acta phys. slov. 28. (1978), No. 2

ACTIVATION ENERGIES OF Ge-S GLASSES AFTER NEUTRON IRRADIATION

PAVEL MACKO*, VLASTA MACKOVÁ*, Bratislava

In the paper some experimental data on the influence of neutron irradiation on changes of activation energies in Ge-S glasses are presented. The changes were calculated from temperature dependences of d.c. and a.c. electrical conductivities, and by measuring the transmission coefficient in GeS_8 samples. Simultaneously, the influence of radiation defects on the changes of electrical conductivities and the transmission coefficient are documented. A qualitative interpretation is based on an assumed connection between the concentration of unsaturated bonds and the concentration of defects in the investigated glasses.

ЭНЕРГИИ АКТИВАЦИИ СТЁКОЛ Ge-S ПОСЛЕ ОБЛУЧЕНИЯ НЕЙТРОНАМИ

В работе приведены экспериментальные данные о влиянии излучения нейтронов на энергии активации стёкол Ge-S, расчитанные из температурной зависимости электропроводности для постоянного и переменного тока или же из измерений коэффициента пропускания для образцов стекла GeS_8. Одновременно продемонстрировано влияние радиационных дефектов на изменение электропроводности, а также коэффициента пропускания. Приведённая качественная интерпретация явления исходит из предположения, что существует связь между концентрацией ненасыщенных связей и концентрацией дефектов в исследованных стёклах.

I. INTRODUCTION

It is well known that the existence of 10^{16} to 10^{20} unsaturated bonds per 1 cm^3 is an inner property of semiconductive glasses. One possibility of some modification of transport parameters in glasses is provided by influencing these bonds. Some years ago it was shown [1] that bonds may become saturated by tempering glasses in the vicinity of transformation temperature. The existence of unsaturated bonds in GeS_x glasses was later proved [2]. In our previous papers [3], [4] a possible influence of unsaturated bonds by radiation defects created in the glassy semiconductors by bombarded neutrons was discussed on the basis of our experimental results.

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* Department of Physics, Slovak Technical University, Gottwaldovo nám. 19, CS-880 19 BRATISLAVA.

II. SAMPLE PREPARATION

The samples used in our experiments were prepared from the Ge-S glasses using the technology introduced in [4] and [5]. The processes of formation of this type of chalcogenide glasses together with many experimental data are given in [6] and [7]. Samples of various thickness were cut from $GeS_{1.35}$ and GeS_8 glass ingots (always from one ingot for a series of measurements). All samples were irradiated by fast neutrons with an energy $E_n = 2$ MeV and integral neutron flux densities ranging from 10^{16} ncm^{-2} to 10^{19} ncm^{-2}. The series 1, 2, 3, 4, and 5 were irradiated by integral densities (in $n\,cm^{-2}$) zero, 1×10^{16}, 1×10^{17}, 1×10^{18}, and 1×10^{19}, respectively. The temperature during irradiation did not exceed 40 °C. Surfaces of each sample were finished before measurement (also after irradiation) with regard to the requirements of the corresponding measurement method. Where needed, contacts were prepared on the samples in the manner described in [4].

