Temperature Dependence of the Structure Factor of As_2Se_3 Glass Up to the Glass Transition

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The temperature dependence of the structure factor of glassy As_2Se_3 has been measured. Surprising results were found for the first peak, which shows a large increase in intensity from 40 K to the glass transition temperature, T_g; in contrast the second peak decreases in this range. The first peak corresponds to interlayer correlation in the glass. Its increase indicates a smoothing of the layers which may lead to layers slipping past one another, thus decreasing the viscosity above T_g.

Certain materials form glasses when cooled rapidly from the liquid state.[1,2] These materials undergo a glass transition, which is most dramatically demonstrated by a rapid increase in the viscosity, from a value appropriate to a liquid to that of a solid, as the temperature is decreased to T_g (the glass transition temperature). The nature of the glass transition, whether kinetic, thermodynamic, or some combination of these, is still unresolved. Until now, measurements have focused primarily on thermodynamic properties which reflect the influence of relaxational effects at the transition.[3-5] Several models have been developed to describe the relationship of such data to T_g (Refs. 6–11) but they give little indication of the microscopic behavior of the glass.

We have taken a new approach to the problem. Although it is known that the overall structure of the liquid and the glass are very similar, no work has previously been done to probe changes in the structure of the glass as T_g is approached. We have measured changes in the x-ray structure factor of As_2Se_3 glass as a function of temperature from 40 K to T_g (460 K). Our results give important insight into the microscopic mechanism which determines the glass transition. We chose As_2Se_3 since it is an excellent glass former which is easily made by cooling the melt. Its average coordination number of 2.4 satisfies Phillips's criterion,[12] which states that the best glass formers should have coordination numbers between 2 and 3. In addition, As_2Se_3 is one of the chalcogenide semiconductors which have been widely studied and for which there is considerable thermodynamic data at the glass transition.[13]

Crystalline As_2Se_3 is a layered structure[14] with each layer consisting of linked, twelve-membered rings of alternating As and Se atoms. The forces between adjacent layers are very weak compared to those within each layer.[15] There is a Bragg

diffraction peak at $k = 1.26$ Å^{-1} known to correspond to the interlayer separation.

The glassy structure is characterized by several diffuse peaks in the structure factor $S(k)$. The first four peaks from our x-ray data are shown in Fig. 1. The derived radial-distribution-function calculation gave results in agreement with those of other studies.[16-18] These show that the short-range order of the crystal exists in the glass, i.e., the nearest-neighbor distance is only slightly larger in the glass and the coordination numbers are unchanged. There has been some controversy over the structural significance of the first diffraction peak ($k_{p1} = 1.2$ Å^{-1}) in the glass; it is believed to be due either to layering or to the presence of large molecular clusters[19,20] such as As_4Se_6. A neutron diffraction measurement[21] indicates the presence of the first diffraction peak in the liquid.

Our experiment focused on the temperature dependence of the peak intensities of the first diffraction peak at $k_{p1} = 1.27 \pm 0.004$ Å^{-1} and the second diffraction peak at $k_{p2} = 2.23 \pm 0.004$ Å^{-1}.
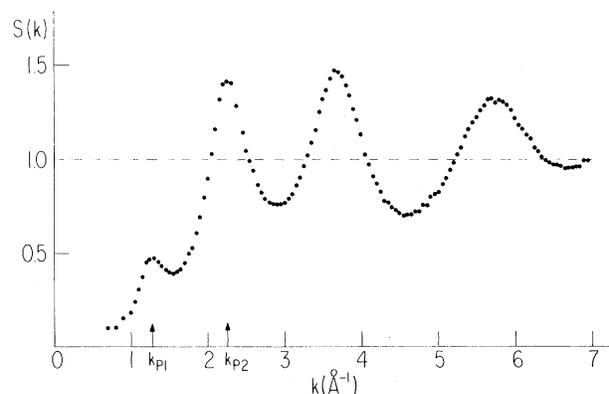

