Neutron and X-ray Scattering Studies

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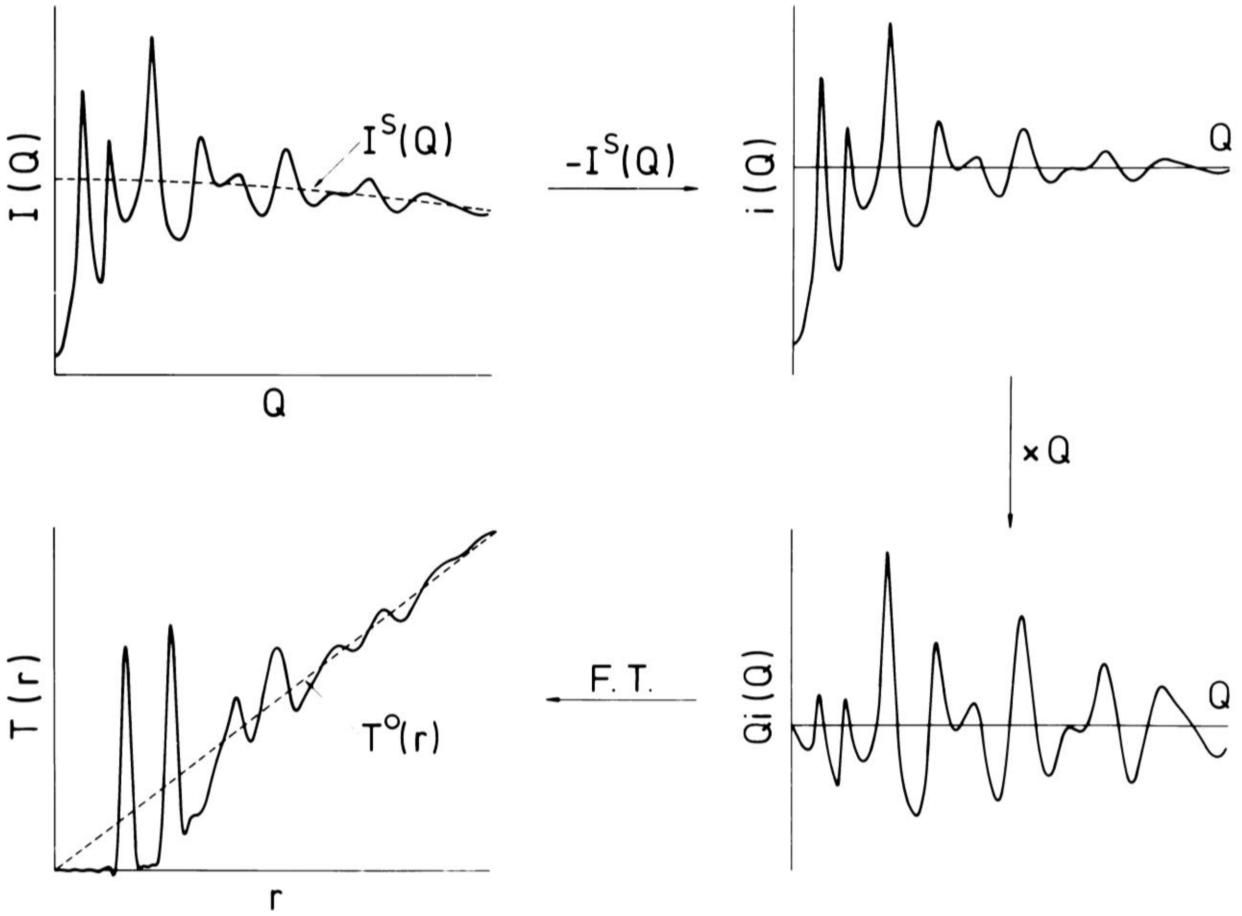
Outline

- Review interpreting correlation functions
- Some more examples
- Inelastic neutron scattering
- Small angle scattering
- Molecular species