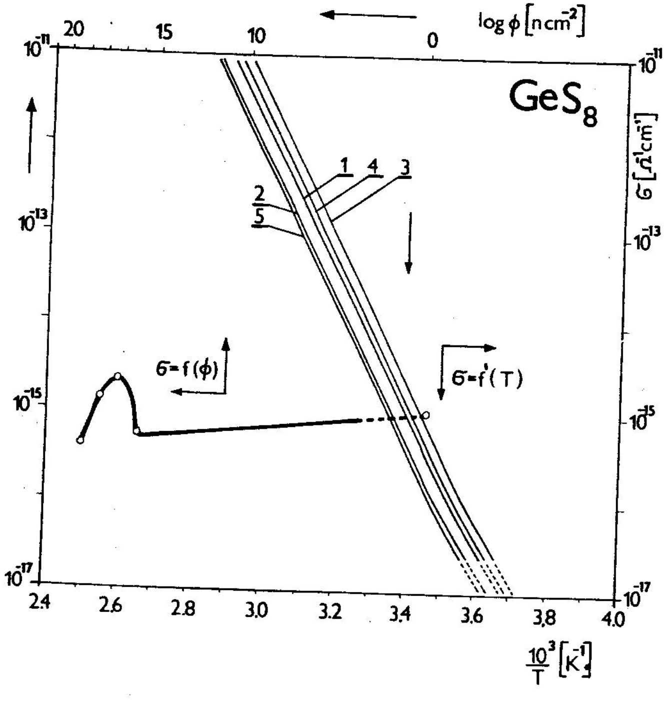

Fig. 1. Temperature dependence of d.c. electrical conductivity in $GeS_{1.35}$ glasses at varying irradiations (1, 2, 3, 4, and 5 corresponds to fluxes 0, 10^{16}, 10^{17}, 10^{18}, and 10^{19} $n\,cm^{-2}$). The d.c. electrical conductivity versus integral neutron flux density at $T = \text{const}$.

III. EXPERIMENTAL RESULTS

In order to determine the activation energy the following dependences were measured: i) d.c. electrical conductivity versus temperature (always at $\Phi_i = \text{const}$); ii) a.c. electrical conductivity versus temperature (at $\Phi_i = \text{const.}$) for the frequency $\omega = 10^4$ Hz; iii) transmission coefficient versus integral neutron flux density.

The temperature dependences were measured within the range 100 K to 400 K, the limiting factors being resistivity of samples at low temperatures and transformation temperature of the glasses (GeS_8), respectively.

The d.c. conductivity was measured by the IM-6 device made by Radiometer Co. The corresponding results of d.c. electrical conductivity temperature dependences in $GeS_{1.35}$ and GeS_8 samples are plotted in Fig. 1 and Fig. 2, respectively.

The temperature dependence of a.c. electrical conductivity in samples irradiated by various integral neutron flux densities was measured at the frequency $\omega = 10^4$ Hz using the Tesla BM 484 device with selective nanovoltmetre Unipan.

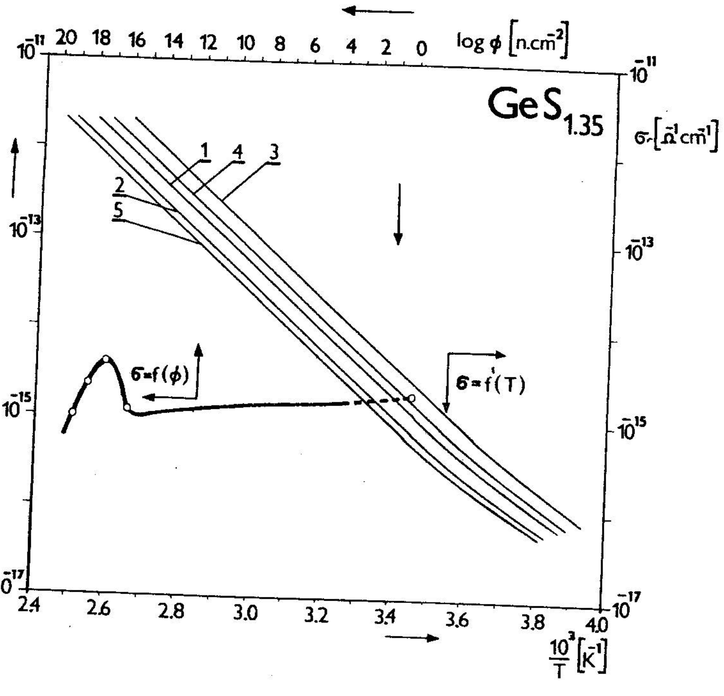

Fig. 2. Temperature dependence of d.c. electrical conductivity in GeS_8 glasses at varying irradiations of samples, and d.c. electrical conductivity as a function of Φ at $T = \text{const}$.

The graphs of temperature dependence of a.c. electrical conductivity are shown in Fig. 3 ($GeS_{1.35}$ samples) and Fig. 4 (GeS_8 samples).

The transmission coefficient of the GeS_8 samples (series 1, 2, 3, 4, and 5) was measured using a PERKIN-ELMER apparatus at the temperature 22.5 °C. The record of the transmission coeffieient as a function of frequency for all samples with the thickness of 0.95 ± 0.005 mm is illustrated by graphs in Fig. 5.

