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Meyer-Neldel rule and further Meyer-Neldel rule in chalcogenide glasses from point of view of barrier-cluster model

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The objective of the paper is to present a consistent explanation of the Meyer-Neldel rule (MNR) together with the “further MNR”. The explanation, is based on the barrier-cluster model and the assumption that recombination are accompanied with emitting a series of phonons (each with the energy ΔE). The total probability of the multi-phonon emission decreases with the growth of the number of the phonons. The “further MNR” takes into account the fact that the phonons produced during the recombination process are intensively absorbed by free electrons in sub-band of low average mobility.

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1. Introduction

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

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

where σ_o is a constant and W – activation energy [1-6].

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 determines the activation energy W. The point intersection of this line with the ordinate axis yields the value of the pre-exponential factor, σ_o.

For many classes of materials, especially organic semi-insulators, chalcogenide glasses, and amorphous silicon samples experimental evidence suggests that a correlation exist between the activation energies and pre-exponential factors of the form [7-23]

$$\ln \sigma_0 = bW + \ln \sigma_{00} \qquad (2a)$$

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

$$\sigma_0 = \sigma_{00} \exp(\frac{W}{kT_0}) \qquad (2b)$$

where

$$b = 1/kT_o \qquad (3a)$$

The parameter

$$E_{MN} = kT_o \qquad (3b)$$

is often called the Meyer-Neldel characteristic energy. From relations (3a, 3b) it follows that $b = 1/E_{MN}$.

The relation (2b, 3) gives the dependence of the pre-factor σ_o on the activation energy W and represents the Meyer-Neldel empirical rule (called also the compensation rule). The constant σ_{oo} used to be called the Meyer-Nedel pre-exponential factor.

For the electrical conductivity of the above mentioned materials it holds that

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

This rule is valid in disorder materials even when W is varied by doping, by surface absorption, by illumination of samples or by preparing films under special conditions. This rule has also been observed with liquid semiconductors and fullerens. Moreover, the validity of the MN rule has been reported with chalcogenide glasses. In the case of glass alloys this rule was observed when W varied with a change of their composition. The electrical conductivity in the dark was measured as a function of temperature for this purpose. In works [7, 9,10,14] the change of the activation energy W was obtained by the influence of an electric field or by light.

The MNR was first described by W. Meyer and H. Neldel in 1937 [16]. Up to now there does not exist a generally accepted theory explaining satisfactorily the MN rule.

Shimakawa and Abdel-Wahao [24] reported an observation of the MNR with different chalcogenide glasses. They found the following correlation between

σ_{00} and E_{MN} :

$$\ln \sigma_{00} = p + q.E_{MN} \tag{5}$$

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 [25-34].

In the present paper, we intend to explain the MNR and 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.

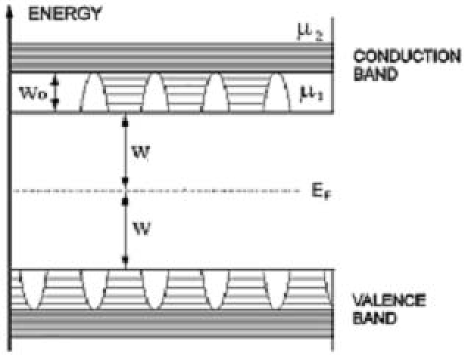

Fig. 1 Electronic spectrum of chalcogenide glass

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”.

2. Barrier-cluster model of non-crystalline semiconductors

2.1 Barrier-cluster model – basic information

The barrier-cluster model assumes that an amorphous semiconductor consists of microscopic regions separated from each other by potential barriers. [35-46]. The microregions 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 [47-51] 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.

2.2. 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 [35-46]. 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 [36, 45, 46].

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.

