. This formula describes the so-called Urbach's margin of optical absorption. In this case, at higher temperatures (that is, above a certain value T_o), the quantity T is identical to the thermodynamic temperature. For temperatures below T_o, T_o should be substituted for T in this formula (1). Thus, below T_o, the exponential tails do not depend on temperature. The value T_o is a kind of characteristic temperature for a given material. For the crystalline materials mentioned, this value is about 100 K. It seems quite strange that, although the exponential tails in these crystalline materials are relatively long [1], there does not exist a generally accepted explanation Urbach's rule, not even in this particular case.

The exponential tails in the case of amorphous semiconductors occur more or less regularly. They tend to fit Urbach's formula (1), too. However, the characteristic temperature T_o is considerably higher for amorphous semiconductors than for crystals. It may even reach room temperature. At higher temperatures (above T_o), the slope of the tails, ln $\alpha(\mathrm{h}f)$, changes with temperature in accordance with the Urbach margin (Urbach's rule). 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.

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 [5,6], 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-Keldyš effect [7, 8]. Its nature is in tunneling of the Bloch states into 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 [9] investigated the problem of absorption in a direct 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 [1] 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 [1,4]. 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 these tails of density states may have an exponential shape as well. According to Mott [1], 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 $\ln\alpha(\mathrm{h}f)$ 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 [3], 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 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.

2 Barrier model

The barrier model assumes that an amorphous solid consists of microscopic regions separated from each other by potential barriers. The barriers restrict the transition of low energy conduction electrons from one region to the other. Such electrons behave between barriers in particular regions of material in a similar way as electrons in a crystal do. The author, to some extent, used this idea already to explain physical properties of non-crystalline semiconductors (see [10-12]).

In Fig. 1, the electron spectrum of an amorphous semiconductor, based on the barrier model, is shown.

The potential barriers are depicted inside the conduction and valence bands of an

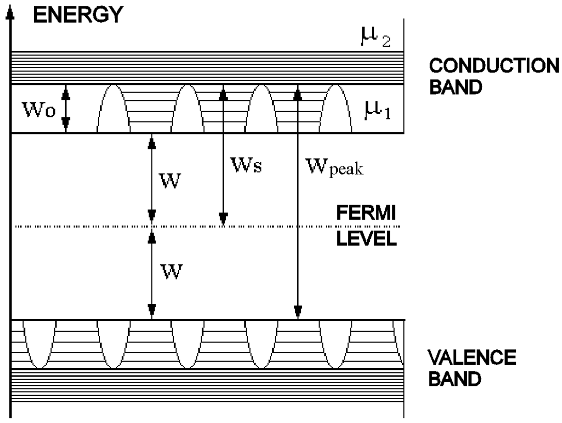

Fig. 1 The electron spectrum of an amorphous semiconductor.

amorphous material, separating individual localized energy states at the edge of the band. The electron levels between barriers, due to the small dimensions of the microscopic regions, exhibit a distinct discrete character [10]. At the lower margin of the conduction band, a sub-band with carriers (μ_1) of low average mobility is created. Situated above the Fermi level, on the energy level W_s, which corresponds to the peaks of barriers, mobility changes rapidly. The states with energy above the peaks of barriers are delocalized. They create a sub-band with a high average mobility (μ_2).

Quite a similar situation occurs at the edge of the valence band. In further considerations, we will limit ourselves to the electron type of transport.

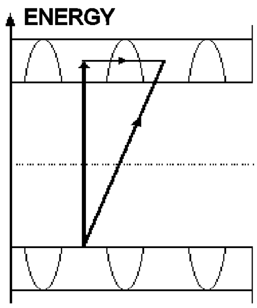

Fig. 2 The optical transition of an electron connected with tunneling trough potential barrier.

Transport in the region of energy levels lower than the tops of barriers is connected with a tunneling mechanism through the potential barriers. Under common conditions, the contribution of the carriers from a low-mobility sub-band to the overall conductivity is small and that the carriers from the high-mobility sub-band will contribute the most. Thus, it is clear that the activation energy of an amorphous material as a whole becomes a highly questionable quantity. At higher temperatures, it is determined substantially by the height of the potential barriers, so that the value W_s corresponds to it. At lower temperatures, however, the transport in a region below the peaks of barriers may dominate, and the corresponding activation energy will obviously be lower; with decreasing temperature, it will approach the W value.

The potential barriers are important not only for the electrical transporting properties of a semiconductor, but for optical phenomena. The existence of barriers induces a relatively strong electron-phonon interaction, which allows significant energy participation of phonons in optical absorption at higher temperatures. On the other hand, in optical absorption at lower temperatures, the tunneling of electrons through the potential barriers plays an important role (Fig. 2). It is related to the low number of possible combinations inside the localized region. The discrete levels of neighboring regions provide more possibilities for combination. Thus, the potential barriers will influence several optical phenomena in a non-crystalline semiconductor.

The energy spectrum of an amorphous solid, from the point of view of a barrier model, is thus to a large extent similar to that of a crystalline solid. A more pronounced difference is at the margins of bands, not only in the mobility of carriers but also in optical absorption near the "optical edge". In the simplest (and of course, only a special) case, the barrier model may correspond to a polycrystalline model of an amorphous solid, to which we attribute fine-grain, polycrystalline structure. Obviously, this model may also explain physical properties of many nanocrystalline materials.

3 Light absorption from the point of view of a barrier model – a range of higher temperatures

The starting point of the following considerations is an assumption that in non-crystalline semiconductors (and quite exceptionally in the crystalline ones, too) proper conditions occur for a distinct absorption of light, with phonons participating in the energy exchange [13]. This process is shown in a simplified form in Fig. 3.

The potential barriers create conditions for a strong electron-phonon interaction. This may be connected with localization of carriers in the vicinity of zone borders, caused by presence of potential barriers [10-12]. At that, the barriers are not stiff but they are subject to temperature motion as they are connected with real physical objects. This offers new possibilities for the electron-phonon interaction. The details of this interaction remain unknown. Not regarding this, however, we assume that an electron in an optical transition accepts not only the energy of a photon but also the phonon energy [13]. Thus, the whole energy accepted is

$$\mathrm{h}f + W_{phon} \tag{2}$$

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

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 (Fig. 3).

Under these assumptions, the transitions on levels just below the barrier peaks will be more probable for two reasons. The first one is a high probability of tunneling on levels of neighboring microregions. 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. Let us denote the energy needed for optical transitions on levels just below the peaks of barriers, as W_{peak}. If the photon energy $\mathrm{h}f$ is less than W_{peak}, absorption can take place only in the case where the "missing" energy

$$W_{peak} - \mathrm{h}f$$

is supplied by the phonon field.

The number of electrons that can acquire such energy from a phonon field depends on temperature and is thus determined by the expression

$$\exp\left[-\frac{W_{peak} - \mathrm{h}f}{2kT}\right] \tag{3}$$

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 this expression. For the absorption coefficient, in accordance with (3), it can be written

$$\alpha \approx \exp\left[\frac{\mathrm{h}f - W_{peak}}{2kT}\right] \tag{4a}$$

$$\ln \alpha = \frac{\mathrm{h}f - W_{peak}}{2kT} + \mathrm{const} \tag{4b}$$

or, for a particular (constant) temperature

$$\ln \alpha = \mathrm{h}f + \mathrm{const} \tag{5}$$

which is a mathematical expression of an exponential tail of optical absorption. However, assuming (4b), the slope of tails is also temperature dependent.

Optical absorption with participation of phonons can also be viewed in another way. In a simplified form, we can imagine that, due to incident radiation with the photon energy $\mathrm{h}f$, the valence band as a whole shifts higher by $\mathrm{h}f$. In this way, a new virtual valence band rises, whose forbidden band has a width $W_{peak} - \mathrm{h}f$. From this virtual band, electrons will thermally penetrate into the conduction band.

