

Temperature dependence of the structures of As_2Se_3 and $\text{As}_x\text{S}_{1-x}$ glasses near the glass transition

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(Received 10 May 1983; revised manuscript received 18 October 1983)

The temperature dependence of the x-ray structure factor has been measured for As_2Se_3 and $\text{As}_x\text{S}_{1-x}$ glasses of compositions $x=0.40, 0.33, 0.19,$ and 0.11 . In all of these glasses, a surprising increase in the first-diffraction-peak intensity was observed with increasing temperature while the second-diffraction-peak intensity decreased. These changes were fully reversible. Measurements have been made above the glass transition temperatures T_g for the $\text{As}_x\text{S}_{1-x}$ glasses, where the intensity changes continue the behavior seen below T_g . It is suggested that these results are consistent with the existence of local layering in these glasses and are suggestive of a mechanism for the viscosity decrease above T_g . In addition, for the $\text{As}_x\text{S}_{1-x}$ glasses, plots of the intensities normalized to those at T_g vs T/T_g gave a universal temperature-dependence behavior for all x up to $1.2T_g$.

I. INTRODUCTION

A glass is formed when a liquid is supercooled until it is frozen into a noncrystalline solid. Although glass formation is believed to be due to the failure of the liquid to crystallize,¹ the question remains as to why some materials easily form glasses while others do not. How does ease of glass formation depend on structure?

A great deal of work has been done to determine the structure of glasses using x-ray or neutron diffraction. Such experiments yield a structure factor $S(k)$ which is liquidlike, having broad, diffuse peaks which oscillate about unity at large wave vector. From the Fourier transform of $S(k)$, one obtains the radial distribution function (RDF), which gives average interatomic distances and coordination numbers for the atoms in a glass. The short-range order for the glassy state of a material is often very similar to that of the crystalline state, that is, it has a similar average nearest-neighbor distance and coordination number. Unlike the crystal, however, the glass has no long-range periodic order.

Experiments have been done near the glass transition to investigate the behavior of thermodynamic, transport, and relaxational properties.² For example, there is a rapid increase in the shear viscosity as the liquid is cooled to T_g , the glass transition temperature. One might ask what the effects are on the structure near T_g .

We recently reported³ the first measurements of the temperature dependence of the x-ray structure factor for As_2Se_3 glass from low temperature up to the glass transition. We observed an increase in the first-peak intensity with increasing temperature and a simultaneous decrease in the second-peak intensity. These changes were completely reversible. Crystalline As_2Se_3 has a layered structure, and others have proposed that there is a locally layered structure in the glass. We suggested that our temperature-dependence results were consistent with such proposals, and that they indicate a structural mechanism

for the characteristic drop in viscosity at the glass transition.

Since As_2S_3 has crystalline and glassy structures similar to those of As_2Se_3 , we proposed³ that temperature-dependence measurements of its glassy structure should give similar results. In this paper we describe our results for As_2Se_3 as well as our new experimental measurements of As_2S_3 glass and the nonstoichiometric alloys $\text{As}_x\text{S}_{1-x}$, where $x=0.33, 0.19,$ and 0.11 . The latter were chosen to study the effects of decreasing arsenic content on the structures. When heated, the arsenic sulfide glasses are more resistant to crystallization than As_2Se_3 , and thus the first measurements have been made above the glass transition. The As_2Se_3 and $\text{As}_x\text{S}_{1-x}$ glasses are of interest not only because they are excellent glass formers, but also because many measurements have been made to determine their structures⁴⁻²⁶ and thermodynamic and transport properties.²⁷⁻³⁰

Our results for the $\text{As}_x\text{S}_{1-x}$ glasses are indeed similar to those we reported for As_2Se_3 . The reversible increase in the first-peak intensity and decrease in the second-peak intensity also continue above T_g . We suggest that there is local layering in these glasses. We also observed a universal temperature-dependence behavior for all x when the intensities were normalized to those at T_g and plotted versus T/T_g ; this behavior is apparent up to $1.2T_g$. Certain trends with composition showed differences in the structures.

The paper is arranged as follows. Sec. II gives a brief background description of the glass transition and previous proposals for the structures of these glasses. Details of the experiment follow in the next section. In Sec. IV the results are described, with their implications for the structures and behavior of these glasses near the glass transition. Comparisons to previously proposed structural models are made to put our results in perspective, and further questions arising from them are discussed. The paper is completed by a summary in Sec. V.

II. BACKGROUND

A. Glass transition

Glasses, which range from those with simple structures such as the metallic glasses to the more structurally complex organic and inorganic materials and polymers,^{2,31,32} are each characterized by a glass transition temperature, T_g , often defined as that temperature where the viscosity reaches approximately 10^{13} P (which corresponds to relaxation times on the order of 1 d). The form of the viscosity as a function of temperature varies with the type of glass.^{2,31,33}

At the glass transition there are also changes in thermodynamic properties such as the specific heat, thermal-expansion coefficient, or isothermal compressibility.² These quantities undergo abrupt changes from values appropriate to the supercooled liquid to those typical of the crystalline solid as T is lowered to T_g . The observed glass transition temperature depends on the thermal history of the sample as well as on the time scale of the measurement.^{28,34-36} Certain models have been proposed to describe the temperature dependence of the properties near T_g .^{33,37-46} Theorists have proposed that an equilibrium thermodynamic phase transition should occur in this temperature region, but that the transition cannot be seen experimentally due to the fact that the liquid enters a nonequilibrium state during the time scale of the measurement.^{31,38,45,46}

B. Structures of As_2Se_3 and As_2S_3

The structures of inorganic glasses, including the chalcogenides, have been widely investigated.⁴⁷⁻⁵¹ The chalcogenide glasses include the elemental glasses sulfur and selenium (the chalcogens) and their compounds with germanium and arsenic. Phillips's criterion^{52,53} states that the average coordination number should be approximately 2.4 for the best glass formers, as is true for the As_2S_3 and As_2Se_3 glasses.

The crystalline structures of As_2Se_3 and As_2S_3 are essentially the same (see Fig. 1).⁵⁴⁻⁵⁷ Each arsenic atom bonds to three sulfur (selenium) atom, forming a pyramid with arsenic at the apex. These pyramids are joined into a ring of 12 atoms of alternating arsenic and sulfur (selenium). Each arsenic atoms has three nearest neighbors and each sulfur (selenium) atom has two nearest neighbors; the

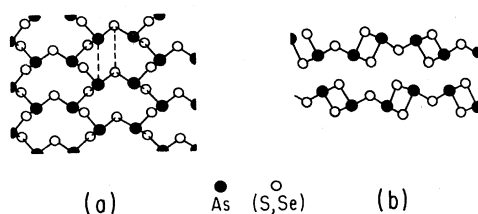


FIG. 1. As_2Se_3 or As_2S_3 crystalline structure: (a) One layer viewed along the (010) direction; the cross-ring distance is indicated by the dashed lines. (b) Two layers viewed edge on. The complexity of the layer structure is evident.

rings are thus interconnected as shown in Fig. 1 to form a layered network structure. Puckering in the rings causes each layer to consist of five different parallel planes of atoms. The layers are believed to be held together by weak van der Waals forces. From low-temperature measurements of the low-frequency zone-center optical modes in the crystals, Zallen and Slade⁵⁷ found the ratio of interlayer to intralayer force constants to be small, indicating no interlayer covalent bonds, although the difference is not as large as in the case of graphite, which has an exactly planar layered structure.

