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Recombination processes, Meyer-Neldel rule and non-exponential decay in disordered semiconductors

I. BANIK
Slovak University of Technology, Faculty of CE, Department of Physics, Radlinského 11,
813 68 Bratislava, Slovak Republic

The article deals with the recombination dynamics of current carriers in disordered semiconductors. It searches for way out to better understanding processes proceeding in disordered semiconductors in steady system as well as in non-stationary one. A model is presented which enables one from unified viewpoint an explanation of Meyer-Neldel rule (including the specific effects connected with the MNR) and also essential features of the non-exponential relaxation.

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1. Introduction

Physical properties of disordered semiconductors are a subject of intensive investigations because of their broad scale of applications in electronics, optoelectronics, solar techniques, etc. [1-9].

In this article we deal with an explanation of two phenomena in a field of the theory of disordered semiconductors. Their essence is still unclear. The first is the empirical Meyer-Neldel rule (MNR) and the second the non-exponential relaxation.

Even though the MNR has been discovered in 1937, there does not exist a generally accepted explanation of it up to now, in spite of there fact that the phenomenon is frequent. It is typical not only for non-crystalline semiconductors (their electrical conductivity) but also for some diffusion processes, phase transitions, catalysis etc. The MNR phenomenon occurs also in modern electronics, e.g. in FET transistors and in CCD imagers.

Similarly, as to the second phenomenon: the non-exponential relaxation is still shrouded by mystery in case of disordered semiconductors (very often called “stretched exponential” relaxation).

As far as it is related to the MNR in the interpretation of the electric conductivity of disordered semiconductors, we recall some experimental facts as follows.

Semiconductors are characterized by the temperature dependence of their electrical conductivity. Most semiconductors exhibit an exponential temperature dependence of the conductivity, σ

$$\sigma = \sigma_0 \exp(-\frac{W}{kT}) \tag{1}$$

where σ_o is a constant and W – activation energy [1-10]. If the logarithm of the conductivity σ is plotted on the ordinate against the reciprocal of the temperature T on the abscissa, a straight line is obtained whose slope one may calculate the activation energy, W. The extrapolated intercept of this line on the ordinate axis yields the value of the pre-exponential factor, σ_o.

For many classes of materials, especially organic semi-insulators, chalcogenide glasses, amorphous silicon…experimental evidence suggest that a correlation exist between the activation energies and pre-exponential factors of the following form [11-28]

$$\ln \sigma_0 = bW + \ln \sigma_{00} \tag{2}$$

where b and σ_{oo} are constant. This relation can be written as

$$\sigma_0 = \sigma_{00} \exp(\frac{W}{kT_0}) \tag{3}$$

here $b = 1/kT_o$. The relation (3) gives the dependence of pre-factor σ_o on the activation energy W and represents Meyer-Neldel empirical rule. Equation (3) is often refereed to as the MN rule or the compensation rule. Constant σ_{oo} is often called the Meyer-Nedel pre-exponential factor and kT_o the MN characteristic energy.

For electric conductivity of upper mentioned group of substances it holds

$$\sigma = \sigma_{00} \exp(\frac{W}{kT_0}) \exp(-\frac{W}{kT}) \tag{4}$$

This rule holds in disorder materials when W is varied by doping, by surface absorption, light soaking or by preparing films under different conditions. This rule has also been observed for liquid semiconductors and fullerens. The validity of the MN rule has also been reported in the case of chalcogenide glasses. In the case of these glasses this rule is observed by variation of W on changing the composition of the glassy alloys in a specific glassy system. Electrical conductivity in dark is measured as a function of temperature for this purpose.

In works [11, 13, 14, 18] the change of activation energy W was caused under influence of an electric field or a light. Up to now there is not the generally accepted theory explaining the MN rule satisfyingly.

MNR has been observed not only with the electric conductivity but also with other processes such as: diffusion, crystallization, catalysis, adsorption, luminescence etc.

An attempt for explanation of MNR (normal MNR, inverse MNR, further MNR), based on the barrier-cluster model, has been published in [29-31]. The next information about the barrier-cluster model can see in [32-40]. A short description of existing models explaining MNR is in the review article [41].

1.1 Specific problems connected with the MNR

In addition to the information introduced up to now on the MNR, we recall here also some specific empirical acquaitance with the MNR. First of all we notice deviations from relations (2-4), observed at smallest activation energy values. In that region of activation energy there appears so called “the inverse MNR”.

The standard MNR is characterized by the function $\ln\sigma_o(W)$ (2). This function is corresponds to a straight line with a positive slope. In some cases, a deviation from this behavior appears in an interval of low activation energies W. In that interval a minimum at W_m appears on the graph $\ln\sigma_o(W)$. The function $\ln\sigma_o(W)$ decreases with W in the interval $0 \le W < W_m$. This decrease was named as the “inverse MNR” in the literature. Examples of this kind of dependences can be found in [41-47]. Published experimental dependences of $\ln\sigma_o(W)$ showed a decrease in the interval $0 \le W < W_m$. This decrease (for sufficiently low positive values of W) can be described approximately by a linear function

$$\ln \sigma_o = \ln\sigma_{oo} - cW \tag{5}$$

where the constant c is positive.

If $W >> W_m$, the function $\ln\sigma_o(W)$ can be depicted as a straight line with a positive slope. This line corresponds to the standard MNR.

As to an explanation of the inverse MNR is concerned one can meets some accesses (approaches) in [42-47]. Presently, there is no generally accepted theory explaining the inverse MNR.

A further open problem connected with the MNR lies in clarifying the so called “further MNR”. It consists in the explanation of experimentally observed correlation between the pre-exponential factor σ_{oo} - which appears in relation (6) - and the parameter E_{NM}. The correlation was discovered and described by Shimakawa and Abdel-Wahao [21] with different chalcogenide glasses. They found the following correlation between σ_{00} and E_{MN}

$$\ln \sigma_{00} = p + q.E_{MN} \tag{6}$$

Here p and q are constants. This relation between the Meyer-Neldel pre-factor σ_{oo} and Meyer-Neldel energy E_{MN} has become known as "further MNR". This problem was dealt with [48-57].

1.2 Problem of relaxation

Another phenomenon - important and unclear until now - which will be treated in this paper is the non-exponential relaxation in disordered semiconductors.