Formula (4a) is of the same kind as the Urbach's formula. It explains the temperature dependence of the slope of exponential tails at temperatures above T_o.

The agreement of the result obtained in this way is also supported by the existence of a focal point of a set of lines $\ln\alpha(\mathrm{h}f,\, T_i)$, determined by the expression (4b). Let us denote the coordinate $\mathrm{h}f$ of a focal point by a symbol $(\mathrm{h}f)_F$. We find this point from the condition that any couple of straight lines, for which $\mathrm{T}_i \neq \mathrm{T}_j$ must pass through it, so that

$$\ln \alpha_i(\mathrm{h}f, \mathrm{T}_i) = \ln \alpha_j(\mathrm{h}f, \mathrm{T}_j)$$

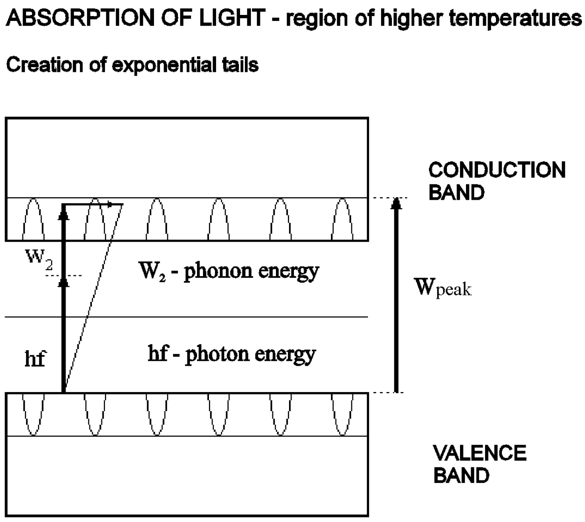

Fig. 3 The optical transition of an electron with phonon-energy participation.

In this way, using (4), we obtain

$$\frac{1}{2kT_i}(\mathrm{h}f - W_{peak}) = \frac{1}{2kT_j}(\mathrm{h}f - W_{peak}) \tag{6}$$

which is always fulfilled provided $\mathrm{h}f = (\mathrm{h}f)_F = \mathrm{W}_{peak}$. Thus, the focal point of straight lines (4b) exists, and at higher temperatures, it determines the "real" width W_{peak} of the forbidden band of a semiconductor by its position on the energy axis. This is in agreement with the statement in the study of Mott and Davis [1]. It also confirms that in the region of higher temperatures, the quantity E_o appearing in (1) corresponds to the value $\mathrm{W}_{peak}/2$.

The formula (4b) does not explain why the slope of exponential tails ceases to change below $T_{o,}$ and the tails only shift in parallel towards lower absorption. We shall consider this in the next part.

3.1 Comparison with experiment

Let us now compare the theory with experiment. The theoretical value of the parameter γ , which appears in (1), is 0.5, as it follows from comparison of (1) and (4). The experimental values of this parameter for some amorphous materials are as follows: Te – 0.47; As_2Te_3 - 0.49; $CdSGeAs_2$ - 0.49; As_2Se_3 - 0.52; As_2S_3 - 0.49; Se - 0.44 etc. It is certainly a good agreement. At the same time, this provides a logical explanation of such a "surprising" fact that the slope of exponential tails is very similar for many different materials. For this, there is no reasonable explanation on the base of similar density of states in the tails near the borders of zones.

The phonon mechanism also explains the fact that the tails can reach relatively deep into the forbidden band. With decreasing temperature, however, this overlap decreases, too. At that, it is remarkable that an interpretation of absorption dependence on the basis of a barrier model does not need to assume an existence of density of states in a forbidden band of an amorphous solid. Existence of a certain density of states inside the forbidden band is not eliminated. It can be supposed, however, that this density is lower than it was estimated up to now [1, 3].

3.2 Optical bandwidth of the forbidden band in non-crystalline semiconductors

The concept of optical bandwidth, E, of the forbidden band in a non-crystalline semiconductor is used relatively often in publications dealing with this kind of matter. It is defined as the energy of photons of monochromatic light to which the conventional value of the absorption coefficient corresponds [$\alpha = 10^2\mathrm{cm}^{-1}$]. Experiments showed that the optical bandwidth, E, is strongly influenced by temperature, T. The functional dependence E(T) (for example, in the case of chalcogenide, non-crystalline semiconductors) has most often a linearly descending characteristic, $\mathrm{E} = \mathrm{E}_o + \mathrm{CT}$. The value $\mathrm{dE/dt} = \mathrm{C} < 0$ represents the temperature coefficient of the optical bandwidth of the forbidden band of a semiconductor. On chalcogenide materials, its values are most often in the range 5-7.10^{-4} eV K^{-1} [1]. In the literature, for example, data are given for As_2Se_3: 7.10^{-4} eV K^{-1} [15]; for Se: 7.10^{-4} eV K^{-1} [1]; for semiconductors of the type As_2Se_3-Sb_2S_3 : 6-7.10^{-4} eV K^{-1} [1]; for As_2S_5 : 6.10^{-4} eV K^{-1} [15]; and for $CdGeAs_2$: 5.10^{-4} eV K^{-1} [16]. These values are rather close to each other, which may not be a plain chance event.

We are going to show that the optical width properties of the forbidden band can be explained well using the barrier model. At that, the value E has a clear physical interpretation. It will be made clear at the same time why the above values are so close to each other. We also assume, however, that the value E as optical width of the forbidden band is, in fact, illegitimate, because its value is influenced significantly by a concentration of phonons. According to the barrier model at higher temperatures, an electron, on absorption of a photon, apart from the energy hf, also acquires the energy of a phonon ε, so that the total energy acquired is hf + ε. In this case, the energy in the region of the exponential tail is considered. Under these circumstances, for the absorption coefficient α, the relation (1) applies.

$$\alpha = A \exp\left[\frac{\mathrm{h}f - W_{peak}}{2kT}\right] \tag{7}$$

Suppose that the coefficient A is, as compared to the exponential term, only weakly temperature-dependent, and that the value of the exponent will have a dominant influence on the coefficient α. From the condition that the absorption coefficient α should have a constant, conventional value of $\alpha = 10^2$ cm^{-1}, we require

$$\frac{\mathrm{h}f - W_{peak}}{kT} = K \tag{8}$$

from which

$$\mathrm{h}f = W_{peak} + CT$$

where K is a constant, k < 0, and C = kK < 0, as in the region of the absorption tail. So, hf - W_{peak} < 0. Under these circumstances, the value hf represents the optical bandwidth E = hf, so that

$$E = W_{peak} + CT \tag{9}$$

It is obvious that at these conditions, the value C = d(hf)/dT < 0 represents the temperature coefficient of the optical width of a forbidden band. The linear dependence obtained fits well the data and dependences found experimentally.

Supposing that diverse values of absorption for different chalcogenide materials are primarily due to different values of the exponential term in the relation (7), the constant K will have almost the same value for these materials. (It is, however, the same as the assumption that the coefficients A are almost identical for different chalcogenides). Very close values of the temperature coefficient C = d(hf)/dT of these materials are a consequence of this as well. It is in good agreement with the values introduced.

Thus, the temperature dependence of optical width E of the forbidden band is not due to a real change of the bandwidth but due to the energy of phonons taking part in an absorption event. With increasing temperature, the contribution of phonons increases as well. This enables absorption of light with a lower energy of photons.

In the region of very high temperatures, deviations from linearity are observed (9). The optical width E decreases more rapidly than would be expected by the expression (9). Obviously, the cause of this effect is absorption of light on free carriers. In such a situation, the absorption coefficient (its value for optical width is 10^2cm^{-1}) consists of two items. Phonons participate only in one of them, which is now less than 10^2cm^{-1}. It corresponds to a lower energy level and, consequently, to a smaller optical width, E. In the low-temperature region, an influence of frozen phonons may also appear. These will be mentioned later.