Results of x-ray- and neutron-diffraction measurements⁴⁻¹¹ are in agreement in that the short-range order of the crystal is present in glassy As_2Se_3 and As_2S_3 , that is, the first- and second-nearest-neighbor distances and coordination numbers are approximately the same. Far-infrared, Raman, and NMR spectroscopy experiments also show that glassy and crystalline As_2Se_3 and As_2S_3 have similar local structures.¹²⁻²¹ The vibrational spectra in the glasses consist of broad peaks centered at frequencies corresponding to the dominant bond-stretching and bond-bending vibrational modes of the nearest-neighbor As—Se (—S) bonds in the crystal.

Diffraction results^{4-6,9,11} and studies of local bonding using electron spectroscopy for chemical analysis⁸ have shown that, as in the crystal, each arsenic atom bonds with sulfur (or selenium), that is, the glasses are chemically homogeneous. Evidence against chemical phase separation was also given by small angle x-ray scattering results²² where there was no indication of voids (of radius 3–50 Å) existing in the bulk glasses, as might be expected if large phase-separated clusters were packed randomly in the glass.

Owing to the lack of long-range periodicity for As_2Se_3 and As_2S_3 , as for all glasses, the structure beyond the short-range order is difficult to determine. RDF analyses^{5,6} indicate that the cross-ring correlation distance (see Fig. 1) is not evident in the glassy structure. Thus the twelfold ring structure as seen in the crystal does not exist unmodified in the glass. The most significant feature in the structure factor for these glasses is the first peak which exists at $k_p = 1.2 \text{ \AA}^{-1}$, a wave vector smaller than that of the first peak for other glasses such as SiO_2 . Its presence may indicate a medium-range ordering in the glass. Since its position corresponds well to that of the interlayer Bragg peak seen in crystalline As_2S_3 and As_2Se_3 , this peak has often been interpreted as signifying the presence of layers in the glass.

Certain models for the glassy structure have been developed which are based on distorting the crystalline structure. Renninger and Averbach⁵ compared the RDF results obtained from their x-ray-diffraction data on As_2Se_3 glass to a microcrystalline model structure, which they developed by appropriately broadening the experimental polycrystalline distribution function with a Gaussian. The microcrystalline model RDF had a peak present at the cross-ring distance, which was not in the experimentally determined RDF. They concluded that a quasi-crystalline layer structure is not present in the glass.

Leadbetter and Apling⁶ and Leadbetter and Wright⁵⁸ performed x-ray- and neutron-diffraction experiments on

arsenic selenide and arsenic sulfide glasses, and compared their results to a model distribution function for a quasi-crystalline distorted layer structure. The function was obtained by expanding the crystalline lattice so as to have the lower density of the glass and convoluting the crystalline distribution function with a damping function⁵⁸ to give correlations that decay within a finite radial distance L . These model distributions with $L=10$ Å for arsenic selenide and 12 Å for arsenic sulfide also contained the peak at the position corresponding to the cross-ring correlation distance. Upon taking the Fourier transform of the model RDF to obtain the model intensity distribution, they found the first-peak intensity to be too small in comparison to the experimental first diffraction peak.

Leadbetter and Apling pointed out, however, that the model RDF's are completely dominated by intralayer contributions, so that interlayer spacings only appear as ripples of wavelength 5 Å. They also concluded from the sharpness of the experimental diffraction peak that the glass consists of layers which have more correlation between them than within them. They used the Scherrer equation⁵⁹ to obtain this interlayer correlation distance, D , and obtained $D=15$ Å for arsenic sulfide and 20 Å for arsenic selenide. For a layer separation of about 5 Å, this means there are approximately four layers correlated for the sulfide and five for the selenide.

In another study, Renninger *et al.*⁶⁰ used a Monte Carlo simulation for the As-Se glasses. They placed the atoms at random positions and allowed them to move while preserving local bonding requirements until the structure gave a model RDF which closely matched the experimental RDF. The model structures giving these fits contained fragments of rings and chains, but no evidence of layering. When using a starting configuration based on a layered structure for the As_2Se_3 glass, however, they also obtained essentially the same good fit to the experimentally determined RDF. Their results thus did not rule out the possibility of layers in the glass.

Lucovsky and Martin¹² and others¹³ have proposed a structural model for As_2S_3 and As_2Se_3 based on their Raman and infrared spectroscopy measurements, in which they observed that certain vibrational modes still follow selection rules determining whether the modes are infrared or Raman active. In this "molecular model," it was suggested that the glass consists of molecular constituents (the AsS_3 or AsSe_3 pyramids) which have bond-bending or bond-stretching vibrational modes at frequencies corresponding to the spectral peaks. The intermolecular coupling modes are believed to be weaker and are thus treated separately. This model successfully fitted the observed frequencies¹² and led to the proposal that the structures of these glasses should consist of these linked molecular units. Others pointed out, however, that because the basic structural unit in the crystal is also the AsS_3 (Se_3) pyramid, the molecular model is not inconsistent with the existence of a more quasilayered structure in the glass.¹⁴

Noting the presence of the first peak in liquid As_2Se_3 in neutron-diffraction data,⁶¹ Phillips²⁴⁻²⁶ proposed that there are stacks of layers, or "rafts," present in the glass which are not microcrystalline. Phillips describes the atomic arrangement in a raft so that it has minimal strain

energy. Chen *et al.*⁶² recently reported seeing domains with diameters of the order of 1000 Å in thin evaporated films of As_2Se_3 using electron microscopy; Phillips⁵² interpreted these domains as a possible coalescence of smaller regions. Important structural differences have been observed, however, between the vapor-deposited films and the bulk glasses of As_2Se_3 and As_2S_3 . The film structure changes after annealing, and there is evidence of like-atom bonds⁶³⁻⁶⁵ and structural heterogeneities⁶⁶ which are not found in the bulk. These films have been modeled as consisting of large molecular clusters.^{64,65}

III. EXPERIMENTAL

The samples were prepared by reacting elements of 99.999% purity (obtained from the Alfa Products Corp.). These were placed in proper proportions into quartz tubes which were sealed under a vacuum of 10^{-6} Torr. They were then placed in a rocking furnace for 24 h at 870 K for the As_2Se_3 sample and 770 K for the $\text{As}_x\text{S}_{1-x}$ samples. The furnace was then turned off and the samples were allowed to cool to room temperature.

Chips of the bulk glass samples were then placed between two squares of 7.5- μm Kapton plastic and melt-squeezed at temperatures above the liquidus temperature to form flat samples of thickness 50 μm and diameter 3–5 mm. After the scattering experiments were completed, the flat samples were analyzed using an electron microprobe. This analysis gave the composition of the samples and it also revealed any inhomogeneities of size 1 μm or larger in the samples. In addition, samples of the bulk glasses were analyzed for composition by atomic absorption spectroscopy. The compositions determined for the samples are listed in Table I with corresponding values of T_g determined by Myers and Felty.²⁷ The samples of As_2Se_3 and As_2S_3 ($x=0.40$) and the glasses of compositions $x=0.11$ and 0.19 were found to be homogeneous. One of the samples of composition $x=0.33$ was found to be inhomogeneous. Its composition varied by $\Delta x = \pm 0.06$ from the average of 0.33 when comparing one-half of the sample to the other. The temperature-dependence data for this sample was in agreement with that of the other samples of the same composition which were homogeneous.

For the high-temperature measurements, the samples were held vertically in a sample holder mounted on a goniometer, oriented for transmission of x rays. The samples were heated by a flow of nitrogen gas which passed through a Nichrome heater coil. For the low-temperature measurements, a Helix Displex cryostat was mounted to the diffractometer. The samples were again oriented for x-ray transmission as attached to a sample holder mounted on the cold finger of the cryostat. The temperature was regulated to within ± 5 K. The x-ray setup consisted of a computer-driven Picker four-circle diffractometer. $\text{Cu } K\alpha$ x rays ($\lambda=1.5418$ Å) were used, generated by either a Rigaku rotating anode or a Picker standard x-ray tube.

