acta phys. slov. 36 (1986), No. 2

ON THE RELATIONSHIP BETWEEN ULTRASONIC AND ELECTRIC LOSSES IN AMORPHOUS Se

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An experimental study of acoustic and electric losses in amorphous selenium in the temperature range 200—300 K and the frequency range 1—100 kHz is presented. From similar temperature dependences, the conclusion that the same hopping mechanism of atoms, respectively ions, is responsible for both kinds of losses in the viscoelastic range, has been drawn. Using a theoretical model for this kind of the hopping process, the number of natural polaronic defects has been estimated. The influence of thermal treatment and pressure on the mechanism of losses is discussed too.

О ВЗАИМОСВЯЗИ МЕЖДУ АКУСТИЧЕСКИМИ И ЕЛЕКТРИЧЕСКИМИ ПОТЕРЯМИ В АМОРФНОМ СЕЛЕНЕ

В работе приведены результаты экспериментального изучения акустических и электрических потерь в аморфном селене в области температур 200 – 300 K и диапазоне частот 1 – 100 кГц. На основе простых температурных зависимостей сделано заключение о том, что один и тот же прыжковый механизм атомов или ионов вызывает оба типа потерь в упруговязкой области. Исходя из теоретической модели для такого типа прыжкового процесса, было вычислено число поляронных дефектов. Обсуждается также влияние термической обработки и давления на механизм потерь.

I. INTRODUCTION

The presence of the connection between dynamic electric and dynamic mechanical properties of polymeric materials has long been known. This connection was attributed to tight bonds of electric dipole moments with the amorphous network. According to this supposition the movement of the dipole moments should be influenced by the viscosity of the material and so the dynamic properties in both cases are determined by the dynamic viscosity. The detection of such a connection also in anorganic polymeric material by Eisenberg and Tobolsky [1], studied later by Fiedler and al. [2], was a little surprising. In [1] and [2] an analogical mechanical and electric behaviour of Se was demonstrated at a very low frequency of the order Hz and kHz, respectively. The existence of the dipole moments in Se was not proved and therefore the obtained results were surprising and not clear.

The possibility to ascribe both electric and acoustic properties of many amorphous materials to the same physical origin was suggested by the pioneering work of Anderson [3] on the bipolaronic defect states. The basic feature of this model, developed by several authors [4], [5], [6] and connected with the conception of the tunneling-atom-theory proposed by Anderson, Halperin and Varma [7] makes it possible to connect the movement of polaronic defects with movement of atoms and so explain the observed very low temperature cross-electromechanical experiments performed by Schickfus and al. [8]. According to the recently published theoretical analysis of Russo and Ferrari [9] the intimate valence alternation pairs make also a contribution to these effects, which are obviously mathematically described by the two-level-system theory.

The question was if there exists some relationship between the very low temperature observations and the observations in a glas-forming temperature region that enables us to explain the same approach. In the past fifteen years the electric processes in amorphous materials have been explained in terms of mobility gaps, hoping processes and similar transport phenomena and no attention has been given to polarization effects. Only some authors predicted [10] or directly observed the effects which can be contributed to the dipole moments created by bipolaronic centres bounded to the network [14]. Therefore we have started experimental acoustic and electric investigations in the 20—100 kHz frequency range on the same samples of amorphous Se. The frequency range was chosen where the relaxation effects are clearly manifested for an appropriate temperature range and, on the other hand, the ionic transport and contact phenomena are negligible.