Recently, non-exponential decay of excited states of condensed matter has attracted much attention [58-60]. For example, Leonelli and Brebner have investigated time-resolved spectroscopy of the visible emission band in $SrTiO_3$, and found that the fast emission decay involves monomolecular process while the slow decay process involves bi-molecular process [59]. Itoh and Wada have studied photoconductivity in anatase crystal (TiO_2) induced by super-band-gap light excitation at 300 K, and found that the photocurrent decays nonexponentially and persists over 3000 seconds [60]. The time dependence can be partially fitted by a stretched exponential function:

$$I(t) = I(0)\exp\left[-(t/\tau)^{\beta}\right] \tag{7}$$

where τ =1,7 ~ 3,6 sec and β = 0,21 ~ 0,25 depending on the excitation energy. However, the physics underlying the phenomena is not clear and no reliable theory has been constructed that explains the origin of the stretched exponential behavior [61-64].

Below we will submit an explanation of connections between the MNR and the non-exponential (stretched-exponential) relaxation in disordered semiconductors.

2. An explanation of the Meyer-Neldel rule in disordered semiconductors

In this paragraph we present possible explanation of the Meyer-Neldel rule in non-crystalline semiconductors, e. g. in chalcogenide glasses, or in amorphous silicon and so on. It is based on assumption that the physical processes in non-crystalline semiconductors can be explained in a frame of the barrier-cluster model. This model was described in author’s foregoing works.

We assume that activation energy of a semiconductor influences recombination process of current carriers. Then we show than an increase of activation energy of a non-crystalline semiconductor decreases probability of recombination of carriers. This process necessary influences equilibrium concentration of conduction electrons (carriers) and subsequently electric conductivity of the semiconductor. As a result we obtain the relation identical with that one representing empirical Meyer-Neldel rule.

2.1 The barrier-cluster model

The barrier-cluster model assumes that there are not energy levels of significant concentration in forbidden band of a non-crystalline semiconductor. The barrier-cluster model assumes that there exist potential barriers in the non-crystalline semiconductor, which separate the certain microregions – clusters, and in this way, they hinder the transport of the carriers at the margin of the conduction or valence bands [32-40].

The barriers have also an influence upon the optical absorption at the optical absorption edge. The optical absorption at low temperatures is usually accompanied with tunneling of the carriers through the potential barrier.

2.2 Recombination

A transition of an electron from conduction band to valence band in a non-crystalline semiconductor proceeds predominantly by production of phonons. The total energy of produced phonons will correspond to that one released in electron transition. Further we shall assume that in a substance under consideration dominates phonon production which average energy is ΔE. It means that phonon production of other phonons is negligible. At the transition of an electron from conduction band to valence band gained energy $2W$ is used in production of N phonons each of them has energy ΔE so that $2W = N\Delta E$ or

$$N = 2W/\Delta E \tag{8}$$

Let w_1 be probability of production one phonon which energy is equal to ΔE. Probability $w_N$of production N phonons of equal energy due to the electron – lattice interaction will be

$$w_N = (w_1)^N \tag{9}$$

If we write down probability w_1 as

$$w_1 = \exp(-\varepsilon_1) \tag{10}$$

where ε_1 is a positive value, then probability w_N one can write with respect to (9,10) as

$$w_N = \exp(-N\varepsilon_1) = \exp(-\varepsilon_1 2W/\Delta E) = \exp(-bW) \tag{11}$$

where the constant b is given by

$$b = 2\,\varepsilon_1/\Delta E \tag{12}$$

Relation (11) gives at the same time the probability of recombination; it means the transition probability of an electron from conduction to valence band. That one is proportional to the probability of production N phonons and too proportional to the $\exp(-bW)$. With an increase of activation energy probability of recombination according to (11) exponentially decreases.

2.3 Equilibrium concentration of conduction electrons

An equilibrium concentration n of conduction electrons in a semiconductor is result of two opposite processes: one is a process of generation and the other one is a process of recombination of carriers. In equilibrium (or steady) state it holds

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{gen}} = (\mathrm{d}n/\mathrm{d}t)_{\mathrm{recom}} \tag{13}$$

A number of free electrons generated in a unit time is given as

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{gen}} = G = C_1\exp(-W/kT) \tag{14}$$

where C_1 is a constant.

For a recombination process we suppose that the relation

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{recom}} = R = n.C_2 \exp(-bW) \tag{15}$$

is valid. Here C_2 is a constant. The number of recombinations in a unit of time is proportional to the number n of the electron – hole (e-h) pairs as well as to the probability (11) production N phonons at the electron transition.

In equilibrium state it valid $R = G$, so that

$$C_1 \exp(-W/kT) = n.C_2 \exp(-bW) \tag{16}$$

From that relation follows for equilibrium concentration n of free carriers

$$n = C_{oo} \exp(bW) \exp(-W/kT) \tag{17}$$

where C_{oo} is determined by the constants C_1 and C_2.

2.4 Electric conductivity

It is known that electric conductivity σ is proportional to n: $\sigma \approx n$. If mobility of carriers is independend on activation energy W (or that dependence is negligible) one can write with respect to (17)

$$\sigma = \sigma_{oo.}\exp(bW) \exp(-W/kT) \tag{18}$$

respectively

$$\sigma = \sigma_o(W) \exp(-W/kT) \tag{19}$$

where σ_{oo} is a constant and

$$\sigma_o(W) = \sigma_{oo} \exp(bW) \tag{20}$$

If we put

$$b = 1/kT_o = 1/E_{MN} \tag{20b}$$

the relation (18) takes the form which is identical with dependence (4)

$$\sigma \approx \sigma_{oo} \exp(W/kT_o) \exp(-W/kT) \tag{21}$$

The relation (20) acquires the form

$$\sigma_o \approx \sigma_{oo} \exp(W/kT_o) \tag{22}$$

which expresses the Meyer-Neldel rule (3).

Remark: The relations (18, 19) which gives the MNR, can also be obtained in another way (as it will be shown at the end of the paper) than by using relations (14, 15). These relations correspond to the single-molecular type of the recombination. Alternative relations – which will be introduced later - correspond to the bi-molecular recombination. The MNR will hold also in this case. This implies that the reasoning about the inverse MNR and further MNR will also be valid.

