

ATTEMPTS TO INTERPRET DIELECTRIC BEHAVIOUR IN Cu-DOPED $\text{GeS}_{1.5}$ GLASS

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Dielectric behaviour in $\text{GeS}_{1.5}$ glasses containing up to 5 at % Cu has been evidenced by the thermally stimulated depolarization (TSD) method. The TSD peak ($T_{\text{max}} = 260\text{--}330\text{ K}$, $\nu = 0.12\text{ Ks}^{-1}$) shifts towards lower temperatures and increases in size with increasing Cu content. The origin of the peak is discussed alternatively in terms of heterogeneous and homogeneous polarization, respectively. After a proper thermal treatment an additional TSD peak due to interfacial polarization was observed in glass doped with 3 at % Cu. The latter is most probably connected with the formation of Cu_2GeS_5 polycrystalline spherulites in the glassy matrix during the heat treatment. Long-range diffusion of ionized Cu atoms is suggested to account for both the dielectric behaviour and the effects of annealing.

ОБ ИНТЕРПРЕТАЦИИ ДИЭЛЕКТРИЧЕСКИХ СВОЙСТВ СТЕКЛА $\text{GeS}_{1.5}$ С ПРИМЕСЬЮ МЕДИ

Диэлектрические свойства стекол $\text{GeS}_{1.5}$, содержащих вплоть до 5% примеси меди, были доказаны при помощи метода термически стимулированной деполаризации. С увеличением содержания меди максимум деполаризации ($T_{\text{max}} = 260\text{--}330\text{ K}$, $\nu = 0.12\text{ K/c}$) сдвигается в сторону более низких температур и его величина растёт. Обсуждаются две альтернативы происхождения этого пика, основанные соответственно на предположении об однородной и неоднородной поляризации. После соответствующей термической обработки в стекле с примесью меди 3% наблюдался дополнительный максимум деполаризации, обусловленный поляризацией в результате скопления зарядов на поверхностях включений. Этот максимум, по всей вероятности, связан с образованием поликристаллических сферулитов Cu_2GeS_5 в кристаллической решётке стекла во время термообработки. Для объяснения как диэлектрических свойств, так и эффектов, связанных с отжигом, предполагается наличие действующей диффузии ионизированных атомов меди.

I. INTRODUCTION

Since the work of Kolomic [1] it has been well established that the conductivity of chalcogenide glasses is relatively insensitive to impurities. According to Mott [2] the covalent bonding requirements of impurities are satisfied in the glasses. There are, however, a few deviations from such a behaviour [3, 4]. Liang et al. [3] ascribed the conductivity changes in Cu-doped As_2Se_3 glasses to either a decrease in the gap or an increase in the coordination number. The latter explanation is similar to that provided by Mott [4], who assumed the presence of four-coordinated copper in glassy As_2Se_3 . Recently, Watanabe et al. [5] have found a large increase in the dc conductivity in Cu-doped amorphous $\text{Ge}_{0.42}\text{S}_{0.58}$ as a consequence of a reduction of disorder in the glass structure. We have found that glasses with an almost identical composition exhibit dielectric behaviour [6]. The present paper is an attempt to clarify the origin of the dielectric behaviour. As pointed out by Owen [7], dielectric relaxation has not been observed in wide-gap chalcogenide glasses such as As_2Se_3 , As_2S_3 . The glasses in the system Ge-S represent evidently an exception, since a dielectric polarization could be found in undoped GeS_x glasses, too [8, 9].

II. EXPERIMENTAL

In the course of the present investigation we have used the TSD method, based on thermally stimulated depolarization of a previously polarized capacitor with the glassy dielectric [10]. Disc-shaped samples¹⁾ ($\Phi = 7.5\text{ mm}$, $d = 0.8\text{ mm}$) with coated dag electrodes were used for both TSD and dc conductivity measurements.

