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THE TEMPERATURE DEPENDENCE OF THE ABSORPTION COEFFICIENT OF ULTRASOUND IN AMORPHOUS As_2Se_3 DOPED WITH Cu AND I

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The absorption coefficient of longitudinal ultrasonic waves in amorphous $As_2Se_3 \,.\, Cu_{0\cdot06}$, $As_2Se_3 \,.\, Cu_{0\cdot12}$, $As_2Se_3 \,.\, Cu_{0\cdot25}$ and $As_2Se_3 \,.\, I_{0\cdot06}$ was measured in the frequency range of (20—100) Mc/s by the pulse echo method. The samples were of cylindrical shape and their bases were polished with a plan-parallelism of 1×10^{-3}mm.

The attenuation was measured continuously in the temperature range of 150—340 °K. For temperature variation the simple cryostat with a continuous sliding of the sample was used. The rate of change of temperature was about 0.3 deg min^{-1}. It follows from the measurements that at the given frequency and temperature range an increase of temperature causes a monotonic increase of the absorption coefficient similarly as we observed recently in pure amorphous As_2Se_3. Both kinds of impurities cause an increase of absolute values of the absorption coefficient in measured samples. The investigation of the frequency dependence of the absorption coefficient at room temperature proved its non quadratic character. This indicates the existence of relaxation mechanisms, but in the investigated temperature interval and at the frequencies the clean-cut relaxation peaks were not observed.

I. INTRODUCTION

Recent investigations [1], [2], [3] of the pure amorphous As_2Se_3 and As_2Se_3 with the impurities of Cu and I showed that the impurities influence the propagation of the mechanical waves, which becomes rather obvious in the ultrasound range (tens of Mc/s) by a velocity change of the propagation of the ultrasonic longitudinal waves and by the increase of their attenuation at room temperature. This fact is significant because in the amorphous semiconductors impurities cause only small changes of electric conductivity in comparison with those in the crystalline ones [4]. It is due to the fact that for the mechanical properties of an amorphous system not only the short range arrangement

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but also the character of the couplings between individual structural units, ordered regions, is important and this is markedly influenced by the atoms of the impurities, which arrange — make better or worse — bonds by their embodiment into the amorphous net, while for the electric properties the short arrangement is of a decisive importance.

In the present paper we continue our previous investigations of the amorphous As_2Se_3 [3] mainly by a more detailed examination of the temperature dependence of the attenuation of longitudinal ultrasonic waves. It shows that this dependence has another character than that for crystalline materials and with regard to the non-quadratic character of the frequency dependence it is not possible to use common relations directly.

II. EXPERIMENTAL TECHNIQUES AND RESULTS OF MEASUREMENTS

The attenuation coefficient has been determined by the graphical and numerical evaluation of the echo picture obtained by the one-probe or two-probe method by recording the passing of the ultrasound impulses (3—10) μs along the investigated samples. The following samples were used for measurements: $As_2Se_3.Cu_{0.06}$ % at, $As_2Se_3.Cu_{0.12}$ % at, $As_2Se_3.Cu_{0.25}$ % at, $As_2Se_3.I_{0.06}$ % at ... All of them were cylindrical shape (14 ÷ 24) mm in length and (15 ÷ 16) mm in diameter. The faces of the samples were carefully ground and polished so that they were both flat and parallel. The lengths of the stamples were thus constant near the area of the faces with an error of less than 1 μm. With regard to the low electric conductivity of the samples the faces were plated by Au or Ag layer less than 1 μm in thickness. For excitation and detection of longitudinal ultrasonic waves *X*-cut quarz transducers plated on one side or on two sides were used (5 ÷ 10) mm in diameter and with basefrequencies at (6 ÷ 11) Mc/sec. Dehumidified silicon oil M-200, M-500 or salol were used to bind acousticly the transducers to the samples. The used bonds were of ≈ 1 μm thickness or thinner.

