Attenuation and Velocity of Ultrasonic Waves in Amorphous Selenium in the Vicinity of the Glass Transition

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Attenuation and velocity of longitudinal ultrasonic waves have been measured in a-Se in the vicinity of the glass transition. Both quantities are shown to be affected significantly by the stabilization process below the glass transition temperature T_g. Equilibrium values of sound velocity are also reported for the range 25 °C to 45 °C. The decrease (increase) of attenuation (velocity) during stabilization is reversed at higher temperatures. The connection of both quantities is discussed in terms of an effective temperature which allows the approximate determination of equilibrium values of attenuation (and possibly of other structure related properties) from measurements performed in nonequilibrium states.

1. Introduction

Because of its simple chemical constitution amorphous bulk Selenium has very early been considered as a model glass and its vitrification was studied mainly by dilatometric and by viscosity measurements. A review of this early work may be found in Reference [1]. Despite longstanding and intensive efforts to determine the structure of vitreous Se there still remain considerable uncertainties [2-12]. While the general view is that Se in its glassy form is made up of a mixture of Se_8-rings and polymeric chains, the existence of Se_6-rings has also been suggested [5, 6] and estimates of the relative amounts of each species differ widely. Studies of elastic properties using high frequency elastic waves are not very numerous [13-15]. Some data on longitudinal sound velocity are also reported in Reference [16]. Elastic constants usually agree within a few percent. Among their temperature derivatives more serious discrepancies are found.

Changes of properties with time have been reported for Se about fourty years ago by Jenckel [1, 17]. These effects called "stabilization" or "after-effects" are typical for glasses in general [17, 18]. Effects of this type concerning thermal properties of a-Se have recently been reported by Cornet and Rossier [20] and by Stephens [21] and concerning various properties of glassy Se and Se-Te alloys by Das et al. [22]. In view of the accuracy available with ultrasonic techniques it is very probable that discrepancies among the results of different investigators are at least in part due to differing sample properties resulting from different thermal histories. In any case the impor-

tance of the stabilization process seems to have been underestimated since none of the papers [13-16] (and very few of Refs. [2-12]) give an account of thermal history apart from sample preparation. This article reports on experiments on propagation of ultrasonic waves in samples of carefully controlled thermal history including in particular data on attenuation on which almost no results have been published so far and, for the first time, equilibrium values of sound velocity below 30 °C.

2. Experimental

Ultrasonic measurements were performed using conventional commercially available pulse echo equipment. Attenuation was determined by matching a calibrated exponential to the echo train. Velocity was calculated from the travel time of the echoes by use of a delay generator the accuracy of which was improved by continuous recalibration with a quartz-stabilized digital counter. Transducer influence was corrected for as described elsewhere [23].

In order to determine the frequency dependence of attenuation it would be desirable to cover as wide a frequency range as possible. An upper limit to this range is set by the increase in attenuation with frequency at about 40 MHz. Thus an extension would be possible only towards lower frequencies which would require making the samples as large as possible. As a compromise a diameter of 22 mm and a minimum length of 7 mm was chosen for the cylindrical samples allowing in principle measurements from 3 MHz upwards due to the rather low velocity of sound in a-Se.

Preparation of the specimens was started with quenching a melt from about 300 °C to room temperature to produce ingots of roughly cylindrical shape. To yield meaningful attenuation data the

samples must meet rather stringent geometrical requirements. Faces must be plane and parallel within 10^{-4} radians. This was accomplished by a lengthy grinding and polishing procedure. 99.999% pure Se shot as well as Se doped with 130 ppm Cl plus 40 ppm Te was used as starting material. Within experimental error both types of samples yielded identical results.

Because of the large size of the samples the cooling rate during quenching is strongly inhomogeneous and cannot be controlled throughout the sample. The duration of mechanical preparation may not be set in advance and usually differs for different specimens. It is thus not surprising that results show considerable scatter at this stage due to the fact that essential parts of the thermal history are not sufficiently under control. Fortunately this situation can be remedied. According to Chang and Bestul [24] amorphous Se may be brought to a supercooled liquid equilibrium state which is independent of previous thermal history upon heating to a temperature above 310 K for approximately one hour. Thus it is possible to erase effects resulting from different thermal conditions during preparation. All samples used in this investigation were heated to 42 °C for one hour. Indeed it was confirmed that previous discrepancies had disappeared by this heat treatment.