3. Inverse Meyer-Neldel rule

3.1 Explanation of the inverse MNR based on the barrier-cluster model

We propose that the phenomenon of the inverse MNR is closely connected with a recombination radius of carriers in noncrystalline semiconductors. We interpret the recombination radius as follows: It is the maximal distance between carriers under which (at a given width $2W$ of forbidden gap) more or less localized particles *e* and *h* (electron-hole pair *e-h*) are still able to recombine in a disordered material. At larger distance of two particles *e-h* the recombination (at the same width $2W$ of forbidden gap) is impossible. Further we assume that the recombination radius in disordered semiconductors depends on the width $2W$ of the forbidden gap. Arguments for this assumption will be discussed later.

Our MNR model assumes (as before) that the carrier recombination is accompanied by emission of a series of monoenergetical phonons. The number N of emitted phonons is proportional to the width $2W$ of forbidden gap,

$$N \sim 2W \tag{23}$$

Our further hypothesis says: there is a correlation between the number N of emitted phonons at the recombination and the recombination radius. In another words, if there are more phonons at the recombination, then an electron will have a higher chance to recombine with a hole at some larger distance. Otherwise the recombination will not be realized.

Let the recombination distance R be proportional to the number N of phonons resulting from the recombination act ($R \sim N$). According to (23) $N \sim 2W$. This implies

$$R \sim W \tag{24}$$

At low activation energy W, the recombination radius will be small. It restricts probability of recombination. As a consequence the effect of the inverse MNR takes place.

The probability P_R of the presence of a hole in the sphere of radius R in the centre of which an electron is present - and then the probability of their mutual recombination is proportional to R^3 ; $P_R \sim R^3$. With respect to relation (23,24), one obtains

$$P_R \sim W^3 \tag{25}$$

The recombination probability will influence also the recombination radius and the quantity W^3.

3.2 Revised relation for recombination probability

The result (25) necessitates a correction of relation (11), which gives recombination probability of *e-h* pair in the existing standard model. Relation (11)

$$w_N \sim \exp(-bW) \tag{26}$$

has to be corrected in to the form

$$w_N \sim P_R.\exp(-bW) \tag{27}$$

and, with respect to (25) into the form

$$w_N \sim W^3 \exp(-bW) \tag{28}$$

Relation (28) represents the improvement of relation (11). For the number n of carriers recombined during the unit time, one can write

$$(dn/dt)_{\text{recom}} = R = n.C_3 W^3 \exp(-bW) \tag{29}$$

In the equilibrium state, it holds

$$(dn/dt)_{\text{gen}} = (dn/dt)_{\text{recom}} \tag{30}$$

for all free electrons whose number generated during unit time is given as

$$(dn/dt)_{\text{gen}} = G = C_1 \exp(-W/kT) \tag{31}$$

where C_1 is a constant. We obtain

$$C_1 \exp(-W/kT) = n.C_3 W^3 \exp(-bW) \tag{32}$$

From this relation it ollows for equilibrium concentration n of free carriers that

$$n = C_{oo} W^{-3} \exp(bW) \exp(-W/kT) \tag{33}$$

where C_{oo} is determined by the constants C_1 and C_3.
For conductivity $\sigma \sim n$, it is evidently valid that

$$\sigma = \sigma_{oo.}W^{-3}.\exp(bW)\,\exp(-W/kT) \qquad (34)$$

One can write

$$\sigma_o = \sigma_{oo}\,W^{-3}\exp(bW) \qquad (35)$$

or

$$\ln \sigma_o = \ln \sigma_{oo} + bW - 3\ln W \qquad (36)$$

This relation gives the dependence $\ln\sigma_o(W)$ in a wide interval of activation energies W, including low values of W. This is the generalization of relation (2) providing more complex view on the problem of the MNR.

At high values of W, the term bW dominates; $bW >> -3\ln W$ in relation (36), so approximately

$$\ln \sigma_o = \ln \sigma_{oo} + bW \qquad (37)$$

This relation corresponds to the standard MNR.
At sufficiently low values of the activation energy $bW << -\ln W$. In such a case, the relation

$$\ln \sigma_o = \ln \sigma_{oo} - 3\ln W \qquad (38)$$

may approximately be accepted. Relation (38) that we have obtained corresponds well to the decrease of $\ln\sigma_o$ with the increase of the activation energy W in the interval where the inverse MNR take place.

Remark: If one replaces the relation (36) by the relation $R = cW + R_o$, where R_o is a constant - the relation (36) will take the form

$$\ln \sigma_o = \ln \sigma_{oo} + bW - 3\ln(W+a) \qquad (39)$$

One can see that for $W \to +0$, $\sigma_0(0) = \sigma_{00}/a^3$. If $\sigma_{00}/a^3 > 1$ then in accord with experiment $\ln\sigma_0 > 0$ stays positive and finite. For W > 0 the course of the function (39) will be nearly similar to the function (36).

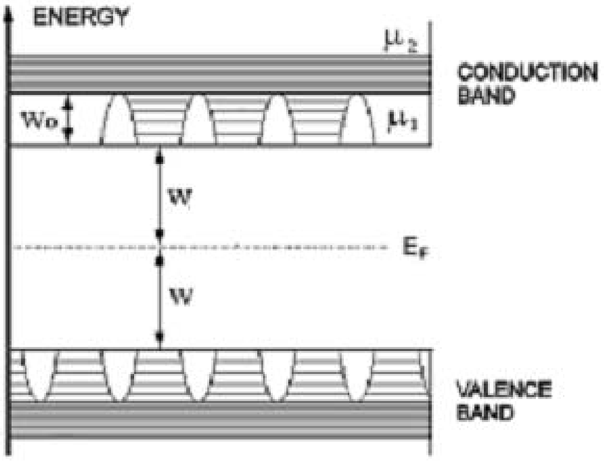

Fig. 1 Electronic spectrum of chalcogenide glass

4. Further Meyer-Neldel rule

In the present paragraph, we intend to explain the "further MNR" for chacogenide glasses. The explanation, concerning a disorder semiconductor, is based on the barrier-cluster model. The basic assumption of this model is that recombinant electron transitions from energies above the forbidden gap to energies in the valence band are accompanied with emitting a series of phonons (each with the same energy ΔE). The total energy of these phonons is equal to the width of the forbidden gap of the semiconductor. The number of the phonons emitted during the recombination process is higher if one chooses a wider forbidden gap. The total probability of the multi-phonon emission decreases with the growth of the number of the phonons. Consequently, the recombination probability of carriers decreases with growth of the width of the forbidden gap. The decrease in the recombination probability causes an increase of the equilibrium concentration of free electrons in the conduction band which means an increase of the electrical conduction. In this sense it is essentially possible to interpret the electrical conductivity in the agreement with the NMR.