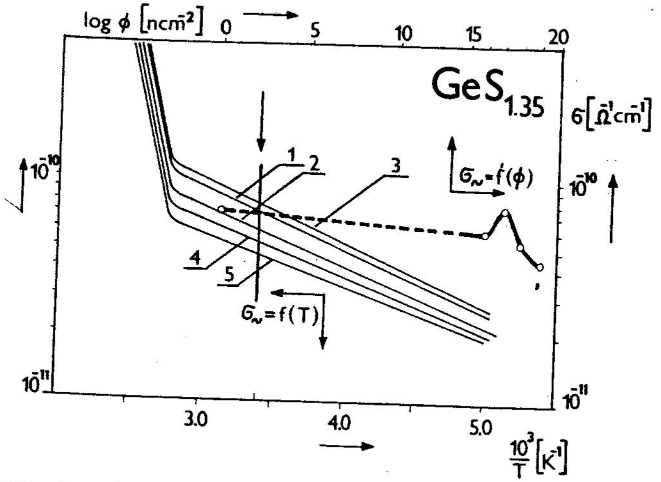

Fig. 3. Temperature dependence of a.c. electrical conductivity in $GeS_{1.35}$ samples (integral neutron flux density Φ taken as a parameter) and the dependence $\sigma_{\sim} = f'(\Phi)$ at $T = \text{const}$.

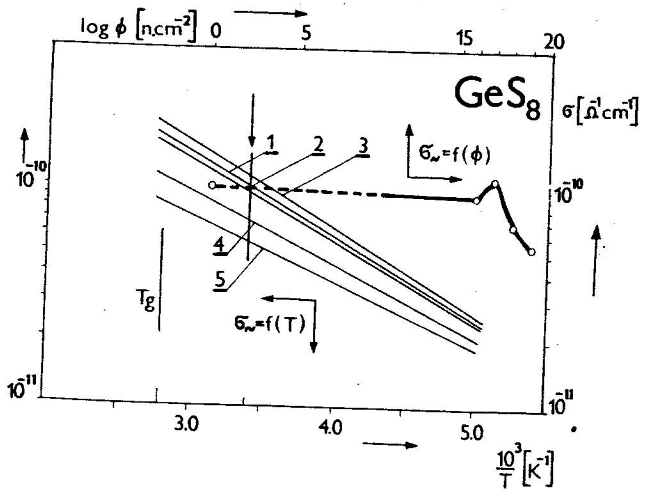

Fig. 4. Temperature dependence of a.c. electrical conductivity in GeS_8 samples (Φ taken as a parameter), and $\sigma_{\sim} = f'(\Phi)$ at $T = \text{const}$.

IV. DISCUSSION OF RESULTS

From the course of the temperature dependence of d.c. electrical conductivity at $\Phi = \text{const}$ (right-hand side in Figs. 1 and 2) the values of activation energy $E_1 = E_C - E_F$ and $E_2 = E_A - E_F$ can be calculated for the samples of both glasses.

From the course of the temperature dependence of a.c. electrical conductivity energies E_2 and E_3 can be calculated, the latter characterizing the activation energy of hopping between the localized states in bands (or in the vicinity of E_F) in the same glass.

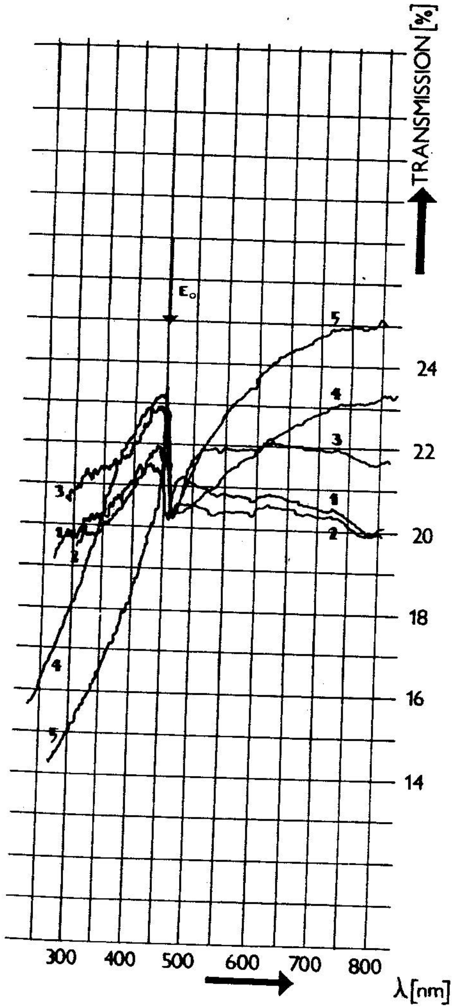

Fig. 5. The changes of the transmission coefficient in irradiated GeS_8 samples as a function of impinging irradiation wavelength.