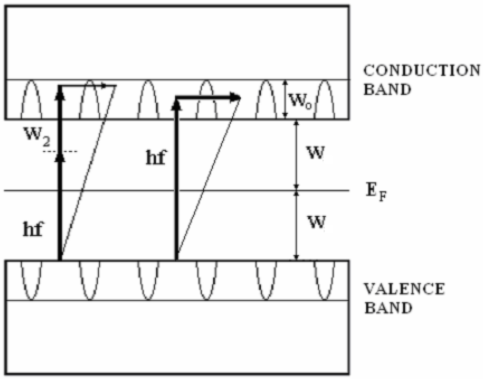

Fig. 2 Electronic spectrum of a non-crystalline semiconductor and optical transition at some higher (left) and lower (right) temperature

2.3 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 [35-46]. 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

$$hf + W_{\text{phon}} \tag{6}$$

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.

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 is small. 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 [36].

$$\alpha \sim \exp(hf/2kT) \tag{7}$$

or, for a given (constant) temperature

$$\ln \alpha \sim hf + \text{const} \tag{8}$$

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 [36]. 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 [36]

According to [35, 43,45, 46] the probability p of a single tunneling of an electron across a parabolic barrier is proportional to the expression

$$p \sim \exp\left[-A\left(2W + W_o - (hf + CT)\right)\right] \tag{9}$$
$$p \sim \exp\left(A\left(hf + CT\right)\right)$$

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

$$\alpha \sim \exp\left(A\left(hf + CT\right)\right)$$

In this way, not only the existence of exponential tails of α at low temperatures can be clarified, but also their parallel temperature shift [35-46]. 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.

3. The explanation of the meyer-neldel rule in chalcogenide glasses

We assume that the activation energy of a disordered semiconductor is a clue parameter in the theory of the recombination process of current carriers. We will show than an increase of the activation energy of a non-crystalline semiconductor lessens the probability of the recombination of the carriers. This increase necessarily affects the equilibrium concentration of the conduction electrons (carriers) and subsequently the electric conductivity σ of the semiconductor. We will obtain theoretically a relation for σ identical with what has been known as the empirical Meyer-Neldel rule.

3.1 Dependence of conductivity *σ* on activation energy *W*

The barrier-cluster model assumes that there are no energy levels of significant concentration in the forbidden band of a non-crystalline semiconductor.

A transition of an electron from the conduction to valence band in a non-crystalline semiconductor proceeds predominantly by some production of phonons. The total energy of produced phonons corresponds to that one released in electron transitions. Further we shall assume that in a substance under consideration production of phonon with an average energy ΔE sominates. It means that production of other phonons is negligible. The energy $2W$ gained during the transition of an electron from the conduction to valence band is used up in the production of n phonons. As we assume that each of them has energy ΔE, we write $2W = n\Delta E$ or

$$n = 2W/\Delta E \qquad (10)$$

Let w_1 be the probability of producing one phonon of energy ΔE. The probability w_n of producing n phonons of this same energy (due to the electron – lattice interaction) will be

$$w_n = (w_1)^n \qquad (11)$$

If we write down the probability w_1 as

$$w_1 = \exp(-\varepsilon_1) \qquad (12)$$

where ε_1 is a positive value, then probability w_n can be written as

$$w_n = \exp(-n\varepsilon_1) = \exp(-\varepsilon_1 2W/\Delta E) = \exp(-bW) \qquad (13)$$

where the constant b is given by

$$b = 2\,\varepsilon_1/\Delta E \qquad (14)$$

Relation (13) gives in fact the probability of a recombination; it means the transition probability of an electron from the conduction to valence band. This is proportional to the probability of producing n phonons, i.e. proportional to the exp($-bW$). With an increase of the activation energy, the probability of the recombination according to (13) exponentially decreases.

3.2 Equilibrium concentration of conduction electrons

The equilibrium concentration n of the conduction electrons in a semiconductor is a result of two opposite processes: the a process of generation and the process of the recombination of carriers. In the equilibrium state it holds

$$(dn/dt)_{gen} = (dn/dt)_{recom} \qquad (15)$$

The number of free electrons generated during a unit time is given as

$$(dn/dt)_{gen} = G = C_1\exp(-W/kT) \qquad (16)$$

where C_1 is a constant.