The TSD procedure started with the polarization of the capacitor at a temperature T_p for a time t_p . After this time the system was cooled down to 90 K under the applied bias and then shortcircuited by a resistor $10^{11}\ \Omega$ connected in parallel with the electrometer input. A thermocouple monitored the temperature of the sample, heated at a uniform heating rate of 0.12 Ks^{-1} .

To avoid electrode polarization during the dc conductivity measurements, the temperature region was restricted to temperatures below T_g . The bias of 20 V was applied at T_p to establish the dielectric polarization with subsequent cooling to 90 K. When raising the temperature of the sample, only a pure conductivity current was observed²⁾.

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¹⁾ The glass preparation will be published elsewhere [11].

²⁾ Possible dependence of the polarization on temperature is neglected.

III. RESULTS

The TSD records of a set of $\text{GeS}_{1.5}$ glasses containing various amounts of copper are reproduced in Fig. 1. Here, instead of the current density $j(T)$ (the apparent conductivity σ_a defined as current density) the electric field intensity ratio is replotted as a function of temperature for the heating rate $v = 0.12 \text{ K s}^{-1}$. Bucciet al. [10] developed an exact analysis of discrete monoenergetic TSD peaks in terms of some kinetic parameters such as relaxation time τ_0 and activation energy A , respectively. Their analysis does not immediately apply to glasses, where distributed dielectric relaxations are expected. This is definitely also the case for the $\text{GeS}_{1.5} + x$ at % Cu glasses. Namely, for a given composition the temperature T_{max} (unless a saturation is reached). The situation is similar to the one in organic polymers, where several distributed polarization processes were detected [12]. van Turnhout [12] suggested to analyze TSD peaks from distributed polarizations by which of the two kinetic parameters is distributed. As a matter of fact, the multistage depolarization procedure applied to the set of curves from Fig. 1 indicated that most probably both τ_0 and A are distributed. Nevertheless, in

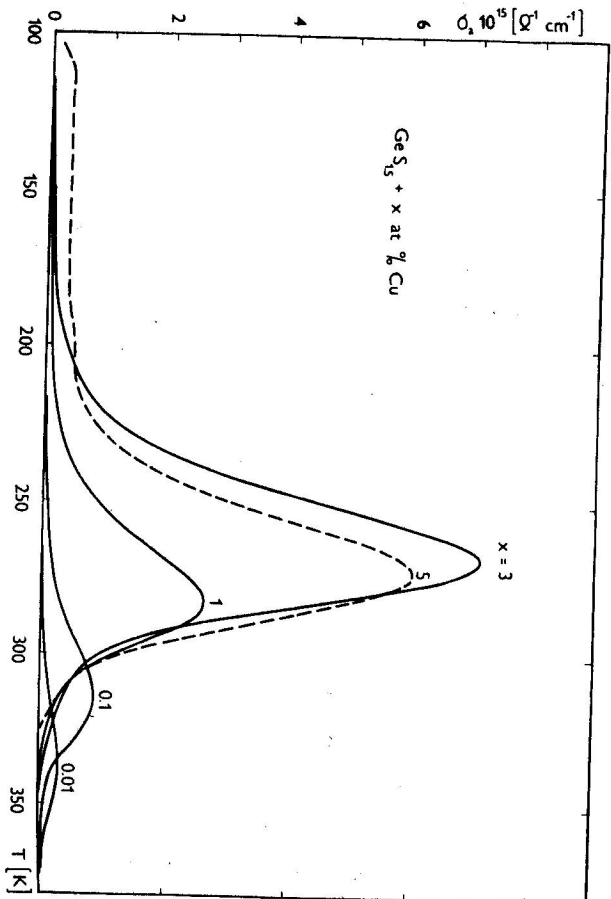


Fig. 1. A family of TSD thermograms of Cu-doped $\text{GeS}_{1.5}$ glasses, $v = 0.12 \text{ K s}^{-1}$. The broken line corresponds to a glass with 5 at % Cu, which was partially crystalline without additional heat treatment.