FIG. 1. The x-ray structure factor for glassy As_2Se_3. The first peak is located at $k_{p\,1} = 1.27 \pm 0.004$ Å^{-1}; the second peak at $k_{p\,2} = 2.23 \pm 0.004$ Å^{-1}.
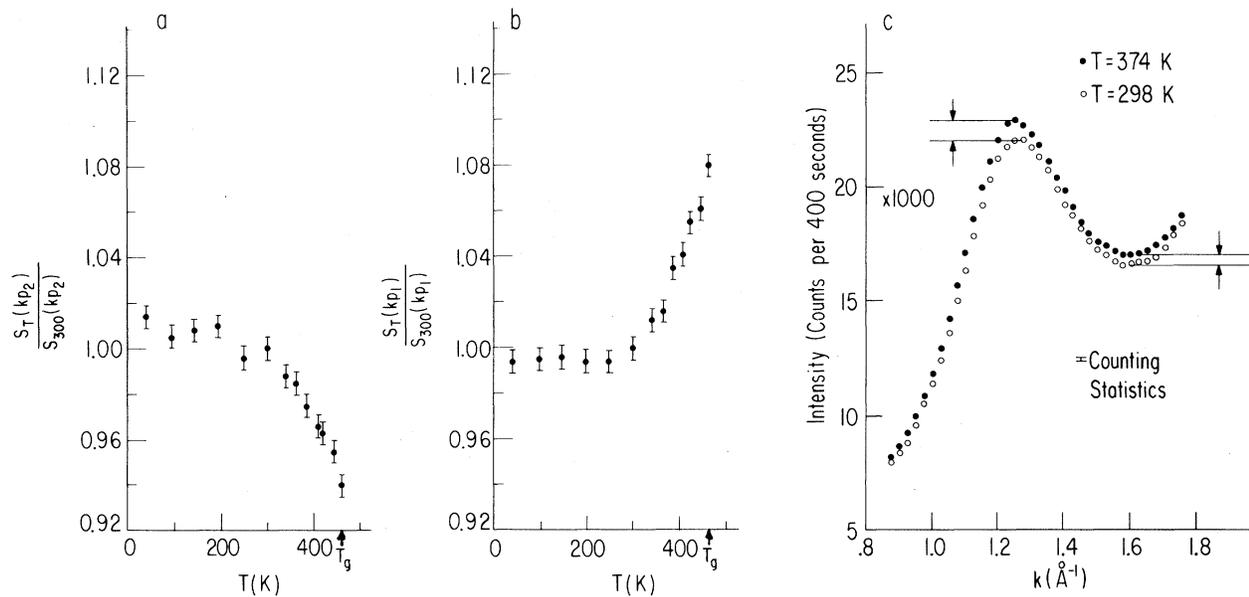
FIG. 2. Ratio of the intensity $S(k_p)$ at temperature T to the intensity at room temperature (300 K): (a) for the second peak at k_{p2}; (b) for the first peak at k_{p1}; (c) intensity of the entire first peak at two temperatures (298 and 374 K). The change with T at the peak is larger than the change at the first minimum.

Since the entropy increases the structure should become more disordered as T is raised. One would therefore expect that the intensities of the structure factor peaks should decrease in a manner similar to that of the Bragg diffraction peaks of a crystal.

The glass was prepared by heating elements of 99.999% purity under a vacuum of 10^{-6} Torr to 870 K in a rocking furnace for 24 h. Chips of this bulk glass were each placed between two squares of 7.5 μm Kapton film and heated to 650 K while being squeezed to form thin samples of about 50 μm thickness. These samples were oriented for x-ray transmission with use of Cu K_α x rays ($\lambda = 1.5418$ Å). Both a standard tube source and a Rigaku rotating anode x-ray source were used with a Picker diffractometer. Low-T measurements were made with a Helix displex cryostat; high-T experiments were made by directing heated nitrogen gas over the sample. The temperature regulation was accurate to ± 5 K. Care was taken to assure that we were always measuring the intensity of the peak of the structure factor even though the peaks shift slightly with temperature. Above 300 K, the linear expansion coefficient (determined by $\alpha = k^{-1} dk/dT$) from the second-peak shift was found to be $(5.9 \pm 1.0) \times 10^{-5}$ K^{-1}, while that from the first peak was $(1.2 \pm 0.2) \times 10^{-4}$ K^{-1}.

The temperature dependence of the second peak

is shown in Fig. 2(a). The intensity decreases with increasing temperature as expected for greater disorder. The decrease of about 7% over the entire temperature range is quite large, however. Below 200 K, the intensity remains relatively constant. Similar behavior has been seen in metallic glasses.[22,23]

Figure 2(b) shows the temperature dependence of the first peak. The *increase* of the intensity with increasing temperature is quite surprising; it indicates that order is increasing on that length scale as the glass is heated. The change of 9% over the whole temperature range is very large. At the lowest temperatures the intensity changes very little with T.