Figure 2(a) is a plot of the structure factor $S(k)$ for the As_2Se_3 glass (the structure factors for the $\text{As}_x\text{S}_{1-x}$ glasses are shown in Fig. 7). These were obtained from room-temperature profiles taken between $2\theta=3^\circ$ and $2\theta=117^\circ$

TABLE I. Compositions determined for the glasses studied, and the corresponding glass transition temperatures, liquidus temperatures, and linear thermal-expansion coefficients.

Composition ^a for As _x S _{1-x} samples	T _g (K) ^b	T _l (K) ^b		Linear expansion coefficient (10 ⁻⁵ K ⁻¹)		Average
				α ₁	α ₂	
0.11±0.01	307±5	439±5	T < T _g T > T _g	17.0±1.0	6.5±1.0	10.0
0.19±0.01	358±5	499±5	T < T _g T > T _g	6.4±1.0	5.5±1.0	5.8
0.33±0.01	433±5	561±5	T < T _g T > T _g	13.0±1.0	6.4±1.0	8.6
0.40±0.01	478±5	581±5	T < T _g T > T _g	4.7±1.0	4.1±1.0	4.3
				10.8±1.0	6.6±1.0	8.0
			T < T _g T > T _g	5.8±1.0	3.4±1.0	4.2
				11.0±1.0	6.1±1.0	7.7
An As ₂ Se ₃ sample ^c	460±5	645±5	T < T _g	12.0±2.0	5.9±1.0	7.9

^aCompositions were determined by both electron-microprobe analysis for the samples used in the x-ray experiments and by flame atomic absorption spectroscopy for samples of the bulk glasses used to prepare the x-ray samples. The composition results were within error of each other, except for the samples of composition $x=0.11$, for which the microprobe analysis was unreliable, due to the samples being soft and giving a poor polish (causing increased scatter of the emitted x rays) and loss of sulfur under the electron beam.

^bReference 27.

^cReference 3.

at intervals of 0.2°. The counting time per point gave a statistical error at the peaks of approximately ±0.6% for As₂Se₃ and ±1% for the As_xS_{1-x} samples. The procedure used to convert the measured intensity to a structure factor is described in detail elsewhere.^{67,68} This

method includes appropriate corrections for air scattering, absorption in the sample, coherent and incoherent (Compton) scattering, and polarization effects due to the monochromator.

Figure 2(b) shows the pair correlation function $g(r)$ for As₂Se₃. The pair correlation function is related to the RDF and structure factor as

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{1}{2\pi^2\rho_0 r} \int_0^\infty k [S(k) - 1] \sin(kr) dk, \quad (1)$$

where ρ_0 is the average number density and $4\pi r^2 \rho(r)$ is the RDF. The pair correlation function gives the probability that a pair of atoms are separated by a distance r . For a binary alloy, $g(r)$ is a weighted average of the three partial correlation functions giving correlations between type AA , BB , and AB atoms. For As₂Se₃, the first and second peaks were found to be at $r_1 = 2.40 \pm 0.05$ Å and $r_2 = 3.60 \pm 0.05$ Å, in agreement with those from diffraction studies previously reported.⁴⁻⁶

The experiments involved measuring the variation with temperature of the intensities of the first two peaks in $S(k)$. The intensities of the peaks were measured at the position of the maximum, k_p , which varied with temperature due to thermal expansion. Below room temperature, no shifts of the peaks were observed. Above room temperature the peak shifts were measured for each glass, from which the coefficients of linear expansion were calculated by

$$\alpha_p = \frac{1}{k_p} \frac{dk_p}{dT}. \quad (2)$$

The thermal-expansion coefficients α_1 and α_2 derived from the temperature shifts of the first and second peaks are listed in Table I.

The samples were recycled to room temperature after every temperature-intensity measurement. This was done to check for any irreversible changes arising from anneal-

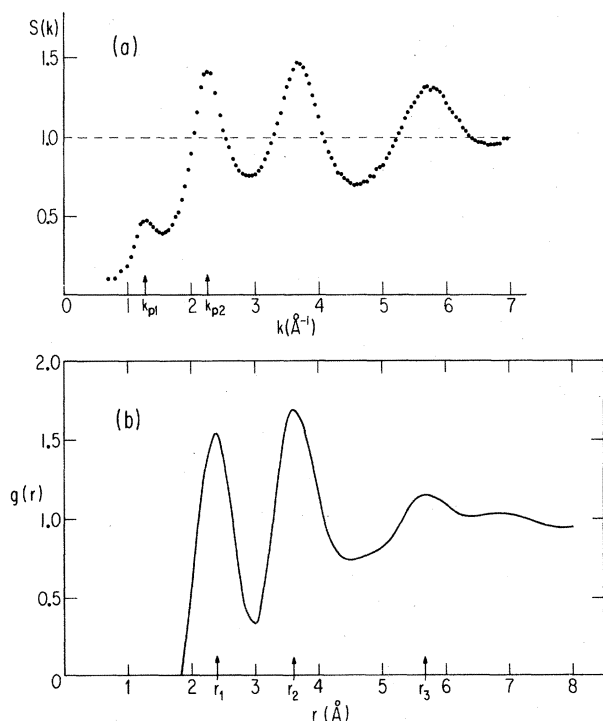


FIG. 2. (a) Structure factor $S(k)$ for As₂Se₃. The positions of the first two peaks are indicated, at $k_{p1} = 1.27 \pm 0.004$ Å⁻¹ and $k_{p2} = 2.23 \pm 0.004$ Å⁻¹. (b) The pair correlation function $g(r)$ calculated for As₂Se₃. The spurious structure introduced by a finite wave-vector cutoff in the Fourier transform has been suppressed for $r < 1.88$ Å.

ing during heating, changes in sample shape at high temperature, and fluctuations in the x-ray source intensity. The first- and second-peak intensities were measured sequentially at each temperature. At low temperatures, the sample position changed due to thermal contraction of the cold head, so the careful realignment was necessary to keep the sample in the focal plane of the x-ray beam.

The temperature dependence of the background (primarily Kapton scattering) was measured in the regions of k_{p1} and k_{p2} . At low temperatures there were no changes observed in the background intensity; at high temperatures, there was a slight decrease in intensity with increasing temperature.

IV. RESULTS AND DISCUSSION

A. Temperature dependence

In glasses as in crystals, intensity maxima normally decrease with increasing temperature because of increases in vibrational amplitude.^{68,69} Figure 3 shows the results of the temperature-dependence measurements for As_2Se_3 . The second peak was observed to decrease with increasing temperature, as one might expect with more structural disorder. The results for the first peak are dramatically different. The peak was observed to *increase* as the temperature increased; the changes were large, approximately 11% over the entire temperature range.⁷⁰

Figures 4(a)–4(h) contain temperature-dependence results for the alloy glasses $\text{As}_x\text{S}_{1-x}$. In all of these glasses, the first-peak intensity was observed to increase and the second-peak intensity to decrease as the temperature was raised. Furthermore, these trends continued above the glass transition temperatures for all of these glasses.

These changes were *reversible* and were not annealing effects; upon recycling to room temperature the intensity

was reproducible. Each point in Figs. 3 and 4 represents an average of several independent counting measurements, where ratios of the high-temperature to room-temperature intensity were in agreement among the several samples measured for each glass. At the highest temperatures for the $\text{As}_x\text{S}_{1-x}$ glasses, where the samples were beginning to soften, the intensity was initially monitored until it stabilized, indicating that the sample had flowed into a stable shape. Measurements taken for subsequent runs at that temperature were found to be reproducible; in addition, the temperature dependence at lower temperatures was again checked and found to reproduce the results obtained prior to the high-temperature runs.

