D.C. ELECTRICAL CONDUCTIVITY OF GE-S AND GE-V-S SYSTEM GLASSES, THE MEYER-NELDEL RULE

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D.C. electrical conductivity of Ge-S and Ge-V-S glassy systems were studied. It was found that so called Mott minimum metallic conductivity is function of activation energy of d.c. electrical conductivity for all studied glasses. The explanation based on idea of exponential tail of valence band edge and the p-type of electrical conductivity in extended states close to the mobility edge of valence band was suggested.

INTRODUCTION

The temperature dependence of d.c. electrical conductivity (σ) of semiconductors can be represented by the relation [1,2]:

$$\sigma = \sigma_0 \exp\left[\frac{-\Delta E}{kT}\right] \quad , \tag{1}$$

where pre-exponential factor σ_0 is called Mott minimum metallic conductivity [1] and ΔE is activation energy of d.c. electrical conductivity.

Linear dependence of log σ_0 vs. ΔE for many organic and inorganic semiconductors was observed [3-8]. The temperature dependence of d.c. electrical conductivity then can be described by so-called Meyer-Neldel (M-N) rule [9]:

$$\sigma = \sigma_0' \exp\left[-\frac{\Delta E}{kT}\right]^{(1-\alpha)} , \qquad (2)$$

where $\alpha = T/T_0$ and T_0 is constant, so-called characteristic temperature.

The great attention was paid to M-N rule especially for study of organic semiconductors but universally valid model on the base of these studies was not suggested. One of the possible explanation of the M-N rule was suggested by Roberts [10] but his assumption of unreachable temperature T_0 contradicts reality. In the model of Roberts the function describing concentration of the free carriers at the temperature T_0 is discontinuous. This fact is in the contradiction with the experiment and thus the model of Roberts can be far from the real situation.

The aim of this work is to prove validity of the M-N rule for semiconducting chalcogenide glasses of Ge-S and Ge-V-S systems and to propose possible more universal explanation of the M-N rule. The 49 semiconducting glasses of Ge-S and Ge-V-S systems from the whole glass-forming areas of both systems were used for study.

EXPERIMENTAL PART

The glasses of $Ge_x S_{100-x}$ system (nine compositions from the whole glass-forming area), $15 \le x \le 44$, were prepared by conventional method of direct synthesis from elements of 5N purity in evacuated quartz ampoules. Glassy samples of $Ge_x V_y S_{100-y-x}$ system (40 samples), $15 \le x \le 44$ and $0.005 \le y \le 0.5$ were prepared by modified method of synthesis, for details see [11]. The absence of crystalline inclusions and the homogeneity of the samples were checked by measurements of optical transmissivity and X-ray diffraction. The chemical composition was checked by electron microprobe with energy dispersive X-ray analyzer. Neither microcrystals nor optical inhomogeneities were found.

The temperature dependence of d.c. electrical conductivity was studied for all 49 glasses of different chemical compositions. All samples were cut to the square-shaped plates (area from 30 to 40 mm², thickness $d \sim 2$ mm). The samples were contacted with aquadac and covered by molybdenum plate contact of area ~ 1 mm². Temperature dependence of the dark d.c. electrical conductivity was determined from measurements of V-A characteristic by using computer

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aided arrangement with Keithly 615 electrometer at the temperature ranging from 100 to 300 °C and at the air pressure $p \sim 1$ Pa. At the temperatures below 100 °C unnegligible error due to very high d.c. electrical resistivity was observed. For more details, see [12].

RESULTS AND DISCUSSION

The specific resistivity of all studied glasses at room temperature were within the interval $10^{11} - 10^{13} \Omega \text{cm}$. The nonlinearities in dependence of log $\sigma = f(1/T)$ were observed at temperatures below 100 °C. That is why only data measured at the temperatures above 100 °C were taken into account, as it was mentioned above.

For all 49 studied glasses dependence of preexponential factor σ_0 and activation energy of d.c. electrical conductivity ΔE was found, see figure 1. This dependence can be described by following equation:





• - Ge-S; + - Ge-V-S; $\ln \sigma_0 = 21.9 \Delta E - 19.2$; coef. of determination = 0.901; $T_0 = 529 \text{ K}$; $\sigma'_0 = 4.8 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$

In
$$\sigma_0 = 21.9 \ \Delta E - 19.2$$
, (3)

which confirms, that the M-N rule for Ge-S and Ge-V-S glasses is fulfilled.