3. Results

Typical data of the attenuation constant α as a function of frequency f at different temperatures are shown in Figure 1. Measurements were made using different X-cut Quartz transducers at their fundamental and odd harmonic frequencies. An average value of λ/a^2 dB per unit length (where λ is the wavelength of sound in the specimen and a is the transducer radius) was used to correct for diffraction losses. All other apparent losses were shown to be negligible from 5 MHz upwards. As in many other amorphous solids [25, 26] ultrasonic attenuation shows a linear frequency dependence in a-Se. Apparent deviations from linearity at 3 MHz and 4 MHz are due to systematic errors caused by the transducer mounting which was used to facilitate changing the transducers quickly on a particular sample in the course of measurements at a fixed temperature.

Because of this frequency dependence it is convenient to use $\alpha\lambda$, the attenuation per wavelength, which is independent of frequency. In Fig. 2 $\alpha\lambda$ is plotted as a function of temperature. The sequence
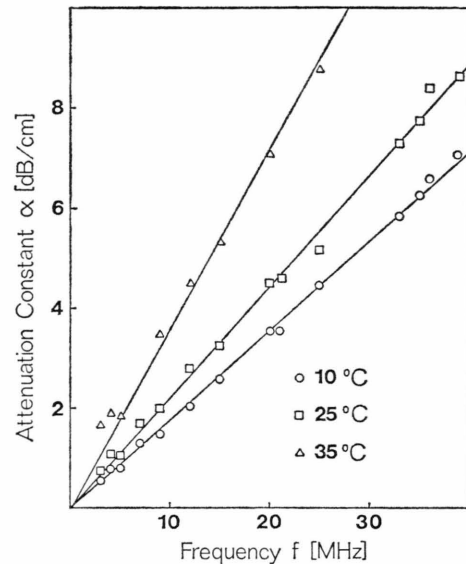

Fig. 1. Attenuation constant α for longitudinal waves as a function of frequency at different temperatures.
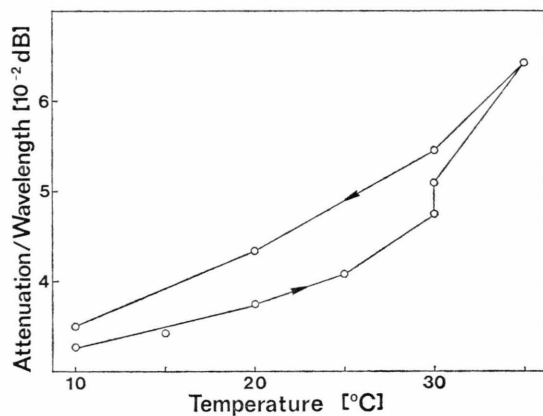

Fig. 2. Attenuation per wavelength ($=\alpha\lambda$) as a function of temperature. Arrows indicate the sequence of measurements.

of measurements is indicated by arrows. A strong increase in attenuation with temperature is observed. It is seen that attenuation is not uniquely determined by temperature. The "cooling" branch shows a different dependence on temperature than the previous "heating". Since viscosity decreases strongly with increasing temperature [27], it could be suspected that sample faces and parallelism could have deteriorated while samples were kept at 35 °C, resulting in higher apparent losses. A check of sample geometry after the measurements ruled out this possibility. Thus a genuine increase in intrinsic attenuation is observed reflecting the influence of thermal history on the

particular properties of a sample. Therefore a plot like Fig. 2 is not very useful without information on this thermal history, including the measurement process.

To gain some information on reproducibility the measurements, of which Fig. 2 is an example, were performed in parallel on three samples which previously had been stored at room temperature (around 24 °C) for six weeks. During the course of the measurements all three samples were kept in the thermostat at the same temperature except for the short periods needed for transducer coupling (performed at room temperature) which in turn affected each sample in a similar way. It was thus assured that the thermal history of all samples was as far as possible identical. On account of the rather high uncertainty of a single attenuation reading, $\alpha \lambda$ was determined for each sample at each temperature from the slope of α-values in the entire accessible frequency range as indicated in Figure 1. Since after each change of a transducer some time was needed for the sample to again assume the measurement temperature and since the velocity of sound c was also measured (results are shown in Fig. 3) it took
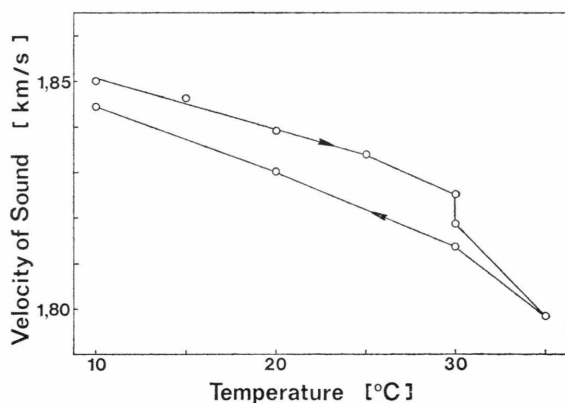