The "further MNR" takes into account the fact that – if we explain it from the viewpoint of our barrier-cluster model – the phonons produced with the energy ΔE during the recombinsation process are intensely absorbed by free electrons with energies corresponding to a low-mobility sub-band inside the conduction band (i.e. in an interval where potential-energy barriers have to be considered).

Owing to the presence of the barriers, the electrons undergo a strong interaction with the phonons and this implies a considerable absorption of the phonons of the "recombination" origin. In the transport of electrons in the lower part of the conduction band, we have to respect a tunnelling through the barriers. Owing to the absorption of the "recombinant" phonons, some free electrons go over to higher energy levels, and this is connected with an increase of the tunnelling probability. This causes a remarkable enhancement of the mobility of electrons in this sub-band. We present a mathematical expression for the electrical conductivity of the disordered semiconductor in agreement with the empirical relation based on the "further MNR".

4.1 Barrier-cluster model of non-crystalline semiconductors

The barrier-cluster model assumes that an amorphous semiconductor consists of microscopic regions separated from each other by potential barriers [32-40]. The micro-regions are interpreted as clusters in this model. The model is based on the idea that some low-dimensional covalent systems, e.g. chalcogenides, could form special configurations (similar to fullerenes or nanotubes) – clusters. Cluster structures of chalcogenide glasses, and their physical properties, were studied in [8-9, 65-67] using computer's simulations. The concept of clusters enable to explain some important properties of chalcogenide glasses, such as the absence the EPR signal, as well as X- ray examination results.

The potential barriers impede (restrict) the transition of low energy conduction electrons from one region to another (Fig. 1, 2). Such electrons behave in regions between barriers in a similar way as electrons do in a crystal. The potential barriers can be drawn inside the conduction (or valence) band of an amorphous material as objects separating individual localized energy states at the edge of the band.

The electron levels between barriers, due to the small dimensions of the inter-barrier regions, exhibit a distinct discrete character. At the lower margin of the conduction band, a sub-band with carriers of low average mobility (μ_1) is created. The states with energies above the peaks of barriers are delocalized. They create a sub-band with a high average mobility (μ_2). Thus, it is clear that the activation energy of an amorphous material should not be defined by one value. At higher temperatures, it is determined substantially by the height of the potential barriers. 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 than its hight temperature value. Quite a similar situation occurs at the edge of the valence band.

4.2 Optical absorption

The potential barriers influence significantly the optical absorption at the optical absorption edge. We have to consider a strong electron-phonon interaction, which implies that an electron can also take the energy of a phonon at the optical transition and thus, the total energy taken by an electron equals the sum of the photon and phonon energies. This enables to explain the existence of exponential tails at the optical absorption, which penetrate deeply inside the forbidden band of the semiconductor [29-40]. Another important factor - as far as the influence of barriers on optical phenomena is concerned - is that the absorption of light in the region of the absorption edge at low temperatures is usually connected with a tunneling of carriers through potential barriers. Thus, the absorption process is influenced by the barriers.

Employing this idea we can explain successfully not only the creation of exponential tails at the optical absorption edge, but also their temperature dependences both at high and at low temperatures [32-40].

The optical absorption in most crystalline solids is characterized by a sharp edge of the absorption band. The absorption band near its border in the case of non-crystalline semiconductors is smeared out and creates a tail extending deeply into the forbidden band. As a rule the profile of the tail is exponential. The exponential tails at high enough temperatures often fit Urbach´s formula. The slope of the tails changes with a temperature decrease. At lower temperatures, the slope of the tails ceases to vary with a temperature decrease. However, a certain parallel shift towards lower absorption is observed.

4.3 The exponential tail

High temperature range: The starting point in the following discussion is an assumption that the potential barriers in non-crystalline semiconductors under proper conditions enable to explain the absorption of light with phonons participating in the energy exchange [32-40]. We assume that an electron in the optical transition receives not only the energy hf of a photon but also the phonon energy W_{phon} (Fig. 2). Thus, the whole received energy is

$$hf + W_{\mathrm{phon}} \qquad (40)$$

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

In principle, a photon can be absorbed only when its energy is sufficient to cause a transition of the electron into the conduction band. However it should be taken into account, that optical transitions on the energy levels lying just near 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 micro regions offer more possibilities of combination. However, one has to consider the tunneling of electrons through the barriers.

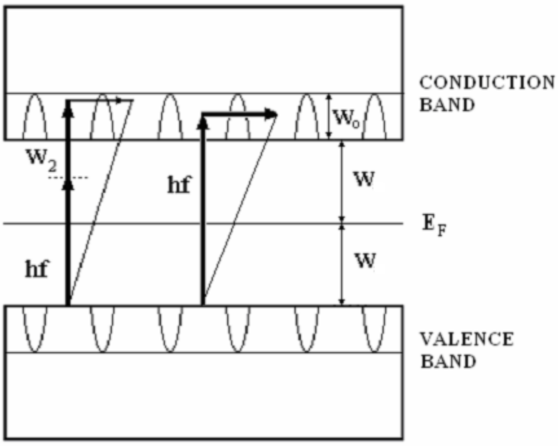

Fig. 2. Electronic spectrum of a non-crystalline semiconductor and optical transition at some higher (left) and lower (right) temperature

Under these assumptions, the transitions to levels just below the barrier peaks will be more probable for two reasons. The transitions to lower levels are less significant since the a small tunneling probability. The second reason consists in the strong electron-phonon interaction in the presence of the barriers. The number of electrons that can acquire advantageous energy from a phonon field depends on the temperature. The number of electron transitions during an irradiaton of the material by „low energy" photons (and thus, also the coefficient of optical absorption α) is directly proportional to the phonon concentration corresponding to the minimum energy needed for the transition. For the absorption coefficient, we can writte [30]

$$\alpha \sim \exp(hf/2kT) \qquad (41)$$

or, for a given (constant) temperature

$$\ln \alpha \sim hf + \text{const} \tag{42}$$

This is a mathematical expression of an exponential tail of the optical absorption [1,2]. However, the slope of the tails is also temperature dependent. Formula is of the same kind as Urbach's formula.

