

Ultrasonic velocities and thermal expansion coefficients of amorphous $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{90}\text{Te}_{10}$ alloys near glass transitions

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Precise measurements of the ultrasonic velocities and thermal expansivities of amorphous $\text{Se}_{80}\text{Te}_{20}$ and $\text{Se}_{90}\text{Te}_{10}$ alloys are reported near the glass transition. The samples are produced by liquid quenching. The longitudinal and transverse velocities are measured at 10 MHz frequency using the McSkimin pulse superposition technique. The thermal expansivities, α , are measured using a three-terminal capacitance bridge. The α -values show a sharp maximum near the glass transition temperature, T_g . The ultrasonic velocities also show a large temperature derivative, dV/dT near T_g . The data are discussed in terms of existing theories of the glass transition. The continuous change in α shows that the glass transition is not a first-order transition, as suggested by some theories. The samples are found to be deformed by small loads near T_g . The ultrasonic velocities and dV/dT have contributions arising from this deformation.

1. Introduction

The transition that occurs between a glass and the supercooled liquid is called the glass transition. The manifestation of this depends upon crystallization processes being sluggish [1]. The free volume model [2, 3] and the entropy model [4] are generally used to understand the behaviour of transport properties, especially the viscosity, near the glass transition. Experimental results indicate that, generally, the viscosity, η , varies as

$$\eta = A \exp [B/(T - T_0)], \quad (1)$$

where A and B are constants and T is the temperature, above the "ideal glass transition temperature", T_0 . Since the "ideal glass transition temperature", T_0 , is lower than T_g , there is speculation about the nature of the structural transition at T_0 . For many systems it is known that A , B and T_0 are not constant over the complete temperature range between T_M , the melting point, and T_g [5]. Some tetrahedrally-bonded network glasses, for example SiO_2 and GeO_2 , show $T_0 = 0$ and not T_g is manifested in a differential scanning

calorimetry (DSC) experiment. Also, it is known that if the entropy values of some liquids (obtained from the measurement of the specific heat, C_p) are extrapolated, they intersect the entropy curve of the crystal at some temperature T_s [6]. This means that entropy of the glass is smaller than that of the crystal below T_s .

Since this is incompatible with the nature of entropy, S , it is necessary that C_p decreases very sharply below T_g . If C_p of the glass is to change so as to preserve $S_{\text{glass}} > S_{\text{crystal}}$, then the resultant variation of C_p would look like a λ -transition (a second-order phase transition where the variation of C_p , α etc. resemble a λ) [7].

These experimental facts suggest that there could be an ideal glass-to-liquid phase transition masked by kinetic phenomena. The Gibb's entropy model [4] was the first to suggest the existence of such an ideal phase transition. Recently, the free volume model has been modified using the percolation theory [3]. This model suggests a first-order liquid-glass transition.

To study the behaviour at T_g careful measure-

ments of ultrasonic velocity and thermal expansion have been attempted. The measurements of ultrasonic velocities are carried out at 10 MHz. Transverse and longitudinal velocities were measured with a resolution of 0.05% and an absolute accuracy of 1%. The measurements of thermal expansion were performed using a three-terminal capacitance bridge and a six-decade ratio transformer. These give a length resolution of 0.2 nm.

2. Details of experimental measurements

2.1. General experimental details

The measurements have been performed on $\text{Se}_{90}\text{Te}_{10}$ and $\text{Se}_{80}\text{Te}_{20}$ samples. The Se-Te system was chosen because the Se-rich alloys can be easily produced as good samples, with a minimum of internal macroscopic voids. This helps in the ultrasonic velocity measurements. Also, earlier work [8] has shown that the T_g of these samples is quite low, less than 60°C in both cases. This low T_g makes the measurements relatively easier. The samples were produced by liquid-quenching sealed quartz ampoules in ice-water. The ampoules were carefully opened to produce cylindrical samples of diameter about 6 to 8 mm and of length 10 to 15 mm and DSC and X-ray diffractometry were used to confirm the formation of amorphous phases.

2.2. Experimental measurement of ultrasonic velocity

A pulse-echo interferometer has been used for ultrasonic measurements [9]. This unit employs the McSkimin pulse superposition technique [10, 11]. The samples were carefully polished so that opposite faces are parallel (maximum error 0.01 mm). Then the sample and the transducer were bonded together and placed in close contact with a metal block (see Fig. 1). A bonding material capable of working at temperatures up to 60°C is needed and 1, 3 dihydroxy benzene has been used in this work. Care was taken to see that the sample was not heated while the bond was made. The temperature was varied by changing the power supplied to a heater wound on the block. The sample was lightly spring-loaded to preserve the integrity of the bonding between the transducer and the sample. The arrangement was enclosed in a metal container which was soldered, using Wood's metal, to a flange. This facilitates evacuation of the sample chamber to a vacuum of 10^{-6} torr. This ensures that any thermal link

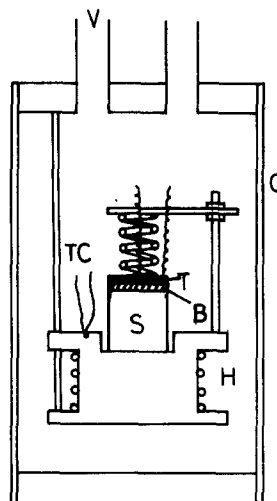


Figure 1 Schematic diagram of sample arrangement for ultrasonic measurements. T: transducer; S: sample; H: heater; B: bond; TC: thermocouple; C: calorimeter; V: vacuum connection.

between the sample and the outside environment is negligible. Normally, a stability in temperature of 0.01 K is achieved for 10 min. The measurements were made while the sample was slowly heated at an average rate of 5 to 6 K h^{-1} . Both longitudinal and transverse velocities have been measured so that the differences in behaviour at glass transition can be easily noted.