To check that the first-peak increase was not due to an increase in the surrounding intensity, such as a rise in the tail of the second peak, scans of the peak and its surroundings were made at room temperature and at high temperature. As shown in Fig. 3(c) for As_2Se_3 , the intensity of the peak is rising much faster than that of the tails. Similar results were obtained for the $\text{As}_x\text{S}_{1-x}$ glasses of compositions $x=0.40$ and 0.11 [Figs. 5(a) and 5(b)].

1. Implications for the structure and behavior near T_g

The temperature dependence of the first peak indicates that there is *increasing* order with increasing T on the length scale corresponding to $1/k_{p1}$ in the glass. To our knowledge, a reversible increase in the intensity of a structure-factor peak with increasing temperature has been reported only for ^4He below the superfluid transition.⁷¹

The reversible increase with increasing T of the first-peak intensity is inconsistent with behavior as described by the Debye-Waller factor. Not only does the intensity increase with increasing temperatures, but even at low temperatures it continues to change.

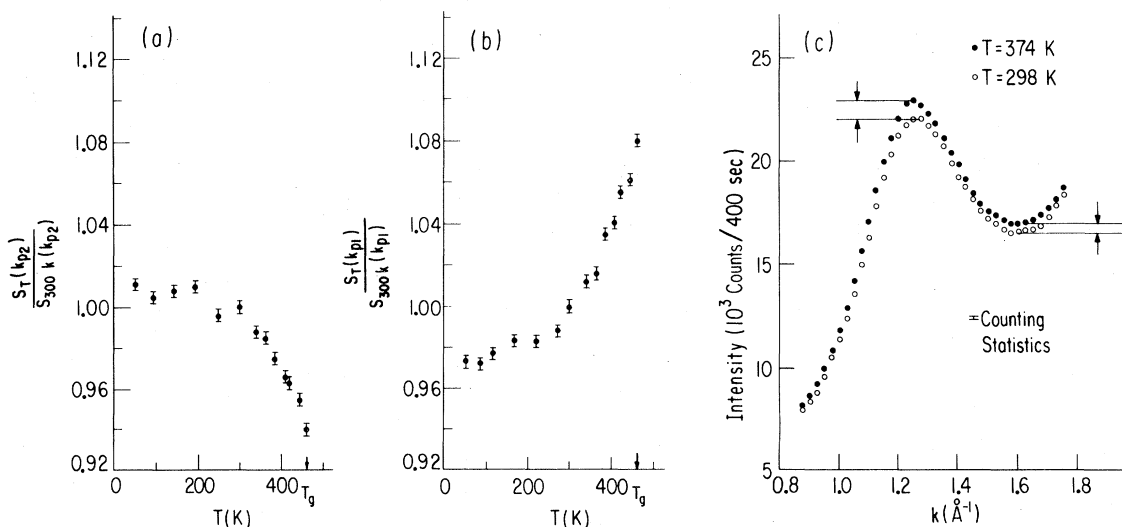


FIG. 3. Ratio of the intensity at temperature T to the intensity at 300 K for the As_2Se_3 glass: (a) for the second peak at k_{p2} ; (b) for the first peak at k_{p1} ; (c) the diffraction pattern for the first peak at two temperatures (298 and 374 K). The change with T at the peak is larger than the change at the tails of the peak.

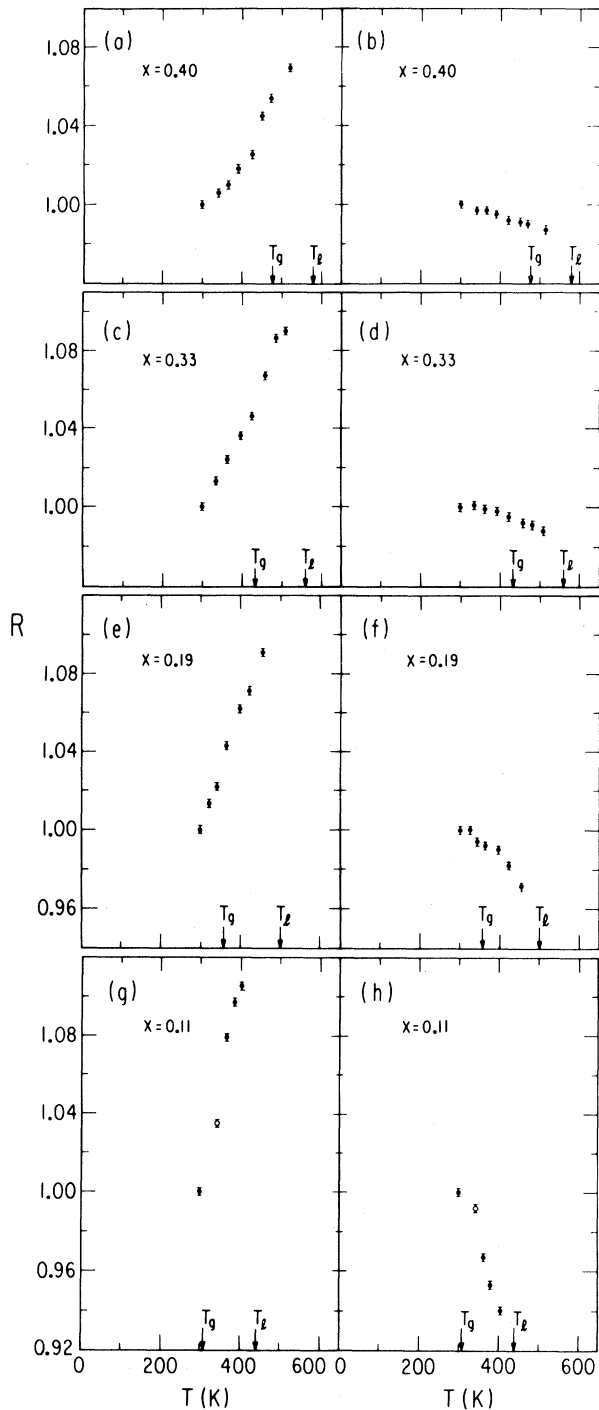


FIG. 4. (a)–(h): Temperature dependence of the intensities of the first peak (shown in the left column) and of the second peak (shown in the right column) for the As_xS_{1-x} glasses of compositions $x=0.40, 0.33, 0.19,$ and 0.11 . The intensities are normalized to those at room temperature; thus $R = S_T(k_p) / S_{300\text{K}}(k_p)$. The glass-transition temperatures (T_g) and liquidus temperatures (T_l) are indicated for each composition.