Low temperature range: At low temperatures, only photons with sufficient energy can be absorbed in the material. There are not enough phonons with sufficiently high energies to realize the high-temperature mechanism. The optical transition of an electron can be virtually divided into two parts [32-40]. The first (Fig. 2) is a vertical transition onto an energy level inside its own localized region; the second represents a (horizontal) tunneling transition onto a level in an adjacent inter-barrier region. Thus, absorption of a photon in a low-temperature mechanism is connected with the tunneling of the electron through a potential barrier. The barrier model explains in this case the temperature dependent parallel shift of the exponential tails [30].

According to [32-40] the probability p of a single tunneling of an electron across a parabolic barrier is proportional to the expression

$$p \sim \exp\,[-A\,(2W + W_o - (hf + CT))] \tag{43}$$
$$p \sim \exp\,(A\,(hf + CT))$$

A similar relation will be valid for the optical absorption coefficient α, so that

$$\alpha \sim \exp\,(A\,(hf + CT))$$

In this way, not only the existence of exponential tails of α at low temperatures can be clarified, but also their parallel temperature shift [32-40]. The barrier-cluster model allows to elucidate also other optical phenomena, including electroabsorption, photo-conductivity and photoluminesence, without an a priori consideration of exponential tails of the state density inside the forbidden gap of the disordered semiconductor. It allows also to explain the MNR.

The most important phenomena observed in non-crystalline semiconductors can be explained on the basis of the barrier-cluster model. This model allows explanation not only of a number of important optical and electrical features of chalcogenide glasses, but also the results of *X*-ray structure measurements. The closed-cluster structure can explain the absence of an ESR signal in the case of chalcogenide glasses. This model provides a new explanation for the density of states within the forbidden band of a semiconductor and explains why the attempts at identification of gap-states by various optical and other methods fail.

5. YM model of „further MNR“

Soon after the discovery of the „further MNR“ by Shimakawa and Abdel-Wahao [21] in different systems of chalcogenide glasses, similar strong correlation between the values of σ_{oo} and E_{MN}, namely

$$\ln \sigma_{00} = p + q.E_{MN} \tag{44}$$

was observed by Wang and Chen [48] for C_{60} films at different stages of the growth process and at different gate voltages of the field effect transistor. It has also been reported in *a*-Si:H produced by different techniques [49].

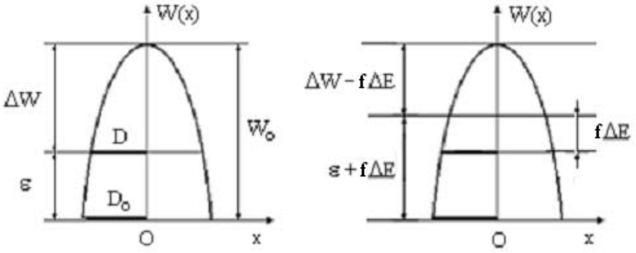

Fig. 3 The parabolic potential barrier

Recently, Mehta, Kumar and co-workers reported the "further MNR" in various chalcogenide glasses paying heed to thermally activated photoconduction, high-field conduction, and non-isotermal crystallization [50-54]. The correlation between σ_{00} and E_{MN} is explained in [55-57] by the multiple excitations associated with the phonon energy Δ*E*, as described above.

To explain the puzzle about the „further MNR“ Yelon and Movaghar proposed a YM model [55]. According to this model, the MNR arises naturally for kinetic processes in which Δ*E* is the energy of a kinetic barrier and for which Δ*E* is large compared to the energies of the excitations which contribute to the activation, as well as to *kT*. Yelon and co-workers suggest that optical phonons are the source of the excitation energy in such a process, showing the "further MNR". It is assumed that many phonons are involved in the trapping and de-trapping of electrons, either by a cascade or multi-phonon process. Yelon and Movaghar explained the MNR with an entropy term, which may change the pre-factor by many orders of magnitude. It applies equally well to crystalline and amorphous materials.

Emin [68] presented an extensive calculation of the optical – phonon assisted transition rates for a non-adiabatic hopping of electrons in a solid. He calculated the jump rates, associated d.c. conductivity, a.c. conductivity, and electric-field dependence of the d.c. conductivity, for a crystal in the strong-coupling small-polaron regime. He found that these transport properties manifest a qualitatively different behavior in the case when the temperature is above or well below the optical-phonon temperature. In the low-temperature regime, the energy-conserving processes, which involve the absorption of the minimum amount of vibrational energy, provide the dominant contribution to the thermally activated jump rates. At sufficiently high temperatures, the multi-phonon processes dominate the transition rate; the high-temperature jump rates are also activated, although with a different activation energy than that which characterizes the low-temperature regime. In the complementary weak-coupling regime, the jump rate is characterized by the dominance of those processes which involve the absorption or emission of the minimum number of phonons consistent with the requirements of energy conservation. Once again two distinct temperature domains manifest themselves: a low-temperature, thermally activated, regime and a high-temperature, non-activated, regime. Emin calculated the hopping rates due to multi-phonon effects as a lattíce-relaxation phase shift. As can easily be seen, the MN energy depends on ln *S*, whereas, the hopping rate depends upon exp(-*S*).

Emin´s calculatins give the prediction that

$$\ln\sigma_{00} = r - \exp\left(\frac{h\nu_o}{E_{MN}}\right) \tag{45}$$

Here it has been assumed that *r* is a constant. Yelon and Movaghar have found $r = -9.8$ and $h\nu_o = 78.2$ meV for the best fit of Eq. (45) to the data of Ref. [55-57]. They observed that the deviation of the data from this fit is very similar to that of Eq. (6), which also has two adjustable parameters.