These results are not due to annealing effects but are completely reversible. The sample was repeatedly recycled to room temperature where we measured the same starting intensities of the two peaks. To our knowledge this is the first time in any material that the structural order has been observed to increase, on any length scale, as the temperature is raised.

As a further check of the first-peak behavior, we measured the intensity both at and surrounding the peak at two temperatures [Fig. 2(c)]. We wished to determine whether its increase was due to an overall background increase, possibly from a rise in the tail of the second peak. Our results show the first peak to be rising much faster than

its surrounding background. This also demonstrates that the rise in intensity at the peak is real and not an experimental artifact. We also measured the temperature dependence of the scattering with only the Kapton present. At low temperatures we found no temperature dependence of this background intensity at either peak position. Above 300 K there was only a slight decrease of intensity at each position. The effect of the background subtraction would be to enhance the temperature dependence seen in Fig. 2(b). We have not as yet extended our measurements above T_g since above that temperature, as the sample softens and changes shape, it is much more difficult to obtain reliable intensity information.

We believe our data to be consistent with the existence of local layers in the glass. If molecular clusters were present, the increase of the first peak would indicate that more clusters were forming or that they were becoming spatially better correlated as the temperature rises. The formation of clusters seems unlikely because it must be reversible as our data indicates; thermal energy provided to the clusters would presumably prevent their increased correlation. Also we observe a different thermal expansion for the first peak than for the second which indicates that these wave vectors must relate to different objects or at least to different directions in the local order of the glass. The structural picture we suggest is of crimped, disordered layers in the glass. Estimates from the first-peak width have indicated[18] that on average four layers are correlated.

Most importantly, we believe our results give an explanation for the onset of diffusive behavior at the glass transition. The increase of the first peak implies that the layering is becoming enhanced, i.e., the layers become smoother as the temperature rises. As the layer becomes smoother, they can eventually slip past one another as T increases above T_g and thus account for the rapid drop in viscosity. This description is in contrast to a model proposed by Phillips[24] for As_2Se_3, in which the viscosity change at T_g is said to be due to edges of layers slipping past one another in a direction perpendicular to the layers. Our model is consistent with the interpretation of temperature-dependent viscosity data,[25] infrared spectra,[26] and Raman spectra[27] in which it is proposed that the layers remain intact while the forces between layers weaken above T_g. However, in our model we can be much more specific and correlate this drop in viscosity with the actual smoothing out of the layers.

At the same time that the layers are getting smoother, the second-peak decrease indicates decreasing order within each layer. In the absence of a quantative microscopic model for this behavior, we propose the following qualitative arguments. As the liquid is cooled, structural defects are presumably frozen into the glass. A particular layer, for example, may contain rings of atoms not numbering twelve, which causes defects in the ideal layer structure, pushing atoms out of the layer and causing it to crimp. Other defects such as open rings or bonding between layers could also reduce interlayer correlation. Because of these defects, the glass could have a large strain energy (E_S) which is comparable to the bonding energy (E_B). If the difference between the bond energy and the strain energy released by breaking a bond $(E_B - E_S)$ is small compared to $k_B T$, it would be possible to break or bend bonds as the temperature rises, allowing atoms to relax into the layers, thus making them smoother. Within the layers themselves there would be less ordering, in agreement with our measurements on the second peak. It is possible that the enhanced planar ordering may be accounted for by a similar model as that proposed for explaining the behavior of reentrant-nematic liquid crystals.[28]

To summarize, we have, for the first time, studied structural changes in As_2Se_3 glass over a wide range of temperature up to T_g. We believe our results are the only known observation for any isotropic material indicating an increase of structural order with increasing temperature. Our data lend support to the structural model of layering in the glass and indicate a very plausible explanation for the decrease in viscosity as the temperature rises above T_g. Such an explanation is the first attempt to understand the microscopic nature of the glass transition in an excellent glass former.

There are other materials which readily form glasses and which have a first diffraction peak giving some indication of layering; such glasses include As_2S_3, GeS_2, and $GeSe_2$. We might expect similar behavior for the temperature dependence of the structure in this entire class of glass formers.

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