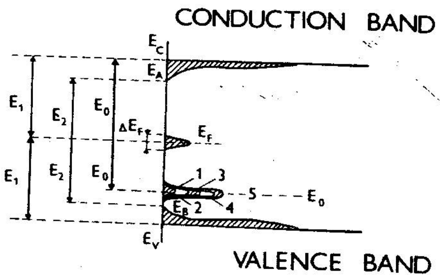

Fig. 6. The density-of-state model (energy diagram) for GeS_8 samples.

Table 1

$GeS_{1.35}$	GeS_8
$E_1 = 0.715$ eV	$E_1 = 1.64$ eV
$E_2 = 0.51$ eV	$E_2 = 1.33$ eV
$E_3 = 0.053 - 0.0507$ eV	$E_3 = 0.078 - 0.061$ eV
$E_3\ (\Delta\Phi) = 0.0023$ eV	$E_3\ (\Delta\Phi) = 0.017$ eV
	$E_0 = 2.74$ eV

From the frequency dependence of the transmission coefficient (Fig. 5) at various Φ the optical activation energiy E_0 is determined in the GeS_8 glass type.

The influence of radiation defects on changes in the courses of the investigated parameters is documented by the dependences on the integral neutron flux densities (at $T = \text{const}$) of d.c. and a.c. electrical conductivities (left-hand side in Figs. 1, 2, and right-hand side in Figs. 3, 4, respectively). These graphs supplement the experimental results published in [3] and, especially in [4]. The extremal values (at $\Phi_{opt} \doteq 10^{17}$ n cm^{-2}) are in correspondence with the radiation defects concentration $N_D \doteq 10^{19}$ defects per cm^3 [3], which agrees (in order) with the concentration of the unsaturated bonds. This effect proves the mutual interaction between radiation defects and unsaturated bonds in bombarded glasses that yields saturation of bonds and optimalization of transport phenomena.

From Figs. 1, 2, 3, and 4 it is clear that whilst there are no changes in activation energies E_1 and E_2 with varying integral neutron flux density, the activation energy E_3 is affected by the created radiation defects. This means that: i) at lower temperatures the influence of radiation defects causes changes in activation energies, and ii) at higher temperatures the influence of radiation defects on changes in activation energy values E_1 and E_2 is negligible and yields some changes in electrical conductivity values only. Simultaneously, a comparison of the courses in Figs. 1 and 3 confirms that activation energies of the E_2-type are practically equal (in $GeS_{1.35}$ we have $E_2 = 0.51$ eV and $E_2 = 0.53$ eV).

In Fig. 5 an increase of extremes in the transmission coefficient with the degree of irradiation in GeS_8 glasses is observed. The shape of curves documents the "purification" process of the band in such a structure with a simultaneous enlargement of localized-defects-states regions in the vicinity of the energy E_0. The primarily point radiation defects form in the integral density range over 10^{17} n cm^{-2} some aggregates of defects, thus enlarging localized states regions in the band. As a consequence, a change of optical parameters appears and an observable drop of electrical conductivity values in the above mentioned neutron flux range is obtained.

There are only very few papers devoted to the optical parameters of Ge-S glasses. Except for [6] and a brief note in [5] the only papers which deal with this topic are [8] and [9] (from another aspect).

The calculated values of activation energies for $GeS_{1.35}$ and GeS_8 together with the energy model of GeS_8 (Fig. 6) are in Table 1 where $E_3\ (\Delta\Phi)$ denotes the change in activation energy due to the variation of the integral neutron flux density in the range 10^{16} n cm^{-2} to 10^{19} n cm^{-2}.

V. CONCLUSION

The summing up of experimental facts suggests that there is a relation between the concentration of unsaturated bonds and the concentration of radiation defects created by neutrons in the investigated glasses. The extremes in the measured values of electrical conductivities enable to estimate the concentrations of unsaturated bonds on the material. Obviously, the suggested model (Fig. 6) represents only a schematic sketch of the energy spectrum.

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Received June 27th, 1977