2.3. Experimental measurement of thermal expansion coefficients

Precise measurements of the thermal expansion coefficients have been made using a three-terminal capacitance bridge set-up [12]. The capacitance, C , of a parallel-plate capacitor formed between one fixed copper plate and a copper plate placed on top of the sample was measured (see Fig. 2). The plate on the sample was placed in position using springs. The total compressional load on the sample was about 0.05 N. This was necessary to prevent the plates being disturbed by vibrations. The space between the plates was evaluated and the change in the capacitance was directly related to the change in the thickness of the sample. Capacitance was measured using a six-decade ratio transformer. A resolution of 1 part in 10^6 was achieved for an experimental capacitor of 10 pF. A 1 pF standard capacitor was used as a reference. The cell has been calibrated using OFHC copper and quartz standards [13]. For precise detection, a Brookdeal 9503 precision lock-in amplifier has

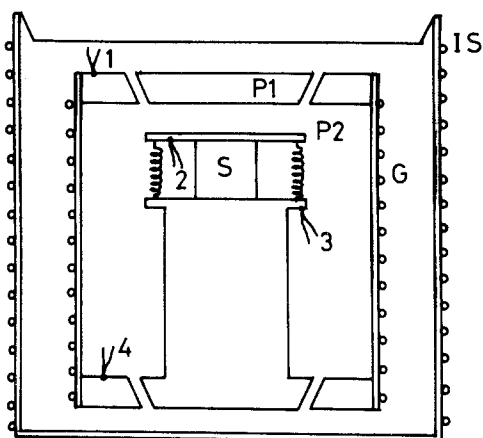


Figure 2 Schematic diagram of cell arrangement for thermal expansivity measurements. S: sample; 1 to 4: thermocouples; G: guard; P1, P2: active capacitor plates; IS: isothermal shield.

been used. The temperature of the cell assembly was controlled using a proportional temperature controller. The cell was shielded by an isothermal shield, the temperature of which was controlled manually by operating a variable power supply. An overall gradient of 0.5 K and a stability of about 0.2 K was achieved.

The sample was polished to a parallelism of about $\pm 10 \mu\text{m}$ error and was so placed in the cell that the distance between the two capacitor plates was between 0.5 and 0.3 mm. This produced a capacitance of about 10 to 20 pF so that the resolution was good. The cell was kept at each temperature for about 45 min so that equilibrium could be attained. The measurements were initially taken on as-quenched samples, up to the glass transition. Then they were cooled at a rate of about 2 K h^{-1} and became stabilized, the measurements were then repeated on the stabilized glasses (one controlled cooling from T_g is believed to stabilize the samples completely [14]). Measurements were performed on both $\text{Se}_{90}\text{Te}_{10}$ and $\text{Se}_{80}\text{Te}_{20}$ samples.

3. Results

3.1. Results of ultrasonic velocity measurements

The results of the ultrasonic velocity, V , measurements near the glass transition are shown in Figs 3 and 4. The value of dV/dT (the change in velocity, V , with respect to temperature, T) is negative and dV/dT is a minimum near T_g . There is, however, no abrupt change in the value of dV/dT

near T_g . On the other hand, the magnitude of dV/dT continuously increases. Above the glass transition region there is some tendency for $|dV/dT|$ to decrease again. In Figs 5 and 6, the variation of $V^{-1} dV/dT$ is shown as a function of temperature. It is to be mentioned that no functional form for the variation of the ultrasonic velocity is available and, hence, the differentiation is carried out numerically.

3.2. Results of thermal expansion measurements

The values of C^{-1} (C is the capacitance between the active plates) which are experimentally measured, are plotted in Figs 7 and 8. Once again, no numerical curve-fitting has been undertaken. The data for C^{-1} against T shown in Figs 7 and 8 show very small scatter. Also, the total change in C^{-1} for the $\text{Se}_{90}\text{Te}_{10}$ sample is much smaller than that for the $\text{Se}_{80}\text{Te}_{20}$ sample. This is because the expansivity of the $\text{Se}_{90}\text{Te}_{10}$ sample is almost the same as that of the copper used for making the cell: this leads to a larger error in the measurements.

The values of expansivity, α , for the two samples are plotted in Figs 9 and 10. The plots indicate a rapid increase in α near the T_g for each sample. In the $\text{Se}_{90}\text{Te}_{10}$ sample, a small shift in T_g is noticed. An important observation is that near T_g the value of C^{-1} is time dependent. A decrease in C^{-1} is initially noticed which is followed by an increase. This is confirmed by the fact that the sample is permanently deformed. A typical variation is shown in Fig. 11.