6. Futher MNR from the point of view of the barrier-cluster model

6.1 Basic idea

The phenomenon for which the “further MNR” applies is caused – we believe – by the strong absorption of the phonons (that we characterize by the same value of energy) by the free electrons having energies in a low-mobility sub-band of the conduction band. The transport of electrons in this sub-band is via the tunneling across potential-energy barriers (Figs. 1, 2). The absorption of phonons by these electrons implies that electrons jump on higher energy levels at which the tunneling probability is enhanced. This means a remarkable enhancement of the mobility of the electrons. Having in mind disordered semiconductors, we will present a mathematical derivation of their electrical conductivity. As we will show, our final result for the electrical conductivity agrees well with the empirical “further MNR” (6).

NOTE: The free electrons in the low-mobility sub-band interact strongly with phonons right owing to the presence of the barriers. Hence we may state that the considerable absorption of the mono-energy phonons is of the “recombination type”.

6.2 Derivation of an expression corresponding to the “further NMR”

Let us consider an electron with an initial energy E_1 (Fig. 3). It can tunnel with this energy through a parabolic barrier with a probability p_1. When a phonon with the energy $\Delta E = E_2 - E_1$ is absorbed, the electron is excited on the energy level E_2. The greater tunneling probability in the low-mobility sub-band (below the top of the barriers) causes an enhancement of the electron mobility and then also of the electrical conductivity. Formally it implies an enhancement of the value of σ_{00} in expression (4) from the initial value σ_{00} to the value $\sigma'_{oo} > \sigma_{oo}$.

With the usual MNR (not with the “further NMR”), the formula for the conductivity reads

$$\sigma \sim \sigma_{oo} \exp(W/kT_o) \exp(-W/kT) \tag{46}$$

When phonons are absorbed, the value of the electron mobility becomes higher, and the formula for the electrical conductivity should read

$$\sigma' \sim \sigma'_{oo} \exp(W/kT_o) \exp(-W/kT) \tag{47}$$

with $\sigma' > \sigma$. We will show that

$$\sigma'_{00} = \sigma_{00} \exp[Af\,\Delta E] \tag{48}$$

Or

$$\ln\sigma'_{00} = \ln\sigma_{00} + Af\Delta E \tag{49}$$

where *f* is a constant, *A*-constant characterizing the parabolic barrier, and ΔE is the energy of the absorbed phonon. It follows from relations (12, 20b) that

$$\Delta E = 2\varepsilon_1 kT_o = 2\varepsilon_1 E_{MN} \tag{50}$$

where $E_{MN} = kT_o$ is the Meyer-Neldel energy. From relations (49, 50), we obtain the formulas

$$\ln\sigma'_{00} = \ln\sigma_{00} + 2Af\varepsilon_1 E_{MN} \tag{51}$$

or, if we employ the denotation $p = \ln\sigma_{oo}$, $q = 2Af\varepsilon_1$

$$\ln\sigma'_{00} = p + qE_{MN} \tag{52}$$

This formula is identical with the mathematical expression of the “further MNR” (6).

6.3 Derivation of the auxiliary relation (48) Tunneling through the parabolic potential energy barrier

In the case of a parabolic barrier (Fig. 3), the dependence of the potential energy $W(x)$ of an electron on its position can be expressed as

$$W(x) = -ax^2 + W_o \tag{53}$$

where W_o is the height of the barrier measured from the bottom of the conduction band and *a* is the "narrowness" of the barrier. If $W(x)$ is inserted into the semi-classical formula for the tunnelling probability of a particle, one obtains [32-40]

$$p(\varepsilon) \sim \exp(-A\Delta W) \tag{54}$$

Where

$$A = -\frac{\pi}{\hbar}\sqrt{\frac{2m}{a}}, \qquad \Delta W = W_o - \varepsilon \tag{55}$$

and m is the mass of the tunnelling electron. The quantity ε is the energy of the tunnelling particle measured with respect to the bottom of the conduction band (Fig. 3).

If the average energy of electrons is increased – as we can suppose - proportionaly to the ΔE (by $f\Delta E$, f is a constant), the value of the parameter ΔW decreases to the value $\Delta W - f\Delta E$. The tunneling probability is changed from the value p top the value p':

$$p \sim \exp(-A\Delta W) \tag{56}$$

$$p' \sim \exp[-A(\Delta W - f\Delta E)] \tag{57}$$

The change of the mobility of carriers

The change of the tunneling probability means that correspondingly the mobility of the carriers is changed from μ to μ'

$$\frac{\sigma'_{00}}{\sigma_{00}} = \frac{\mu'}{\mu} = \frac{p'}{p} \tag{58}$$

so that

$$\mu \sim \exp(-A\Delta W) \tag{59}$$

$$\mu' \sim \exp[-A(\Delta W - f\Delta E)] = \mu \exp[Af\,\Delta E] \tag{60}$$

It follows from relations (56-58) that

$$\sigma'_{00} = \sigma_{00}\,\exp[Af\Delta E] \tag{61}$$

This expression is identical with expression (48). Thus, we may state that relation (52), corresponding to the "further MNR", has been proved.

Remarks: The MNR in modern era

Pichon et al. [69] have reported an interesting technological application of the MNR. According to their analysis, the Meyer-Neldel effect in the sub-threshold region of thin-film transistor active layer could be a diagnostic tool to quantify the quality of the active layer. The implication of fhe Meyer-Neldel behavior for oxidizing gas detection in phthalocyanine thin films was proposed by Goldie [70]. Widenhorn et al. [17] have explained the temperature dependence of the forward current of a silicon diode in terms of the MNR. They have demonstrated that a real diode follows the MNR. It is shown that MNR is due to a shift of the current from ideal-diode to a high-injection-diode behavior.

Takechi et al. [71] suggested that an exponential tail-state distribution model combined with the MNR can be used to describe the sub-threshold characteristics of amorphous $\mathrm{InGaZn0_4}$ thin-film transistors (a-IGZO TFTs).

Most recently Ielmimi et al. [72] reported that the structural relaxation and crystallization in phase-change memory (PCM) devices could be interpreted by the MNR allowing for: (a) the development of a new temperature dependent analytical model for the structural relaxation and (b) a unified interpretation of the structural relaxation and crystallization, with a physical ínterpretation of the pre-exponential Arrhenius time by many-phonon thermal excitation. Similarly, Savransky and Yelon [73] reported the interpretation and consequences of the MNR for conductívity of a large number of memory cells of a GeSbTe phase-change memory alloy.