Naturally, the concept of optical width is an issue of convention. We dare, however, to express doubts about the suitability of introducing such a designation for the value E. That is to say, it does not give a true picture of a real situation in the region of the forbidden band. In our opinion, a value obtained by extrapolation of the linear dependence (9) to the region of very low temperatures (T → 0 K) should instead be considered the optical width of the forbidden band.

Notes:

(1) The relation (2) can also be obtained in such a way that, according to (7), we express the coefficients α_1 and α_2 for two different temperatures, T_1 and T_2, and then apply the requirement $\alpha_1/\alpha_2 = 1$, assuming that the pre-exponential factors A_1 and A_2 are approximately equal, so that $A_1/A_2 = 1$ is true.

(2) For the coefficient C, its value can also be roughly estimated from the expression

$$C = Kk = \frac{\mathrm{h}f - W_{peak}}{T} \tag{10}$$

but the value W_{peak} is problematic in materials and is unknown in most cases. For this reason, it is better to determine C from the relation C = Δ(hf)/ΔT, where the value W_{peak} does not appear any more. On the contrary, the relation (10) enables us to determine the value W_{peak} for a semiconductor from a known value of the coefficient C. Apart from it, the validity of this consideration is restricted to a linear segment of the dependence E(T), and that, in our consideration, the pre-exponential factor A was assumed temperature-independent.

For example, for an amorphous semiconductor As_2Se_3 (at T = 343 K is hf = 1.5 eV and W_{peak} = 1.76 eV) we obtain C = -7.10^{-4} eV K^{-1}. The experimentally determined value (1) is C = -7.10^{-4} eV K^{-1}. This is really a very good agreement.

3.3 Influence of pressure on an optical width of the forbidden band in non-crystalline semiconductors

In the monograph [1], the reader can also read about the influence of all-round hydrostatic pressure on an optical width of the forbidden band. The authors state some "discrepancies" in this field of research, which, in their opinion, are "only hard to grasp". They are the surprising consequences that result for the optical width E of the forbidden band of a non-crystalline semiconductor from the thermodynamic relation

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\alpha_V}{\chi_k}\left(\frac{\partial E}{\partial p}\right)_T \tag{11}$$

where α_V is the volume thermal expansion coefficient and χ_k is the coefficient of volume compressibility of the semiconductor. These values are defined by the relations

$$\alpha_V = \frac{1}{V}\left(\frac{dV}{dT}\right)_p, \quad \chi_k = -\frac{1}{V}\left(\frac{dV}{dp}\right)_T$$

The authors analyze the experimental data, published in a number of papers [17-20], from a thermodynamic point of view, and they conclude that the first term $(dE/dT)_V$ on the right side of this equation must have an enormously high negative value in non-crystalline semiconductors. They find this very surprising, as this value is usually small in crystalline materials. At that, the values

$$\frac{\alpha_V}{\chi_k}\left(\frac{\partial E}{\partial p}\right)_T$$

are practically identical for amorphous and crystalline materials, and they are relatively very small.

From the point of view of a barrier model, this problem can be explained in a quite natural manner. While in crystals the change of the optical width is connected with a real change of the forbidden band, which is, first of all, due to a change of interatomic distances, it is different with non-crystalline semiconductors. In these, according to the barrier model, the change of the width E is, in the first instance, caused by a change of phonon concentration. This is strongly influenced by temperature, practically equally at the changes

$$\left(\frac{dE}{dT}\right)_p \text{ and } \left(\frac{dE}{dT}\right)_V$$

that is, with an isobaric as well as isochoric change. This is why the values must be comparable with each other and considerably higher than those in crystals. And since the first term is high, the other one must be high too.

The influence of pressure on the optical width E of the forbidden band rests in a dependence of the parameter W_{peak} on pressure, p. Pressure lowers the value of this parameter as it similarly does with the width of the forbidden band of a crystal. Therefore, the influence of pressure will be practically equal on both types of material. If a narrow enough pressure range is assumed, we can consider the dependence W_{peak}(p) as linear, so that

$$W_{peak} = W_{0peak} - k_p p \tag{12}$$

where k_p is a constant. After putting this into the relation

$$C = \frac{\mathrm{h}f - W_{peak}}{T} \tag{13a}$$

we obtain

$$C = \frac{\mathrm{h}f - W_{0\,peak} + k_p p}{T} \tag{13b}$$

or

$$CT = \mathrm{h}f - W_{0\,peak} + k_p p \tag{14}$$

Under the condition $\alpha = 10^2$ cm^{-1}, it will be E = hf. So it follows that

$$C = \left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_p, \quad k_p = -\left(\frac{\mathrm{d}E}{\mathrm{d}p}\right)_T \tag{15}$$

Based on relations (11), (14), and (15), it can be written

$$\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_V = C - \frac{\alpha_V}{\chi_k} k_p \tag{16}$$

Both terms on the right side of this expression are negative, as C is negative, and k_p is positive. At that, the second term on the right side is relatively very small while the first one is large. From this, the value $(\partial \mathrm{E}/\partial \mathrm{T})_v$ must have a still higher negative value.

There is no "discrepancy". It suits the purpose if the value E is assigned the right meaning ascribed by the barrier model, and everything becomes understandable. The heart of the matter is that with the non-crystalline semiconductors, the value E is strongly influenced by temperature at isobaric as well as at isochoric processes via phonons, which participate at the absorption event. The apparent disagreement relates to the fact that the above-defined optical width E of the forbidden band of a non-crystalline semiconductor does not actually represent any real width of a forbidden band of a non-crystalline material. An analogously defined optical width of a forbidden band on common crystalline semiconductors would express the real width of the forbidden band quite well, and the influence of temperature would be substantially lower. This difference seemed misunderstood by Mott and Davis [1].

4 Optical absorption from the point of view of a barrier model – low temperature range

At low temperatures (below T_o), absorption of light in a non-crystalline semiconductor can essentially take place only in a simplified form depicted in Fig. 4. It is a low-temperature mechanism of absorption. Only photons with sufficient energy, exceeding $2W$, can be absorbed by the material. There are not enough phonons with sufficiently high energies to realize the high-temperature mechanism of absorption (described in the preceding part), at which the forbidden band was overcome due to the sum of energies of photons and phonons.

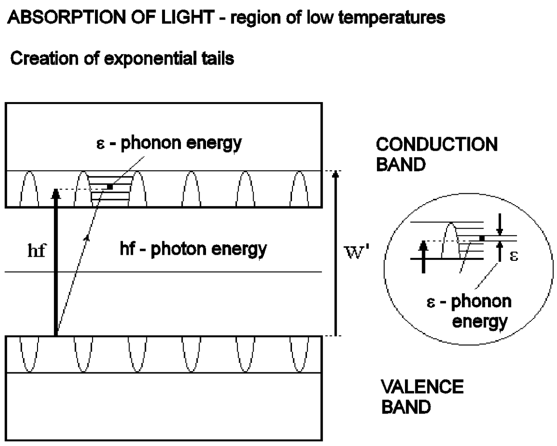

Fig. 4 The optical absorption in low-temperature region.

The ”skewed” optical transition of an electron (as depicted in Fig. 4) can be virtually divided into two parts [21]: The first part is a vertical transition onto an energy level inside its own localized region (without tunneling); the second part represents a horizontal tunneling transition onto a real level in an adjacent localized region. Thus, absorption of a photon in a low-temperature mechanism is connected with tunneling of the electron through a potential barrier.

At lower temperatures (below T_o), absorption of light in the vicinity of an optical absorption edge could principally run without a tunneling process, that is, within a single localized region. The probability, however, of such transitions is small due to a distinctly discrete character of the lowest levels, as well as to a small number of such levels in a single microregion. Therefore, absorption connected with tunneling to adjacent regions is more probable.