As the viscosity, η , decreases, the sample deforms due to the small load (0.05 N) applied by the springs. To quantify these changes in length, caused by deformation, sample thickness measurements were made at different temperatures as a function of time. These results are plotted in Fig. 12. It is seen that C^{-1} varies linearly with time. A least-squares fit was performed and the slopes were determined. It is shown that $\log m(T)$, where m is the slope, varies linearly with T^{-1} . (See Fig. 11b.)

4. Discussion of results

4.1. Ultrasonic velocities

If the glass transition is considered to represent the transition from a liquid to a glass, the ultrasonic velocity should be expected to decrease above T_g . This is because ultrasonic velocities in liquids are usually much smaller than those in a

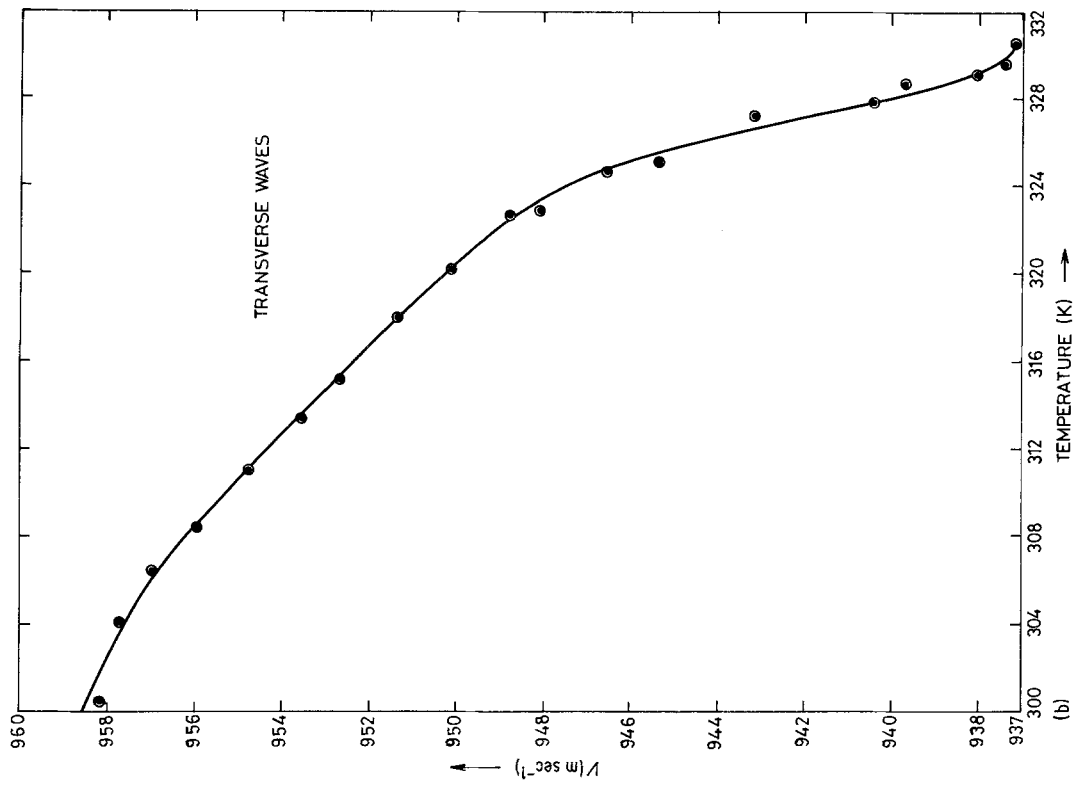
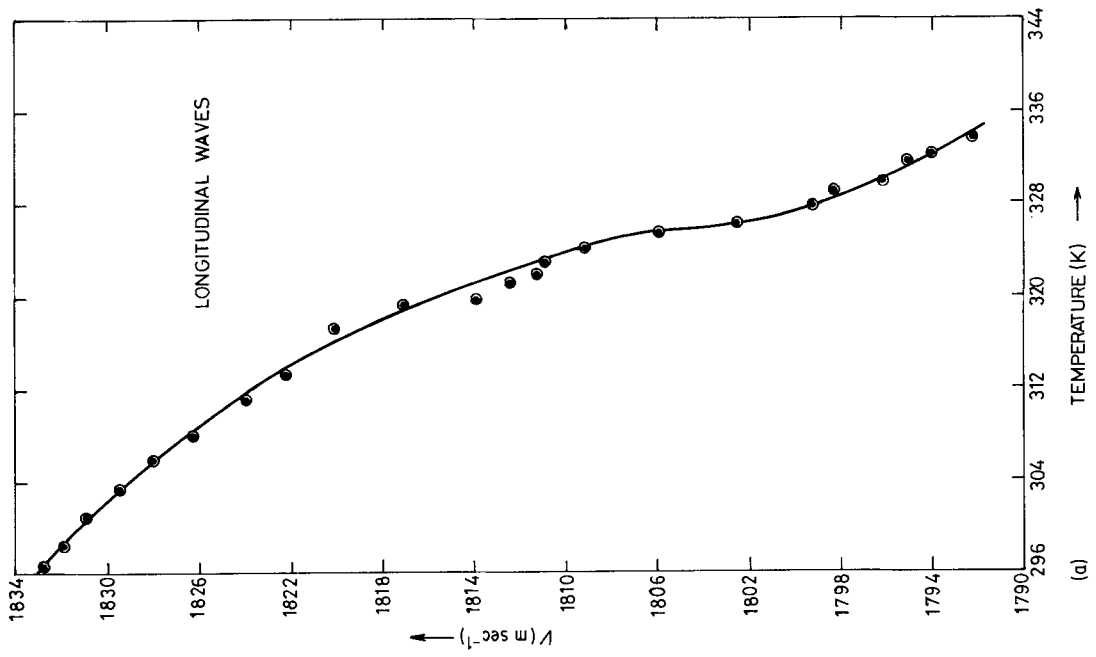