II. EXPERIMENT AND RESULTS

Low frequency ultrasonic measurements on solid materials are possible only on sufficiently large samples. Amorphous selenium rods ($\Phi = 8$ mm and $l =$ 30—60 mm) were prepared by rapid cooling of the Se-melt in an evacuated quartz glass ampule. Plates of 1 mm thickness were cutt off from each end of rods for electric measurements. The acoustic measurements were made using a reverbation technique. Quartz transducers were used to excite a mechanical resonator by the Se rod. The arrangement is illustrated in Fig. 1. The electric losses represented by the real part of a.c. conductivity were measured using a conventional audiofrequency bridge. The typical temperature dependences of both the ultrasonic attenuation and a.c. conductivity are shown in Fig. 2. The appearance of a new dominant mechanism is clearly seem from the sudden change in the slope of these dependences. Together with the real part of a.c. conductivity the imaginary part connected with capacitance changes due to polarization was performed. Using the

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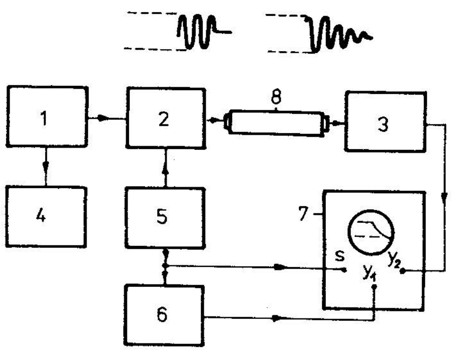
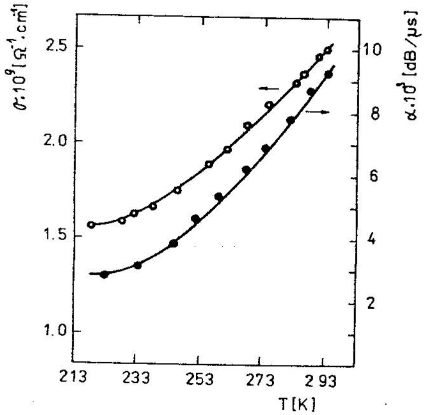
Kronig--Kramers formulas the measured values were compared with the real part values and good agreement was found. The small increase of a capacitance in the used temperature range is proof of the increase of polarizations. The results of measurements made at other frequencies in this region have shown a similar dependence but little shifted in the absolute values. Apart from these principal experiments the influence of the pressure and thermal treatment on the losses were investigated. In Fig. 3, the dependence of a.c. conductivity versus pressure for different frequencies is plotted for a slowly cooled (about 0.1 Ks^{-1}) sample. The effect of thermal treatment on the structure of the investigated samples is illustrated in Fig. 4 by a series of photographs made by a scanning electron microscope (SEM). This treatment changes the absolute value of losses and the slope of the pressure dependences as illustrated in Fig. 5.





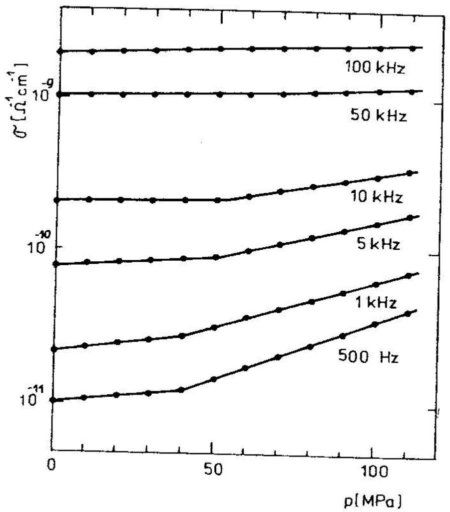


Fig. 1. The scheme of the used reverberation method: 1 — generator of the harmonic signal, 2 — gate, 3 — amplifier, 4 — frequency counter, 5 — pulse generator, 6 — generator of exponential decay, 7 — scope, 8 — sample with transducers.

Fig. 2. The temperature dependences of ultrasound longitudinal waves attenuation α and a.c. conductivity σ.

Fig. 3. The pressure dependence of the a.c. conductivity of slowly cooled Se at different frequencies.