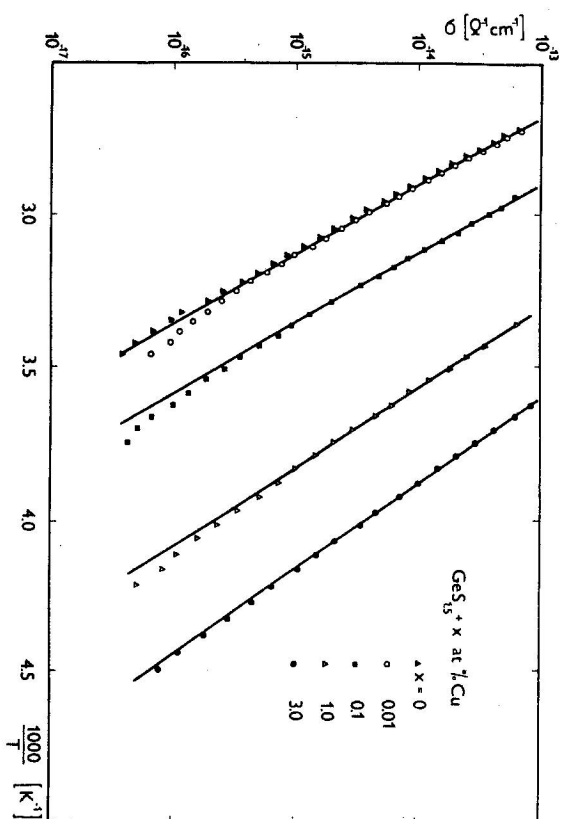


Fig. 2. dc conductivity of the Cu-doped $\text{GeS}_{1.5}$ glasses. The parameters σ_0 and A_0 are listed in Table 1.

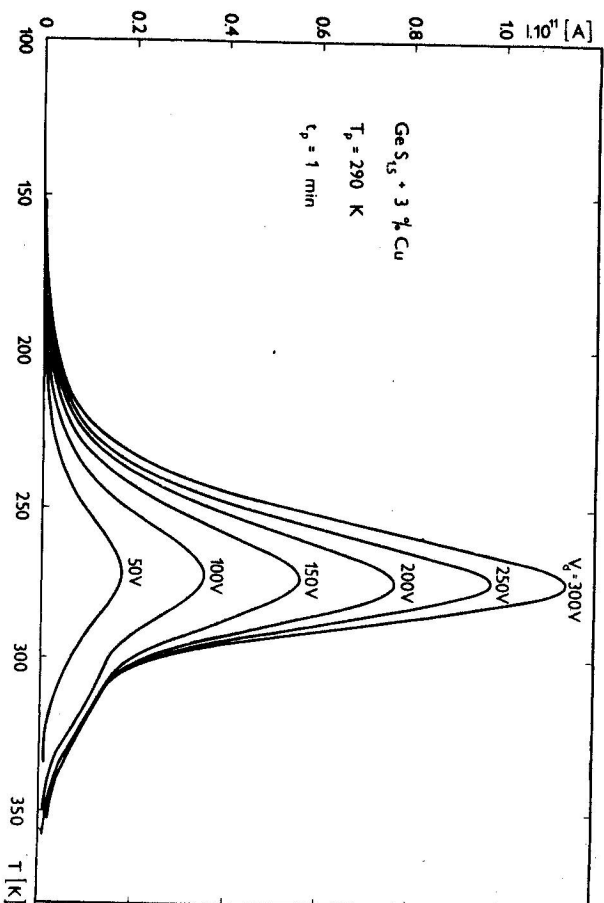


Fig. 3. The effect of bias voltage on the j - T thermogram.

Table 1 the activation energies A_{TSD} for each glass composition are given, obtained from the last heating run close to T_{max} . It is evident that the energies are not much lower compared with the corresponding energies A determined from dc conductivity measurements (Fig. 2). A correspondence between A_{TSD} and A might be obvious from Table 1. At present, no conclusive explanation is available for the finding that the energies do not coincide precisely.

