Comment on "Rigidity Percolation in the Germanium-Arsenic-Selenium Alloy System"

Elastic constants (EC) on two sets of alloy glasses with low-As and high-As content were examined[1] recently as a function of composition, i.e., average coordination number $\langle r\rangle$ in the range $2<\langle r\rangle<3$. Both sets of samples, according to Halfpap and Lindsay (HL),[1] display an increase in the longitudinal (C_{11}) and transverse (C_{44}) EC near $\langle r\rangle\simeq 2.4$. These experiments, stimulated by ideas of Phillips[2] and Thorpe[3] were interpreted as evidence of mean-field rigidity percolation in elastic networks.

Several years ago Ota *et al.*[4] also measured EC of binary Ge-Se glasses in the same $\langle r\rangle$ range and found a rapid increase near $\langle r\rangle=2.6$ instead of $\langle r\rangle=2.4$. In this Comment I provide an alternative interpretation to these EC experiments and discuss the apparent discrepancy between these results. My interpretation of these macroscopic results correlates well with the one inferred earlier from a microscopic probe[5] of network rigidity.

In Fig. 1 the lower panel [Fig. 1(b)] reproduces HL's results for C_{11}, and those of Ota *et al.* are given in the upper panel [Fig. 1(a)] for comparison. HL's results strikingly demonstrate that a first-order threshold, discontinuity in $dC_{11}/d\langle r\rangle$, i.e., kink in C_{11}, occurs near $\langle r\rangle=2.5$ and 2.7 for the high- and low-As-content glasses. In addition, a second-order threshold, discontinuity in $d^2C_{11}/d\langle r\rangle^2$, is observed near $r\simeq 2.4$, particularly in the results of Ota *et al.* [Fig. 1(a)]. I also note that the saturation value of C_{11} as $\langle r\rangle\rightarrow 3$ in the low-As-content glasses is substantially higher than for the high-As-content glasses.

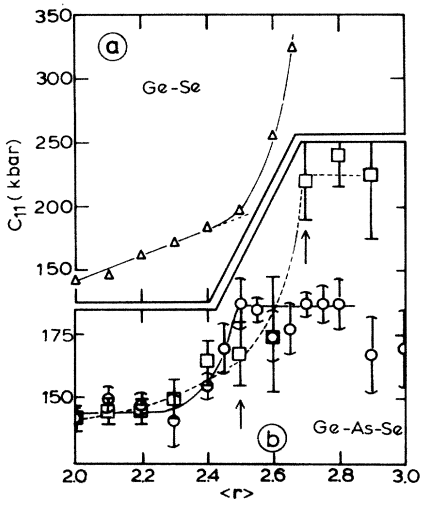

FIG. 1. (a) C_{11} of Ge_xSe_{1-x} glasses plotted as a function of average coordination number $\langle r\rangle=2(1+x)$ from the results of Ota *et al.*, Ref. 4. (b) C_{11} as a function of $\langle r\rangle$ for ternary Ge-Se-As glasses taken from Ref. 1. The squares and circles correspond to low- and high-As-containing glasses. Note that C_{11} rises rapidly near $\langle r\rangle=2.4$ and 2.6 for the high- and low-As glasses, resulting in kinks at the arrows. The smooth lines through the data are a guide to the eye.

The elastic kinks in these glasses apparently arise as a result of two distinct types of molecular fragments present in these networks: one built of optimally coordinated pyramidal $As(Se_{1/2})_3$ units and the other of overcoordinated tetrahedral $Ge(Se_{1/2})_4$ units. For the As-based fragment the mechanical and chemical thresholds coincide at $\langle r\rangle=2.40$. This accounts for the kink in C_{11} observed by HL near $\langle r\rangle=2.5$ in their high-As content glasses. For the Ge-based fragment, however, the mechanical threshold (at $\langle r\rangle=2.40$) deviates from the chemical one (at $\langle r\rangle=2.67$) with the important consequence that microscopic and macroscopic probes of glass networks respond differently to the rigidity threshold. For example, in the Mossbauer experiments[5] on Ge-Se glasses the mechanical threshold is indeed observed close to $\langle r\rangle=2.4$. However, in the EC measurements which use ultrasound of wavelength $\lambda\simeq 10^{-2}$ cm, the glass network is sampled on a scale much coarser than the molecular fragment size (10^{-7} cm) and the tail of the kink obscures the elastic threshold. For this reason the results of Ota *et al.*[4] and those of HL on their low-As content glasses are both consistent with only a second-order transition near $\langle r\rangle=2.40$. In the latter results, the kink in C_{11} near $\langle r\rangle=2.7$ I associate with rigid Ge-containing fragments filling up the glass network. The lower saturation value of C_{11} in the As-rich glasses is understood in terms of a reduced stiffness of the pyramidal units in relation to the tetrahedral units, which largely derives from a reduced coordination number since the Ge-Se and As-Se single-bond strengths are nearly the same. Thus models of glass networks based on specific molecular fragments[2,5] which phase separate provide a good basis to understand rigidity percolation kinks in alloy glasses. To avoid inconsistencies, these kinks must be identified and distinguished from elastic thresholds associated with longer distance scales.

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