The simultaneous increase of the first-peak intensities and decrease of the second-peak intensities with increasing temperature imply that there is more order on one length scale and less on another as the temperature rises. These

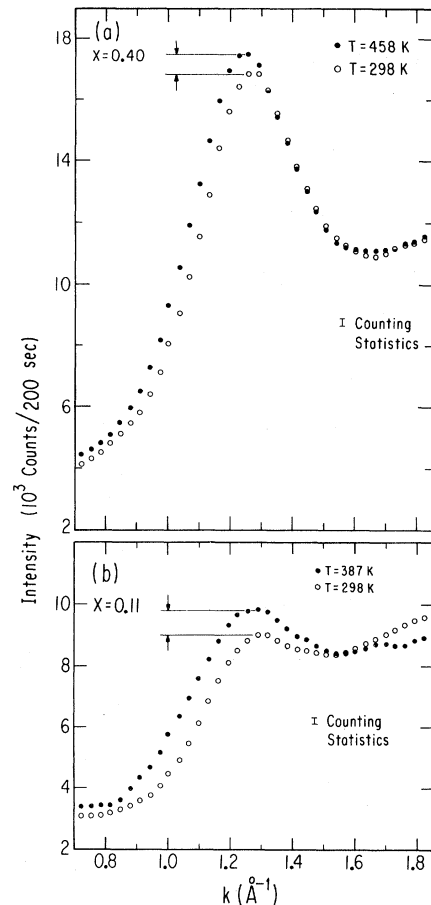


FIG. 5. Scans of the first peak in the As_xS_{1-x} glasses at two temperatures for (a) $x=0.40$ and (b) $x=0.11$.

results are suggestive of a competition of ordering taking place in the glassy structure. In addition, the difference in thermal expansion measured from the first- and second-peak shifts with temperature (almost a factor of 2 in some cases) indicates that they refer to possibly two different entities or different local directions in the glass.

We believe the structural changes with temperature are consistent with the existence of local layering in the glass. These layers are not microcrystalline, but are proposed to be crimped and disordered. The temperature dependence of the second diffraction peak, which is related to intralayer interatomic distances, indicates that order is decreasing within the layers as the temperature increases. At the same time, the first diffraction peak, related to interlayer separation, is increasing in intensity with temperature, indicating that the layering is becoming enhanced. There may be interconnected rings of atoms in each layer which consist of various numbers of atoms. Since the 12-atom ring is favored by the crystalline structure, any deviation might cause atoms to randomly stick out of the layers due to their strained bonding arrangements, allowing significant crimping of the layer. As the temperature rises, the thermal energy provided may allow the atoms to relax their strained bonding arrangement, making the layer smoother. Thus the structural changes couple together; the decrease of order

within the layers smooths out the crimped layer, causing an increase in correlation between layers.

As the layers become smoother, they may eventually begin to slide past one another, since as in the crystal, the forces between layers are expected to be weak. Since the glass is isotropic, it would consist of groups of the layered subunits arranged randomly. As T rises there could be a cooperative effect of these groups of layers sliding past each other which would eventually cause the characteristic drop in viscosity above T_g . This description thus gives insight into the microscopic behavior of the glass near the glass transition.

The temperature-dependence results do not seem consistent with associating the first peak with large clusters in the glass. It is unlikely that the increase of the first-peak intensity indicates that such clusters are becoming better correlated as the temperature rises, since increasing thermal energy would presumably reduce this correlation, not increase it. If the rise in the first peak is associated with the formation of more or larger clusters, this would have to be a reversible formation, and it is not clear how this could happen.

2. Comparison to other models for As_2S_3 and As_2Se_3

Our proposal for the existence of crimped, disordered layers in glassy $\text{As}_2(\text{S,Se})_3$ is clearly consistent with the suggestions of Leadbetter and Apling⁶ for layering. The poor fit to the structure which was found by Renninger and Averbach⁵ and Leadbetter and Apling⁶ with their quasicrystalline models is consistent with a very disordered arrangement within the layer, perhaps similar to the one we suggested. Leadbetter and Apling⁶ proposed that there may be more correlation between the layers than within them; our data suggest that this interlayer correlation increases as T rises.

The interpretations of several temperature-dependent Raman, infrared, and NMR spectroscopy measurements also lend support to a layering model. The experiments of Finkman and co-workers,^{14,15} Bishop and Taylor,¹⁶ Taylor *et al.*,¹⁷ and Kawamura *et al.*²³ led each of these groups to suggest that there are layers present not only in the glass, but up to and possibly above the melting temperature. The large thermal expansion for As_2S_3 we observed above T_g indicates that the separation between layers grows as the temperature increases, but the continuing intensity increase with T indicates that the layers are still correlated above T_g . Thus the layers do not float apart or break up until a higher temperature is reached. Taylor *et al.*¹⁷ suggested this would occur above the melting temperature in As_2Se_3 . For As_2S_3 , Kawamura *et al.*²³ used extrapolations from their data to suggest that very near melting the restoring force for the low-frequency-layer shear mode would vanish. Although our data were not taken very near or above the melting point for As_2S_3 due to the samples softening and changing shape, there must be a temperature region where the peak will begin to decrease with increasing T , which could indicate the loss of interlayer correlations. Kawamura *et al.*²³ also found that the shift of the low-frequency Raman mode was reversible between room temperature and 483 K, which may be re-

lated to the reversibility of our temperature-dependence results.

Phillips's model^{24-26,52,53} for noncrystalline, layered stacks in the glass is also consistent with our picture. Our proposal that the drop in viscosity is caused by the smoothing and subsequent shearing of the layers as the temperature rises above T_g contrasts, however, with his idea of the layer edges of one stack "flaking" or "peeling" the edges of another.

Tanaka observed a reversible photostructural change induced by light absorption in As_2S_3 evaporated films^{72,73} (not bulk glasses as in the present experiments). His observation of the decrease in intensity of the first peak at low temperature after illumination is not unlike the changes seen in the present experiment, but there are substantial differences. Tanaka's x-ray measurements were made at room temperature after many hours of illumination at low T ; thus the structure "remembered" its previous conditions. The results of the present work showed no "memory" of the low-temperature state. The results obtained in this experiment were present immediately upon temperature equilibration; to test this, the intensity was monitored at 10-sec intervals for As_2S_3 at both room temperature and 465 K and no drift in intensity occurred.

Since light exposure affects electronic and optical properties of these glasses,⁷⁴⁻⁷⁶ it is important to ask whether x rays, which have a much higher energy, might have sufficient intensity to cause the structural changes seen in this experiment. An estimate made of the intensity of x rays incident on the samples in this experiment gave the value 0.01 mW/cm². This is much smaller than that used to create paramagnetic defects (typically 1 mW/cm²). Since the energy per photon is on the order of 1000 times larger for x rays than for visible photons, this means there are about 10⁵ fewer photons per second incident on the sample per unit area for the x rays used in the present experiment than for the light exposures typically used.

Using measurements of the effects of pressure on the optical properties of amorphous semiconductors including As_2S_3 and As_2Se_3 , Kastner⁷⁷ has noted certain trends occurring with atomic composition. Recently, Weinstein *et al.*⁷⁸ found similar pressure-optical effects in amorphous GeS_2 , and concluded that the structure is a molecular solid, possibly consisting of covalently bonded molecular units such as the model proposed by Phillips *et al.*^{24,25} or a one-dimensional model (i.e., chainlike).⁷⁹ Their interpretations in conjunction with Kastner's results seem consistent with the existence of large molecular units in the As_2Se_3 and As_2S_3 glasses which may be layerlike.

