

## ULTRASONIC RELAXATION AND RETARDATION OF DEFORMATION IN AMORPHOUS SELENIUM NEAR THE $T_g$ POINT\*

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The pure selenium in the amorphous state was investigated by means of both ultrasonic waves and retarded deformation. The distribution of relaxation times was observed in the range of very small values ( $10^{-8}$  s— $10^{-7}$  s) as well as in the range of long relaxation times ( $10$  s— $10^2$  s).

### УЛЬТРАЗВУКОВАЯ РЕЛАКСАЦИЯ И ЗАПАЗДЫВАЮЩАЯ ДЕФОРМАЦИЯ В АМОРФНОМ СЕЛЕНЕ В ОКРЕСТНОСТИ $T_g$ -ТОЧКИ

В работе приводятся результаты исследований чистого селена, находящегося в аморфном состоянии, которые были выполнены с помощью ультразвуковых волн и запаздывающей деформации. Спектр измеренных времен релаксации находится в области очень малых ( $10^{-8}$ — $10^{-7}$  с), а также в области очень больших ( $10$ — $10^2$  с) времен.

### 1. INTRODUCTION

Recently many amorphous semiconductors from the group of chalcogenide glasses have been investigated. Expressive relaxation phenomena due to the motion of the amorphous network were expected, as in the case of silicate glasses. However, measurements have exhibited that at temperatures above  $-190^\circ\text{C}$  there are not any remarkable relaxation maxima. On the other hand, the frequency dependences of ultrasonic absorption were not of a square character and therefore the presence of relaxation processes characterized by a distribution of relaxation times could be supposed. Many authors [1], [2], [3] attempted to describe the distribution by means of a convenient function. However, there were doubts whether this distribution function would keep its form at various temperatures, especially at those around the  $T_g$  point. Therefore we performed the investigation

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of the frequency dependences of absorption in amorphous selenium in the temperature range 0°C—80°C and determined the upper frequency part of the spectrum of relaxation times. The distribution in the range of long relaxation times was obtained by means of the observation of delayed deformation. Determination of these ranges of relaxation times is important mainly in cases, where it is necessary to determine the response of an amorphous network to an acoustical or quasistatistical impulse.

## II. METHODS OF DETERMINATION OF THE RELAXATION TIME DISTRIBUTION

As it is well known the absorption coefficient of ultrasound can be described in the presence of several relaxation mechanisms by means of the relation:

$$\alpha = \frac{\omega^2}{2\rho c^3} \left( \eta_\infty + \sum \frac{\eta_i}{1 + \omega^2 \tau_i^2} \right) = \frac{\omega^2}{2\rho c^3} \eta(\omega),$$

where  $\omega$  is the angular frequency,  $\rho$  the density of material,  $c$  is the velocity of the wave,  $\eta_i$  are the phenomenological viscosities of those relaxation processes whose relaxation times are comparable with the period of ultrasonic wave,  $\eta_\infty$  is the total viscosity of all the processes with relaxation times much smaller than the period of wave. The expression in brackets is called dynamical viscosity  $\eta(\omega)$ .

If the relaxation times are continuously distributed, the product  $\omega\eta(\omega)$  can be expressed as follows:

$$\omega\eta(\omega) = \omega\eta_\infty + \int_0^\infty \frac{H(\tau)\omega\tau d(\omega\tau)}{\omega\tau + \omega^2\tau^2},$$

where  $H(\tau) d\tau$  is the total viscosity of all mechanisms with the relaxation times from  $\tau$  to  $\tau + d\tau$ .  $H(\tau)$  is called the density of the relaxation time spectrum. In the first approximation the expression  $\omega\tau(1 + \omega^2\tau^2)^{-1}$  can be substituted by the  $\delta$  function, as it is presented by Michajlov [7], and then we obtain the following simple relation for  $H(\tau)$ :

$$H(\tau) = \omega[\eta(\omega) - \eta_\infty]_{\omega=1/\tau}. \quad (1)$$

In the case of the constant strain instead of the harmonic strain caused by ultrasonic waves, deformation does not take place immediately either; the medium reaches only gradually through many relaxation actions the new equilibrium state. This problem was discussed in detail by Primack [4]. If  $g(\epsilon)$  is the statistical weight of those relaxation processes whose activation energies are from the unit interval around the value  $\epsilon$ , then the experimentally measured deformation  $S$  as a function of time can be expressed as:

$$\Delta S(t) = \int_0^\infty g(\epsilon) \exp \left[ -At \exp \left( -\frac{\epsilon}{kT} \right) \right] d\epsilon, \quad (2)$$

where  $\Delta S = S_\infty - S$  is the deviation from the equilibrium value  $S_\infty$ ,  $A$  is the frequency factor. The function  $\exp \left[ -At \exp \left( -\frac{\epsilon}{kT} \right) \right]$  is for small  $\epsilon$  approximately equal to 0, for high  $\epsilon$  it reaches the value 1. The inflex point lies at the energy  $\epsilon_0 = kT \ln(At)$ . According to Primack [4] the function  $\exp[-At \exp(-\epsilon/kT)]$  can be replaced by a step dependence which changes its value from 0 to 1 at the activation energy equal to  $\epsilon_0$ . Then the relation (2) can be modified and has the form:

$$\Delta S(t, \epsilon_0) = \int_{\epsilon_0}^\infty g(\epsilon) d\epsilon,$$

and we obtain for the weight of the relaxation process with the activation energy  $\epsilon_0$  the equation:

$$g(\epsilon_0) = -\frac{\partial(\Delta S)}{\partial \epsilon_0}. \quad (3)$$

Using the relation  $\epsilon_0 = kT \ln(At)$  and  $\Delta S = S_\infty - S$ , (3) can be written as:

$$g(\epsilon_0) = \frac{1}{kT} \frac{\partial S}{\partial t}. \quad (4)$$

From the knowledge of the distribution according to the activation energies it is possible, by using the Arrhenian relationship, to calculate the distribution of relaxation times  $\tau$  or  $\ln \tau$ , respectively.

## III. EXPERIMENTAL PROCEDURE

The absorption of ultrasound in selenium at temperatures near to the  $T_g$  point exhibits very high values and therefore bulk samples cannot be used. As a convenient method of measurements in this case Mc Skimin's method [5] was used. The material of a thickness of about several wave lengths was placed between two fused-silica buffers. In order to realize a good acoustical binding, selenium was melted directly on the buffers. The surfaces of the buffer ends had to be polished most carefully. This way of binding secured also a good mechanical connection and hence an easy manipulation with the system. The temperature of selenium was measured by a thermocouple. As for an electronic arrangement a MATEC comparator was used. At temperatures below room temperature the measurement of absorption could be performed on bulk samples of a diameter of 5 mm and a thickness of 5 mm and the use of the buffers was not necessary. The holder with the sample was placed in a thermostat.

The high relaxation times were determined by the frequently used method which consists in observing the retardation of the strain under constant stress. The elongation of the fibres proportional to the stress was indicated by means of a differential transformer. The obtained electrical signal was registered by a printer at conveniently selected intervals of time. The desired temperature of the fibre was secured by placing the fibre in a tempered tube. The length of fibres was 30 cm,

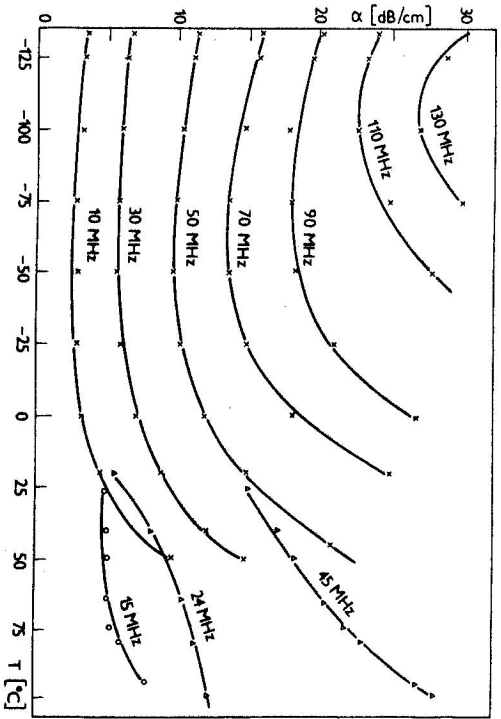


Fig. 1. Temperature dependences of absorption at various frequencies.