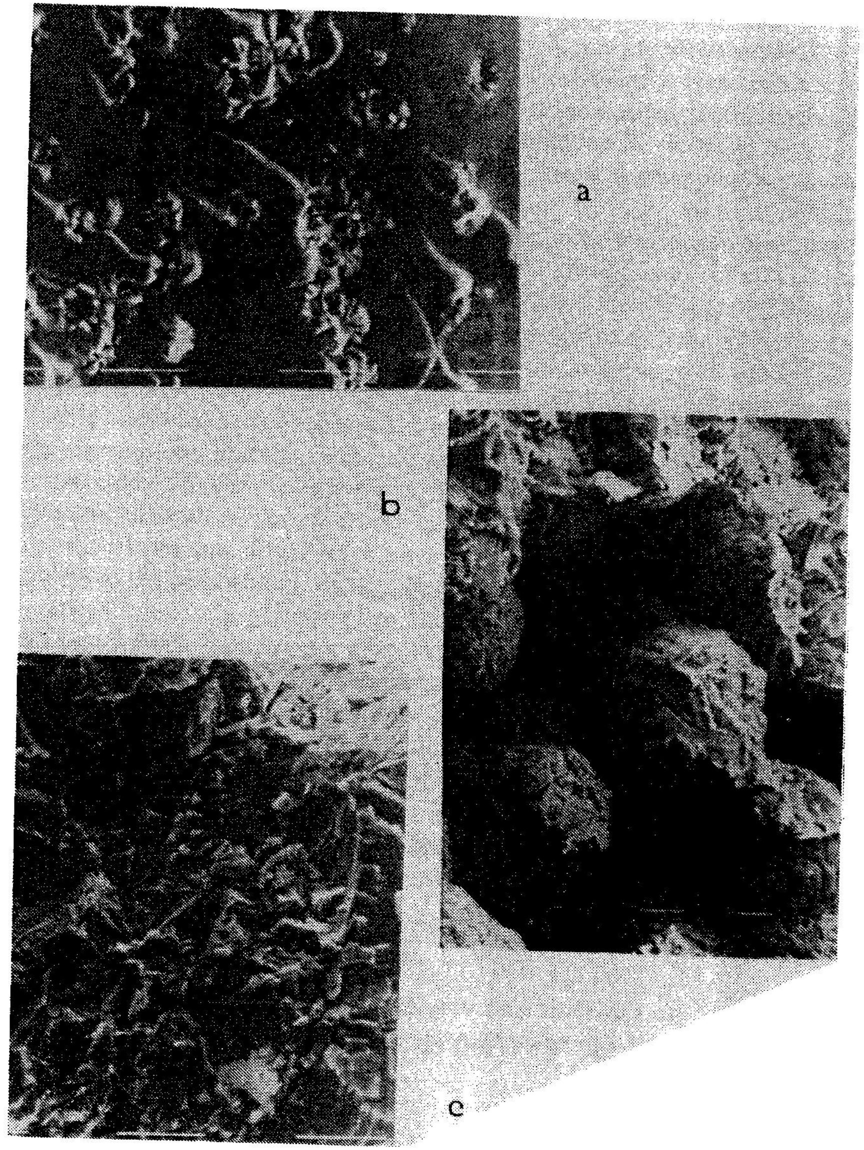


Fig. 4. The photographs of crystallized area inside the Se sample annealed at 60 °C (a), crystalized formations inside the Se sample annealed at 90 °C (b) and internal structure of crystallized (spherulite) units of the sample annealed at 150 °C (c). The samples were annealed for 6 hours. The marks on the photographs represent 10 μm.

