

	<b>Experiment title:</b> Anomalous x-ray scattering study on glassy Ge-Se around the stiffness threshold composition	<b>Experiment number:</b> HS-1562
<b>Beamline:</b> BM02	<b>Date of experiment:</b> from: 03 Oct. 2001 to: 10 Oct. 2001	<b>Date of report:</b> 17 Feb. 2002
<b>Shifts:</b> 21	<b>Local contact(s):</b> Dr. Jean-François Bézar	<i>Received at ESRF:</i>
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### Report:

Mean-field theory [1,2] for network glasses provides a powerful tool to explain the experimentally observed numerous anomalies around the critical composition of the rigidity percolation threshold at an average coordination number,  $\langle r \rangle_c = 2.4$ , where the number of constraints per atom is equal to the degree of freedom. In case of glassy (*g*-)  $\text{Ge}_x\text{Se}_{1-x}$  system, this corresponds to  $x = 0.20$ . The character of the network glass undergoes a steep *first-order-like* transition from easily deformable at  $\langle r \rangle < 2.4$  (*floppy*) to *rigid* at  $\langle r \rangle > 2.4$ . Recently, Boolchand *et al.* [3] demonstrated that results from Raman Scattering, modulated scanning calorimetry, and Mössbauer spectroscopy provide clear experimental evidence for the stiffness transition. The electronic density of states also show abrupt concentration changes around the transition composition [4]. However, there has yet no study that explored the precise variation of the atomic structure with concentration.

Anomalous x-ray scattering (AXS) experiments were carried out at two energies (–15 and –200 eV) below the K edge of each element using a normal  $\omega$ - $2\theta$  diffractometer. To obtain a sufficient energy resolution (to discriminate the elastic signal from the  $K_{\beta}$  fluorescence and Compton scattering contributions) and enough counts in a reasonable data acquisition time, we chose a graphite analyzer crystal with a 40 cm detector arm [4,5], providing the energy resolution of about 45 eV. The samples were prepared by quenching the melts after rocking a quartz ampoule containing the mixed compound. The measurements were performed at room temperature with the reflectance geometry.

We measured five samples ( $x = 0.15, 0.17, 0.25, 0.28, \text{ and } 0.33$ ) in steps  $\Delta Q$  of  $0.5 \text{ nm}^{-1}$ . Fig. 1 shows total structure factors  $S(Q)$  measured at the incident x-ray energy of 10903

eV (200 eV below the Ge K edge) together with the previous results at  $x = 18.5, 19.5,$  and  $0.23$  [4,5]. For clarity, the spectra are shifted against each other by  $0.3$ . The prepeak appeared around  $11 \text{ nm}^{-1}$ , which is clear evidence for the existence of intermediate-range order, shows a systematic decrease in intensity and shifts towards higher  $Q$  with decreasing  $x$ . These concentration variations are very strong around  $x = 0.20$ . On the other hand, the concentration change of the spectra is very small in the  $Q$  range beyond  $15 \text{ nm}^{-1}$ .

As an example of our present AXS results, differential structure factors  $\Delta_i S(Q)$  for  $g\text{-GeSe}_2$  ( $x = 0.333$ ) close to the Ge and Se K edges are shown in Fig. 2 by crosses and circles, respectively, together with  $S(Q)$ . Apparently, the statistical quality of the  $\Delta_i S(Q)$ s is so good that an interpretation of the underlying structural information can easily be given. The shape of  $\Delta_{\text{Ge}} S(Q)$  has a much larger prepeak and a large negative minimum at the position of the first peak in  $S(Q)$  at  $20.5 \text{ nm}^{-1}$ . On the other hand,  $\Delta_{\text{Se}} S(Q)$  has no signal at the prepeak position. Since  $\Delta_{\text{Ge}} S(Q)$  originates from about 27%  $S_{\text{GeGe}}(Q)$ , 68%  $S_{\text{GeSe}}(Q)$ , and 5%  $S_{\text{SeSe}}(Q)$ , while  $\Delta_{\text{Se}} S(Q)$  about 60%  $S_{\text{SeSe}}(Q)$ , 40%  $S_{\text{GeSe}}(Q)$ , and no  $S_{\text{GeGe}}(Q)$ , it is obvious that the prepeak at about  $11 \text{ nm}^{-1}$  is a result of the Ge-Ge correlation. Very similar results are also obtained in the whole concentration range measured from  $x = 0.15$  to  $0.333$ . In order to confirm the above speculation on a quantitative basis and to discuss the relation between the structure and the stiffness transition, it is essential to obtain complete sets of  $S_{ij}(Q)$ s from the present results. Such analyses are now in progress.

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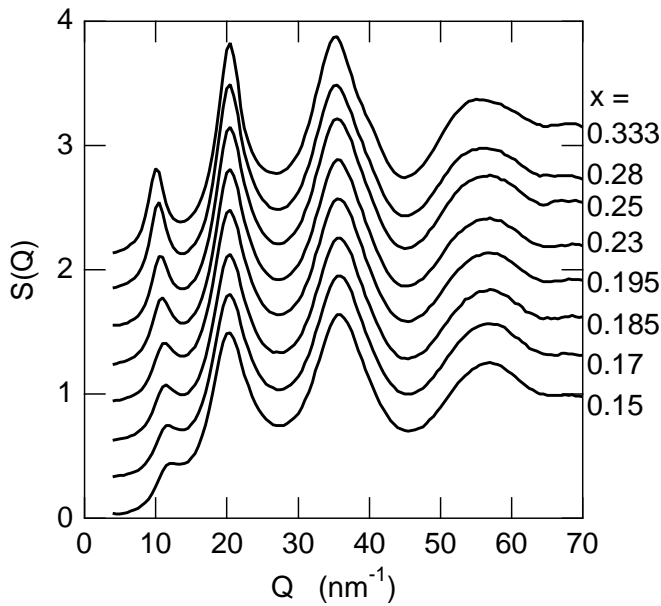


Fig. 1

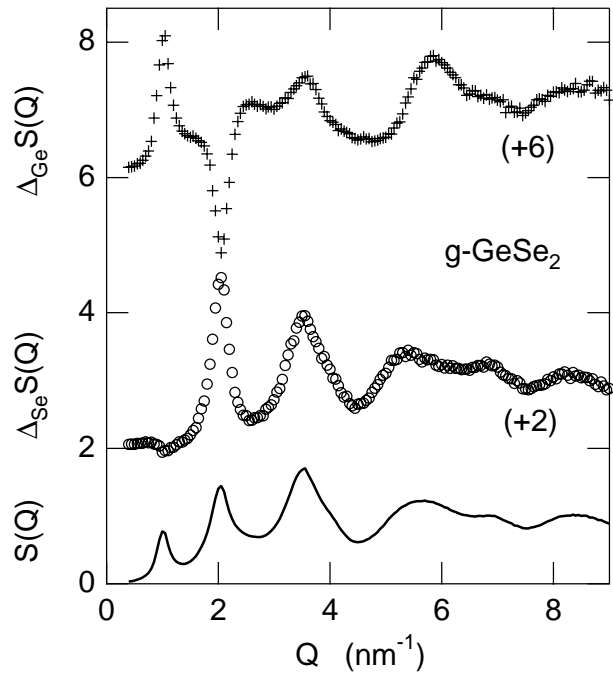


Fig. 2