Fig. 3. Longitudinal sound velocity measured simultaneously with attenuation values shown in Figure 2.

on the average four hours to take all required readings at any one temperature. It was therefore impossible to make all measurements in one continuous cycle. During necessary interruptions the temperature was lowered to around 10 °C. This insures that changes in sample properties occur very slowly and do not have much influence for the periods involved. The terms "heating" and "cooling" are therefore to be understood as roughly

indicating the general direction of temperature changes.

At first each measurement temperature was maintained for about four hours and then changed abruptly. During the 30 °C-measurement a small drift was observed. This temperature was maintained for twelve more hours and another measurement taken after this time resulting in a clearly increased value of $\alpha \lambda$ and a smaller value of c. A similar holding period was kept at 35 °C. At this temperature however no further changes in $\alpha \lambda$ and c were observed which means that the appropriate equilibrium value had been reached by the time measurements were taken on the first sample. Upon cooling to 30 °C however a third, still higher value of $\alpha \lambda$ and a still lower value for c were found. Similar "permanent" changes resulted at 20 °C and 10 °C.

Actually the observed changes are not really permanent. Values along the lower branch in Fig. 2 and the upper branch in Fig. 3 are a result of the previous stabilization process during storage. This process may be understood as a relaxation towards the equilibrium state of the supercooled liquid at the storage temperature. It manifests itself in a slow increase of c and a decrease of $\alpha \lambda$. During rapid heating the material may then exhibit higher velocity and lower attenuation than in the equilibrium state appropriate to the higher temperature. Relaxation then sets in in the reverse direction. This leads to the observed changes at 30 °C. Once equilibrium has been reestablished (as in this case at 35 °C) subsequent rapid cooling will lead to properties similar to those present before storage. The processes involved are therefore reversible over longer periods of time. This has been confirmed through velocity measurements by repeatedly cycling the samples in this way. In fact the steeper slope of the lower branch in Fig. 3 is mainly a result of stabilization which occured during the storage between measurements and does not reflect the true temperature dependence of c in the glassy state. (The temperature derivative of c does show a slight dependence on storage time [28] but the differences are considerably smaller than Fig. 3 would indicate.) This reversibility rules out that the changes shown in Figs. 2 and 3 might be caused by incipient crystallization.

While these data may be called typical for specimens stored for an extended period below the glass transition temperature T_g the specific values do not

represent characteristic properties of the material as such. Therefore the equilibrium values of sound velocity which are independent of thermal history and so represent true material constants were determined in the temperature range from 25 °C to 45 °C. Since these values are approached asymptotically it is not sufficient to just measure c as a function of time and wait until the result seems stationary. To ascertain that a true equilibrium value has been reached, it is necessary to approach it from both sides as suggested in Reference [18]. At temperatures above T_g this may be done in reasonable time by just heating and cooling the samples to the given temperature. Below T_g it is necessary to store the specimens for sufficient time at a temperature below the one for which the equilibrium value is to be determined to insure that the velocity initially is significantly higher than the expected equilibrium value. This may involve storage in excess of one week to find the appropriate value for 25 °C. For still lower temperatures this procedure becomes very time consuming and very soon impossible in practice. Results of these measurements are shown in Figure 4. The points represent average
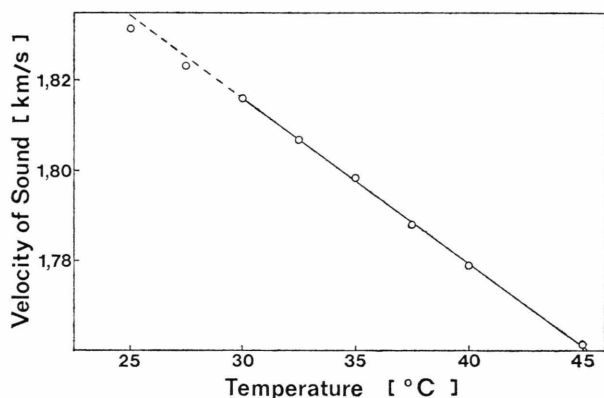

Fig. 4. Equilibrium values of sound velocity as a function of temperature.

values obtained for four samples. Scatter among the individual specimens used was within ± 1.5 m/s. It is perhaps surprising that values below 30 °C deviate from a linear extrapolation from the results at higher temperatures. Due to the procedure outlined above it is not possible that this be a consequence of not waiting long enough for equilibrium to be adequately approximated. In particular the value at 25 °C has been rechecked carefully several times.