For the recombination process we suppose that the relation

$$(dn/dt)_{recom} = R = n.C_2 \exp(-bW) \qquad (17)$$

is valid. Here C_2 is also a constant. The number of recombinations per unit time is proportional to the number n of the electron – hole (e-h) pairs as well as to the probability (13) production n phonons at the electron transition. In the equilibrium, $R = G$, so that

$$C_1 \exp(-W/kT) = n.C_2 \exp(-bW) \qquad (18)$$

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

$$n = C_{oo} \exp(bW) \exp(-W/kT) \qquad (19)$$

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

3.3 Electrical conductivity

It is known that the electrical conductivity σ is proportional to n: $\sigma \sim n$. If the mobility of carriers is independent of the activation energy W, one can write with respect to (19 14) the relations

$$\sigma = \sigma_{oo}.\exp(bW) \exp(-W/kT) \qquad (20)$$

or

$$\sigma = \sigma_o(W) \exp(-W/kT) \qquad (21)$$

where σ_{oo} is a constant and

$$\sigma_o(W) = \sigma_{oo} \exp(bW) \tag{22a}$$

If we put

$$b = 1/kT_o \tag{22b}$$

the relation (20) takes the form which is identical with dependence (4)

$$\sigma \sim \sigma_{oo} \exp(W/kT_o) \exp(-W/kT) \tag{23}$$

The relation (22) acquires the form

$$\sigma_o \sim \sigma_{oo} \exp(W/kT_o) \tag{24}$$

which expresses the Meyer-Neldel rule (2b...3).

4. YM model of „further MNR“

Soon after the discovery of the „further MNR“ by Shimakawa and Abdel-Wahao [24] in different systems of chalcogenide glasses, similar strong correlation between the values of σ_{oo} and E_{MN}, namely

$$\ln \sigma_{00} = p + q.E_{MN} \tag{25a}$$

was observed by Wang and Chen [25] 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 [26]. Recently, Mehta, Kumar and co-workers reported the "further MNR" in various chalcogenide glasses paying heed to thermally activated photoconductíon, high-field conduction, and non-isotermal crystallization [27-31]. The correlation between σ_{00} and E_{MN} is explained in [32-34] by the multiple excitations associated with the phonon energy ΔE, as described above.

To explain the puzzle about the „further MNR“ Yelon and Movaghar proposed a YM model [32]. According to this model, the MNR arises naturally for kinetic processes in which ΔE is the energy of a kinetic barrier and for which ΔE 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 excitatíon 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 [52] 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 transitíon 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

$$\ln \sigma_{00} = r - \exp\left(\frac{h\nu_o}{E_{MN}}\right) \tag{25b}$$

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. (25) to the data of Ref. [32-34]. They observed that the deviation of the data from this fit is very similar to that of Eq. (5), which also has two adjustable parameters

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

5.1 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”.

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”.

5.2 Derivation of an expression correspon-ding 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 $\sigma'_{00} > \sigma_{00}$.

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

$$\sigma \sim \sigma_{oo} \exp(W/kT_o) \exp(-W/kT) \qquad (26)$$

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

$$\sigma' \sim \sigma'_{oo} \exp(W/kT_o) \exp(-W/kT) \qquad (27)$$

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

$$\sigma'_{00} = \sigma_{00} \exp[Af\Delta E] \qquad (28)$$

or

$$\ln \sigma'_{00} = \ln \sigma_{00} + Af\Delta E \qquad (29)$$

where f is a constant, A-constant characterizing the parabolic barrier, and ΔE is the energy of the absorbed phonon.

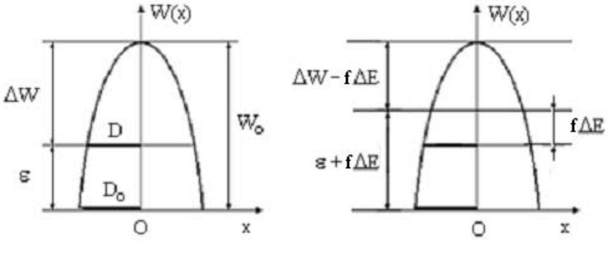

Fig. 3 The parabolic potential barrier

It follows from relations (14, 22b) that

$$\Delta E = 2\varepsilon_1 k T_0 = 2\varepsilon_1 E_{MN} \qquad (30)$$

where $E_{MN} = kT_0$ is the Meyer-Neldel energy. From relations (14, 22b), we obtain the formuls

