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Temperature dependence of the structure factor of GeS_2 glass

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We have measured the temperature dependence of the first two peaks in the structure factor of GeS_2 glass. The first peak shows an increase in intensity between 300 and 523 K. The second-peak intensity is practically independent of T in this range. This anomalous behavior is similar to that found in As_2Se_3 and As_xS_{1-x} glasses which also appear to have a short-range order corresponding to layers.

One expects in general that as the temperature of a solid is raised it will become more disordered. An exception to this of course is if the sample can anneal while it is at the elevated temperatures, in which case one would find an irreversible change in the structure. When the sample is recooled to its initial temperature it will no longer have its original structure but will show increased short-range order. It therefore came as a great surprise when it was discovered[1] that certain glasses showed the opposite effect, namely that certain components of the short-range order reversibly increased upon raising the temperature. Because it was reversible, this was clearly not an annealing effect.

In those experiments, x-ray diffraction measurements as a function of temperature showed that the intensity of the first small peak in the structure factor of glassy As_2Se_3 increased with temperature rather than decreased. The first peak was located at wave vector $k_{p_1}=1.27$ Å^{-1}. This change in $S_T(k_{p_1})$ occurred over the entire temperature range measured: $50 \leq T \leq 460$ K. Since the glass transtion temperature T_g for As_2Se_3 is 460 K the sample would soften and flow at higher temperatures. In a subsequent series of experiments[2] on As_xS_{1-x} glasses it was possible to perform x-ray diffraction measurements from room temperature to temperatures considerably above the glass transition temperature. In those studies it was also found that the intensity of the first peak in the structure factor increased with temperature while the other peaks decreased. This behavior was observed both above and below the glass transition temperature. It was also found in the As_xS_{1-x} glasses that the rate of increase in the first-peak intensity scaled inversely with the value of T_g for the alloy. That is, a universal curve for all x was obtained if $S_T(k_{p_1})/S_{T_g}(k_{p_1})$ was plotted versus T/T_g.

The crystal structures[3] for both As_2Se_3 and As_2S_3 are identical. They are layered materials with each layer consisting of linked, 12-membered rings of alternating As and S(Se) atoms. The forces between adjacent layers are very weak compared to those within each layer. The first peak in the glass structure factor has often been interpreted[4,5] as being due to short-range order in the amorphous state which is similar to the layering observed in the crystal. This is plausible since the Bragg peak associated with the interlayer spacing in the crystal is very close to k_{p_1}, the position of this first peak in the glass. If this interpretation of the peak is correct, the fact that this peak increases upon raising the temperature while the others do not, could imply that the layer structure in the glass is becoming more ordered. This remarkable result according to this structural model thus relies on the fact that the sample has a short-range layered structure. Although other structural models have been proposed for these glasses,[6] interpretation of these results in terms of layering appears the most natural.

The question naturally arises whether this phenomenon, an increase in the first peak in $S_T(k)$ with temperature, will be observed for all glasses which have a layered structure as their crystalline counterpart or whether it is particular to the As_2Se_3 structure. For that reason we have studied the glass GeS_2. Crystalline GeS_2 also has a layered structure,[7] but the structure within each layer is different from that within each As_2Se_3 layer. Germanium has a higher coordination number than arsenic and there is a larger percentage of sulfur atoms in GeS_2 than there is in As_2S_3.

We have performed both x-ray diffraction and neutron diffraction on samples of GeS_2 glass. The samples were made in a quartz ampoule by heating elements of 99.999% purity under a vacuum of 10^{-6} Torr to 1223 K. It was held at this temperature in a rocking furnace for 24 h. The liquid was then quickly quenched in water. For the x-ray work, chips of the bulk glass were polished and etched until they were about 50 μm thick and were then held between two squares of 7.5-μm Kapton film. These samples were oriented for x-ray transmission. Cu $K\alpha$ x-rays ($\lambda=1.5418$ Å) were used. The temperature was varied by flowing heated nitrogen gas past the sample. The temperature was stable to ±5 K. In measuring the peak intensity as a function of temperature care was taken to account for the shift in the peak due to thermal expan-

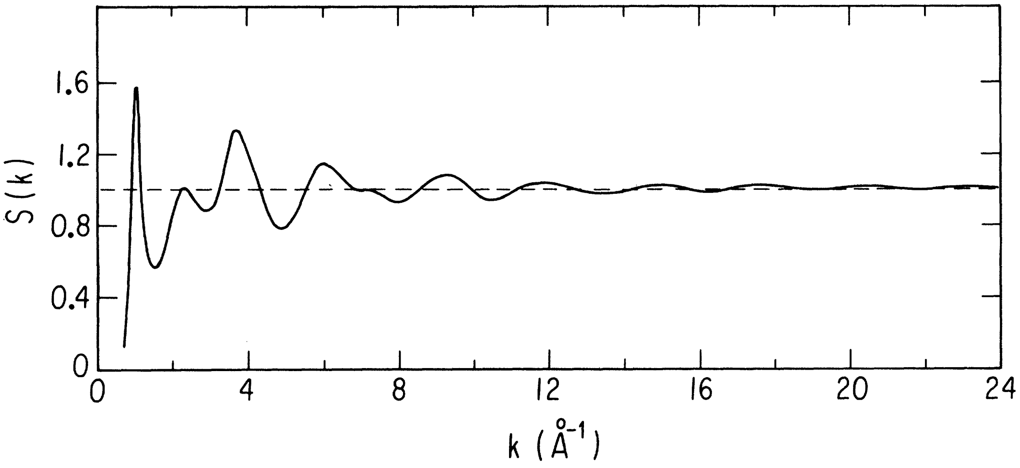

FIG. 1. Static structure factor for GeS_2 glass as measured by neutron diffraction.