Figure 3 (a) Velocity of longitudinal waves in a $\text{Se}_{80}\text{Te}_{20}$ sample near the glass transition. (b) Velocity of transverse waves in a $\text{Se}_{80}\text{Te}_{20}$ sample near the glass transition.

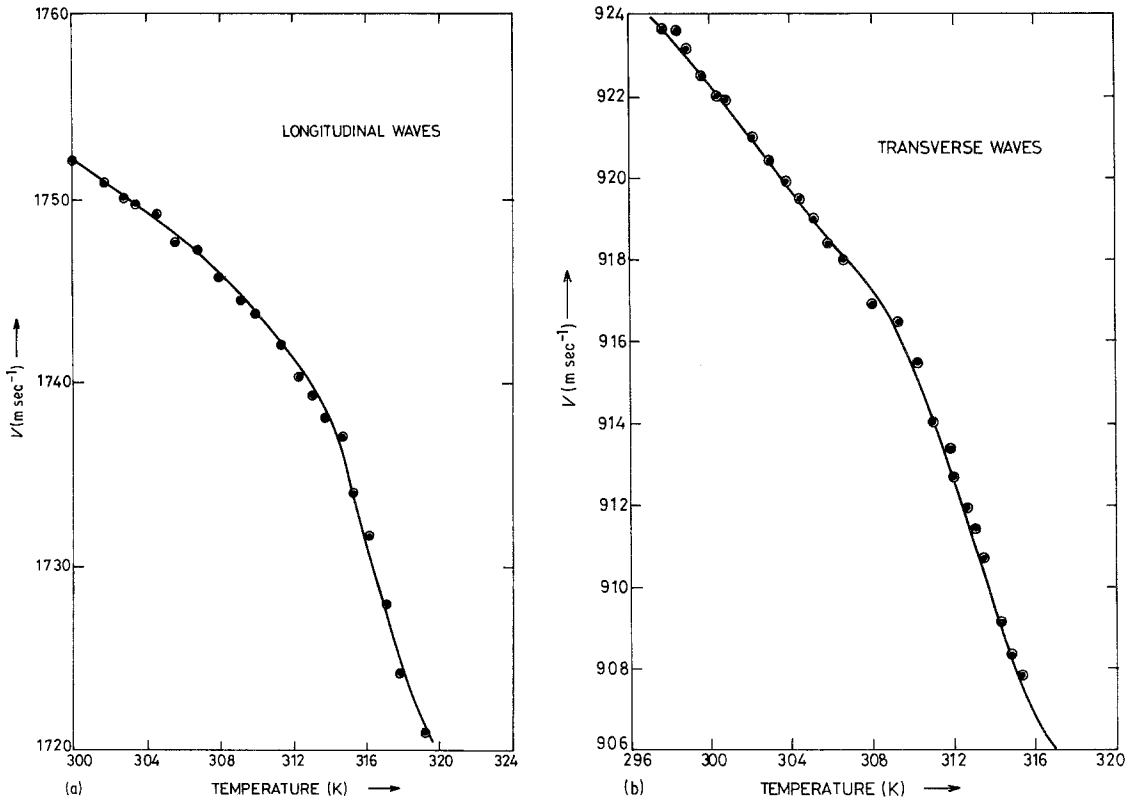


Figure 4 (a) Velocity of longitudinal waves in a $\text{Se}_{90}\text{Te}_{10}$ sample near the glass transition. (b) Velocity of transverse waves in a $\text{Se}_{90}\text{Te}_{10}$ sample near the glass transition.

solid phase. The basic ideas of propagation of acoustic waves in glasses and liquids have been discussed by many workers and are summarized by Landau and Lifshitz [15]. According to their discussion, when a highly viscous liquid is deformed, the mechanical deformations exist for a time, τ , after the deformation force is removed. If ω is the frequency of mechanical disturbance (the acoustic waves in our case) then, for $\omega\tau > 1$, the material behaves as a solid and, for $\omega\tau < 1$,