The precision of these data does not allow to decide whether there is a pronounced bend or whether the points should rather be approximated by a smooth curve. For the temperature dependence of sound velocity in the region of the supercooled liquid in equilibrium as determined between 30 °C and 45 °C the results in Fig. 4 yield:

$$(1/c)\,(\mathrm{d}c/\mathrm{d}T) = - (2.05 \pm 0.05) \cdot 10^{-3}\,(°C)^{-1}\,.$$

This value is in good agreement with the temperature dependence which follows from the data reported by Dzhalilov and Rzaev [16] in the range 42 °C to 60 °C while the velocities themselves in Fig. 4 are about 1% lower than the corresponding extrapolated values from Reference [16]. Sound velocities from Refs. [13-15] are all within the interval given by the values of Figure 3. It appears that the samples used in this investigation exhibit lower attenuation than the ones studied by Graham and Chang [13]. However because of the scarce data given there a quantitative comparison is difficult.

4. Discussion

The changes in $\alpha\lambda$ and c turning up in Figs. 2 and 3 reflect structural changes in the material which affect most properties. In thermodynamic treatments usually an ordering parameter is used to characterize the actual structural state. This parameter may be replaced by the so called "fictive temperature" $\overline{T}$ which in Ref.[18] is defined as "that temperature at which a glass would find itself in equilibrium if brought there sufficiently quickly from its actual state − the pressure being kept fixed". If a single ordering parameter is sufficient to characterize the structural contribution to the changes of observed properties the state of a specimen may be described by giving its actual temperature T together with the fictive temperature $\overline{T}$.

The basic similarity between the plots of $\alpha\lambda$ vs T and c vs T indicates a close relationship between these two quantities. This is demonstrated quite clearly in Fig. 5 where all $\alpha\lambda$-values of Fig. 2 are plotted against the corresponding c-values of Figure 3. All points line up neatly to justify the assumption that this relationship is singlevalued. In this case it must be possible to find a single parameter as a function of which both quantities may be described. On the model of the concept of fictive temperature it is proposed to define an "effective temperature" T_{eff} to serve as this parameter as
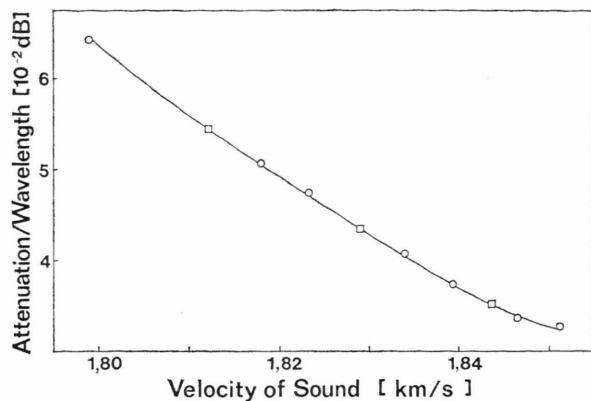
Fig. 5. Attenuation per wavelength as a function of corresponding sound velocity (data of Figs. 2 and 3). Values of upper branch in Fig. 2 are marked by squares.

follows: T_{eff} of an arbitrary state at which a certain property (eg the velocity of sound) has a value c_1, is that temperature at which the equilibrium value of this property equals c_1. The relation of T_{eff} to $\overline{T}$ is illustrated in Figure 6. It is assumed that at an
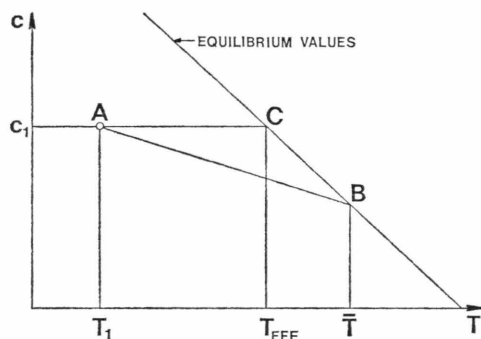

Fig. 6. Schematic representation of the relation between actual temperature T_1, effective temperature T_{eff} and fictive temperature $\overline{T}$.

actual temperature T_1 a particular specimen has a velocity c_1. During a rapid increase in temperature the velocity would change along the line AB (corresponding to the temperature coefficient of c in the glassy state i. e. at fixed structure). At point B the specimen would find itself in equilibrium. This point therefore corresponds to the fictive temperature $\overline{T}$. On the other hand at point C the equilibrium value corresponds to T_{eff}. It could be said that the specimen has a sound velocity c_1 as if it were in its equilibrium state at the temperature T_{eff}.