4.1 Tunneling through a parabolic barrier

In the case of a parabolic potential barrier (Fig. 5a), the dependence of potential energy $W(x)$ of an electron on its position can be denoted as

$$W(x) = -ax^2 + W_o \tag{17}$$

where the constant W_o means the height of the barrier from the bottom of the conduction band, and the quantity a determines the "narrowness" of the barrier. If we put (17) into a semi-classical approximation of a general formula for the probability of tunneling of a particle with mass m,

$$p(\varepsilon) \approx \exp\left\{-\frac{2}{\hbar}\int_{x_1}^{x_2} \langle 2m\,[W\,(x) - \varepsilon]\rangle^{1/2}\, dx\right\} \tag{18}$$

we obtain

$$p(\varepsilon \approx \exp\left\{-\frac{2}{\hbar}\int_{x_1}^{x_2} \left\langle 2m\left[-ax^2 + \ W_0 - \ \varepsilon\right]\right\rangle^{1/2} dx\right\} \tag{19}$$

where $\hbar$ $(= h/2\pi)$ is the Planck constant, and the difference $x_1 - x_2$ gives the barrier width on the energy level ε. The integration limits are a function of energy ε of the tunneling particle. They can be determined from the condition $W(x) = \varepsilon$, thus from the equation : $-ax^2 + W_o - \varepsilon = 0$. Its solution is

$$x_{1,2} = \pm\sqrt{\frac{W_o - \varepsilon}{a}} \tag{20}$$

Within the limits given by (20) the integral becomes

$$\int_{x_1}^{x_2} \left\langle\left[-ax^2 + W_0 - \varepsilon\right]\right\rangle^{1/2} dx = \frac{\pi}{2}\frac{W_0 - \varepsilon}{\sqrt{a}}$$

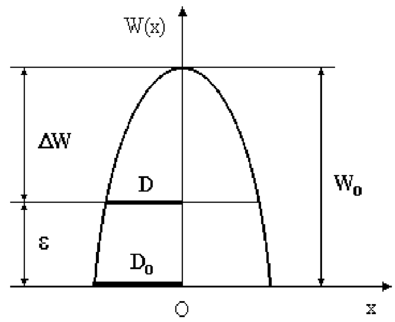

Fig. 5a The parabolic potential barrier - dependence of potential energy $W(x)$ of an electron on its position.

The probability of tunneling can be then expressed as

$$p(\varepsilon) \approx \exp\left\{-\frac{\pi}{\hbar}\sqrt{\frac{2m}{a}\,(W_0 - \varepsilon)}\right\} \tag{21}$$

or in the form

$$p(\varepsilon) \approx \exp\{-A\Delta W\} \tag{22}$$

where

$$A = \left\{-\frac{\pi}{\hbar}\sqrt{\frac{2m}{a}}\right\} \tag{23}$$

$$\Delta W = W_0 - \varepsilon \tag{24}$$

The quantity ΔW means the *"energy depth"* of the tunneling particle versus the peak of the parabolic potential barrier.

4.2 Probability of absorption

It may seem at first sight that phonons play no role in low-temperature absorption. However, it is not the case. The problem is connected with a clearly discrete character of energy levels in the region between barriers (below barrier peaks). A jump of an electron onto a real level of a neighboring localized region usually needs small "tuning", that is, a small correction of the photon energy by a certain value δW. This energy is supplied by low-energy phonons, which are also present in the material at lower temperatures. Apart from that, the transfer of an electron from one localized region to another is, in fact, always dependent on interaction with phonons.

The coefficient of optical absorption α, under the low-temperature mechanism described above, is, as can be supposed, proportional to the product of two probabilities: p_1 being the probability of tunneling through a potential barrier onto a corresponding energy level ε, and p_2 being the probability of occurrence of a phonon with the small correction energy δW. For probability p_1 of tunneling, we can write, according to (22)

$$p_1 \approx \exp[-A\Delta W] \tag{25}$$

The probability of occurrence of phonons with energy higher than δW can be expressed as

$$p_2 \approx \exp\left[-\frac{\delta W}{2kT}\right] \tag{26}$$

Thus, it can be written for the coefficient α

$$\alpha \approx p_1 p_2 \approx \exp[-A\Delta W] \exp\left[-\frac{\delta W}{2kT}\right] \tag{27}$$

Since, for the energy difference ΔW between the level corresponding to the peak of a barrier and the energy level on which the tunneling takes place,

$$\Delta W = 2W + W_o - \mathrm{h}f \tag{28}$$

we arrive at the expression

$$\ln \alpha = A\mathrm{h}f - B(T) - C \tag{29}$$

which is a mathematical expression for the exponential tail of optical absorption in a logarithmic scale. The term

$$B(T) = +\frac{\delta W}{2kT} \tag{30}$$

which depends on temperature, will cause a parallel shift of the straight lines towards lower absorption with decreasing temperature. Just this effect is typical for low-temperature absorption in non-crystalline semiconductors.

The change of behavior of exponential tails around T_o is caused by a change of mode (mechanism) of optical absorption with decreasing temperature. The increase of slope of the tails stops when the slope reaches a certain value, corresponding to the transition to a low-temperature absorption mode. The high-temperature absorption mode loses its significance and the low-temperature mechanism prevails. Naturally, the transition from one mode to another is continuous.

4.3 Comparison with the experiment

As it follows from experiment, the parameter A (that is, the slope of $\ln\alpha$ (hf)), which appears in (29), acquires a value in the range of 15-22 eV^{-1} for various amorphous semiconductors. This enables us to estimate the parameter and "narrowness" of the potential barrier using (23). An approximate limit obtained according to this formula is

$$0.1 \text{ J m}^{-2} < a < 0.2 \text{ J m}^{-2}$$

On the basis of the parameter a, electroabsorption can be explained as well (see section 5).

4.4 To the question of frozen phonons

Let us return to the question: Why, at lower temperatures, do the absorption curves cease to change their slope below a certain temperature, and only a parallel shift of the tails towards lower energies occurs? This phenomenon was explained in the above text by a transition from the high-temperature mechanism of absorption to the low-temperature one, connected with tunneling through potential barriers. However, questions can be asked: Can the so-called frozen phonons contribute to this phenomenon? How should such phonons be interpreted from the point of view of a barrier model?

A possible contribution of frozen phonons to absorption at lower temperatures does not contradict the barrier model in any way. Essentially, it can be understood in the following way: At very low temperatures, when there are just a few thermal phonons in the material, an absorption of a photon with an energy hf smaller than the width of the forbidden band can occur in such a way that the necessary difference in the energy of an electron is supplied by some defect (instead of a thermal phonon). The defect releases a certain dose of energy through its transition to a lower state. Thus, a frozen phonon is, in fact, a metastable state within an amorphous structure. The energy of the frozen phonon is released by an interaction of an electron with a defect (with the material structure), which triggers a transition of the material (defect) to a lower energy state. Naturally, absorption in the presence of frozen phonons leads to a gradual structural change in an amorphous solid, which is, up to some extent, an analogy of tempering. In this interpretation, frozen phonons can complement other explanations of mechanisms of absorption processes. After all, several mechanisms will participate in real processes related to absorption of light. The mechanism associated with frozen phonons is only one of them. Therefore, conflict among different absorption mechanisms is not essential in theoretical considerations, as they do not exclude each other; they may work simultaneously and in parallel.

4.5 Optical production of phonons?

Chalcogenide amorphous semiconductors are distinguished by a strong electron-phonon interaction. On absorption of light, a photo-production of phonons may also occur. They can influence the absorption process. Initially, low optical absorption can increase due to phonons produced by light itself, even at a low temperature. This process must play an important role in the measurement of absorption at very low temperatures. At low temperatures, the concentration of light-produced phonons can prevail over the concentration of phonons with a thermal origin. This phenomenon may apply in some crystalline chalcogenides, too.