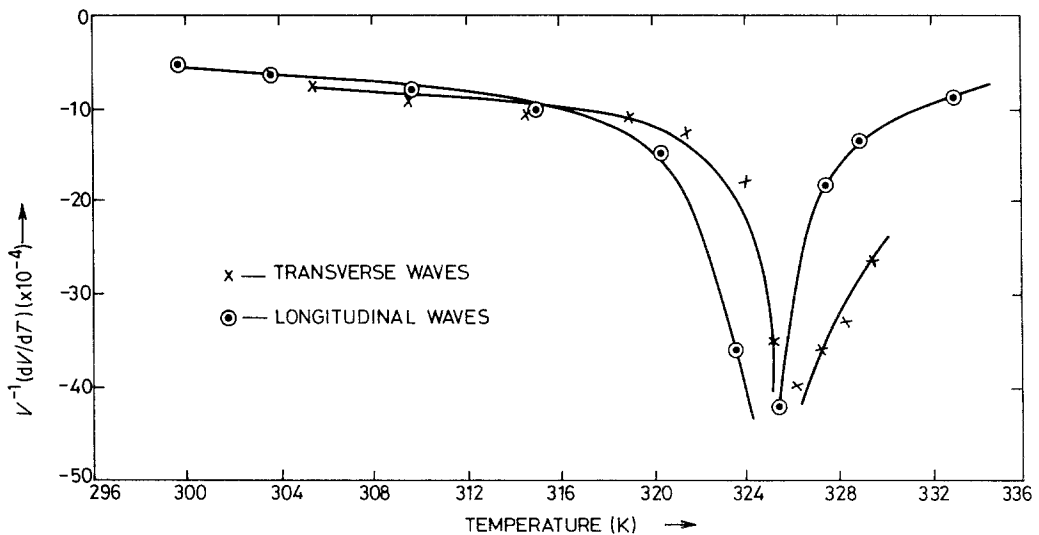


Figure 5 Variation of $V^{-1}(dV/dT)$ near the glass transition for a $\text{Se}_{80}\text{Te}_{20}$ sample.

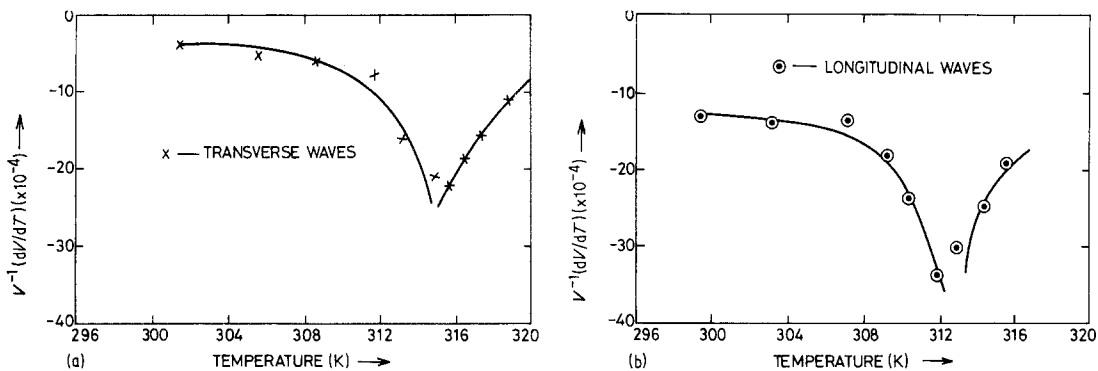


Figure 6 Variation of $V^{-1}(dV/dT)$ near the glass transition for a $\text{Se}_{90}\text{Te}_{10}$ sample. (a) Transverse waves, (b) longitudinal waves.

the material behaves like a liquid. τ is related to η and the modulus of rigidity, μ , by

$$\eta \approx \tau\mu. \quad (2)$$

On this basis, the behaviour of the ultrasonic velocities in our samples can begin to be understood. Above T_g , η decreases exponentially, and

gradually the rigidity disappears and shear waves will propagate only if $\omega\tau > 1$. Thus it would be expected that the ultrasonic velocities would decrease rapidly above the glass transition. For transverse waves, the velocity should go to zero well above T_g and the longitudinal velocity should asymptotically attain the value in the liquid near