In order to determine T_{eff} in practice equilibrium values of one of the quantities must be known. In

the present case the values of Fig. 4 have to be used. Figure 4 as a consequence of the definition given above may be interpreted as representing a plot of c vs T_{eff}. Under the assumption of a unique relationship between $\alpha\lambda$ and c however a plot of $\alpha\lambda$ vs T_{eff} will in the same way be equivalent to the temperature dependence of equilibrium values of attenuation. It should therefore be possible to deduce equilibrium values from measurements in arbitrary nonequilibrium states. In Figure 7 such a plot of
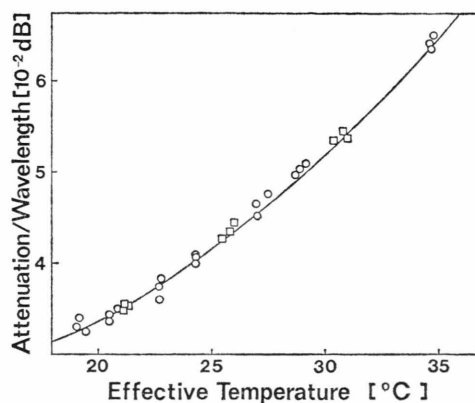

Fig. 7. $\alpha\lambda$ as a function of effective temperature. Values corresponding to the upper branch of Fig. 2 are marked by squares. This diagram corresponds to a plot of equilibrium values.

$\alpha\lambda$ vs T_{eff} is shown where the data taken on all three samples are included to provide an indication of experimental accuracy and reproducibility. It appears that the concept of an effective temperature seems applicable within experimental error.

Some caution concerning this interpretation is in order: 1. The determination of T_{eff} below $25\,°C$ rests on an extrapolation of equilibrium values of c to the temperature in question and is therefore uncertain. 2. Though the data within experimental accuracy support the assumption of a unique relation between $\alpha\lambda$ and c (which is closely related to the question whether or not a single ordering parameter is sufficient) this is not proved generally. It should be noted that in the region of interest sample properties do not deviate very much from equilibrium properties. It would be necessary to check if the assumption still holds for values which have been reached after widely differing thermal histories. Measurements of the rate of approach to equilibrium after different storage periods seem to indicate problems in this respect.

Although the phenomenological concepts of $\overline{T}$ and T_{eff} will not directly contribute to a better understanding of the basic processes underlying the relaxation phenomena, they still seem to have some practical value. Even if the assumption of a single ordering parameter should prove oversimplified $\overline{T}$ could serve in good approximation as a measure of the integral effects of thermal history. Giving a value of $\overline{T}$ would still be preferable to no information on the state of a particular specimen and would facilitate comparison of results of different investigators. The concept of effective temperature should be applicable also to other properties and allow the approximate determination of equilibrium values without performing the time consuming procedure necessary to measure them directly.

The effects of thermal history on elastic properties reported here seem closely related to the effects reported by Cornet and Rossier [20], Stephens [21] and by Das et al. [22]. One difference must be noted however: In Ref. [20] it is claimed that T_g and the height of the endothermic peak showing up in DTA-measurements reach a saturation value within a 100 hour storage period at 20 °C and that these saturation values remain the same at higher holding temperatures below T_g. This contrasts with the observation that sound velocity continues to increase for a long time. It is true that the rate of increase becomes extremely small after 100 hours. After storage periods of several months however values of c are obtained which exceed the ones given in Fig. 3 by almost 10 m/s. While this behaviour qualitatively corresponds to what one would expect for glasses in general this is not so for the observations reported in Reference [20].

There is at present no theory which would allow to quantitatively relate the absorption mechanism to a specific structural model. The linear frequency dependence has in general been attributed to relaxation processes having a wide distribution of relaxation times. These processes are thought to be due to atoms moving in a double potential well [26, 29] or to weakly bound atoms moving in microcavities [30]. It seems that this latter model could be applicable to the ends of polymeric chains in a-Se. Qualitatively the decrease in attenuation during stabilization could then be attributed to a conversion of chains to rings, a process which has been suggested by Stephens [21] to explain his thermal relaxation data.

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