5 Electroabsorption

Under electroabsorption, the influence of absorption of a non-crystalline solid by an external electric field is understood [1]. As experiments show, an increase of optical absorption in non-crystalline semiconductors is observed in a 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 the energy of the absorbed photon.

Kolomiec *et al.* [22] observed electroabsorption in the amorphous semiconductor As_2S_3. In their study [23], results of measurements of the absorption coefficient, as well as changes of the coefficient caused by the electric field, are presented for semiconductors As_2Se_3, $(As_2Se_3)_{0.95}(As_2Te_3)_{0.05}$, and $(As_2Se_3)_{0.91}(As_2Te_3)_{0.09}$. The measurements were carried out in the field of 10^7 Vm^{-1}. Similar results for $(As_2Se_3)_{0.95}(As_2Te_3)_{0.05}$ are presented in Mazec *et al.* [24].

5.1 Explanation of electroabsorption based on a barrier model of an amorphous solid

As said previously, absorption of light in the region of exponential tails at temperatures below T_o is connected with tunneling of an electron through a potential barrier. At that, the absorption coefficient is proportional to the probability of tunneling. As we will show, a strong electric field influences the tunneling probability of an electron through a barrier and, thus, the value of the absorption coefficient as well. This is the essence of the explanation of absorption on the base of a barrier model.

5.1.1 Tunneling through a barrier in an electric field

During tunneling of an electron through a barrier without an external electric field (see Fig. 5b), the energy of the electron does not change. In an external electric field, the electron energy will continuously increase or decrease depending on whether the tunneling process runs in the direction of the acting electric force or in the opposite direction. This is true at least in the one-dimensional (1D) case, which is considered now. The three-dimensional (3D) case will be treated later.

The probability of tunneling a particle with energy ε through a parabolic potential barrier of the type (17) in the absence of external electric field is described in a semi-classical expression by the formula (19). If tunneling takes place in a homogenous electric field with an intensity E, the electron energy ε will be a function of position [25]. In the case depicted in Fig. 5b, where the origin of the x-axis is placed in the middle of the barrier in question, it can be written

$$\varepsilon(x) = \varepsilon_o + eED \pm eEx \tag{31}$$

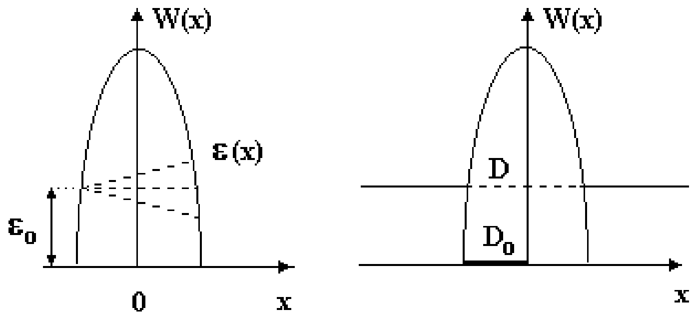

Fig. 5b The tunneling process trough potential barrier in electric field.

where $2D$ is the barrier width on the energy level ε_o, and ε_o represents the initial energy of the tunneling particle. The positive upper sign before the last term applies when the particle energy increases in the field; the negative sign applies on decreasing particle energy. (See Fig. 5b).

By putting the formulae (31) and (23) into (19), we obtain

$$p(\varepsilon) \approx \exp\left\{-\frac{2}{h}\int_{x_1}^{x_2}\left\langle 2m\left[-ax^2 + W_0 - \varepsilon_0 - eED - eEx\right]^{1/2} dx\right\rangle\right\} \tag{32}$$

The lower limit of integration, x_1, is obtained from the condition $W(x_1) = \varepsilon_o$, the upper limit, x_2, from the condition $W(x_2) = \varepsilon_o + eED + eEx_2$, whereby for $W(x)$, the relation (17) is true. Thus

$$x_1 = \sqrt{\frac{W_0 - \varepsilon_0}{a}} \tag{33}$$

$$x_2 = \frac{eE \pm \sqrt{(eE)^2 + 4a\left(W_0 - \varepsilon_0 - eED\right)}}{2a} \tag{34}$$

After performing the integration, we obtain

$$p(\pm E) \approx \exp\left[-A\left(W_0 - \varepsilon_0 \mp eED + \frac{(eE)^2}{8a}\right)\right] \tag{35}$$

where A is given by the formula (23). Supposing that the last term appearing in parentheses in the exponent of this formula is negligible compared to the previous one, the relation can be re-written as

$$p(\pm E) \approx \exp\left[-A\left(W_0 - \varepsilon_0 \mp eED\right)\right] \tag{36}$$

Such a transition is conditioned by fulfilling the inequality

$$\frac{(eE)^2}{8a} \ll eED \tag{37}$$

from which, after calculating the parameter a from the relation (33) and considering that $D = x_1$, we obtain

$$eED \ll 8(W_o - \varepsilon_o).$$

Its physical sense is immediately clear. In the region sufficiently far from the top, this condition is usually fulfilled satisfactorily. We will return to the question of the validity of this condition during the numerical examination of the problem.

If we put $E = 0$ in the relation (36), we obtain probability $p(0) = p$ of tunneling without an external field

$$p \approx \exp\left[-A\left(W_0 - \varepsilon_0\right)\right] \tag{38}$$

Therefore, the relation (36) can also be expressed as

$$p(\pm E) \approx p \exp\left[\mp AeED\right] \tag{39}$$

From this it is clear that the probability of tunneling in an electric field increases in one direction and decreases in another direction as compared with the original value for $E = 0$.

5.1.2 Derivation of relations for electroabsorption

According to the barrier model of an amorphous solid, the absorption coefficient in the temperature range below T_o is directly proportional to the probability of tunneling related to the respective energy level. However, two different probability values should be considered during absorption in electric field: the probability of tunneling p($+E$) in the direction of an acting electric force and the probability p(-E) in the opposite direction. The probability p($+E$) of tunneling in the direction of an electric force is greater whereas the probability p(-E) in the opposite direction is smaller than the probability p of tunneling without a field. These two changes caused by a field do not, however, compensate each other. This fact itself leads to the influence of the field on absorption and is thus the very reason of the electroabsorption.

As overall the probability P(E) of tunneling an electron in an electric field with intensity E, the sum p($+E$) + p($-E$) = p(E) will be considered for the one-dimensional (1D) case, where the probabilities p($+E$) and p($-E$) are given by (39). This is quite similar in the absence of an electric field, with $E = 0$. The overall probability of tunneling in the absence of a field, P(0), is thus P(0) = p(0) + p(0) = 2p(0) = 2p, where for p, the relation (38) holds true.

Let us further suppose that a relative change of absorption under the influence of the field is directly proportional to the relative change of the overall probability of tunneling, P, that is, that the relation

$$\frac{\Delta\alpha}{\alpha} = \frac{\Delta P}{P} = \frac{p\,(+E) + p\,(-E) - 2p}{2p} \tag{40}$$

applies. From (33) and (34) we obtain

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{2}[\exp\ (AeED + \exp(-AeED) - 2)] \tag{41}$$

Supposing that $AeED \ll 1$ *(this condition is usually fulfilled as we will demonstrate numerically)*, the exponential functions appearing on the right-hand side of this relation can be expanded into the Taylor series, limiting consideration to the first three terms of this expansion. In this way, we obtain

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{2}(AeED)^2 \tag{42}$$

If, for $D = x_1$, we substitute the relation (33), we obtain

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{2}(AeE)^2\frac{W_0 - \varepsilon_0}{a} \tag{43}$$

which says that the relative change (increase) of the absorption coefficient caused by an electric field is directly proportional to the square of intensity of the electric field. This agrees with observations.