Okamoto et al. [74] derive universal MNR in the reciprocal temperature domain on the basis of the Laplace transform representation of thermally activated quantities, by a mathematical analogy with the generalized Kramers-Kronig relations in an adequate frequency interval. If the MNR bears universality, it should originate from certain mathematical grounds, similarly as the Kramers-Kronig relations link the real and imaginary parts of the complex susceptibility. Okamoto et al. tried to pursue the generalized MN relations in terms of the Laplace transform. They demonstrated that it appears in the limited temperature region specific to each physical system, when some realistic conditions are guaranteed.

NOTE: In review [41] the new observations in MNR are discussed in case of chalcogenide glasses.

7. Relation between MNR and relaxation

The Meyer-Neldel rule gives relations between physical quantities in steady states. In our case, this refers to the electric conductivity of a non-crystalline semiconductor (namely to its pre-exponential factor) and the value of the activation energy. On the other side, a non-exponential (stretched exponential) function describes the behavior of a non-stationary relaxation process. Despite that difference in their nature there is a well-defined relation between these phenomena.

Our goal is to suggest a sight on both phenomena. This attempt will also support the work [58], namely the "diffusive model" described there.

7.1 Diffusive model of relaxation

In work [58] a relaxation process in 2-D system (at surface recombination) has been studied by computer methods proceeding after an initial optical impulse activation of current carriers. The initial concentration of carriers before the impulse was considered as zero, and closely after the optical impulse application, the concentration was considered as a positive constant everywhere on the observed area of the surface. The initial distribution of carriers has been modeled by the method of "random shooting".

The above described model assumes the following:

Both types of carriers (*e* and *h*) execute chaotic Brownian motion in disordered materials. This motion is simulated by computer means.

Further, it is assumed that the recombination pair *e-h* has a non-zero probability to recombine only if an electron undergoing the Brownian motion approaches a hole at a sufficiently small distance (smaller than r_0). The circle of radius r_0 represents in the planar case a recombination region. One can imagine that such a relaxation circular area exists around each hole.

Probability P of the electron recombination per second is the same everywhere inside the circular area.

Computer simulation showed [58] that the relaxation had at first an exponential and later achieved a non-exponential (stretched exponential) behavior. The transition from the exponential to the stretched relaxation appears after a certain time, which depends on several parameters. The authors have investigated the influence of single parameters of the model on the relaxation process. In the modeling they have varied the radius r_0, the recombination probability P of the pair, and characteristics of the Brownian motion under consideration.

It seems to us that the model presented in [58] represents a plausible simplified view on relaxation processes in disordered semiconductors. Subsequently we intend to modify it. We do intend to submit an integrated (more complex) model, which should be able to explain not only relaxation but also MNR. The model that we want to elaborate will agree with our early published concept of the MNR based on the barrier-cluster model (BCM) of a non-crystalline semiconductor. The BCM has been presented in [29-40, 75-79].

7.2 Integrated MNR-R model

The integrated MNR-R (Meyer-Neldel rule – relaxation) model arose by the synthesis of two approaches: our MNR model [29-32] and relaxation model (published in [58]). Contrary to the original relaxation model, it takes some new important facts into consideration:

a) The integrated model postulates a dependence of the recombination probability P (close free carriers *e-h*) on activation energy W by the same way as it follows from our MNR model. This probability is proportional to exp($-bW$) according to relation (11)

$$P \sim \exp(-bW)$$

b) The integrated model (contrary to the original one) permits also to study phenomena at which are simultaneously effective both, thermal and optical excitation. These phenomena are either of steady as non-steady type. This enables to model also processes connected with MNR.

c) The integrated model takes into consideration a dependence of the recombination probability P on the radius range in accordance with the relation (25). This way explains the essence of the "inverse MNR" phenomenon.

d) Contradictory to the original 2D relaxation model, the integrated model has generally a 3D character. The recombination regions are not circular surfaces but spheres of radius r_0.

e) "The further MNR" phenomenon can also be included into the integrated model. This is connected with an increase of the mean mobility of free carriers, caused by absorption of mono-energetic phonons produced at recombination. This leads to an increase of the electric conductivity.

7.3 The relaxation from point of view of the integrated model

If a certain concentration of carriers (constant in the whole volume of a semiconductor) is excited by an optical pulse, then in the first phase of relaxation will be always dominate the recombination of the carriers which have been created directly inside recombination regions. This first stage of the relaxation development will always have an exponential course. An expressive recombination will become observed at high free carrier concentrations, when majority free electrons will occur in the recombination regions. This stage of the process will have a short duration at low concentrations. Soon after the beginning of the relaxation a carrier deficit will appear. The diffusive (Brownian) flow of carriers into those regions from their neighborhood will slow down. The phase of non-exponential relaxation begins.

Validity of relations (14, 15) ergo (thus) relations

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{gen}} = C_1\exp(-W/kT \tag{62}$$

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{recom}} = n.C_2 \exp(-bW) \tag{63}$$

leads at the stationary state to relations (3,4), which express the MNR. From (63) it follows that a relaxation process in a semiconductor will have an exponential course

$$n(t) = n_0 \exp(-Ct) \tag{64}$$

where C is a constant. Such a case is in principle occurs when certain conditions are fulfilled. Very often non-exponential relaxations are observed. Our relations (62, 63) such eventuality do not offer. How can this discrepancy be explained?

Two recombination variants are hidden here. The relation (63) corresponds to a mono-molecular recombination. Everything indicates that this sort of recombination dominates at high free carrier concentrations in a semiconductor. It justifies the assumption that nearby *e-h* pairs are created.

7.4 Two types of the relation between NMR and R

The type of the recombination (whether it is single- or bi-molecular) depends on the dominant factor determining the rate of the recombination. If the main hurdle of the recombination process is the Brownian diffusion (which enables the production of near *e-h* pairs), then the recombination process is bi-molecular. If the main reason of why the rate of the recombination is limited is a small probability P for the recombination of electrons with near holes, then the recombination is single-molecular. The deficit dn of *e-h* pairs due to their recombination is proportional to the number n of the pairs. This is a consequence of a constant probability P for each pair. When all (or almost all) carriers are to be paired, an exponential character of the relaxation follows.