Expressing dc conductivity as $\sigma_{\text{dc}} = \sigma_0 \exp(-A/kT)$, the σ_m values listed in Table 1 are of the order of $10^{-14} \Omega^{-1} \text{cm}^{-1}$. We will return to this point once more in connection with the discussion of the conduction mechanism, since most chalcogenide glasses are characterized by σ_0 from the interval $10^2 - 10^3 \Omega^{-1} \text{cm}^{-1}$.

The dielectric relaxation, characterized by the peaks in Fig. 1, is linear with regard to the voltage bias, as indicated by Fig. 3. Hence, an analysis of the peaks in terms of the Debye parameters is justified. Taking the curves from Fig. 1 and the expression for a dispersion of low frequency permittivity

$$\epsilon_1 - \epsilon_\infty = \frac{1}{\epsilon_0 v} \int_0^\infty \sigma_a dT \quad (1)$$

a strong influence of Cu doping on permittivity dispersion has been found — see Table 1³⁾.

Let us note that the shoulder on the high-temperature side of the TSD peak at 270 K in Fig. 3 is non-linear with respect to the bias. From our point of view the slower process might be due to a polarization of the electrodes and will, therefore, be excluded from further considerations.

IV. DISCUSSION

In our previous paper on thermal, structural and dielectric properties of Cu-doped Ge-S glasses [11] the dielectric behaviour was discussed in terms of the

Table 1

x	A_{TSD} [eV]	A [eV]	σ_m ($\Omega^{-1} \text{cm}^{-1}$)	A_{TSD}/A	$\epsilon_1 - \epsilon_\infty$
0.01	0.72	0.88	0.08	0.82	1.5
0.1	0.73	0.88	0.8	0.83	3.8
1.0	0.67	0.75	0.3	0.89	11.4
3.0	0.61	0.71	0.8	0.86	31.3
3.0 ⁴⁾	0.67	0.76	0.07	0.87	—

³⁾ The glass containing 5 at % Cu was partially devitrified.

⁴⁾ Heated up to $T_r = 325^\circ \text{C}$.

Maxwell-Wagner polarization of a heterogeneous dielectric, assuming phase separation of the glasses. In the course of the present discussion this conception will be reconsidered. It will be shown that an alternative explanation based on the assumption of a macroscopically homogeneous polarization in the glasses accounts more adequately for the observed behaviour. The effect of Cu doping on dc conductivity is compatible with the dielectric behaviour, which fact seems to confirm a close relationship between the two processes.

IV. 1. DISCUSSION OF THE DIELECTRIC RELAXATION

a) The Maxwell-Wagner-Sillars model of polarization

As pointed out by Charles [13], partial devitrification or phase separation can produce significant effects on the dielectric behaviour in glasses. In some cases the shape factors and concentrations of separated phases can be estimated from the dielectric measurements. Prior to an analysis of the influence of the Cu content on the TSD spectra from Fig. 1, it is worth mentioning that the $\sigma_a - T$ thermogram belonging to 0.01 at % Cu is essentially identical with that of the pure $\text{GeS}_{1.5}$ glass [8, 9]. In terms of the model the gradual shift of the peak toward lower temperatures with increasing Cu content might imply formation of a highly conducting species (σ_2 , ϵ_2) within the basic glass matrix characterized by the conductivity σ_1 and the permittivity ϵ_1 . This follows from the fact that the time constant of a dielectric containing highly conducting elongated spheroids is given as

$$\tau = \frac{\epsilon_0 \epsilon_1 (n-1) + \epsilon_2}{\sigma_2}, \quad (2)$$

n being the spheroid shape constant. Similarly, the growing area under the thermograms from Fig. 1 may reflect an increasing volume fraction q of the separated phase. The latter finding becomes evident when expressing the aftereffect constant $K = (\epsilon_2 - \epsilon_\infty)/\epsilon_\infty$ in the form [13]

$$K = \frac{q(n^2 \epsilon_1)}{\epsilon_1(n-1) + \epsilon_2} \quad (3)$$

and using (1) for $\epsilon_2 - \epsilon_\infty$.