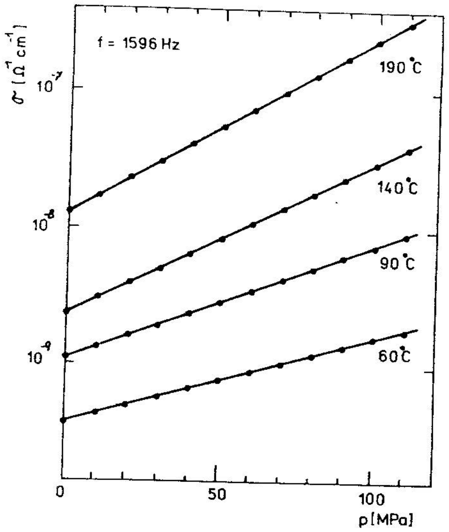


Fig. 5. The pressure dependence of the a.c. conductivity at 1596 Hz of annealed Se at different temperatures for 6 hours.

III. DISCUSSION

The observed increase of acoustic and electric losses can be interpreted using a distribution of relaxation times. Introducing this function for the mechanical case as

$$H(\tau)=\frac{\mathrm{d}\,(E_s-E_\infty)}{\mathrm{d}\tau}$$

where E_s and E_∞ are the static modulus and the modulus at very high frequencies, respectively, and for the electric case as

$$y(\tau)=\frac{\mathrm{d}\,(\varepsilon_s-\varepsilon_\infty)}{\mathrm{d}\tau}$$

where ε_s and ε_∞ are the static and very high frequency dielectric permittivity, respectively. The losses can be written as

$$\alpha=\frac{\omega}{2\varrho v^2}\int_0^\infty \frac{H(\tau)\omega\tau}{1+\omega^2\tau^2}\,\mathrm{d}\tau$$

$$\sigma=\omega\varepsilon_0\int_0^\infty \frac{y(\tau)\omega\tau}{1+\omega^2\tau^2}\,\mathrm{d}\tau\,.$$

Only the integrant can be temperature dependent and so the similarity of the temperature dependences can be a proof that the same mechanism is responsible for both relaxation processes. To roughly estimate the distribution function in the

first approximation, $H(\tau)$ or $y(\tau)$ is often taken equal for $\omega\tau\neq 1$ and so we can conclude that $H(\tau)$ and $y(\tau)$ are constant for $T<T_c$ and proportional for $T>T_c$.

The question is what kind of microscopical mechanism is responsible for such similar behaviour. Obviously a.c. conductivity is interpreted on the basis of (the so-called) hopping processes and mostly the hopping of electrons between two localized states is supposed. In ultra--acoustic losses the hopping processes are clearly connected with the hopping of atoms or their groups in a new quasi-equilibrium state. The coincidence of distribution in both cases can be a proof that the mechanism of electric losses in this temperature range should be also connected with the movement of the amorphous network. Thus we deal here with a shift of polaronic centres, which could be actually understood as a "hopping" of polaronic centres tightly bonded to the amorphous network together with the hopping of atoms, respectively ions. Such hopping, connected with the network movement can be in case of an electric field stimulated by an interaction of effective electric dipole moments with the electric field and in the acoustic case by the deformation potential created by the acoustic waves. Therefore we can use theories in which the calculations of losses are based in both cases on over-jump of atoms or ions through the potential barriers, distributed on a large scale. Calculations extending this approach to the case when a small difference between minima exists also without an external force were performed by Braciník [11] for the acoustic case and by Pollak and Pike [12] for the electric case. In such a case thermally activated over-jumping must be possible and absorption is caused by the asymmetry of population similarly as in all two-level-system conceptions. In principle the kind of excitation is not important. The situation will be controlled by the distribution of energetical differences and by the height of barriers. The above mentioned authors supposed homogeneous distributions of Δ differences and an equal width of all W barriers which can be from an interval $W_0<W<W_0+\bar{W}$. No correlation between these quantities was supposed. Under such simplified conditions they obtained the following expressions

$$\sigma(\omega,\,T)=\frac{1}{6}\,\pi\omega e r_0^2 N_e k_B T(\bar{\Delta}\bar{W})^{-1}\,\mathrm{tgh}\,(\bar{\Delta}/2k_BT)$$