It should be emphasized that the relation between the NMR and R is markedly different with low and high concentrations of the carriers in disordered semiconductors. If the carrier concentration is sufficiently high (from the viewpoint of the integrated model), the preponderant majority of free electrons are in recombination regions. The recombination is single-molecular and relations (62, 63) hold. The validity of the MNR is connected with an exponential relaxation process. The electrical conductance of the sample is proportional to the total number of the free electrons in the whole volume of the sample. However, the number of recombination events is proportional to the number of electrons finding themselves in the recombination regions.

If the recombination region penetrates almost the whole volume of the sample, the calculations under considerations will be approximately the same. The relaxation of the electrical conductivity will be exponential and the NMR will hold for it. When the concentration decreases during the relaxation, the character of the relaxation becomes changed from the exponential to a non-exponential one. Simultaneously the validity of the NMR ceases to hold, or one may say, its validity is restricted to some relatively narrow interval of the electrical conductivity.

7.5 Analytical approximation of the nonexponen tial relaxation and MNR

At lower carrier concentrations the recombination possesses a bi-molecular character. In this case, relation (63) can be replaced by the relation

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{recom}} = n^2.C_2 \exp(-\, bW) \qquad (65)$$

The production of neighbouring pairs by the mechanism of Brownian motion will be at low electron concentrations approximately proportional to the product $n_1.n_2 = n^2$ where $n_1 = n_2 = n$ is electron (hole) concentration. This is so despite that the intrinsic carrier the character of the recombination in the recombination regions alone is mono-molecular.

Solely from a mathematical viewpoint, two equations suggest when the MNR rule is valid and simultaneously, when the relaxation possesses a non-exponential character. They read

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{gen}} = C_1 \exp(-2W/kT) \qquad (66)$$

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{recom}} = n^2.C_2 \exp(-\, bW) \qquad (65)$$

In the stationary case, these equations give the normal-MNR

$$\sigma = \sigma_{oo}.\exp(b'W) \exp(-W/kT) \qquad (18b)$$

or

$$\sigma_o \approx \sigma_{oo} \exp(b'W) = \sigma_{oo} \exp(0.5\, bW) \qquad (20b)$$

so that relations of type (3, 4) are still valid in this case. Consequently, the previous considerations - concerning inverse MNR and further MNR – maintain their validity.

From (66) it follows that after a certain initial carrier excitation,

$$n = \frac{1}{Kt + \dfrac{1}{n_0}} \qquad (67)$$

where $n(t = 0) = n_o$ and K is a constant. The obtained relation (67) does not describe the stretched exponential course but the non-exponential course similar to it in many respects (sufficiently large t). The difference of this course from the stretched exponential one, which is observed in the modelling according to the work [58], should consist most likely in details the influence of the Brownian motion. Relation (65) does not include all details of the Brownian motion. Probably this is the cause of why the relaxation process resembles only in a limited sense the stretched exponential one.

8. Discussion

We suppose that the best approach, leading to the understanding of the relation between the MNR and relaxation, is one which is given by the integrated MNR-R model. This model, instead of analytical results, gives only numerical ones, and this is disadvantageous. The best feature of the integrated model is that it expresses details connected with the Brownian motion of particles. We suppose that just as a result of the Brownian motion of particles, the relaxation possesses frequently exhibit a stretched exponential course. (It is in agreement with [58].)

With the modeling according to the integrated MNR-R model, no input information is given concerning the type of recombination. However, the type of the thermal generation has to be given. Then a problem arises, because we have two different relations for the thermal carrier generation at the mono-molecular and bi-molecular mechanism of the recombination. It is a dilemma that we are unable to answer yet.

The application of two different formulations represents the only possibility how to avoid a paradox to which another way of thought could lead. For the moment, it seems to be possible to solve the problem separately – first for one concentration region and then for another – as these come out from the integrated model. In an interval of low carrier concentrations, the recombination seems to be bi-molecular.

In a case of low concentrations - in agreement with relation (65, 66) - the validity of the MNR is unequivocally accompanied by a non-exponential type of relaxation in a broad interval (several orders) of values of the electric conductivity. It appears that the majority of published works deal just with this second case.

On the other side, relation (62) is here replaced by relation (66) for the thermal excitation of free carriers. The question arises: Is such an expression of a thermal excitation in disordered materials acceptable?

We point out: the concept of phonons in disordered semiconductors is always open. We leave this question open. This is a subject for discussion. The integrated model suggests means for testing this problem. The model includes processes which we are not able to describe in a form of equations. These processes we can quantitatively describe by using numerical modeling methods. Such modeling does not offer an analytical expression, which is considerable disadvantage. Then one relies on compromises.

It is to be stressed that in integrated model the type of the recombination is neither given nor postulated. It results from mechanism of model alone.

The relations (65, 66) offer an explanation of MNR and of the non-exponential relaxation in large intervals of temperatures and activation energies. This agrees with reality. Relation (66) is valid also when modeling is implemented in frame of the integrated model. This model may become what enables a good understanding of processes in disordered materials. Non-exponential relaxation due to Brownian motion according to the relation (67) perhaps can be modified into the expression of stretched exponential form.

9. Conclusion

This paper offers a reader several views concerning relation between MNR and relaxation in disordered semiconductors. We have made an attempt to create a unified view on two significant and characteristic phenomena observed in disordered semiconductors. We bear in mind the clarification of the essence of the Meyer-Neldel rule and inquire the relaxation in disordered semiconductors.

The starting point of the present consideration is the model MNR described in preceding works by author and also the diffusive model of relaxation reported in work [58]. The two views presented above are unified in the suggested integrated MNR-R model. In this work essential features of this model are described. On the ground of this model it will be possible by the use of numerical methods to model both stationary and non-stationary processes in disordered semiconductors under conditions of optical and thermal excitation of current carriers. At the moment the model is subjected to a futher elaboration. Results obtained will be published in the next author's works. Of course, many questions remain still open.

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[*] Corresponding author: ivan.banik@stuba.sk