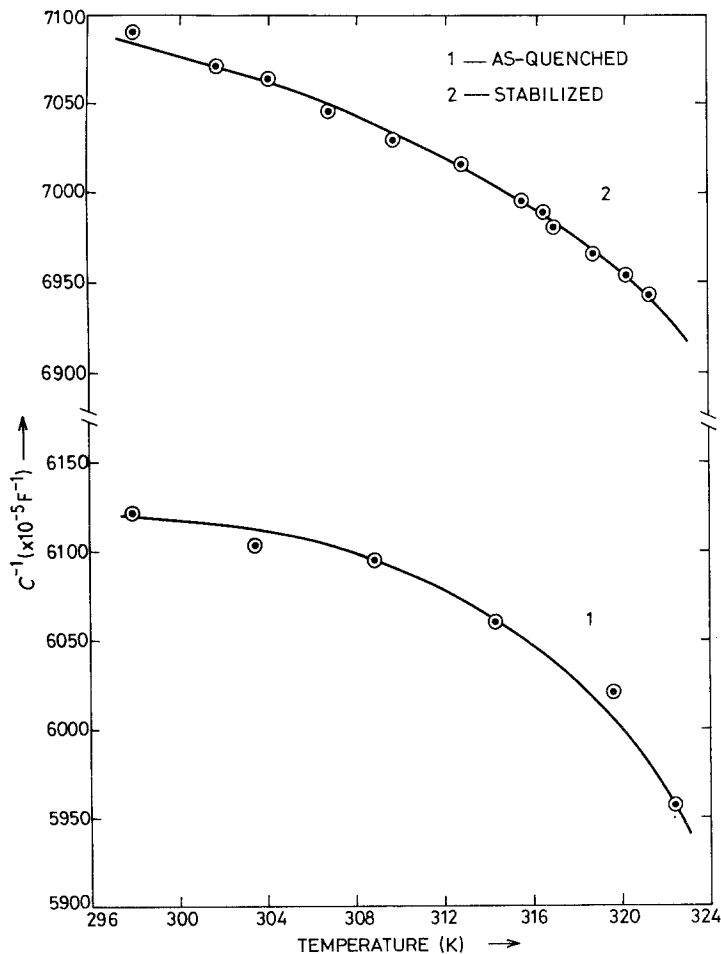


Figure 7 Variation of C^{-1} with temperature for a $\text{Se}_{80}\text{Te}_{20}$ sample.

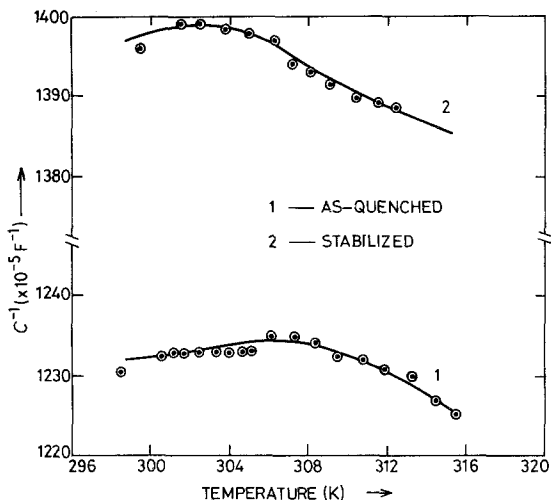


Figure 8 Variation of C^{-1} with temperature for a $\text{Se}_{90}\text{Te}_{10}$ sample.

T_M . The velocity of transverse waves is about 900 m sec^{-1} and that of longitudinal waves is about 1700 m sec^{-1} for our samples. These are

roughly 50% or less of the values for typical crystalline solids. If it is expected that the longitudinal and transverse velocities are substantially smaller in the liquid phase, then the reason for the decrease in the magnitude of $V^{-1}(dV/dT)$ above T_g is not clear. The total change in ultrasonic velocities from room temperature to T_g is also quite small (about 20 to 30 m sec^{-1}). It is expected that the value of $|V^{-1}(dV/dT)|$ should start decreasing well above T_g (nearer to T_M) rather than within 4 to 5 K of T_g . Not many measurements of ultrasonic velocities near T_g are available. The results are similar to those obtained for amorphous Se by Kittinger [16].

No measurements were taken at temperatures well above T_g since the thermal expansion measurements showed that samples tend to contract above T_g , even for small loads. In the ultrasonic velocity measurements, also, a small spring load is used. Noticing that the changes $V^{-1}(dV/dT)$ are very small, it is quite possible that the apparent decrease in $|V^{-1}(dV/dT)|$ above T_g is due to a small con-

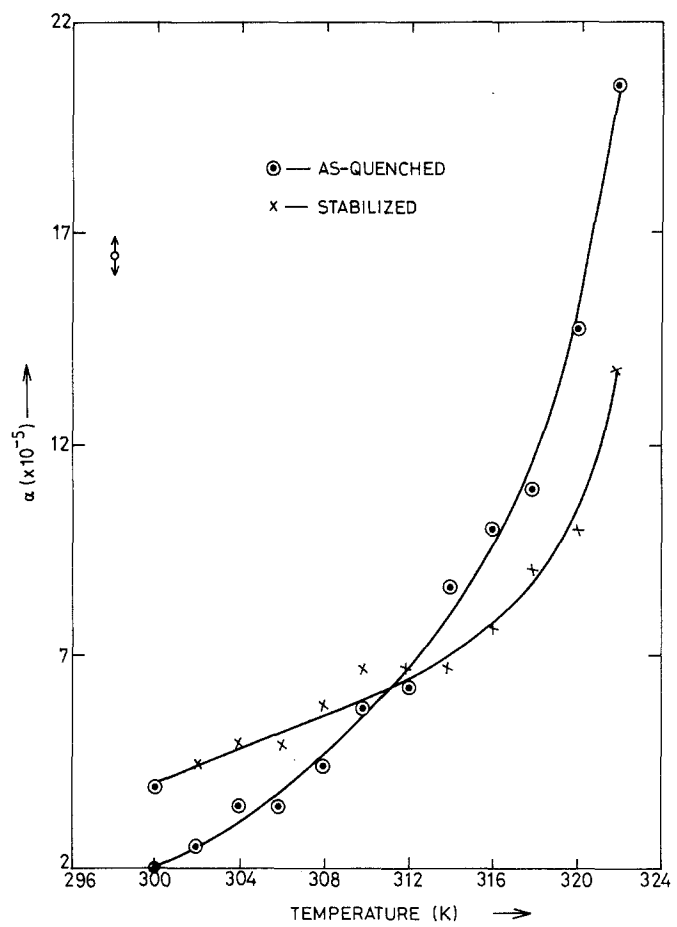


Figure 9 Thermal expansion coefficient of a $\text{Se}_{80}\text{Te}_{20}$ sample near the glass transition.

