Journal of Ovonic Research Vol. 7, No. 1, January - February 2011, p. 15 - 20

AN EXPLANATION OF THE INVERSE MEYER-NELDEL RULE IN DISORDERED SEMICONDUCTORS

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In this article we present basic idea which enables to explain the inverse Meyer-Neldel rule in disordered semiconductors.

(Received January 27, 2011; accepted February 1, 2011)

Keywords: Disordered semiconductor, Meyer-Neldel rule, Inverse Meyer-Neldel rule, Condensed matter, Compensation rule, Barrier-cluster model

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]. Most semiconductors, including noncrystalline ones, exhibit an exponential temperature dependence of the electric conductivity σ,

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

where σ_o is a constant and W an activation energy [1-9].

For many classes of materials, especially organic semi-insulators, chalcogenide glasses, amorphous silicon…experimental evidence suggests that there exists a correlation between the activation energies and pre-exponential factors of the form [10-27]

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

where b ($b > 0$) and σ_{oo} are constants. Relation (2) gives the dependence of the pre-factor σ_o on the activation energy W and represents the empirical Meyer-Neldel rule (MNR). Equation (2) is often referred to as the normal, standard MNR, or the compensation rule. The constant σ_{oo} is often called the Meyer-Nedel pre-exponential factor and $E_{MN} = kT_o$ is the MN characteristic energy. For the electrical conductivity of the group of substances mentioned above it holds that

$$\sigma = \sigma_{00} \exp(\frac{W}{kT_0}) \exp(-\frac{W}{kT}) \tag{3}$$

Here $b = 1/kT_o = 1/E_{MN}$. This rule is valid for disordered materials where W varies with doping, with surface absorption, light exposition or when films are produced under different conditions. This rule has also been observed for (with) liquid semiconductors and fullerenes. The validity of the MNR has also been reported with chalcogenide glasses. In the case of these glasses, this rule has been observed as result of variation of W fllowing changes in the composition of the glassy alloys in specific glassy systems.

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MNR has been observed not only with the electric conductivity but also with other processes such as: diffusion, crystallization, catalysis, adsorption, luminescence etc. MNR was first observed in 1937 [28]. Although many attempts have been done to explain this phenomenon, there does not still exist a widely accepted theory of MNR. A short description of existing models explaining MNR is in the review article [10]. An attempt for explanation of MNR and further MNR, based on the barrier-cluster model, has been published in [29-31].

The standard MNR is characterized by the function $\ln\sigma_o(W)$. 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 $0 \leq W < W_m$. This decrease was named as the "inverse MNR" in the literature. Examples of this kind of dependences can be found in [32-37]. Published experimental dependences of $\ln\sigma_o(W)$ showed a decrease in the interval $0 \leq W < W_m$. This decrease (for sufficiently low positive values of W) can be described approximately by a linear function

$$\ln \sigma_o = \ln\sigma_{oo} - cW \tag{4}$$

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 [32-37]. Presently, there is no generally accepted theory explaining the inverse MNR.

2. Inverse MNR from point of view of the barrier-cluster model

2.1 Explanation of the normal MNR in the framework of the barrier-cluster model

Before treating the inverse MNR, we recall the standard MNR explanation based on the barrier – cluster model [29-31]. This model will also be used as a starting point for the explanation of the inverse MNR.

In the frame of the barrier – cluster model, we succeeded in explaining the essence of the standard MNR. The barrier – cluster model assumes [38-41] that there are no energy levels on some significant concentration in the forbidden band of a non-crystalline semiconductor. A transition of an electron from the conduction band to valence band in a non-crystalline semiconductor proceeds predominantly with the assistance (by production) of phonons. The total energy of the produced phonons should correspond to that one released in the electron transition. Further we will assume that in a substance under consideration dominates phonon production with the average energy E_o. This means that phonon production of the other phonons is practically negligible. At the transition of an electron from the conduction band to valence band, the gained energy $2W$ is due to N phonons, such that each of them has the energy $E_{o,}$ so that $2W = NE_o$ or

$$N = 2W/E_o \tag{5}$$

Let w_1 be the probability of the production of one phonon with the energy E_o. Probability w_N of the production of N phonons of the same energy (due to the electron – lattice interaction) will be

$$W_N = (w_1)^N \tag{6}$$

If we write down the probability w_1 as

$$w_1 = \exp(-\varepsilon_1) \tag{7}$$

where ε_1 is a positive value, then the probability w_N one can be written with respect to (6,7) as

$$w_N = \exp(-N\varepsilon_1) = \exp(-\varepsilon_1 2W/E_o) = \exp(-bW) \tag{8}$$

where the constant b is

$$b = 2\,\varepsilon_1/E_o \tag{9}$$

Relation (8) gives actually the probability of recombination: the transition probability of an electron from the conduction to valence band. This is proportional to the probability of the production of N phonons and proportional also to the exp(-bW). With an increase of activation energy the probability of recombination, according to (8), exponentially decreases.