Before trying to interpret the M-N rule it is necessary to emphasize that validity of equation (3) for glasses of both studied systems showes that mechanism of d.c. electrical conductivity is independent on chemical composition.

For better analysis of our results it is useful to make clear meaning of the slope and absolute term of equation (3). From the common form of equation (3):

$$\ln \sigma_0 = A \ \Delta E + B \quad , \tag{4}$$

it is obvious that the slope A means reciprocal energy and absolute term B is the logarithm of the constant quantity of pre-exponential term. We can write:

$$A = \frac{1}{kT_0} \text{ and } B = \text{In } \sigma_0^{\prime}, \qquad (5)$$

and then we can deduce from the equations (1), (4) and (5) equation (2) for the M-N rule. Equation (2) can be rewritten in the form:

$$\sigma = \sigma_0' \exp\left[\frac{\Delta E}{kT_0}\right] \quad \exp\left[-\frac{\Delta E}{kT}\right] \quad , \tag{6}$$

Comparing of equations (1) and (6) (if the M-N rule is valid) it is possible to express pre-exponential term σ_0 in equation (1) in following form:

$$\sigma_0 = \sigma'_0 \exp\left[\frac{\Delta E}{kT_0}\right] \quad , \tag{7}$$

If the M-N rule is valid then it is evident from equation (7) that the pre-exponential term σ_0 in equation (1) is not constant and depends on constant terms σ'_0 and T_0 and on the value of activation energy of d.c. electrical conductivity ΔE , as well. To interpret the temperature dependence of d.c. conductivity we can start from the assumption of validity of the M-N rule expressed by equation (6) and from Davis-Mott model of d.c. electrical conductivity of non-crystalline semiconductors [13].

Carrier mobility in the localized states is described by Davis-Mott model as follows:

$$\mu_{\rm V} = -\frac{eD}{kT} \quad , \tag{8}$$

where μ_v is mobility of carriers in extended states close to the mobility edge of valence band (studied chalco-

genide glasses are of p-type of conductivity) and D is diffusion coefficient. Pre-exponential term in equation (1) is then expressed:

$$\sigma_0 = e^2 DN(E_{\rm v}) \exp\left(\frac{\gamma}{k}\right) \quad , \tag{9}$$

where $N(E_v)$ is density of extended states near the mobility band edge, $\gamma \sim 4.10^{-4}$ eV K⁻¹ is the constant of temperature dependence of ΔE . (Speaking about the density of states, then owing to spatial fluctuation of their density we have in mind the effective density of states and effective mobility, as well.) Diffusion coefficient $D = 1/6 v R^2$, v is the electron frequency of order of 10^{15} s^{-1} [14] and R is the distance of two adjacent potential wells (mean free path of order of bond length) [14]. Under the assumption that D is constant, equation (9) implies that $N(E_v)$ is the only one non-constant quantity. The value of this quantity can be expressed as a function of energy, in this case as the function of activation energy of d.c. electrical conductivity ΔE . Then we define Fermi level $E_{\rm F}$ as energy at which the density of localized states under discussion is the lowest and ΔE is zero. Under assumption of exponential tailing of the localized band states [10], the density of extended states close to the mobility edge of valence band can be expressed:

$$N(E_{\rm v}) = N(E_{\rm F}) \exp\left[\frac{\Delta E}{kT_0}\right] \quad , \tag{10}$$

where $N(E_{\rm F})$ is density of states close the Fermi level that is related to density of states at the mobility edge of valence band (and thus could not be related to summary density of states at the Fermi level). Equation (9) together with equation (10) then gave the following form:

$$\sigma_0 = e^2 DN(E_{\rm F}) \exp\left[\frac{\Delta E}{kT_0}\right] \exp\left(\frac{\gamma}{k}\right) \quad , \tag{11}$$

which is for:

$$\sigma_0' = e^2 DN(E_F) \exp\left(\frac{\gamma}{k}\right)$$
(12)

equal to the equation (7) and consequently with the expression which under assumption of validity of the M-N rule can substitute the pre-exponential term σ_0 in equation (1). Then we can suggest that the tail of valence band localized states (e.g. energetical dependence of density of localized states at energies greater then energy of mobility edge of the valence band E_V) has for all studied glasses the same exponential behaviour, characterized by value T_0 , see equation (10).