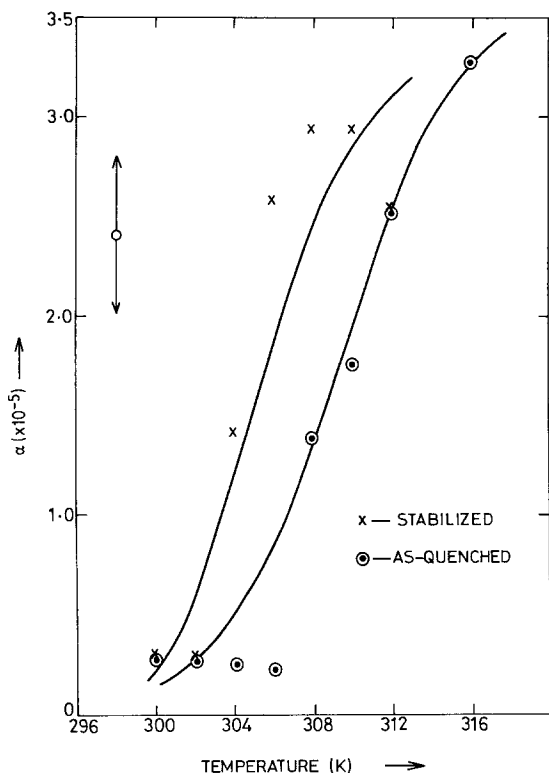


Figure 10 Thermal expansion coefficient of a $\text{Se}_{90}\text{Te}_{10}$ sample near the glass transition.

traction in the length of the sample. The fact that at 5 to 6 K above T_g the rate of contraction of the sample is quite large (see Fig. 12) makes this all the more possible.

The T_g values obtained from ultrasonic measurements are slightly different from these obtained from DSC data. Since T_g depends upon the time taken to perform the measurement, the type of measurements and the history of sample, the ultrasonic velocities and DSC might indicate different values for T_g .

4.2. Thermal expansion coefficients

As already mentioned, the specific heat shows an anomalous behaviour near T_g . Work by Turnbull has shown that C_p near T_g has a nearly reversible maximum. The value near the peak is an extrapolation of the C_p -value of the supercooled liquid [17]. The thermal expansion also shows a peak near T_g [18]. The measurements on thermal expansion reported are rarely very accurate. It is believed that the measurements reported here, though not complete, are more accurate and show a clearer picture of the increase of α near T_g . For

example, earlier work on pure selenium has shown the relaxation of α as a function of time but the results are not very precise [19].

As is clear from the plots, α for these samples shows a sharp but continuous increase near T_g . The behaviour expected from the advanced free-volume model of the glass transition [3] is that of a step increase. In that model, the ideal glass transition is a first-order phase transition where there is a latent heat and a discontinuous change in the specific volume \bar{v} is predicted. The behaviour of C_p shown by this model crudely resembles the data of Turnbull [5] and since the variation of C_p is predicted for the "ideal glass transition" under equilibrium conditions, this might be considered to be correct. In the same paper [5] it is shown that some materials do show a discontinuous change in \bar{v} near T_g . However, our measurements do not show any discontinuous change. There is a continuous change with α rapidly increasing. Thus, the result is not in accordance with expectations based on the existing microscopic free-volume model.

Considering the time-dependent contraction, as the viscosity decreases, the sample loses the solid-like properties and will tend to collapse. The experiment indicates that a metal plate held on top of a cylinder of viscoelastic material moves with constant velocity. This is similar to the behaviour of a metal ball in a viscous medium [20]. In fact, when a ball is moving in an infinite medium, the velocity is inversely proportional to its viscosity. This is the case in our measurements, but the constant of proportionality which depends on the load is not known. If the slope of C^{-1} against time is m , then $m \propto \eta$. Hence, the slope of the $\log m$ against T^{-1} plot is related to the constant in the normal viscosity formula, Equation 1, but there is obviously an unknown constant of proportionality. In addition, T_0 is not known. The measurements of C^{-1} with time show a possible source of error in the measurement of physical parameters near T_g . Even a load of 0.05 N can cause large enough deformations in samples to lead to errors in measurements. This factor, though obvious, is not usually specifically mentioned. Obviously, for very precise measurements near T_g it is necessary to take this factor into consideration and to develop an experimental set-up so that no load is applied to the sample or so that the deformation and flow of the sample is prevented.