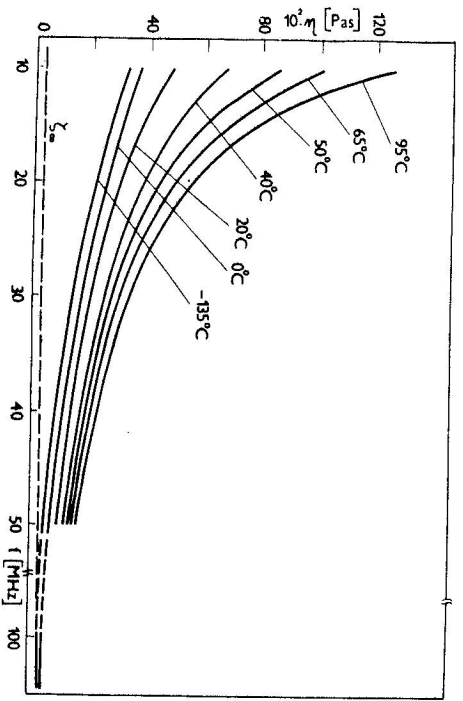
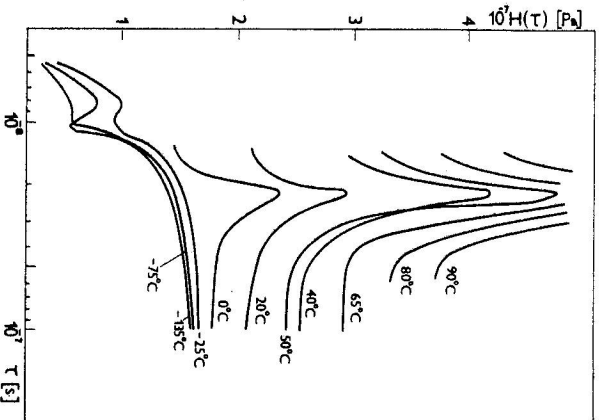


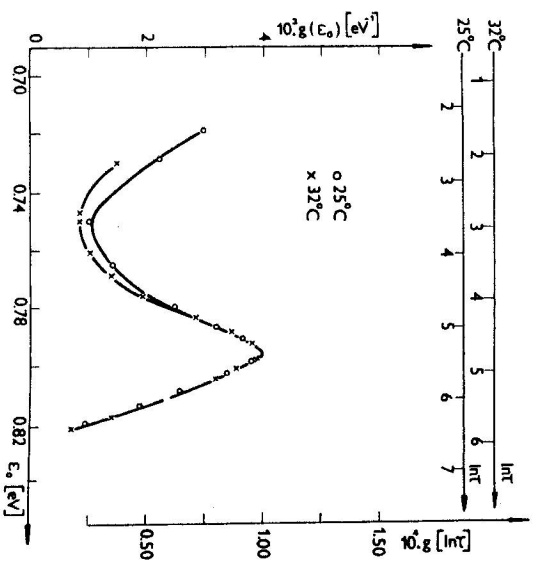
Fig. 2. Dynamical viscosity as a function of frequency at various temperatures.

Fig. 3. Distribution of relaxation times at various temperatures.



their diameter 0.5 mm. Each Se fibre was prepared in the same way but before the measurement the fibres underwent different heating histories. The conditions of measurements were so determined that the plastic deformation was negligible. Each set of temperature dependences was measured on the same fibre.

Fig. 4. Distribution of activation energies and relaxation times in the Se fibre kept for half a year at a constant temperature of 22°C—30°C



#### IV. EXPERIMENTAL RESULTS

The absorption coefficient of ultrasound at frequencies from 10 MHz to 130 MHz at temperatures from  $-190^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  is plotted in Fig. 1. The dynamical viscosity  $\eta(\omega)$  at several temperatures was determined by means of the relation [7]:

$$\eta(\omega) = \frac{2\rho c^3}{\omega} \frac{\alpha c}{\left[1 + \left(\frac{\alpha c}{\omega}\right)^2\right]^{3/2}} = \frac{2\rho c^3}{\omega^2}$$

The value of viscosity that does not change with varying temperature is  $\eta_{\infty}$ . The temperature dependence of viscosity is in Fig. 2. Supposing the presence of a continuous distribution of relaxation times, the density of this distribution can be calculated according to relation (1). The results obtained are in Fig. 3.