Owing to the exponential decrease of density of states near the mobility edge, we consider the assumption about fast decrease of mobility in localized states very close to the mobility edge E_{γ} to be realistic. Then dominant mechanism of conductivity can be carrier motion in the extended states close to $E_{\rm v}$. It is necessary to add several notices to this assumption. Mechanism of electrical conductivity is deduced usually from the order of value of pre-exponential factor σ_0 in equation (1) without knowing of width of localized states above $E_{\rm v}$ (in the case of p-type conductivity). If the width of localized states is $\Delta E_{\text{lok}} \leq 0.2$ [2,14,15,] then it can be shown that, at the usual temperature region of measurements $(T \sim 400-550 \text{ K})$ of d.c. electrical conductivity of semiconductors with high specific resistivity, about 10 % of carriers can be directly excited over localized states close to the band edge to extended states near the mobility edge. Assuming the difference of carrier mobility in extended and localized states in order 10³ [14], the carriers excited to the extended states close to the mobility edge should significantly contribute to d.c. electrical conductivity. This suggestion is in accordance with the idea of Mott and Davis based on the fact that in the case when the width of localized states at the band edge is smaller then ~ 5 kT it can be expected carriers' moving in extended states [14]. We suppose, that the width of localized states at band edge is probably a little greater than 5 kT, but difference of carriers' mobility in extended and localized states can cause dominant role of the carriers excited to the extended states near the mobility edge.

Activation energy and pre-exponential term for all studied glasses are described by equation (3). Thus from equations (4) and (5) arise that both σ'_0 and T_0 are constant for all studied glasses and their values are $\sigma'_0 = 4.8 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ and $T_0 = 529 \text{ K}$.

Compositional independent values of both above mentioned parameters then have to be connected with such a property of studied glasses which is independent on chemical composition. This compositional independent property which would be connected with p-type of electrical conductivity is existence of nonbonding two-electronic states of chalcogen called lonepair (LP) states. LP states create a top of valence band of sulphur-based chalcogenide glasses in the whole glassforming region [4,16,17]. It means that the top of valence band of all studied glasses is created by fulfilled nonbonding atomic orbitals of sulphur. The steepness of exponential decrease of density of localized states in tail of valence band is then probably more affected by interaction of atomic orbitals called "configuration distortion" [16] than by fluctuation of bond lengths and of bonding angles as it happens when the top of valence band is created by bonding molecular orbitals. This fact implies that chemical composition does not affect significantly energetical dependence of density of states.

Interpretation of σ'_0 and T_0 is not clear so far. On the base of equation (12) we can report σ'_0 as a minimal conductivity at the smallest density of states connected with d.c. electrical conductivity, i.e. localized states with density $N(E_{\rm F})$. The characteristic temperature T_0 , i.e. the temperature at which specific d.c. electrical conductivity is the same for all studied glasses, corresponding to the energy $kT_0 \sim 368 \,{\rm cm}^{-1}$ (expressed in the units used in the far-IR spectroscopy). This energy is from the region of fundamental vibrations of studied glass and it can be taken as the most probable that the tails of localized states at the valence band edge is closely connected with energy of these fundamental vibrations.

CONCLUSION

The validity of Meyer-Neldel rule for glasses of Ge-S and Ge-V-S systems was proved by temperature dependence of specific d.c. electrical conductivity. The p-type conductivity in extended states close to the mobility edge of valence band was supposed as possible mechanism of d.c. electrical conductivity for studied chalcogenide glasses. States at the top of valence band are created by fulfilled atomic orbitals of sulphur, socalled lone-pair. For interpretation of experimental data we suppose exponential behaviour of localized state tail at valence band edge, in accordance with Roberts [10]. The possible explanation of insensitivity of d.c. electrical conductivity to changes neither germanium content nor vanadium content in the studied glasses can be connection between mechanism of electrical conductivity and existence of lone-pair states.

