

ONE WAY TO EXPLAIN THE MEYER-NELDEL RULE

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In this article 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.

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1. Introduction

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

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right) \quad (1)$$

where σ_0 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_0 .

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].

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

where b and σ_{00} are constant. This relation can be written as

$$\sigma_0 = \sigma_{00} \exp\left(\frac{W}{kT_0}\right) \quad (3)$$

here $b = 1/kT_0$. The relation (3) gives the dependence of pre-factor σ_0 on the activation energy W and represents Meyer-Neldel empirical rule. Equation (3) is often referred to as the MN rule or the compensation rule. Constant σ_{00} is often called the Meyer-Nedel pre-exponential factor and kT_0 the MN characteristic energy.

For electric conductivity of upper mentioned group of substances it holds

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

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 fullerenes. 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.

2. Barrier-cluster model of 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 [29-40]. The barriers have also an influence upon the optical absorption at the optical absorption edge. The influence of the barrier is caused in the first line by their inducing a strong electron-phonon interaction. The strong electron-phonon interaction results in the fact that on optical transition, apart from the energy of a photon, an electron can also take the energy of a phonon. On such a transition, the total energy taken by an electron equals the sum of the photon and phonon energies.

Another important factor - as far as influence of the barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually accompanied with tunneling of the carriers through the potential barrier. Due to this, the absorption process is influenced by barriers. These facts enable us to explain successfully not only the creation of the exponential tails at the optical absorption edge, but also their temperature dependence at high, as well as at low, temperatures.

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.

3. An explanation of the Meyer-Neldel rule in semiconductors

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.

Dependence of conductivity σ on activation energy W

The barrier-cluster model assumes that there are not energy levels of significant concentration in forbidden band of a non-crystalline semiconductor.

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

$$n = 2W/\Delta E \quad (5)$$

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

$$w_n = (w_1)^n \quad (6)$$

If we write down probability w_1 as

$$w_1 = \exp(-\varepsilon_1) \quad (7)$$

where ε_1 is a positive value, then probability w_n one can write with respect to (6,7) as

$$w_n = \exp(-n\varepsilon_1) = \exp(-\varepsilon_1 2W/\Delta E) = \exp(-bW) \quad (8)$$

where the constant b is given by

$$b = 2 \varepsilon_1/\Delta E \quad (9)$$

Relation (8) 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 (8) exponentially decreases.

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

$$(dn/dt)_{\text{gen}} = (dn/dt)_{\text{recom}} \quad (10)$$

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

$$(dn/dt)_{\text{gen}} = G = C_1 \exp(-W/kT) \quad (11)$$

where C_1 is a constant.

For a recombination process we suppose that the relation

$$(dn/dt)_{\text{recom}} = R = n.C_2 \exp(-bW) \quad (12)$$

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 (8) production n phonons at the electron transition.

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

$$C_1 \exp(-W/kT) = n.C_2 \exp(-bW) \quad (13)$$

From that relation follows for equilibrium concentration n of free carriers

$$n = C_{oo} \exp(bW) \exp(-W/kT) \quad (14)$$

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

Electric conductivity

It is known that electric conductivity σ is proportional to n : $\sigma \approx n$. If mobility of carriers is independent on activation energy W (or that dependence is negligible) one can write with respect to (14)

$$\sigma = \sigma_{oo} \exp(bW) \exp(-W/kT) \quad (15)$$

respectively

$$\sigma = \sigma_o(W) \exp(-W/kT) \quad (16)$$

where σ_{oo} is a constant and

$$\sigma_o(W) = \sigma_{oo} \exp(bW) \quad (17)$$

If we put $b = 1/kT_o$, the relation (15) takes the form which is identical with dependence (4)

$$\sigma \approx \sigma_{oo} \exp(W/kT_o) \exp(-W/kT) \quad (18)$$

The relation (17) acquires the form

$$\sigma_o \approx \sigma_{oo} \exp(W/kT_o) \quad (19)$$

which expresses the Meyer-Neldel rule (3).

4. Discussion

The question arises: Is n't the starting point of upper described method concerning the Meyer-Neldel rule in contradiction with the laws of statistics for steady states of a system? If this is so then the further question emerges: is it going on a system in an equilibrium state? After all non-crystalline substance is always far from equilibrium, it is in a metastable state.

5. Conclusions

Validity of the Meyer-Neldel rule in non-crystalline semiconductors can be explained assuming that recombination transition of an electron from conduction band to valence band is conditioned by emission of number monoenergetical phonons which total energy corresponds to the width of forbidden band (and so to the energy extracted in transition). Probability of such complex process is determined by number of emitted phonons. This probability exponentially decreases with increasing number of phonons and consequently with width of the forbidden band. The probability of recombination influences equilibrium concentration of free electrons in conduction band and subsequently electric conductivity. In such a way we have finally obtained the relation which is equivalent to the Meyer-Neldel rule.

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