The temperature changes of the sample, fixed in a simple holder with a Cu cover were obtained in a specially adapted low-temperature equipment by control of the level of the refrigeration medium (liquid nitrogen) and by a continuous slow shifting of the sample holder into the thermal field of the whole cryostat system. Thus it was easy to reach the speed of temperature change of 0.3 deg. min^{-1} or considerable lower. To measure the temperature a Cu-constantan thermocouple was used, the thermo-junction of which was placed on the surface of the middle part of the cylindrical sample. The temperature gradient check proved that at a speed of temperature change lower than 0.1 deg min^{-1}, the temperature gradient was smaller than 0.5 deg cm^{-1} (in the long samples). The influence of the temperature gradient became evident only in those cases when the temperature change rate was several centigrades per minute, mainly in the liquid acoustic bond as a result of the sample deformation and thus also of the thickness changes of the binding layer. Under these circumstances the phase changes cause considerable distortion of the attenuation ratio as a result of the fact that the electric pulse detected by the transducer is proportional to the integral of the pressure distribution on the transducer. The phase changes are also important at temperatures in the range of the gradual solidification of the binding liquid, therefore it is necessary to be very careful when estimating the temperature dependence of the attenuation. Similar difficulties occur also in solid acoustic bonds at temperatures causing such changes of dimensions of the quartz transducer and the measured sample that a partial or complete destruction may result.

The original measurements of the frequency dependence of the longitudinal ultrasonic waves attenuation were extended to the frequency of up to 100 Mc sec^{-1}. The results of these measurements are shown in Fig. 1.

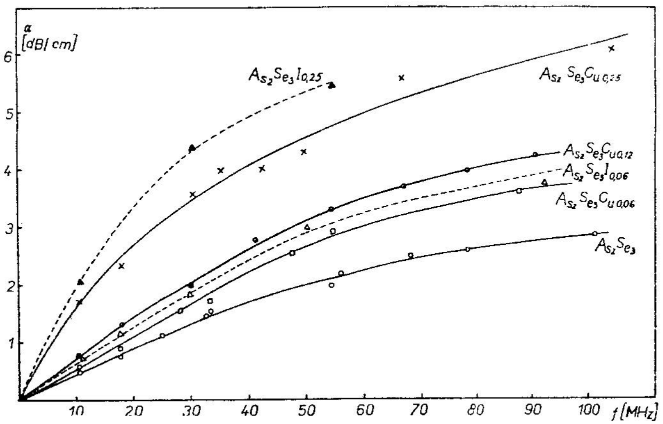

Fig. 1. The frequency dependence of the attenuation coefficient of pure amorphous As_2Se_3 and As_2Se_3 with the impurities of I and Cu, at room temperature.

It is evident from the picture that conclusions mentioned originally for the frequency range of (3.5 ÷ 25) Mc sec^{-1} may be extended also for higher frequencies in the following sense:

1) the dependence of the attenuation coefficient as a function of frequency is for all the samples less than quadratic and therefore typical for amorphous materials.

2) The impurities of I and Cu increase the attenuation due to further

dispersive mechanisms regardless of whether the impurities increase (Cu) or decrease (I) the velocity of the longitudinal ultrasonic waves in the corresponding frequency range.

The dependence of the attenuation coefficient as a function of temperature has been measured for the above mentioned samples in the temperature range of about (150 ÷ 340) K. Since a mechanical disturbance of the bond resulted for various diameters of transducers and acoustical binders, the individual measurements are plotted within a temperature range. The transducers, smaller in diameters, allowed to reach lower temperatures. In this way it was possible to measure nearly at the temperature of liquid nitrogen with salol and a polished and on one side plated transducer 5 mm in diameter. Temperature dependence of the attenuation will be discussed in the following parts of this paper.

In Fig. 2 the results of measurements in the sample are shown with a Cu impurity of a concentration of 0.06 % at. At both measurements the bond of silicon oil M 200 and the two-probe method were used. It is evident that the temperature decrease leads to a decrease of the attenuation coefficient; This curve is in the boundary region at a frequency in the range of 50 Mc sec^{-1} marked by a dashed line.