Partial devitrification of the glasses containing more than 1 at % Cu after a proper thermal treatment was proved in our previous paper [11]. The change in the TSD spectrum induced by thermal treatment is evident from Fig. 4 and Fig. 5. A remarkable change could be observed when heating the sample containing 3 at % Cu up to $T_r = 325^\circ \text{C}$. This temperature corresponds fairly well to the temperature region at which the crystallization of the Cu_2GeS_3 phase takes place [11]. For

glasses containing less than 1 at % Cu no changes in the dielectric behaviour could be detected in accordance with the thermal differential analysis [11]. The additional TSD peak located at $T_{\max} \sim 120$ K (Fig. 5) is related to the presence of spheruloids of the separated Cu_2GeS_3 phase observed directly by the electron transmission microscopy — Fig. 6. The actual height of the 120 K peak is much greater than the measured one, since a considerable amount of the charge circulates the circuit prior to depolarization. Summarizing, the thermally treated (T_r) glasses containing more than 1 at % Cu are definitely phase separated. On the other hand, occurrence of phase separation in the virgin glass with 3 at % Cu is open to discussion, presented further.

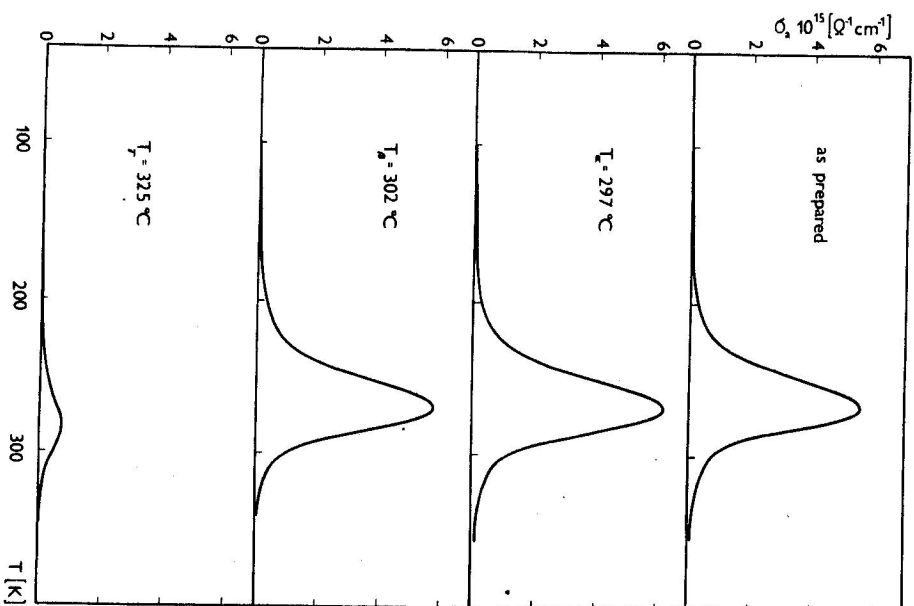


Fig. 4. TSD thermograms of a $\text{GeS}_{1.5} + 3$ at % Cu glass measured after heating the glass up to T_r , T_b and T_r , respectively.