The relation (43) enables us also to explain the dependence of relative absorption $\Delta\alpha/\alpha$ on the photon energy hf. However, although the photon energy does not appear explicitly in the indicated formula, the quantity ε_o depends on it. On optical absorption of photons with energy hf, the electrons excite onto the levels inside the conduction band, the highest of which rests at ε_o above the bottom of the conduction band. At that, the relation

$$\varepsilon_o = \mathrm{h}f - 2W \tag{44}$$

holds true, where $2W$ means the actual width of the forbidden band (for the low-temperature region). Substituting this value into (43), we obtain

$$\frac{\Delta\alpha}{\alpha} = \frac{(AeE)^2}{2a}hf + \frac{(AeE)^2\,(W_o + 2W)}{2a} \tag{45}$$

This relation is valid for the one-dimensional model of a sample. We will further show that the three-dimensionality of a real situation leads to the conclusion that $\mathrm{E}^2/3$ should be used in (45), instead of E^2. So we find

$$\frac{\Delta\alpha}{\alpha} = \frac{(AeE)^2}{6a}\mathrm{h}f + \frac{(AeE)^2\,(W_o + 2W)}{6a} \tag{46}$$

and thus, a dependence of the type

$$\frac{\Delta\alpha}{\alpha} = -C_1 \mathrm{h} f + C_2 \tag{47}$$

At that, the positive parameters C_1 and C_2 do not depend on the energy of the absorbed photon. Thus, the relative change of absorption decreases in a linear manner with the photon energy. It is a consequence of the negative sign before the positive value of C_1. This conclusion is in agreement with the experimental data [22-25]. The quantitative comparison will be given later.

5.1.3 Consideration of the "three-dimensionality" of absorption

In a one-dimensional model of a sample, an electron can move during tunneling only in the direction of the acting electrical force or in the opposite direction. Under three-dimensionality, an electron, due to tunneling on absorption in real amorphous material, can move in an arbitrary direction taking an arbitrary angle φ with respect to the vector of electric force. This also demonstrates the influence of the field on electron energy and, thus, on the probability of tunneling as well.

Further, we consider pairs of coupled tunneling processes of an electron; one in a particular direction, the other one in an opposite direction. Such pairs of "coupled" processes of tunneling exhibit different probabilities. For each pair of such inverse tunnel jumps, a relation of the type (39) can be derived which differs from (39) by the expression $E\ \cos\varphi$ instead of E. Similar substitution should also be carried out in the formula (7). For us, however, the average value of the quantity $\Delta\alpha/\alpha$, given by (35), is interesting. We obtain it by first substituting $E^2\cos^2\varphi$ for E^2, and then determining the average of $\cos^2\varphi$ for the angles φ within the range 0-π. It is shown easily that the average value of the expression $\cos^2\varphi$ is 1/3. So we arrive at formula (46), exactly what was to be proven.

5.1.4 Comparison with experiment

Let us first determine theoretical values of the constants C_1 and C_2, which appear in (47), for the amorphous material As_2Se_3 [1]. For calculation, we use data that come from the absorption measurements. The results obtained in this way will then be compared with the values derived from the electroabsorption measurements.

From the absorption measurements, the value A = 20 eV^{-1} results for the given material. From (23) comes a = 0,106 Jm^{-2}. Based on theoretical relations (46 and 47) for the field intensity E = 10^7 Vm^{-1}, we obtain $C_1 = -10.06.10^{-3}$ eV^{-1} or $C_2 = 18.1.10^{-3}$. In the theoretical calculation of C_2 we have put 2W + W_o = 1.8 eV, which is the width of the forbidden band of the semiconductor considered.

By numerical analysis of the results of electroabsorption on the semiconductor in question, the values $C_1 = -7.65.10^{-3}$ eV^{-1}, $C_2 = 14.7.10^{-3}$ are obtained [1]. As can be seen, the results obtained by both methods compare well. We stress that two different parameters were determined at the same time. It is also worth mentioning that two parameters, a and A, although having been derived from absorption, can be used successfully to explain electroabsorption too. And moreover, there was neither fitting nor any selection of auxiliary parameters.

The agreement of theory with experiment, as far as the dependence of relative absorption on field intensity, E, and on photon energy is concerned, was already mentioned.

6 Photoluminiscence in chalcogenide glasses

A common feature of majority of chalcogenide glasses, as far as photoluminescence is concerned, is a distinct Stokesian frequency shift of luminescence radiation as compared with the exciting radiation [4]. While optical excitation is most efficient in the region of photon energies, which are close to the forbidden band width (corresponding to the upper positions of the exponential tails of optical absorption), the energy of photons of luminescence radiation corresponds to about a half of this width. At that, only a minute value of the absorption coefficient corresponds to the frequency region of luminescence radiation. The clarification of this fact belongs to prestigious tasks of the physics of non-crystalline semiconductors. However, the barrier model of a non-crystalline semiconductor supplies a plausible physical explanation of the photoluminescence process in chalcogenide glasses.

6.1 Photoluminescence from the point of view of a barrier model

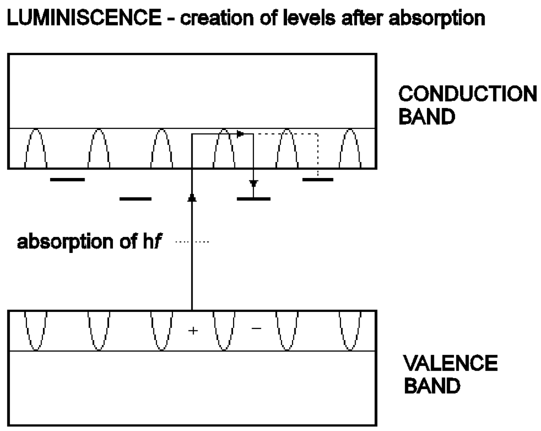

Fig. 6 The energy levels under bottom of the conduction band.

A true picture of the physical nature of photoluminescence in chalcogenide glasses from the point of view of a barrier model is given in Fig. 6 and Fig. 7.

Let us suppose that an electron in the course of optical transition, connected with tunneling, gets to an adjacent or a nearly region (Fig. 6) on an energy level that is just below the peak level of potential barriers. Under these circumstances, the probability of tunneling is high. As we already mentioned, the ”barrier region” of energies is also favorable for an electron-phonon interaction that supports the relevant optical transitions.

At lower temperatures, the excited electron will pass step-by-step on the lowest energy levels from a given localization region. However, in a low-energy state, the probability of its tunneling (and, thus, also its recombination with a hole) will be very small. At that, the carriers (electron and hole) created by absorption will be free only within their own localization region. The wave function of each will be localized 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 a couple arises. As a consequence, a new energy level in the forbidden band is formed. 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, but also in more distant regions. The height of these levels will depend on the distance from the "mother" grain. With increasing distance, these levels will approach the bottom of the conduction band.

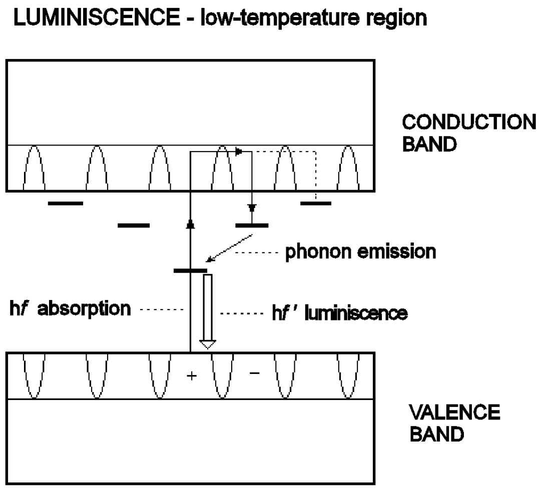

Fig. 7 The photoluminescence from point of view of a barrier model.