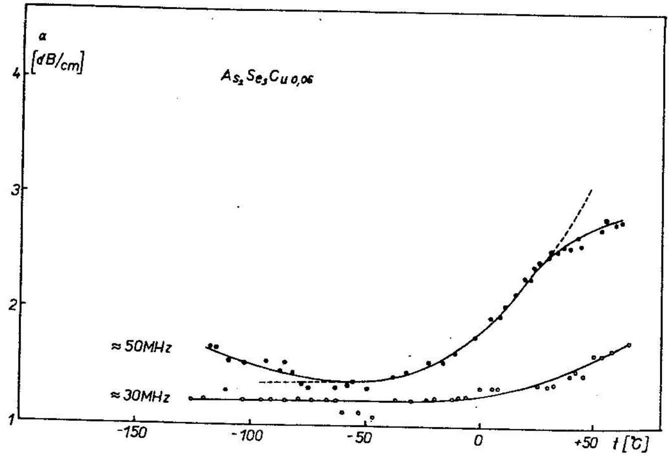

Fig. 2. The temperature dependence of the attenuation coefficient for amorphous $As_2Se_3.Cu_{0.06}$.

We may explain the measured increase of the coefficient of attenuation by the above mentioned change in the binding layer within the solidification temperature range of the binding liquid.

The temperature dependence of the attenuation coefficient for the Cu impurity at the concentration of 0.12 % is shown in Fig. 3. The lower curve has been obtained with an oil bond and the upper one with salol. There are several interesting things on the upper curve. After melting and thus regenerating the previously destructed salol bond, the temperature increased up to +70 °C (denoted +), the further part was detected at a decreasing temperature (denoted Δ). Let us take notice of the pronounced deviation from the full line in the vicinity of +43 °C, which corresponds to the solidification of salol bond. The further values denoted by rings were obtained at a very rapid cooling, to a temperature as low as −170 °C.

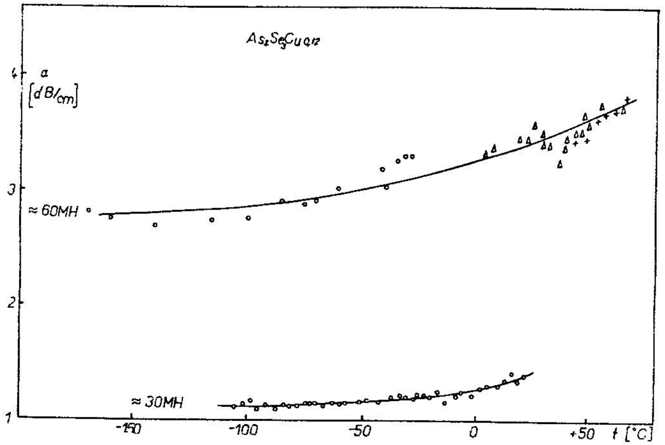

Fig. 3. The temperature dependence of the attenuation coefficient for amorphous $As_2Se_3.Cu_{0.12}$.

The sample of Cu with the concentration of 0.25 %, for which values plotted in Fig. 4 were obtained, presents similar temperature dependences of the attenuation coefficient as those of the above samples. The curves for ranges of 18 Mc/sec, 30 Mc/sec and 50 Mc/sec were obtained with use of the silicon oil, the last one with the use of the salol bond. The curve for 30 Mc/sec with values denoted by × was measured at a decreasing temperature and that denoted with rings at an increasing temperature.

The influence of the impurities of I with the concentration of 0.06 % on the temperature dependence of the attenuation coefficient is shown in Fig. 5.

In all measurements the salol bond was used and the curves for 50 Mc/sec and 90 Mc/sec were obtained with the same bond.

All the plotted temperature dependences in the examined temperature and frequency ranges correspond approximately to the shape of the temperature dependence of the attenuation coefficient for pure As_2Se_3 given in previous papers [3], [5]. The influence of both kinds of impurities Cu and I is more pronounced in the region of higher temperatures, i. e. when approaching the softening point, markedly pronounced in the sample with the impurity of I. In the region of low temperatures the plateau can be seen on all curves, and its starting point shifts with increasing frequency to the region of lower temperatures.