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References

- 1. Nagels P. in: *Amorphous Semiconductors* (ed. M.H. Brodsky), p.113, Springer-Verlag, Berlin 1979.
- 2. Datta T.: Appl.Phys.Commun. 3, 1 (1978).
- 3. Rosenberg B., Bhowmik B., Harder H.C., Postow E.: J.Chem.Phys. 49, 4108 (1968).
- Adler D. in: *Physical Properties of Amorphous Materials* (ed. D.Alser, B.B.Schvartz, M.C.Steele), p.76, Plenum Publish Corporation, New York 1985.
- 5. Arora R., Kumar A.: Phys.Stat.Sol.(a) 125, 273 (1991).
- 6. Spear W.E., Allan D., LeComber P., Gaith A.: Phil.Mag. *B41*, 419 (1980).

- 7. Carlson D.E., Wronski C.R. in: *Amorphous semiconductors* (ed. M.H.Brodsky), p.322, Springer-Verlag, Berlin 1979.
- 8. Staebler D.L., Wronski C.R.: Appl.Phys.Letters 21, 292 (1977).
- 9. Meyer W., Neldel H.: Z.techn. Phys. 18, 588 (1937).
- 10. Roberts G. G.: J.Phys.C: Solid St.Phys. 4, 3167 (1971).
- Černošková E., Černošek Z., Frumar M.: J.Non-Cryst.Solids 161, 331 (1993).
- 12. Černošková E.: PhD Thesis, University Pardubice (1992).
- 13. Davis E.A., Mott N.F.: Phil.Mag. 22, 903 (1970).
- Mott N.F., Davis E.A. in: *Electronic Process In Non-Crystalline Materials*, p.353, Clarendon Press, Oxford 1971.
- 15. Kastner M., Fritzsche H.: Phil.Mag. B37, 199 (1978).
- Kastner M.: Proc.VIIth Int.Conf. on Amorphous and Liquid Semicond. (ed. W.E.Spear), p.504, Edinburgh 1977.
- 17. Mašek J., Velický B.: J.Phys. C42, 133 (1981).

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STEJNOSMĚRNÁ ELEKTRICKÁ VODIVOST SKEL SYSTÉMŮ Ge-S A Ge-V-S, MEYER-NELDELOVO PRAVIDLO

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Na 49 objemových vzorcích skel systémů Ge-S a Ge-V-S byla studována teplotní závislost stejnosměrné elektrické vodivosti. Bylo zjištěno, že pro všechna studovaná skla je hodnota σ_0 (tzv. Mottova minimální kovová vodivost) funkcí aktivační energie ΔE stejnosměrné elektrické vodivosti. To znamená, že u těchto materiálů byla zjištěna platnost Meyer-Neldelova pravidla.

Navržená interpretace Meyer-Neldelova pravidla ukázala, za předpokladu exponenciálních chvostů lokalizovaných stavů u hrany valenčního pásu, že možným mechanismem stejnosměrné elektrické vodivosti je u studovaných chalkogenidových skel děrová vodivost v delokalizovaných stavech u hrany pohyblivosti valenčního pásu. Tyto stavy jsou u chalkogenidových skel tvořeny atomovými orbitaly chalkogenu obsazenými dvěma elektrony, tzv. lone-pair stavy. Interpretace experimentálních výsledků předpokládá exponenciální chvost lokalizovaných stavů u hrany valenčního pásu. Spojení mechanismu elektrické vodivosti s přítomností lone-pair stavů může být vysvětlením skutečnosti, že stejnosměrná elektrická vodivost není významně ovlivněna ani obsahem germania, tedy chemickým složením skel, ani dotací vanadem.

Problematickou zůstává interpretace konstant σ'_0 a T_0 . Na základě navržené interpretace Meyer-Neldelova pravidla se lze na σ'_0 dívat jako na minimální vodivost při nejnižší hustotě stavů spojených s vodivostí, tedy stavů s hustotou $N(E_{\rm F})$. Charakteristická teplota T_0 ,tedy teplota při které je stejnosměrná vodivost všech studovaných skel stejná, odpovídá energii $kT_0 \sim$ 368 cm⁻¹. To je energie z oblasti fundamentálních vibrací studovaných skel a lze pokládat za reálné, že chvosty lokalizovaných stavů u hran pásů budou s energií těchto vibrací úzce souviset.