In [29] it was shown that for the recombination probability w_N of the charge carriers in a disordered semiconductors is

$$w_N \sim \exp(-bW) \tag{10}$$

This implies the relation [29]

$$\sigma_o \approx \sigma_{oo} \exp(bW) = \sigma_{oo} \exp(W/kT_o) \tag{11}$$

This relation characterizes the standard MNR. Here $b = 1/kT_o = 1/E_{MN}$.

2.2 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 localized 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,

$$N \sim 2W \tag{12a}$$

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. According to (12a) $N \sim 2W$. This implies

$$R \sim W \tag{12b}$$

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 (12a,b), one obtains

$$P_R \sim W^3 \tag{13}$$

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

Revised relation for recombination probability

The result (13) necessitates a correction of relation (10), which gives recombination probability of e-h pair in the existing standard model. Relation (10)

$$w_N \sim \exp(-bW) \quad (14)$$

has to be corrected in to the form

$$w_N \sim P_R.\exp(-bW) \quad (15)$$

and , with respect to (13) into the form

$$w_N \sim W^3.\exp(-bW) \quad (16)$$

Relation (16) represents the improvement of relation (10).
For the number n of carriers recombined during the unit time, one can write

$$(dn/dt)_{\text{recom}} = R = n.C_3 W^3 \exp(-bW) \quad (17)$$

In the equilibrium state, it holds

$$(dn/dt)_{\text{gen}} = (dn/dt)_{\text{recom}} \quad (18)$$

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

$$(dn/dt)_{\text{gen}} = G = C_1 \exp(-W/kT) \quad (19)$$

where C_1 is a constant. We obtain

$$C_1 \exp(-W/kT) = n.C_2\, W^3 \exp(-bW) \quad (20)$$

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

$$n = C_{oo}\, W^{-3} \exp(bW) \exp(-W/kT) \quad (21)$$

where C_{oo} is determined by the constants C_1 and C_2.
For conductivity $\sigma \sim n$, it is evidently valid that

$$\sigma = \sigma_{oo.} W^{-3}.\exp(bW) \exp(-W/kT) \quad (22)$$

One can write

$$\sigma_o = \sigma_{oo}\, W^{-3} \exp(bW) \quad (23)$$

or

$$\ln \sigma_o = \ln \sigma_{oo} + bW - 3\ln W \quad (24)$$

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 (24), so approximately

$$\ln \sigma_{o\,=} \ln \sigma_{oo} + bW \quad (25)$$

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

$$\ln \sigma_o = \ln \sigma_{oo} - 3 \ln W \quad (26)$$

may approximately be accepted. Relation (26) that we have obtained corresponds well to the decrease of ln σ_o with the increase of the activation energy *W* in the interval where the inverse MNR take place.

Remark: If one replaces the relation (12b) by the relation $R = cW + R_o$, where R_o is a constant-the relation (24) will take the form

$$\ln \sigma_o = \ln \sigma_{oo} + bW - 3\ln(W+a) \qquad (27)$$

One can see that for W→ + 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 (27) will be nearly similar to the function (24).

3. Coclusions

We present in this paper one of possible explanations of the inverse Meyer-Neldel rule observed in experiments when the electrical conductivity of disordered semiconductors was measured. Our basic idea was to use the barrier-cluster model of disordered semiconductors. We have assumed that at the carrier recombination a series of mono-energetical phonons may be taken into accound. The probability of such recombination decreases with the increase of the number of phonons and so with the increase of the width of the forbidden gap. The decrease of the recombination probability involves an increase of the equilibrium concentration of conduction electrons (holes) and then also the increase of the conductivity. The recombination probability is influenced by the recombination radius. We have assumed that the greater number of emitted phonons, the greater is the recombination radius. Just the dependence of the recombination radius on the number of emitted phonons (and on the width of the forbidden gap) evokes the phenomenon of the inverse MNR.

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