T(*r*) from a Neutron Diffraction Experiment

$$I(Q) = \underset{\text{self}}{I^S(Q)} + \underset{\text{distinct}}{i(Q)}$$



$$T(r) = T^0(r) + \frac{2}{\pi}\int_0^\infty Qi(Q)\,M(Q)\sin rQ\,dQ$$

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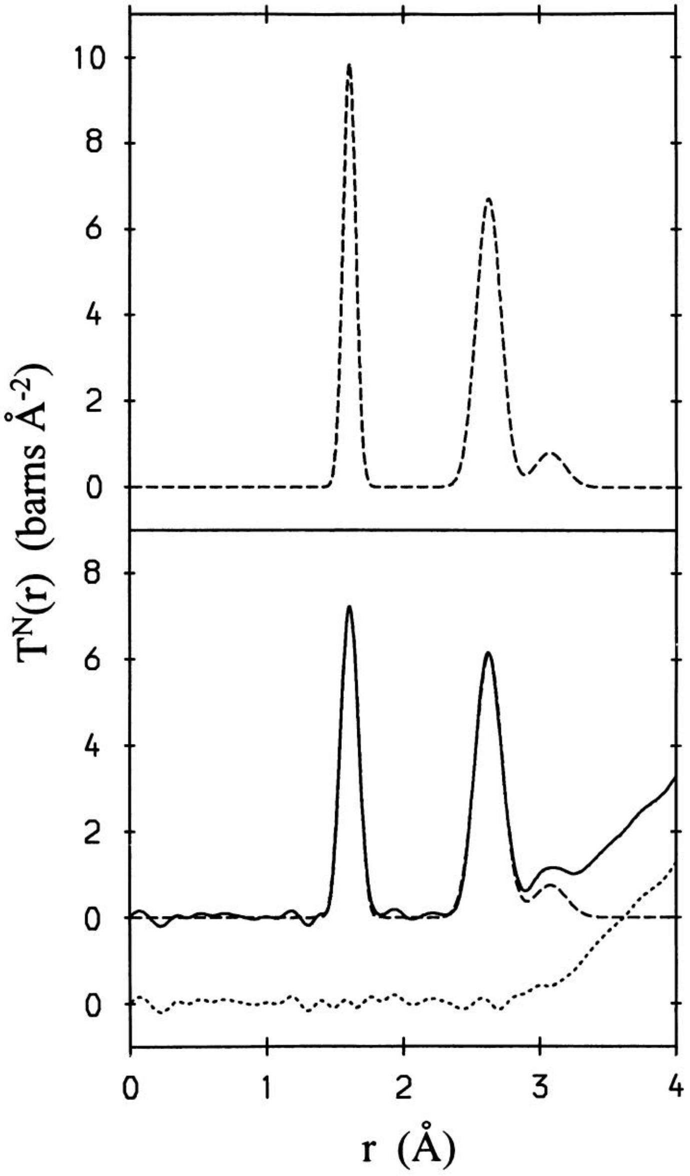
Neutron Peak Fit: Get the Bond length, Distribution and Coordination Number

A fit (dashed lines) to the first two peaks in the neutron correlation function, $T(r)$, for vitreous silica (solid line). The dotted line is the residual and the upper curve is the unbroadened fit. The mean Si–O bond length is 1.608 ± 0.004 Å, with an rms deviation of 0.047 ± 0.004 Å, and the mean O-O distance is 2.626 ± 0.006 Å, with an rms deviation of 0.091 ± 0.005 Å. The Si(O) co-ordination number is 4 and the Si-Si contribution is obtained from the corresponding X-ray data.



The accuracy of fit is given by the rms R-factor

$$R_\chi = \{\Sigma_i[T_{\exp}(r_i) - T_{\text{fit}}(r_i)]^2/\Sigma_i T_{\exp}{}^2(r_i)\}^{½},$$

which is equal to 0.038.

Structural Models of Amorphous Solids

1. Random Network.
    - (a) Hand built.
    - (b) Computer generated.
    - (c) Geometric transformation.
2. Random Coil.
3. Random Sphere Packing.
    - (a) Hand generated.
    - (b) Computer generated.
4. Molecular Model.
5. Crystal Based Models.
    - (a) Limited range of order (finite size).
    - (b) Strained crystal models.
6. Layer model.
7. Amorphous Cluster.
8. Monte Carlo Techniques.
    - (a) Conventional (energy minimisation).
    - (b) Reverse (minimisation of difference from experiment).
9. Molecular Dynamics Simulation.