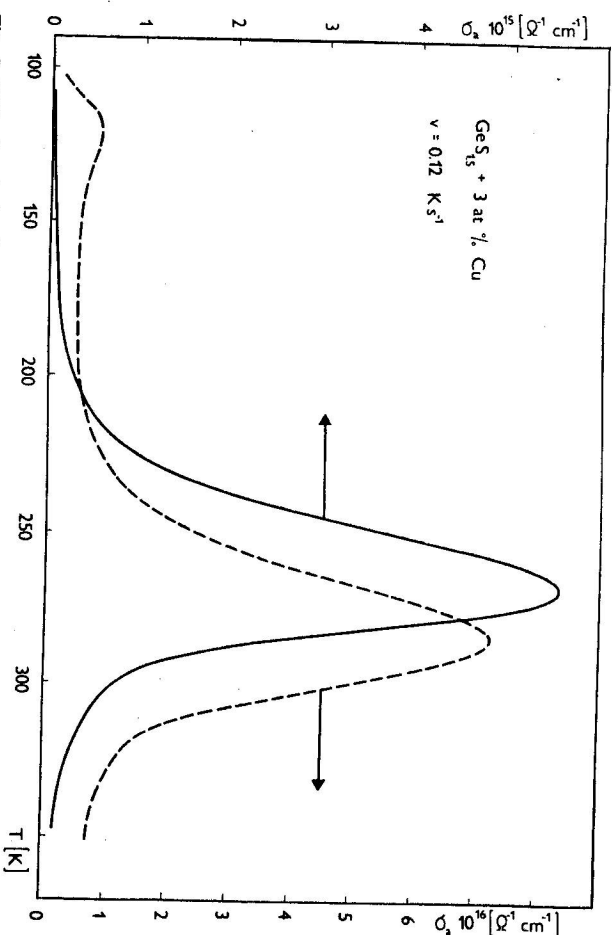


Fig. 5. TSD of a virgin glass is denoted by the solid line, the broken line reflects the TSD spectrum obtained after a heat treatment at $T_r = 325$ °C. Note the additional TSD peak located near 120 K.

The TSD peaks in Fig. 1 are very similar in nature in the sense that they do not exhibit any structure. Then, attributing the TSD to the Maxwell-Wagner-Sillars polarization, even the glasses with the lowest Cu content should be phase separated. The fact that only the TSD of the glass with the highest Cu concentration is influenced by the thermal treatment does not support this hypothesis. Another difficulty arises if we try to explain the changes in the conductivity of the glass with 3 at % Cu after the thermal treatment at T_r — Fig. 7. The conductivity of the glass decreased by almost two orders of magnitude compared with the virgin glass. The crystalline Cu_2GeS_3 is a semiconductor with an activation energy of conductivity of 0.15 eV [14], which is much less than A_{TSD} (0.61 eV). According to equation (2) A_{TSD} should correspond to the activation energy of the conductivity σ_2 of the highly conductive phase ($\sigma = \sigma_0 \exp(-A_{\text{TSD}}/kT)$). Then an increase rather than a decrease in conductivity is expected in the case of phase separation.

The volume fraction 0.03 of the separated Cu_2GeS_3 phase was estimated from Fig. 6. Denoting the diameter of the spheres by d and their diameter when they would touch by D , a ratio $d/D \sim 0.4$ is obtained. Following the calculation made by Champness and Hoffmann [15], touching spheres ($d/D = 1$) are required to account for a change in conductivity exceeding one order of magnitude. Therefore, any attempts to explain the decrease in conductivity assuming electrically isolated regions of polycrystalline Cu_2GeS_3 would fail, too.

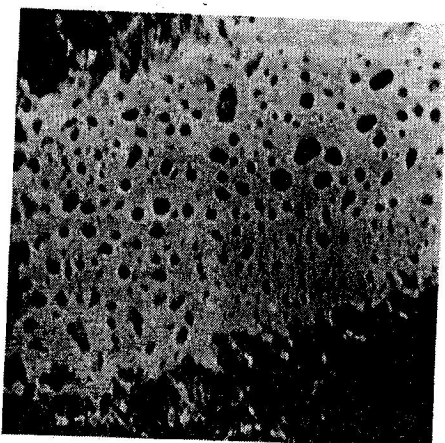


Fig. 6. Evidence for phase separation in glasses with 3 at % Cu after heating up to 325 °C (transmission electron microscopy).