B. $\text{As}_x\text{S}_{1-x}$ glasses: Trends with composition

The temperature-dependence behavior in Fig. 4 showed that each peak in $S(k)$ for the nonstoichiometric glasses had the same behavior as observed for the As_2S_3 glass. When the intensity changes plotted in Fig. 4 were normalized to the intensities at T_g and plotted versus T/T_g , a striking trend occurred. As shown in Figs. 6(a) and 6(b), the temperature-dependence data for the $\text{As}_x\text{S}_{1-x}$ glasses show a universal behavior for all x which is evident up to $1.2T_g$. (The normalized data for As_2Se_3 do not lie on

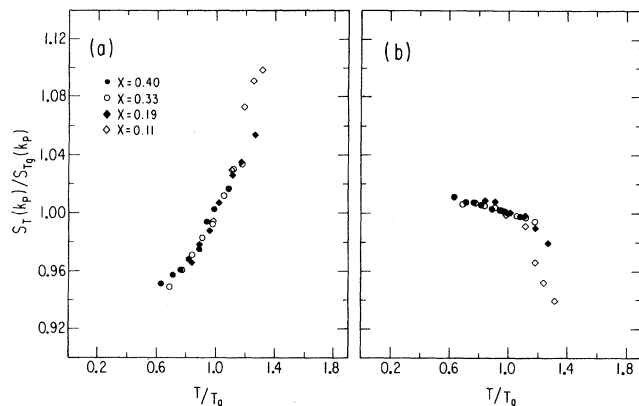


FIG. 6. Plots for the $\text{As}_x\text{S}_{1-x}$ glasses of the temperature-dependence data, renormalized to the intensities at $T_g(x)$, vs $T/T_g(x)$ for (a) the first peak and (b) the second peak. The temperature dependence is universal for all x up to temperatures near $1.2T_g$. The renormalized temperature-dependence data for As_2Se_3 are not plotted since they do not follow this universal behavior.

these universal curves.)

Our results for the structure factors for these glasses indicate that the first peak is not only present for all the compositions, but does not shift appreciably with x (see Figs. 7 and 8). The reversible increase of the first-peak intensity with T and the invariance of k_{p1} with x indicate that the peak corresponds to the same structural entity for all of these glasses; this is suggestive of layering in the structures. Tsuchihashi and Kawamoto⁹ suggested on the basis of their diffraction data that there are layers in the $\text{As}_x\text{S}_{1-x}$ alloy glasses. Further support was given by the data of Kawamura *et al.*²³ who also observed the low-frequency Raman peak for the nonstoichiometric alloys and suggested that there are layers present.

There are trends in our data which indicate the differences in the structures with composition. The second

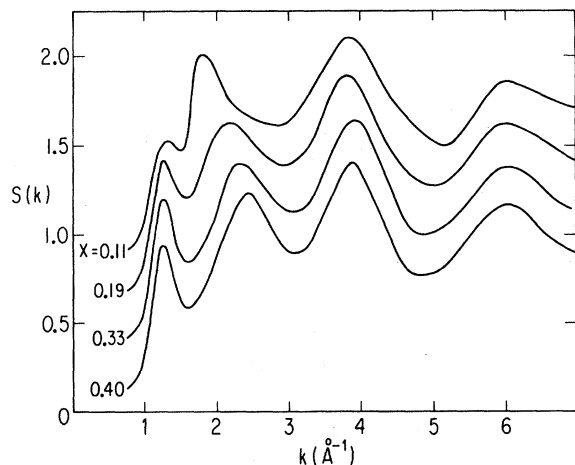


FIG. 7. Structure factors $S(k)$ for the $\text{As}_x\text{S}_{1-x}$ glasses. The curves for compositions $x=0.33, 0.19$, and 0.11 are displaced vertically by $0.25, 0.50$, and 0.75 , respectively.

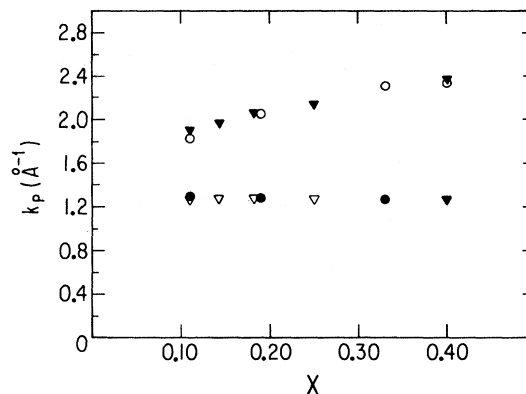


FIG. 8. Positions k_p of the first and second diffraction peaks for the $\text{As}_x\text{S}_{1-x}$ glasses plotted vs composition x . The closed circles are the values of k_{p1} and the open circles are the values of k_{p2} found in these experiments. The open triangles are values of k_{p1} and the closed triangles are values of k_{p2} derived from the diffraction patterns from Ref. 9. There is a monotonic decrease in k_{p2} for decreasing x , but little change in k_{p1} with x .

peak in $S(k)$ does shift to smaller wave vector for less arsenic content (Fig. 8). The thermal expansion calculated from the shift of the first peak with T (Fig. 9) shows an appreciable increase for $x=0.11$. Since the slope of the first peak also showed a tendency to increase with decreasing x (see Fig. 4), a plot was made of the slope, obtained from a least-squares fit to the temperature-dependence data for the first peak, versus the value of the thermal expansion α_1 for $T > T_g$ for each composition. The plot in

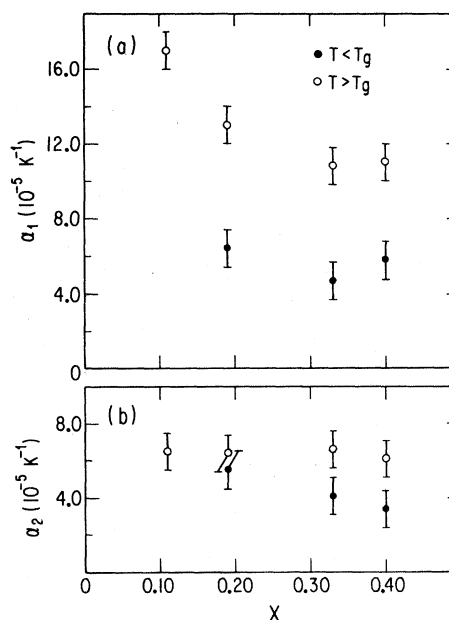


FIG. 9. Coefficients of linear thermal expansion for the $\text{As}_x\text{S}_{1-x}$ glasses plotted vs composition x , as calculated from the shifts of temperature of the first diffraction peak [(a): α_1] and the second diffraction peak [(b): α_2]. Values above and below T_g are indicated.

Fig. 10 indicates that a larger thermal expansion is correlated with a larger rate of increase of the first-diffraction-peak intensity as the temperature rises. (The point derived from the As_2Se_3 data is also plotted for comparison.)

The average thermal expansions above and below T_g were calculated using the expression

$$\alpha_{av}(x) = \frac{1}{3} [2\alpha_2(x) + \alpha_1(x)], \quad (3)$$

which is based on α_2 and α_1 corresponding to two directions, one within a layer and one perpendicular to it, respectively.⁸⁰ As Fig. 11 shows, there is a trend toward increasing thermal expansion of the glasses for low concentrations of arsenic. There is also evidence of deviation from the universal behavior above $1.2T_g$ for the glass of composition $x=0.11$, as shown in Figs. 6(a) and 6(b).

These results imply that there is a new structural entity present in the glasses for decreasing arsenic content. In addition, during our measurements certain irreversible annealing effects were observed for the glasses of compositions $x=0.11$ and 0.19 .

After the samples of composition $x=0.11$ were heated to temperatures near 343 K, the second-diffraction-peak intensity increased and the peak became narrower. The first-peak intensity was unchanged at room temperature after the sample had been heated, but the peak position shifted slightly to larger k . Typical room-temperature diffraction patterns for these samples before heating and after heating to 343 K are plotted in Fig. 12 where these changes are apparent. One sample was heated for 3 h at 343 K, during which time the intensity was monitored and found to be stable. That sample was then cycled between room temperature and 343 K, giving reversible temperature-dependence measurements, which are plotted as the open circles in Figs. 4(g) and 4(h). After heating to $T > 353$ K, the second diffraction peak decreased in intensity and broadened (see Fig. 12). Again the first-peak intensity was the same at room temperature after heating, but the peak appears to have shifted closer to its original position. Between room temperature and $T > 353$ K, the peak-intensity measurements were fully reversible.