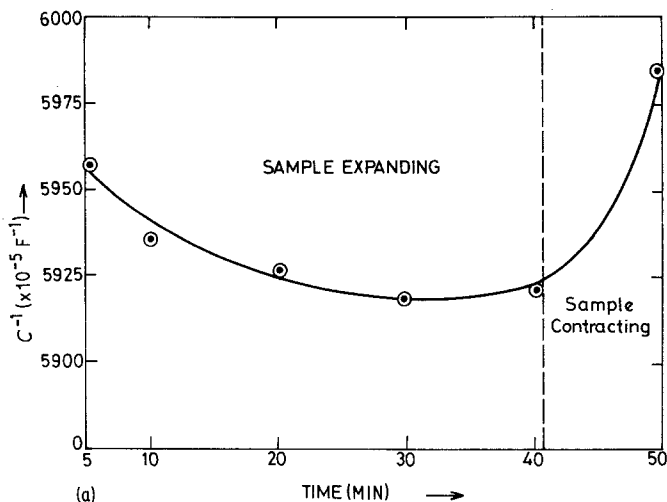
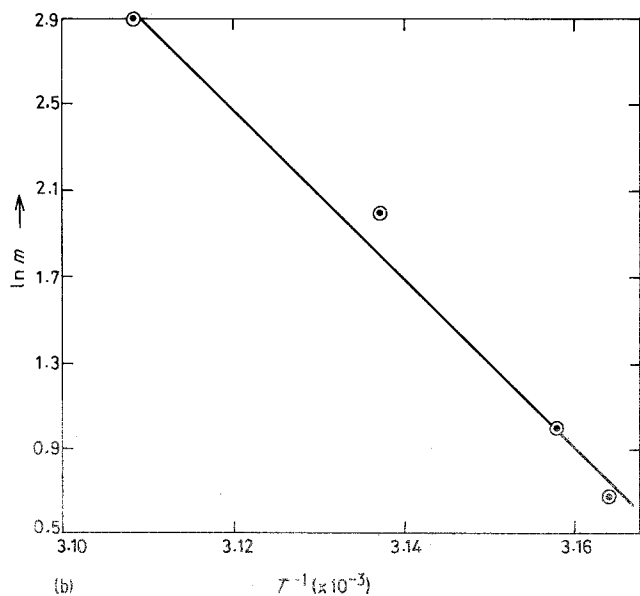


Figure 11(a) Typical variation of C^{-1} near T_g where α increases and then the sample contracts. (b) Variation of $\log m$ with T^{-1} .



5. Conclusions

The change in the experimental values of α shows that the "ideal glass transition" is not of first-order. The continuous increase observed in α would be expected if the transition is of second-order. The ultrasonic velocity measurements and the deformation of the sample under small loads indicate that, in attempts to make precise measurement of physical properties near T_g , the sample mounting configurations should be designed so as to apply no pressure to the sample. In all such measurements the possibilities of errors in measure-

ment due to deformation of sample due to external loads (or even due to gravity) have to be considered.

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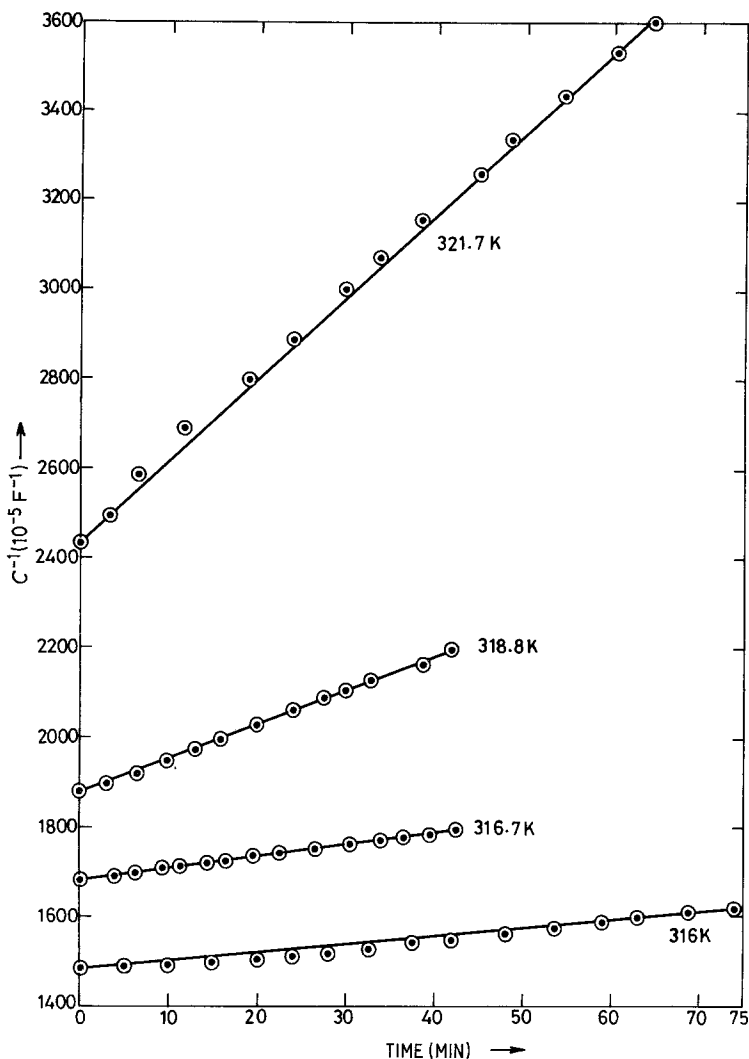


Figure 12 Variation of C^{-1} with time when the sample contracts.

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