From the above reasoning it might be obvious that the Maxwell-Wagner-Sillars model meets with some difficulties when interpreting the thermally induced changes in both dielectric behaviour and dc conductivity. Next, an analysis will be presented which utilizes models of dielectric relaxation in macroscopically homogeneous glasses.

b) Homogeneous polarization models

To account for the dielectric dispersion in both ionically and electronically conducting glasses, Isard [16] assumed inhomogeneities on a scale of a few angstroms. The composite material has a Debye-like dielectric relaxation characterized by a time constant

$$\tau = \frac{\epsilon_\infty \epsilon_0}{\sigma(0)}, \quad (4)$$

$\sigma(0)$ being the conductivity of the material in the limit $f \rightarrow 0$. The shift of the TSD peaks in Fig. 1 toward lower temperatures with an increasing Cu concentration is now attributed to an increase in the conductivity of the glass matrix, cf. Fig. 2. The effect of the Cu doping on the dispersion of the low frequency permittivity cannot be discussed as long as the conductivity mechanism is not specified.

Now, let us examine to what extent the thermal effects on both the dielectric relaxation and conduction in the glass with 3 at % Cu can be accounted for by the present model. Assuming that the peak at $T_{\max} \sim 270$ K is due to a homogeneous polarization, the shift of the peak toward higher temperatures after heating the glass up to T_r is easily explained by the remarkable decrease in conductivity (Fig. 7). The latter statement can be checked quantitatively, supposing in common with

Perlman and Unger [17] that the TSD measurements are approximately equivalent to the $\text{tg } \delta$ measurements with an effective frequency $\omega \sim 0.01$ Hz. The condition for a maximum $\text{tg } \delta$ is evidently $\omega \tau_{\max} = 1$. The TSD is always a maximum when $\tau = \tau_{\max} \approx 100$ s. The temperature T_{\max} is according to Bucci et al. [10] expressed by the relation

$$T_{\max} = \left[\frac{v A_{\text{TSD}} \tau_{\max}}{k} \right]^{1/2}.$$

Thus the temperatures at the maxima of the peaks from Fig. 5 are related as follows:

$$\frac{T_{\max}}{T_{\max}'} \approx \left[\frac{A_{\text{TSD}}}{A_{\text{TSD}}'} \right]^{1/2}$$

From Table 1 ($x = 3^*$, 3) $A_{\text{TSD}} = 0.67$ eV, $A_{\text{TSD}}' = 0.61$ eV and so the value $T_{\max}'/T_{\max} = 1.05$ is expected for the two thermograms from Fig. 5. Experimentally found T_{\max}' and T_{\max} at 285 K and 267 K, respectively, yield a ratio of 1.07 in excellent agreement with the predicted value.

The separated highly conducting polycrystalline Cu_2GeS_3 phase, manifested by the 120 K peak in Fig. 5, cannot contribute to the total conductivity significantly with respect to the d/D ratio of 0.4 [15]. Thus, the discussed conductivity change in the annealed glass is caused primarily by the change in the Cu concentration in the

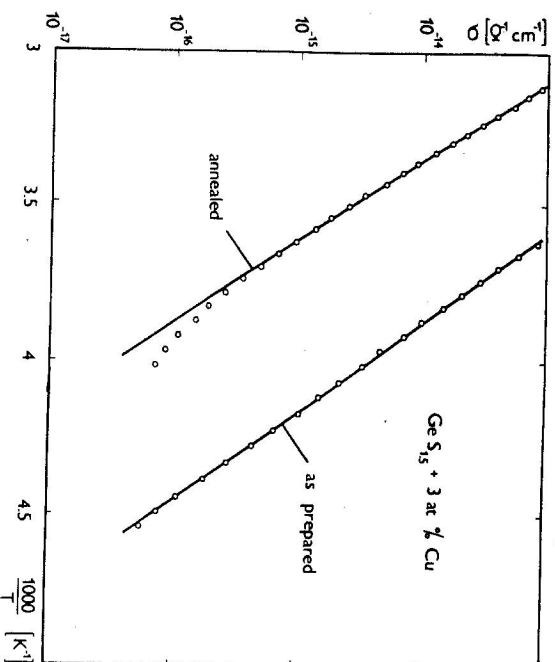


Fig. 7. The effect of heat treatment at $T_r = 325$ °C on the dc conductivity of a $\text{GeS}_{1.5} + 3$ at % Cu glass. for σ_0 and A_{TSD} , see Table 1.