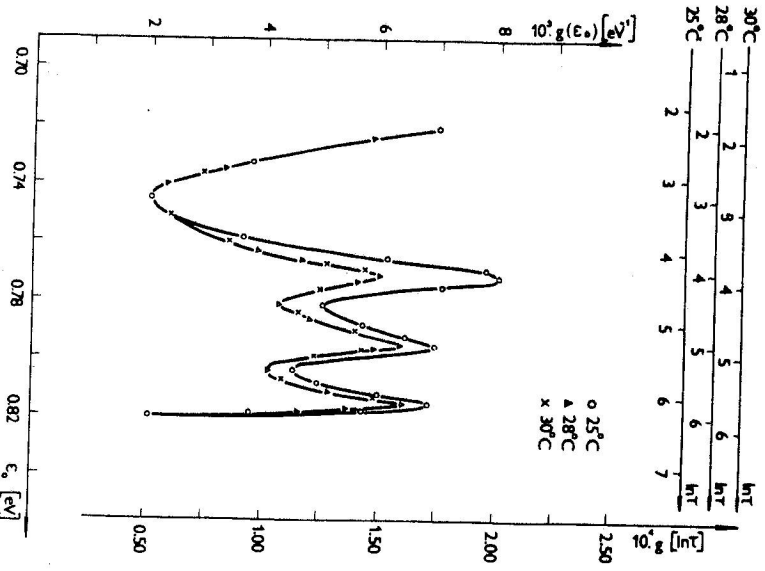


Fig. 5. Distribution of activation energies and relaxation times in the Se fibre kept for 30 days at a constant temperature of  $20^{\circ}\text{C}$

In the region of long relaxation times experiments concerning the retardation of deformation under constant stress were performed. Four types of selenium fibres with different heating histories were investigated. In Fig. 4 there is the distribution of activation energies and relaxation times, respectively, for the fibre heated at temperatures from  $22^{\circ}\text{C}$  to  $30^{\circ}\text{C}$  for half a year. The curves in Fig. 5 represent a fibre kept for 30 days at  $20^{\circ}\text{C}$ . In Fig. 6 there is the distribution in the fibre which was also kept for 30 days at a constant temperature of  $20^{\circ}\text{C}$  but in addition the fibre underwent one temperature cycle near the  $T_g$  point. ( $T_g \sim 32^{\circ}\text{C}$ ). Fig. 7 shows the distribution for the fibre which after being taken out from the melt was immediately put into the refrigerator ( $4^{\circ}\text{C}$ ) and after 7 days was taken out and immediately measured. The activation energies and relaxation times at which the maxima of the distribution function are observed are as follows:

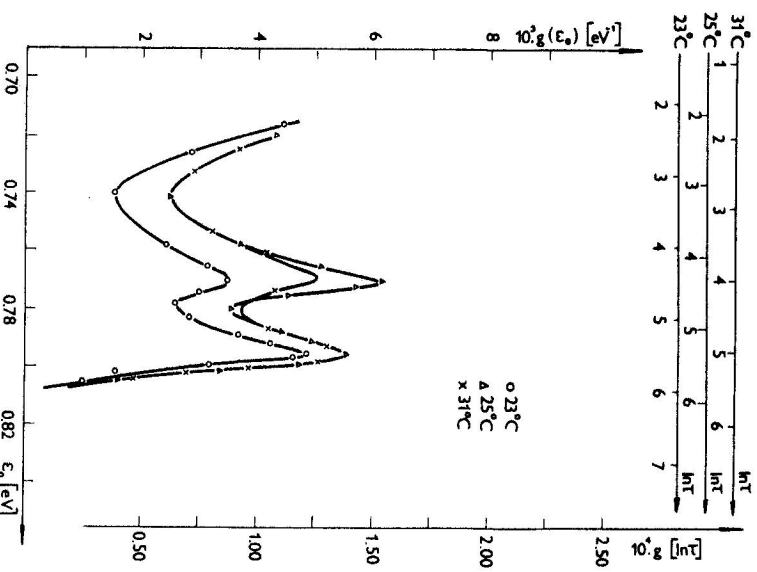


Fig. 6. Distribution of activation energies and relaxation times in the Se fibre kept for 30 days at a constant temperature of  $20^{\circ}\text{C}$ , but before measurement the fibre underwent one temperature cycle near the  $T_g$

other maxima raised at 0.770 eV and 83.4 s, 0.815 eV and 486.6 s. In the third type of fibre the last maximum disappeared and the fourth type exhibits four maxima. Three of them are the same as the previous ones and the new maximum lies at 0.805 eV and 290.1 s. The relaxation times are due to a temperature 25 °C.