On Fig. 6 and Fig. 7, several of these levels are depicted on both sides of the hole (in a one-dimensional model). These levels create a kind of "funnel" of levels, which will play an important role in explaining the process of luminescence. A new energy level will appear not only in adjacent micro-regions but also in the original mother grain (Fig. 7) in which the hole rests. (For simplification we suppose that it did not move.) The electron level in the mother region is the lowest one from among all levels of the funnel. For the luminescence process, this level will be especially important.

At low temperatures, an optically excited electron that has been trapped in some close localization regions on some of these levels, will, with a high probability, gradually get back to the mother region, "descending the stairs of the funnel step by step" (Fig. 7). 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 is not 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, that is, on the lowest level of the funnel mentioned. In its own region, finally, a radiant recombination process with a hole occurs, which is connected with an emission of a luminescence photon. Due to a relatively small height of the mentioned ”final” energy level inside the depth of the forbidden band, the energy of the luminescence photon will be considerably smaller than the energy of the exciting photon. A distinct Stokesian shift will occur.

6.2 The temperature dependence of luminescence

Experiments show that the intensity of photoluminescence is most pronounced at low temperatures, while it decreases significantly with increasing temperature [1,2,4]. Based on the barrier model, this fact can be understood in this way: At low temperatures, an optically excited electron that was trapped in a close localization region begins to move gradually with high probability (by diffusion and tunneling) towards its mother region. At higher temperatures, however, there is a considerable probability of thermal activation of an electron trapped on levels of the ”funnel”. This increases the possibility of the electron departing from the respective hole and leaving the region of the funnel. Such an event may occur either by an activation thermal transition of the electron on energy levels lying above the barrier peaks, followed by moving away in the high mobility band, or by tunneling on the energy levels lying below barrier peaks. However, after departing from the mother localization region, there are many possibilities of non-radiant recombination on various defects of a non-crystalline semiconductor. Through these processes, the overall number of luminescence transitions is decreased.

However, the overall decrease of luminescence with increasing temperature may also be related to absorption of the exciting light by electrons resting on the excited levels, whether on the levels of the conduction band or on the levels belonging to the bound states of an electron-hole system. Moreover, a new absorption may occur sooner than the relevant electron can return to the mother region, that is, sooner than luminescence occurs. This process is more pronounced at higher temperatures, since the concentration of electrons at relevant levels is higher. (The relevant levels are more populated.)

6.3 Influence of a strong electric field on luminescence

An intense electric field, as known from experiments [4], lowers the level of photoluminescence. This fact can be explained by a strong field disturbing the bound pair electron-hole and thus draining the excited electrons from the range of the relevant hole. In this way, the probability of a non-radiant recombination on other types of defects increases, lowering luminescence.

6.4 Time attenuation of luminescence

Experiments carried out at low temperatures show that, at a constant intensity of exciting radiation, the intensity of luminescence in chalcogenide glasses gradually decreases with time. The cause may be that at low temperatures, during absorption of radiation, some electrons get to such states, in which they freeze on energy levels lower than those in the adjacent states. In this way, their transport is practically suspended at low temperatures. The frozen carriers create electric fields, the consequence of which is a decrease in luminescence. At that, the frozen carriers can participate in absorption too, however, without taking part in luminescence transitions.

7 Absorption in the region of a very low absorption coefficient

In the region of very low absorption of a non-crystalline As_2S_3, secondary exponential tails were observed [26, 1] with a considerably lower slope than it was in the case of the tails described above. In other words, in the region of very small absorption at low temperatures, the exponential tails with a high slope turn to small-slope tails.

This behavior of the absorption coefficient of the amorphous As_2S_3 can now be explained on the basis of the barrier model of the amorphous semiconductors. We suppose that the lower part of the absorption curve is caused by the absorption of light on the "induced" energy levels in the forbidden band. We suppose that these levels have the same physical essence as the levels depicted in the forbidden band on Fig. 7. These levels do not exist at 0 K, because they are caused by the existence of localized holes. These thermally "activated" levels create the tail of the density of state in the forbidden band. In our consideration we suppose that this density-tail has an exponential profile. The density of state is falling with decreasing energy. Simultaneously we suppose that the density of state in each energy region of the tail is directly proportional to the density of the localized holes. In these conditions we can write

$$\alpha \cong \exp[-K(2W - \mathrm{h}f)] \exp(-W/kT) \tag{48a}$$

or

$$\ln \alpha = K\mathrm{h}f - W/kT + \mathit{constant} \tag{48b}$$

where $2W - \mathrm{h}f$ is the energy depth of the level (below the conductivity band) that can reach electrons starting from the top of the valence band, if they absorb the energy hf. Most of the absorption occurs on these levels. This relation represents the mathematical expression of the lower exponential tail $\ln\alpha$(hf) in the region of very low absorption. It expresses simultaneously the parallel movement of the tail by increase of the temperature in the direction of the bigger absorption. The temperature movement of the tail by changing $T_1 \rightarrow T_2$ is

$$\Delta \ln \alpha = -\frac{W}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This movement is equal for the whole frequency region of the tail. The theoretical values are in good agreement with experiments.

8 Photoconductivity

The photoelectric conductivity σ of chalcogenide glasses usually exhibits activation dependence in a relatively wide range of temperatures [1, 4, 27]. A relation of the following type can thus express it:

$$\ln\sigma \approx -W_{photo}/kT \tag{49}$$

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

With a further increase in temperature, a distinct maximum can be observed [1, 27]. The curve shape at both sides of this maximum has an exponential character.

8.1 Photoconductivity from the point of view of the barrier model

In the following, we try to outline possible mechanisms of photoelectric conductivity in non-crystalline semiconductors from the point of view of the barrier model. According to [1, 27], the photoelectric conductivity shows a pronounced maximum in dependence on temperature. The shape of the curve σ(1/T) has an exponential character on both sides of this maximum.

Let us divide the problem into three temperature regions.

8.1.1 Mechanism M1

At low temperatures, the absorption of light is connected with the tunneling mechanism, which was described in section 4. The generation factor, which gives the number of carriers created in a volume unit per time unit, is proportional to the probability p of tunneling through the potential barrier on the respective energy level, as well as to the term related to phonon density at a given temperature T. On the basis of the expressions (26-28), it can then be written

$$G = C_1 \exp\left[-A\left(2W + W_o - \mathrm{h}f\right)\right] \exp\left[-\frac{\delta W}{2kT}\right]$$

where C_1 is a constant. At low temperature, the recombination mechanism is bimolecular, so that for the recombination factor R, which gives the number of the excess carriers, recombining in a volume unit per time unit, the following applies:

$$R = C_2 n^2$$

where C_2 is a constant. In a state of a dynamical equilibrium G = R, so that

$$n = C_3 \exp\left[-\frac{A}{2}\left(2W + W_o - \mathrm{h}f\right)\right] \exp\left[-\frac{\delta W}{4kT}\right]$$

where C_3 is a constant determined by the values C_1 and C_2. The symbol n means an equilibrium concentration (density) of the carriers in the conduction band, thus, in both of its sub-bands. At that, the concentration of carriers n_2 in delocalized states is expressed by

$$n_2 = n \exp\left[-\frac{W_o}{2kT}\right] \tag{50}$$

as the statistical distribution of the superfluous carriers between both sub-bands of the conduction band sets relatively quickly, due to a strong electron-phonon interaction. Electrical conductivity σ is directly proportional to the density n_2, so that

$$\sigma \approx n_2 \approx \exp\left[-\frac{A}{2}\ (2W + W_o - hf)\right] \exp\left[-\frac{\delta W}{4kT}\right] \exp\left[-\frac{W_o}{2kT}\right]$$

or

$$\ln\sigma \approx +\frac{A}{2}\mathrm{h}f - \frac{W_o + \delta W/2}{2kT} + C_5 \tag{51}$$

The activation energy of photoconductivity is

$$W_{photo} = \frac{W_o + \delta W/2}{2} \cong \frac{W_o}{2}$$

With increasing temperature, the photoconductivity increases exponentially.