matrix in the course of partial devitrification. Data on the mobility of Cu at the temperatures close to T_g would be valuable to settle this point definitely.

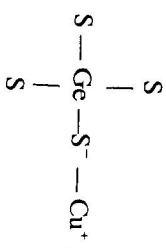
A specific model for the electrical behaviour of semiconducting glasses with copper was suggested by Drake et al. [17]. The authors assumed the presence of both cuprous (Cu^+) and cupric (Cu^{2+}) ions in the glass, the ions being able to exchange an electron. As a result of the transfer a Cu^+ ion has been located in a Cu^{2+} site, forming an inverted pair. The concentration of these inverted pairs, acting as dipoles, is expected to be thermally activated [17]

$$N_d = N_0 \exp \frac{\Delta S}{k} \exp \left(-\frac{\Delta H - q^2/\epsilon_0 \epsilon_d}{kT} \right).$$

Measurements of temperature dependence of the polarization are necessary for checking the theory. Unfortunately, the TSD technique is restricted to a narrow temperature region. A finite cooling rate represents an additional factor which prevented us from observing the desired dependence. Conventional ac bridge techniques are more suitable in this case.

IV. 2. DISCUSSION OF THE CONDUCTION MECHANISM

The large increase in the conductivity of chalcogenide glasses caused by Cu doping was approached by several authors, starting from the changes in the band gap. Liang et al. [3] ascribed the conductivity increase in amorphous As_2Se_3 to the decrease in the gap alone, but a vast increase in the number of hopping paths was suggested as an alternative explanation. According to Mott [4] the four-coordinated copper removes the D^+ centres in amorphous As_2Se_3 so that the Fermi level is no longer pinned and moves toward the valence band. Watanabe et al. [5] provided two tentative explanations for the conductivity of Cu-doped amorphous $\text{Ge}_{0.42}\text{S}_{0.58}$. The former was connected with a downward shift of the Fermi level with Cu negatively charged as a result of supplying one hole. The latter explanation involved reduced disorder in the glass containing copper with a consequent upward shift of the mobility edge. In this case Cu would act as a chain terminator:



The possibility that the charged Cu defects could be mobile has been ignored as yet. The measurements of the ionic transference number performed by Majková [19] revealed a considerable contribution of ions to the conductivity of the glasses $\text{GeS}_{1.5}$ doped with copper. Long-range ionic diffusion in glasses leads to a dielectric

relaxation, which is well established at present [20]. We suggest that the unusually low σ_0 values listed in Table 1 are associated with the ionic conduction, whereas the σ_0 factors of semiconducting glasses are by 3—4 orders of magnitude greater [7]. The effects of annealing on the behaviour of the glasses with a high Cu content provide further indication of a significant mobility of ionized Cu atoms at elevated temperatures.

V. CONCLUSION

Starting from the TSD analysis, the dielectric behaviour in Cu-doped $\text{GeS}_{1.5}$ glasses may be associated with microscopic rather than macroscopic inhomogeneities in the glasses. The glass with the highest Cu content (3 at %) was found to be phase separated after a heating up to 325 °C, the properties of the glasses containing less than 1 at % Cu remained unchanged upon heating.

The mechanism of the dielectric relaxation involves a long-range ionic diffusion of ionized Cu atoms rather than a hopping of electrons between the Cu^+ and Cu^{2+} centres.

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