$$\ln \sigma'_{00} = \ln \sigma_{00} + 2Af\varepsilon_1 E_{MN} \qquad (31)$$

or, if we employ the denotation $p = \ln\sigma_{00}$, $q = 2Af\varepsilon_1$

$$\ln \sigma'_{00} = p + qE_{MN} \qquad (32)$$

This formula isidentical with the mathematical expression of the “further MNR” (5).

5.3 Derivation of the auxiliary relation (28)

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

$$W(x) = -ax^2 + W_o \qquad (33)$$

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 [35-46]

$$p(\varepsilon) \sim \exp(-A\Delta W) \qquad (34)$$

where

$$A = -\frac{\pi}{\hbar}\sqrt{\frac{2m}{a}}, \qquad \Delta W = W_o - \varepsilon \qquad (35)$$

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':

$$p \sim \exp(-A\Delta W) \qquad (36)$$

$$p' \sim \exp[-A(\Delta W - f\Delta E)] \qquad (37)$$

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'

$$\frac{\sigma'_{00}}{\sigma_{00}} = \frac{\mu'}{\mu} = \frac{p'}{p} \qquad (38)$$

so that

$$\mu \sim \exp(-A\Delta W) \tag{39a}$$

$$\mu' \sim \exp[-A(\Delta W - f\Delta E)] = \mu \exp[Af\Delta E] \tag{39b}$$

It follows from relations (36-38) that

$$\sigma'_{00} = \sigma_{00} \exp[Af\Delta E] \tag{40}$$

This expression is identical with expression (28). Thus, we may state that relation (32), corresponding to the "further MNR", has been proved.

6. Remarks: The MNR in modern era

Pichon et al. [53] 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 [54]. Widenhorn et al. [55] 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 lal. [56] suggested that an exponential tail-state distribution model combined with the MNR can be used to describe the sub-threshold characteristics of amorphous $InGaZn0_4$ thin-film transistors (a-IGZO TFTs).

Most recently Ielmimi et al. [57] 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 [58] 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. [59] derived 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 [60] the new observations in MNR are discussed in case of chalcogenide glasses.

7. Conclusions

In this paper we have presented a clarification of the Meyer-Neldel rule and of the "further Meyer-Neldel rule" employing our barrier-cluster model.

We can explain the validity of the Meyer-Neldel rule in non-crystalline semiconductors by assuming that recombination transition of an electron from conduction to valence band is conditioned by emission of a number of equi-energy phonons whose total energy corresponds to the width of the forbidden band (and so to the energy released in the transition). The probability of such a complex process is determined by the number of emitted phonons. This probability exponentially decreases with increasing the number of phonons and consequently with the width of the forbidden band. The probability of recombination influences on the concentration of free electrons in the conduction band and subsequently on the electric conductivity. Using these ideas, we have obtained a relation equivalent to the Meyer-Neldel rule.

We suppose that the validity of the further MNR may be explained within the framework of our barrier-cluster model when we realize that the equi-energy phonons that are produced during the recombination process are strongly absorbed by free electrons in the low-mobility sub-band of the conduction band. The transport of electrons with energies near the lower edge of the conduction band takes place via tunnelling across potential-energy barriers. When the phonons are absorbed, electrons are excited to higher energy levels. This implies a considerable enhancement of the electrical conductivity. This enhancement corresponds well with the empirical relation known as the further NMR.

This result suggests that the barrier-cluster model that was introduced by the author and that was employed successfully in the clarification of the optical absorption, electro-absorption, photocon-ductivity and photoluminescence appears to be generally adequate. The barrier-cluster model seems also to explain why it was difficult to identify reliably the exponential tails of the state density if they penetrate deeply into the forbidden gap. The existence of clusters in chalcogenide glasses enables to clarify some results of X-ray and EPR studies.

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