During the measurements, the diffraction patterns of

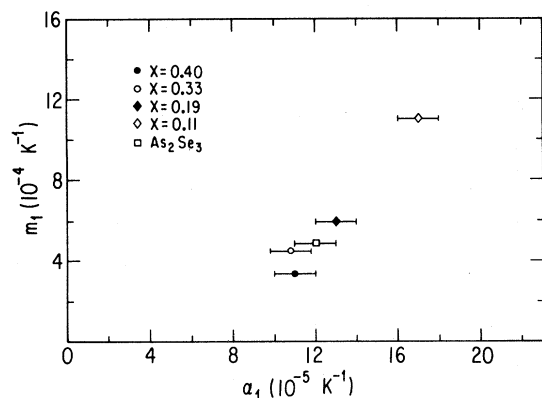


FIG. 10. Plot of the slope m_1 of the temperature-dependence data for the first diffraction peak as derived from a least-squares fit, vs the thermal expansion coefficient α_1 ($T > T_g$).

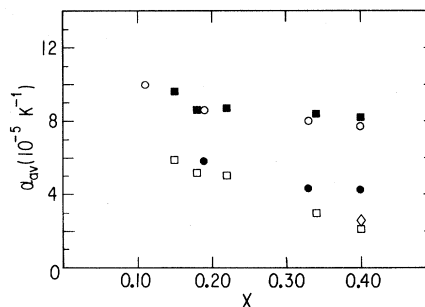


FIG. 11. Plot of the calculated average linear thermal expansion, derived from Eq. (3) for the $\text{As}_x\text{S}_{1-x}$ glasses, vs composition x . Closed circles are the averages for below T_g ; the open circles are averages for above T_g . For comparison, values from Ref. 9, as obtained by measurements with a dilatometer, are plotted as open squares ($T < T_g$) and closed squares ($T > T_g$). The open diamond is derived from thermal-expansion measurements of As_2S_3 glass obtained from the Servo Corp. of America.

the original, unheated samples were not recovered. The samples had actually been “annealing” at room temperature for weeks before the measurements were made. In addition, although the temperature-dependence results for the second peak for $T > 353$ K, plotted as the closed circles in Fig. 4(h), follow the same trend as that near 343 K, the room-temperature normalizations for the data in these two temperature regions are not the same.

A less dramatic annealing effect occurred in the glasses of composition $x=0.19$. After heating for approximately 2–3 h at temperatures between 363 and 423 K, a small peak appeared in the room-temperature diffraction pattern at $k=1.98 \text{ \AA}^{-1}$, superimposed on the second diffraction peak ($k_{p2}=2.05 \text{ \AA}^{-1}$). After subsequent heating, the room-temperature diffraction patterns showed this peak to have grown slightly larger. The peak, once present, caused no change in the temperature-dependence measurements. There were no changes observed at room temperature in the shape or intensity of the first diffraction peak for these samples after heating.

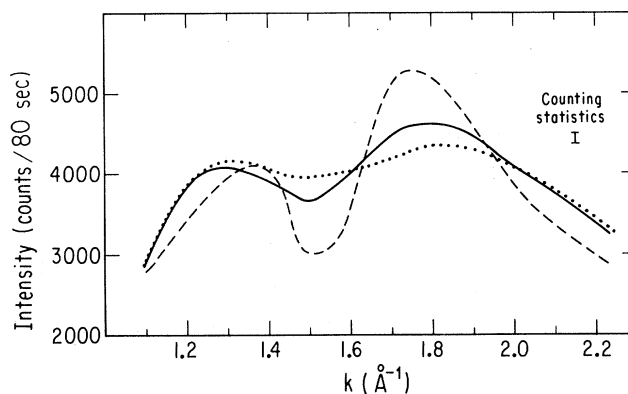


FIG. 12. Room-temperature scans of the first and second diffraction peaks of the $\text{As}_{0.11}\text{S}_{0.89}$ glass. Solid curve: original samples. Dashed curve: samples after heating to 343 K. Dotted curve: samples after heating to $T > 353$ K.

The glasses of compositions $x=0.11$ and 0.19 contain a considerable number of excess sulfur atoms. The most stable crystalline form of sulfur consists of puckered, eight-membered molecular rings held together by weak van der Waals forces.⁸¹ When crystalline sulfur melts, at 392 K, the viscosity decreases and a ring structure is still present. Near 433 K, the viscosity suddenly rises to a maximum and then decreases slowly at higher temperatures. This is known as the polymerization transition,^{82,83} where the ring structures break open to form polymer chains. X-ray measurements on glassy sulfur have indicated that it contains a mixture of rings and chains if the initial liquid temperature is above the polymerization temperature.⁸⁴

Myers and Felty have suggested how the structure in $\text{As}_x\text{S}_{1-x}$ glasses will vary with composition.²⁷ Their measurements of $T_g(x)$ show that at low concentrations of arsenic, the glass temperature falls below the sulfur polymerization temperature. They proposed that sulfur-ring structures will exist in these glasses. Using both differential thermal analysis and thermal-expansion measurements, they observed the sulfur polymerization transition in samples of $\text{As}_x\text{S}_{1-x}$ for $x < 0.20$. (Sulfur rings in glasses of composition $x < 0.20$ have also been detected by chemical means.⁹)

The present experimental results are consistent with the presence of sulfur structural contributions. As the sulfur concentration increases, the position of the second diffraction peak shifts to wave vectors which are closer to those of sulfur (near 1.9 \AA^{-1} for polycrystalline and 1.7 \AA^{-1} for glassy forms). The thermal-expansion increase with increasing sulfur content is consistent with the large thermal expansion of sulfur [the coefficient of linear thermal expansion of crystallized sulfur is $1.18 \times 10^{-4} \text{ K}^{-1}$ within the temperature range 273–373 K (Ref. 85)].

The annealing effects observed in the samples of compositions $x=0.11$ and 0.19 are also suggestive of the presence of sulfur structures. Near 343 K, for $x=0.11$, there may be more sulfur-ring structures forming, giving rise to the sharpening of the second diffraction peak. This is possible since the temperature is above T_g (307 K) for this composition; since the viscosity is lower than at T_g there may be structural rearrangement. The shift of the first peak to wave vectors closer to 1.3 \AA^{-1} is also suggestive of the sulfur glassy structure.⁸⁴ The growth of the peak near 1.98 \AA^{-1} upon heating the glasses of composition $x=0.19$ may be due to the formation of sulfur-ring structures. For both compositions, however, the sulfur structural changes must occur in such a manner that the first peak shows no irreversible change in intensity. Thus we believe that these rings are forming in the connective tissue between the region's layered material or else within the layers such that the layers themselves are not distorted from their original shape.