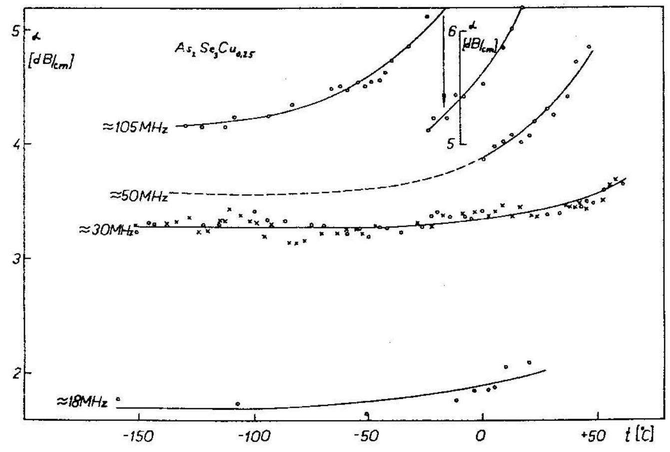

Fig. 4. The temperature dependence of the attenuation coefficient for amorphous $As_2Se_3.Cu_{0.25}$. The part of the curve for 105 Mc/s is displaced in the direction of the axis α.

It is evident from the given dependences that the frequency curves for higher temperatures than room temperature will be shifted to the region of higher attenuations while for lower temperatures they will be below the curves corresponding to room temperature.

The used experimental equipment and especially the properties of the materials used for creating the acoustical bond between the sample and the transducer did not allow to obtain data about the process of the temperature dependence of attenuation in the region below 150 °K, which would enable us to link our measurements to those within the temperature region mentioned in [6], which would have a considerable importance not only for obtaining empirical relations but also for the theory of attenuation of the ultrasound in amorphous systems. Let us remember too that extending measurements of temperature dependences to the region of temperatures close to the softening point of individual samples is dangerous because of the possibility of their tempering by cooling to glass, with different mechanical properties, which may cause destruction. The maximum found in the sample with the impurity of I is probably due to superheating and an insufficient cooling.

The measurements were namely made shortly after plating the bases of the sample in the process of which the sample had been considerably superheated; repeated measurements this maximum was not observed. Therefore it may be expected that the technology of preparation of the sample will reflect not only on the curve of the temperature dependence of the attenuation coefficient but also on the value of this coefficient.

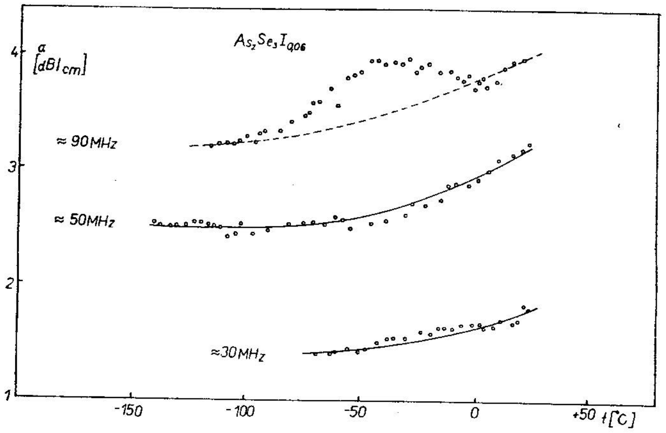

Fig. 5. The temperature dependence of the attenuation coefficient for amorphous $As_2Se_3.I_{0.06}$.