sion. For the neutron work, the sample was placed in a vanadium container. The diffraction was done at the Argonne National Laboratory Intense Pulsed Neutron Source. Time-of-flight techniques were used to measure the diffraction. Measurements were also made of the empty vanadium can in order to perform the background subtraction and of a vanadium rod in order to measure the parameters of the neutron beam.[8]

In Fig. 1 we show the static structure factor, $S_{300\,\mathrm{K}}(k)$, for GeS_2 glass as obtained from the neutron-diffraction measurements. Although we have obtained the structure factor out to a much larger wave vector ($k=160$ Å^{-1}), we have only shown it out to 24 Å^{-1}. At a larger wave vector we find only a flat structure factor with no oscillations. From this data we find that the first peak occurs at $k_{p_1}=1.04$ Å^{-1} and the second peak at $k_{p_2}=2.12$ Å^{-1}, which is in agreement with the measurements of Rowland *et al.*[9]

In Fig. 2 we show the results for the temperature dependence of the intensity of the first two peaks in $S_T(k)$. This was determined from our x-ray measurements. The temperature is varied between 300 and 523 K above which temperature the Kapton film deteriorates. We see in Fig. 2(a) that similar results are obtained for the first peak of the GeS_2 glass as were found for the As_2Se_3 and the As_xS_{1-x} glasses. The first-peak intensity increases with increasing temperature. It was checked that this is not an annealing effect since it is reversible upon raising and lowering T. As shown in Fig. 2(b), the intensity of the second peak is almost independent of temperature over the range of temperature which we studied. The temperature dependence of the Kapton film was also measured at the same wave vector as the two peaks in the glass. When the effect of the scattering from the Kapton film is subtracted from the data it slightly increases the temperature dependence of the first peak.

Although glassy GeS_2 behaves in a qualitatively similar manner to the other glasses studied earlier, the effect is much smaller. The first-peak intensity only increases by 3% upon heating from room temperature to 523 K whereas the first-peak intensity of As_2S_3 increases by approximately 7% over the same temperature range. We note, however, that the glass transition temperature for GeS_2 is[10] 763 K and is thus much higher than it is for the As_xS_{1-x} glasses. In those glasses a universal curve could be made if $S_T(k_p)$ and T were scaled by their values at T_g for each value of x [i.e., plot $S_T(k_p)/S_{T_g}(k_p)$ vs T/T_g]. Thus if T_g were large the change in $S_T(k_p)$ with temperature would be small. This is consistent with the results on GeS_2.

In conclusion we have found that the first peak in the structure factor of GeS_2 glass behaves in a qualitatively

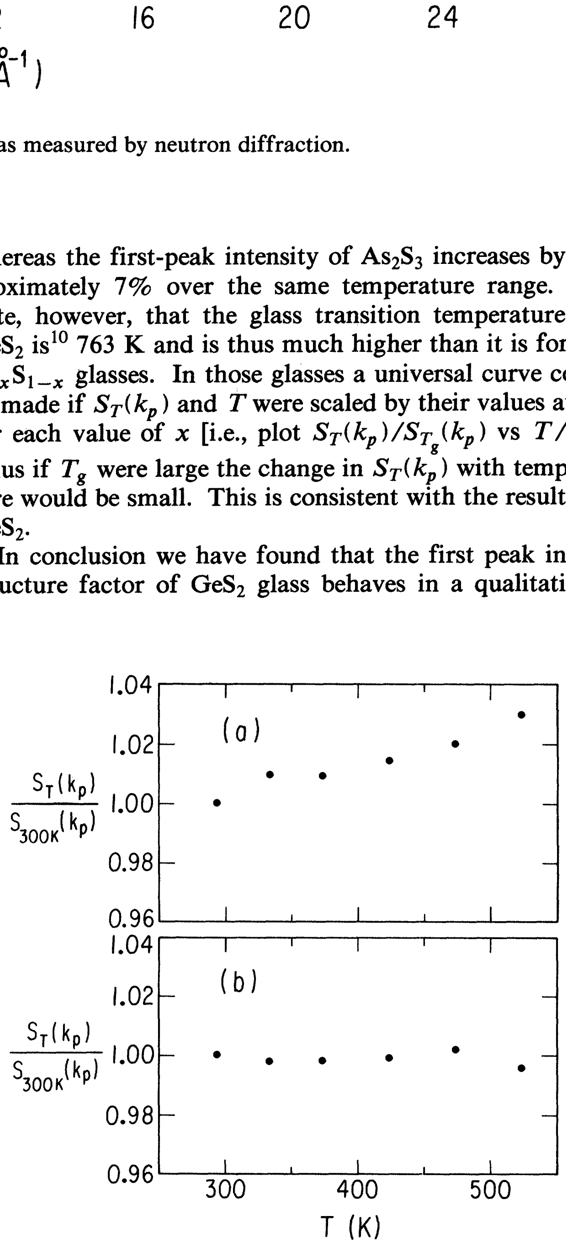

FIG. 2. (a) Temperature dependence of the intensity of the first peak in the structure factor for GeS_2 glass. (b) Temperature dependence of the intensity of the second peak in the structure factor for GeS_2 glass. The temperature dependence of both peaks was measured by x-ray diffraction.

similar manner to the first peak in the glasses previously studied, As_2S_3 and As_xS_{1-x}. The intensity of the peak increases reversibly with temperature. GeS_2 crystal, although layered, does not have the same structure within a layer as does the As_2Se_3 or As_2S_3 crystals. Thus it would appear that the phenomenon of an increase with temperature of $S_T(k_{p_1})$ in glasses is more general than previously realized in that many different structures show the same behavior. As long as there is some remnant of layering in the short-range order of the glass this phenomenon appears to persist.

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