$$\alpha(\omega,\,T)=\frac{1}{8}\,\pi\omega N_a B^2 k_B T(\varrho v^3\bar{\Delta}\bar{W})^{-1}\,\mathrm{tgh}\,(\bar{\Delta}/2k_BT)$$

where N_e and N_a are the numbers of excited over-jumping ions and atoms, respectively. In the first case the excitations are caused by the effectivity dipole moments (er_0), in the second case by the deformation potential B. This mechanism can work only when the temperature achieves a value which permits the over-jumping of the lowest barrier W_0. For a relatively small temperature interval the changes of the hyperbolic tangents will be small and the changes of α and σ will be linear.

Using these relations we have estimated the numbers of charged centres or atoms which participate in the processes. For the values $r_0 = 3.9 \times 10^{-10} - 1.17 \times 10^{-9}$ m, $\bar{\Delta} = 1,6 \times 10^{-20}$ J, $\bar{W} = 8 \times 10^{-20}$ J, $\omega = 2\pi \times 4.1 \times 10^4$ Hz and $\sigma = 2.5 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ we have obtained $N_e = (1.83 \times 10^{19} - 1.67 \times 10^{20})\ cm^{-3}$ and taking the values $B = 4.8 \times 10^{-19}$ J, $\varrho = 4.3 \times 10^3\ kgm^{-3}$, $v = 1.5 \times 10^3\ ms^{-1}$ and $\alpha = 0.71\ Npm^{-1}$ we have obtained $N_a = 1.48 \times 10^{20}\ cm^{-3}$.

We can see that these values coincide, which is not surprising. If we suppose that the loosening of the amorphous network begins in these points, where natural defects are present, the number of hopping atoms will be directly connected with the concentration of charges and a loosening decrease in the motion of these centres will start in the same temperature range. The over--jumping will produce a change of the electric momentum and this will be in an analogical way connected with the mechanical properties as a reorientation of hard dipoles tightly bound to the network.

This model corresponds also to the pressure dependences of a.c. conductivity and structural changes. A.c. conductivity is independent of the pressure in the high frequency region, but in the low frequency range up to 100 kHz some pressure dependence was found. That means that the electron hopping processes responsible for high frequency a.c. conductivity are not influenced by the pressure, but the atomic hopping processes in a low frequency range can be very strongly influenced. In our previous work [13] we have demonstrated that the pressure dependence of the low frequency a.c. conductivity is strongly dependent on the thermal treatment. We have studied these conditions by examining the structural changes called forth by the thermal treatment. It is clearly visible that the thermal treatment leads to the formation of spherulite structural units connected with the creation of many natural defects on the boundaries of spherulites which can be influenced by the pressure. Ultrasonic measurements were made by measuring the velocity dependence on pressure. A weak linear dependence is also due to structural changes but the direct measurements of losses were not possible in spite of an oil medium used in the measurements. Thus we have found the conditions which lead to the growth of atomic hopping processes which contribute to the acoustic and electric losses in the low frequency region.

V. CONCLUSIONS

From our observations we can conclude that a common feature of both the acoustic and the electric losses observed in the viscoelastic temperature region is caused by the same atomic hopping processes provoked by external forces. These hopping processes predominantly occur in natural defects connected with bipolaronic centres. The shift of polaronic centres caused by atomic hopping processes is equivalent to a reorientation of the dipole moments formed by the bipolaronic defect centres. Below some critical temperature this re-orientation is not possible and some effect of "sperrpolarization" occurs similar to the "sperrmagnetization" in amorphous magnetic materials. Above this temperature the increase of polarization losses and acoustic losses with the increasing temperature is linear, which is connected with the relaxation time distribution function.

A suitable thermal treatment of the material leads to an increase in the number of polaronic centres which can participate in these processes. The influence of pressure on the a.c. conductivity can be interpreted as a change of barrier heights, which should be over--jumped at the atomic hopping.

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Received February 12th, 1985