8.1.2 Mechanism M2

Let us consider now the region of medium temperatures. Transfer of electrons from the valence band to the conduction band is now accomplished in the presence of phonons, as described in Section 3. Let us assume, just as in Section 3, that transitions to levels close to the peaks of potential barriers will dominate. Since

$$\mathrm{h}f < 2W + W_o$$

such a transition will be possible only if a phonon supplies the necessary energy

$$2W + W_o - \mathrm{h}f$$

The probability of occurrence of phonons with such a minimum energy and, accordingly, the probability of the relevant optical transition is roughly proportional to the expression

$$\exp\left[-\frac{2W + W_o - \mathrm{h}f}{2kT}\right]$$

The generation factor G is related to this expression as well. It can be written

$$G = K_1 \exp\left[-\frac{2W + W_o - \mathrm{h}f}{2kT}\right] \tag{52}$$

where K_1 is a constant. The equilibrium concentration n of the superfluous carriers in a conduction band will be determined by the condition G = R, where R is the recombination factor (depending on the type of recombination). If a concentration of the equilibrium thermal carriers is small compared with the concentration n of the superfluous carriers of optical origin, recombination of the superfluous carriers will have a bimolecular character, and for the factor R,

$$R = K_2 n^2 \tag{53}$$

where K_2 is a constant. For the equilibrium case G = R, using (52, 53), we obtain

$$n = K_3 \exp\left[-\frac{2W + W_o - \mathrm{h}f}{4kT}\right] \tag{54}$$

where $K_3 = \sqrt{\frac{K_1}{K_2}}$ is a constant.

Only the carriers dwelling in delocalized states, however, cause photoconductivity to a substantial extent. Their concentration will be

$$n_2 \approx n \cdot \exp\left[-\frac{W_o}{2kT}\right] \tag{55}$$

Electrical conductivity of a semiconductor, σ, will be proportional to the concentration n_2 from which, also using expression (54),

$$\sigma \approx \exp\left[-\frac{2W + 3W_o - \mathrm{h}f}{4kT}\right]$$

This result can also be written as

$$\sigma \approx \exp\left[-\frac{W_{photo}}{kT}\right]$$

where

$$W_{photo} = \frac{2W + 3W_o - \mathrm{h}f}{4}$$

is the activation energy of the photoconductivity. Thus, for photoconductivity

$$\ln \sigma \approx -\frac{W_{photo}}{kT}$$

8.1.3 Mechanism M3

At high temperatures, the concentration N of the equilibrium carriers is considerably higher than the concentration n of the excess carriers, and the recombination factor R will be proportional to the product $N \cdot n$, so that

$$R = K_4 N \cdot n$$

At that, for equilibrium concentration

$$N = K_5 \exp\left[-\frac{2W}{2kT}\right]$$

where K_4 is a constant. From the equilibrium condition, R = G and (52), it follows that

$$K_4 n \cdot K_5 \exp\left[-\frac{2W}{2kT}\right] = K_1 \exp\left[-\frac{2W + W_o - \mathrm{h}f}{2kT}\right]$$

from which

$$n = K_6 \exp\left[-\frac{hf - W_o}{2kT}\right]$$

where K_6 is a constant. Using this relation and relation (14), it can be written for photo-conductivity

$$\sigma \approx n_2 = n \cdot \exp\left[-\frac{W_o}{2kT}\right] = K_7 \cdot \exp\left[-\frac{\mathrm{h}f - 2W_o}{2kT}\right]$$

or equivalently

$$\ln \sigma \approx \frac{\mathrm{h}f - 2W_0}{2kT}$$

If $\mathrm{h}f > 2W_o$, then the numerator of the fraction on the right side of this equation will be positive, and with increasing temperature, the conductivity will decrease. This is an explanation for the shape of the curve $\ln \sigma(1/\mathrm{T})$ found experimentally, which shows a distinct maximum. At both sides of this maximum, photoconductivity decreases in an exponential manner. This is in agreement with observations.

For plenty of semiconductors, the mechanism M1 can pass directly to the mechanism M3. In such a situation, the mechanism M2 is not activated. Moreover, the individual mechanisms overlap to a certain extent, and they never appear in a "pure" form.

9 Jump mechanism of electric transport

We will show that the existence of potential barriers leads to the probability $\mathrm{p}_{jump}(x)$ of the jump of a carrier decreasing exponentially with the jump length x, so that

$$p_{jump}(x) \approx \exp[-\beta x] \tag{56}$$

where β is a constant. On the other hand, since the presence of phonons is also required in jumps between levels with a small energy difference δW, the probability of a jump will also be proportional to the expression

$$\exp\left[-\frac{\delta W}{kT}\right]$$

Therefore, the overall jump probability at the distance x will be proportional to the product

$$\exp[-\beta x] \cdot \exp\left[-\frac{\delta W}{kT}\right] \tag{57}$$

Exactly from this relation, the well-known Mott's law

$$\ln \sigma \approx \frac{1}{T^{1/4}} \tag{58}$$

for the jump conductivity [1,2] was derived. Thus, the barrier model can explain even this regular pattern.

9.1 Derivation of the relation (56)

Let us consider, for simplicity, tunneling of carriers through potential barriers at the bottom level of a barrier. Such a case of transport corresponds to low temperatures. At very low temperatures, however, many a carrier gets stuck in metastable positions between the barriers. Denote the probability of tunneling through a single barrier under these conditions by the symbol p. In the course of such tunneling, a carrier will move an average distance d, which corresponds to a mean dimension of a localization region. When tunneling to a double distance, $2d$, the carrier must tunnel through two potential barriers. The probability of such double tunneling is p^2. On tunneling to a distance $3d$, the probability of triple tunneling is p^3, etc. When tunneling to a distance $\mathrm{x} = \mathrm{n}d$, the probability of tunneling is $\mathrm{y} = \mathrm{p}^n$. We find easily that the values d, $2d$, $3d$, ..., create an arithmetic progression, while their corresponding values, p, p^2, p^3, ..., represent a geometric progression. If we turn to an exponential expression of this fact, we realize that an exponential dependence

$$y = p^n = p^{x/d} = [\exp(-\beta d)]^{x/d} = \exp(-\beta x)$$

belongs to the linearly increasing quantity $x = nd$.

At that, the relation $p = \exp(-\beta d)$ holds true, where $\mathrm{p} < 1$. This proves the relation (56).

An analogous process of tunneling to large distances may also concern admixture levels or levels of other defects. Potential barriers mutually isolate all energy states, although it is hard to depict this correctly in such figures as, for example, Fig. 1.

9.2 Notes on electric transport in non-crystalline semiconductors

The barrier model enables us not only to explain many optical phenomena taking place in non-crystalline semiconductors, but electric properties of these materials as well. These problems were solved in various studies [11, 12, 25, 31, 32]. They concerned ohmical transport in the region of low fields, as well as non-ohmical transport in high electric fields.

Certain model elements and concepts close to the described barrier model appear and are used in studies [33-40] in which problems of electric transport in amorphous semiconductors are solved by a method of relaxation constant.

10 Conclusion

The work here shows several non-traditional approaches to the problems of studying of electrical and optical phenomena of non-crystalline semiconductors. It stimulates further and deeper development of theoretical questions related to these problems. The process of development of the theory of non-crystalline materials will be obviously long and laborious. It will be a ”long distance run”. It is likely that more generations of physicists will have to take part in it. That it will not be an effort in vain is already indicated even by current, mostly optical, application possibilities of non-crystalline materials. Solar cells and holographic data recording belong to the prospective possibilities. The research of this vast group of materials, with a wide-ranging spectrum of their physical properties will undoubtedly bring many uses still unknown.

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