#### DISCUSSION

The first remarkable property of the obtained distribution of the relaxation times is the similarity of their course at various temperatures. The fact that the position of the maxima does not change with temperature indicates that the Arrhenian relationship is not valid in our case. However, it is possible that the average value of distribution is shifted in some way. The conclusion that the presence of the

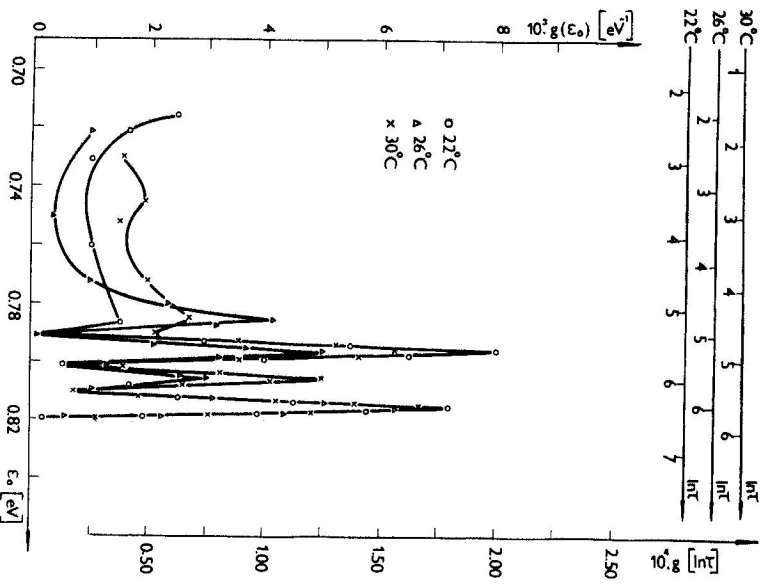


Fig. 7. Distribution of activation energies and relaxation times in the fibre which, after being taken out of the melt, was kept 7 days in the refrigerator at 4 °C and then immediately measured

distribution of relaxation times is related to the non-Arrhenian behaviour of viscosity in oxygen glasses has already been made by Litovitz and Macedo [6].

A further interesting fact is the quantitative increase of the value of the distribution function in consequence of increasing temperature. The complete course of the distribution function is not known yet, but the results in the investigated ranges suggest that it is connected with the statistic of a not closed group that contributes to the relaxation. It seems to be probable that in the high frequency region the relaxation can be caused by the moving of the holes. At rising temperature the free volume increases too, but in such a way that the free volume is distributed in a larger number of holes. However, the energy distribution of holes is preserved.

As regards the distribution of energy barriers resulting from the retardation of deformation, the most remarkable is the fact that the state of tension in the material leads to the rise of second maxima. After keeping the material at constant temperature the strain and also the corresponding maxima disappear. The reason for such a behaviour is in the technology of the fibre preparation. During the processes of being taken out from the melt fibres are cooled irregularly, especially in the radial direction. In the newly created fibre these must exist local strains between different macroscopic areas. The other consequence of irregular cooling is the rise of free volume [8]. Thus the fibre is an unstable material and only keeping the temperature constant for a long time disturbs these factors, and causes a densification of the medium and so diminishes the free volume. If we imagine the hole mechanism of the retardation of deformation, then the jumps of the holes take place first of all in the radial direction because of the radial gradient of the strain.

#### CONCLUSION

The obtained results concerning the relaxation time distribution have shown that the processes in glass at temperatures near the  $T_g$  point are of a cooperative behaviour. Further, on the basis of distribution it can be concluded that the acoustical influence at frequencies above 30 MHz conspicuously increases in the transformation region. The possibility of remarkable acousto-electric or acousto-optic effects can be expected just in this region. In the case of a quasistatistical mechanical influence of the parameters of the network it is necessary to wait at least about 50 s to reach a 90 % reaction of the network. It will be interesting to investigate other parts of the relaxation spectrum and then it will be possible to arrive at conclusions regarding all the rel. mechanisms.

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