The deviations from universal behavior above $1.2T_g$ for the $x=0.11$ glasses may be related to the sulfur polymerization transition, since x-ray measurements on liquid sulfur show increasing prominence of the peak at 1.3 \AA^{-1} near this transition.⁸⁴ For this glass, where the annealing effects we observed were most apparent, one might expect less evidence of the layered network. As shown in Fig. 13,

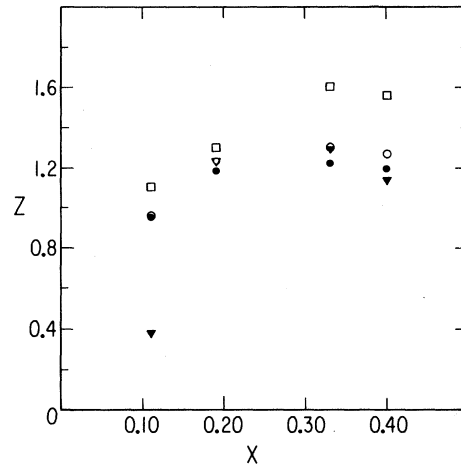


FIG. 13. Variation with composition x for the $\text{As}_x\text{S}_{1-x}$ glasses of the ratios Z , equal to ●: the ratio of the intensities of the first peak to the second peak, calculated at room temperature; ○: this ratio at $T_g(x)$; ▼: the ratio $S(k_{p1})/S(k_{p2})$ computed at room temperature from the structure factors after removing the contributions due to the tails of the peaks; □: the ratio $S(k_{p1})/S(k_{\min})$ where k_{\min} is the wave vector at the first minimum between $S(k_{p1})$ and $S(k_{p2})$. The statistical errors in these ratios are within the size of the points.

the ratios of the intensities of the first peak to the second peak at room temperature show a decrease at small x ; this trend is enhanced when the ratio is calculated at $T_g(x)$. These changes with composition are even more evident when the ratios are calculated from the room-temperature structure factors $S(k)$ after removing the contributions due to the tails of adjacent peaks; as is evident in Fig. 7, the shift of the second peak to smaller k as x decreases makes its contribution to the first peak more pronounced. Finally, the lesser prominence of the first peak at small x is evident from the decreasing ratio of the first-peak maximum to the first-peak minimum in $S(k)$ as x decreases. These trends are all suggestive of fewer layers in these glasses as the arsenic content decreases.

C. Further questions

We have suggested that our temperature-dependence results are consistent with the existence of local layering in the As_2Se_3 and $\text{As}_x\text{S}_{1-x}$ glasses. This description is compatible with the interpretations of many other structural studies which we described. Our observations also present other questions, however, which will now be addressed.

If layers do exist in the glassy structure, their approximate lateral extent remains to be determined. As Leadbetter and Apling pointed out,⁶ the correlation distance within a layer is not synonymous with its size. From their quasicrystalline model, they estimated the intralayer correlation distance to be of the order of 10 \AA .⁶ This may represent a lower limit on the lateral size of the disordered layer.

As the temperature of the glass rises, we proposed that a strained bonding arrangement within the layer may relax and allow the atoms to move into the layers, making them

smoother. This may require the strain energy to be comparable to the bond energy, however, since the thermal energy provided as T rises is very small. This is one possible description; the actual microscopic mechanism for this smoothing, which cannot be determined unambiguously from our data, remains to be found.

We described the changes in thermodynamic properties and the characteristic drop in the viscosity observed as a glass is heated through the glass transition. As Fig. 4 illustrates, we observed no discontinuity or significant change in the slope of the temperature dependence near T_g . Our suggestion for continued interlayer correlations and smoothing of the layers above T_g is consistent with no discontinuity. It may be that the temperature ranges measured above and below the glass transition were too limited to observe a small change in slope at T_g . If there is a more subtle change, such as in the second derivative of the curve, more precise data very close to the transition would be needed to observe it. The question remains as to what sort of change, if any, would be expected at T_g in the temperature dependence of the structure of these glasses.

The universal temperature dependence for the $\text{As}_x\text{S}_{1-x}$ glasses, shown in Fig. 6, illustrates the most puzzling observation from our experiments. The changes in the structures show a behavior which *scales with T_g for all x* . This is very surprising, considering the compositional variations in the structure which we have noted above. There may be a more basic underlying mechanism for the structural changes with temperature for these glasses which has yet to be revealed.

There are other glass-forming compounds whose structure factors contain first peaks at wave vectors near 1 \AA^{-1} . These include the GeS_2 and GeSe_2 glasses and certain alloys of phosphorous and selenium. It remains to be determined whether the structures of these glasses show temperature-dependence behavior similar to what we found in the As_2Se_3 and $\text{As}_x\text{S}_{1-x}$ glasses. In addition, it would be interesting to measure the temperature dependence of the structures of the vapor-deposited amorphous films of As_2S_3 and As_2Se_3 , whose structures after annealing appear similar, but not identical to those of the bulk glasses.

V. SUMMARY

Experimentalists have characterized the glass transition for most glasses by measurements of various properties, including the rise in the shear viscosity as the liquid becomes a glass and changes in the thermal properties such as the specific heat. We have made the first measurements of the changes with temperature in the x-ray structure factors of several excellent glass formers both below and above their glass transition temperatures. These glasses were As_2Se_3 (Ref. 3) and the alloys $\text{As}_x\text{S}_{1-x}$, where $x=0.40$ (As_2S_3), 0.33, 0.19, and 0.11.

Surprising results were found for the temperature dependence of the first-peak intensity. It was observed to increase with increasing temperature up to, and for the $\text{As}_x\text{S}_{1-x}$ glasses, above the glass transition. At the same time, the second-peak intensity was observed to decrease with increasing temperature. The changes were large and

were reversible for both peaks.

The increase of the first-peak intensity indicates that there is *more* order on that length scale at higher temperature; we know of only one other system, liquid ^4He ,⁷¹ where a similar effect was observed. It is also significant that these changes were observed even far below the glass transition; measurements for As_2Se_3 showed that the intensity of the first peak continued to change with T even down to 50 K, the lowest temperature measured.

We propose that our results are consistent with structural models previously given for local layering in these glasses; the first peak corresponds to the interlayer separation in the glass, whereas the second peak relates to correlations within the layers. Since the glassy structure is isotropic, it should consist of groups of these layers which are randomly oriented.

As the temperature rises, we suggest that the layers become smoother (increase of the first-peak intensity) as there is less order within the layers (decrease of the second-peak intensity). As the layers become smoother it may be possible for them to begin to slip past one another. The cooperative effect of the slippage for all the layered groups could lead to the characteristic viscosity decrease near the glass transition.

The temperature-dependence data show no apparent change in behavior above T_g for the $\text{As}_x\text{S}_{1-x}$ glasses; this is consistent with continued smoothing of the layers. This suggestion is supported by the results of other workers who have done high-temperature spectroscopy measurements, and have concluded that there are layers present in the supercooled liquid and in the liquid as well.

Although our results are consistent with local layering in the $\text{As}_x\text{S}_{1-x}$ glasses, there is also evidence of new structural contributions. We observed certain trends with composition and annealing effects (for compositions $x=0.11$ and 0.19). We attribute our observations to the presence of sulfur structures in the sulfur-rich glasses.

The universal temperature-dependence behavior for all x in the $\text{As}_x\text{S}_{1-x}$ glasses, which we observed when the data were scaled to values at $T_g(x)$, indicates that a fundamental mechanism is responsible for relating the increase in the first-peak intensity to the glass transition itself. Our proposal for the smoothing of the layers in these glasses and in As_2Se_3 is one possible interpretation; there is presently no appropriate microscopic model for these glasses with which we can compare our results.

Our measurements constitute a novel approach to investigating the behavior of glasses near the glass transition. The unusual results we obtained may give new insights which were not readily apparent from measurements near T_g of other properties of these glasses.

ACKNOWLEDGMENTS

The author wishes to thank D. Dennison, I. Steele, and A. Davis for assistance with sample preparation and analyses and J. Pluth for technical assistance. Discussions with S. Bhattacharya and H. Fritzsche are gratefully acknowledged. Above all, the patient guidance and constant support and encouragement of my thesis advisor, Professor Sidney Nagel, are deeply appreciated. This work was

supported by National Science Foundation Grant No. NSF-DMR-82-01182 and by National Science Foundation Materials Research Laboratories Program Grant No. 79-

24007, and was submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Chicago.

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