III. DISCUSSION

As it was shown by Ďurček et al. in [5], the coefficient of attenuation within the considered frequency range for pure As_2Se_3 can be expressed by the empirical relation

$$\alpha = A\omega + B\,\frac{\omega^2\tau}{1 + \omega^2\tau^2}\,, \qquad (1)$$

where $A = 2.8 \times 10^{-9}$ dB s cm^{-1}, $B = 8.42 \times 10^{-9}$ dB s cm^{-1} and $\tau = 6.37 \times$ $\times\ 10^{-9}$ s. For such an expression of α it is possible to explain its first — with regard to ω — linear term by the dispersion of ultrasound waves on the static field of deformations around motionless dislocations assuming that the interatomic forces are non-harmonic. The second part of (1) can be explained by the interaction of the acoustic wave and the thermal oscillations and identified with the expression for the attenuation coefficient given by Maris [7] if

$$B = \frac{CT\gamma^2}{2\varrho v^3} \tag{2}$$

where C is the specific heat of the volume unit, ϱ is the density, v the velocity of the ultrasonic waves and γ is the dimensionless Grüneisen parameter. If we require the expression for α in the form of (1) also for samples with impurities — of course with other constants A, B, τ — these would have to depend on the concentrations of impurities. Such dependence is obvious for A in the range of not very low temperatures (since atomic impurities participate significantly in forming bonds between ordered regions and so they determine the character of the static field of deformations in an amorphous structure. The dependence of B on the concentration would be mediated by v, ϱ, C and also γ. However, it should be most pronounced in the relaxation time τ.

Since the second term in (1) contains besides the absolute temperature T also quantities depending on T, namely $C(T)$, $\varrho(T)$, $\gamma(T)$ and first of all $\tau(T)$, there is a possibility of explaining the temperature dependence of the attenuation coefficient from it on the assumption that v varies only negligibly with temperature. The dependence on temperature in the first term of (1) could be namely mediated only through the parameter A, to which the change in the static field of deformations corresponding to the change of temperature would correspond. However, the assumption seems to be acceptable that in the range of very low temperatures the static field of deformations practically does not changed.

The relatively wide plateau in the experimental curves of the temperature dependence of the attenuation coefficient may be explained by the fact that both parts in (1) in this temperature range vary with temperature only to a small extent since to admit mutual compensation, i. e. the increase of one part being compensated by the decrease of another seems to be hardly justifiable. Therefore it is necessary to assume that in the range of the plateau the slight dependence of the second term on temperature is connected in the first place with such a dependence of specific heat and relaxation time on temperature that the whole second part of (1) varies with temperature very slightly. In the very low temperature range, however, the change of total character of this dependence may be expected.

The indicated analysis of the influence of impurities does not respect the own relaxation mechanisms of the atomic impurities. Therefore we shall mention also an other, although formal, approach explaining the measurements. From the frequency dependences shown in Fig. 1 it is easy to obtain the curves for the difference between the attenuation coefficient of samples with impurities and that of the pure amorphous As_2Se_3. These curves have at room temperature a similar character as the similar frequency dependence for pure As_2Se_3, therefore they can be described by an analogous formula as in (1), of course with other constants. It leads in the end to the conclusion that for the samples with impurities it is suitable to express the attenuation coefficient in the form:

$$\alpha = A'\omega + \sum_k B_k \frac{\omega^2 \tau_k}{1 + \omega^2 \tau_k^2}, \tag{3}$$

where the constants A' and τ_k have an analogous meaning as in relation (1) and the summation refers to all kinds of relaxation mechanisms. However the constants B_k — dependent on temperature — there is not such a direct connection with the expression of (2).

IV. CONCLUSION

The obtained temperature dependences of the attenuation coefficient in the given frequency range lead to the opinion that the decrease of temperature causes the decrease of the attenuation coefficient, higher at about room temperature, lower in the low temperature range.

The circumstance that we have not observed conspicuous narrow maxima on the curve of the temperature dependence of the attenuation coefficient and the non-quadratic frequency dependence suggest the existence of a very broad spectrum of relaxation times for the process of the transfer of atoms binding individual ordered regions into an amorphous structure and also for that of the atoms of impurities. Therefore the given explanation of the temperature dependences must be regarded as only a rough approximation and to find a more suitable explanation of the attenuation of ultrasound in amorphous systems.

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