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Even in the Simple Case Component Correlation Functions are Complicated

For a sample with n elements there are $n(n+1)/2$ independent component correlation functions,

$$t_{ij}(r) = 4\pi r \rho_{ij}(\mathrm{r});$$

e.g. for vitreous SiO_2, the components are Si-Si, Si-O and O-O (O-Si is simply related to Si-O). A single diffraction experiment measures a weighted sum of these components,

$$T(r) = \sum_i \sum_j w_i w_j t_{ij}'(r),$$

where the i summation is taken over the atoms in the composition unit and that for j over atomic species (elements). For X-rays, the weighting factors, w, are equal to the number of electrons in the given atom/ion, Z_i, whereas, for neutrons, w is equal to the neutron scattering length, b_i. (The prime on $t_{ij}'(r)$ indicates that it is broadened by the peak function, $P(r)$)

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Extraction of Component Correlation Functions

For a sample containing *n* atomic species, there are *n*(*n*+1)/2 component correlation functions and various techniques exist that allow their complete or partial separation:

1. **Isotopic Substitution** (neutron diffraction).
   Since neutrons are scattered by the nucleus, the isotopes of a given element have different scattering amplitudes (lengths).

2. **Anomalous Dispersion** (neutron and X-ray diffraction).
   The scattering amplitude (X-ray form factor) becomes complex and wavelength dependent in the region of an absorption resonance (edge).

3. **Magnetic Neutron Diffraction.**
   The magnetic correlation function can be used to infer the inter-atomic distances between the magnetic atoms/ions.

4. **EXAFS Spectroscopy.**

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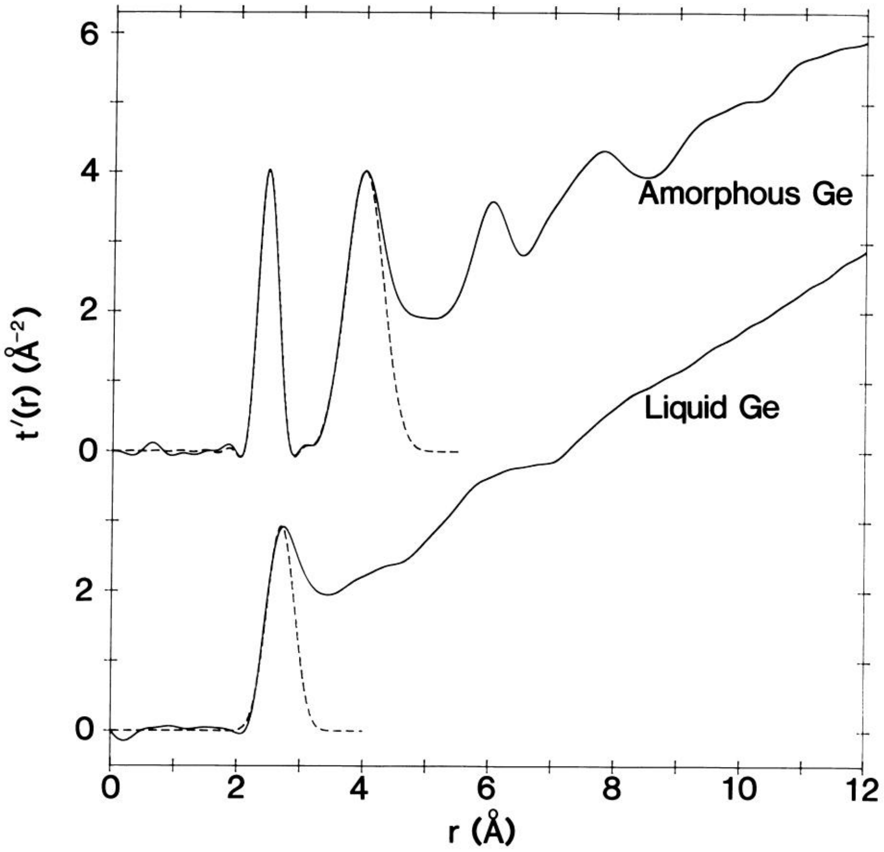
Amorphous & Liquid Germanium

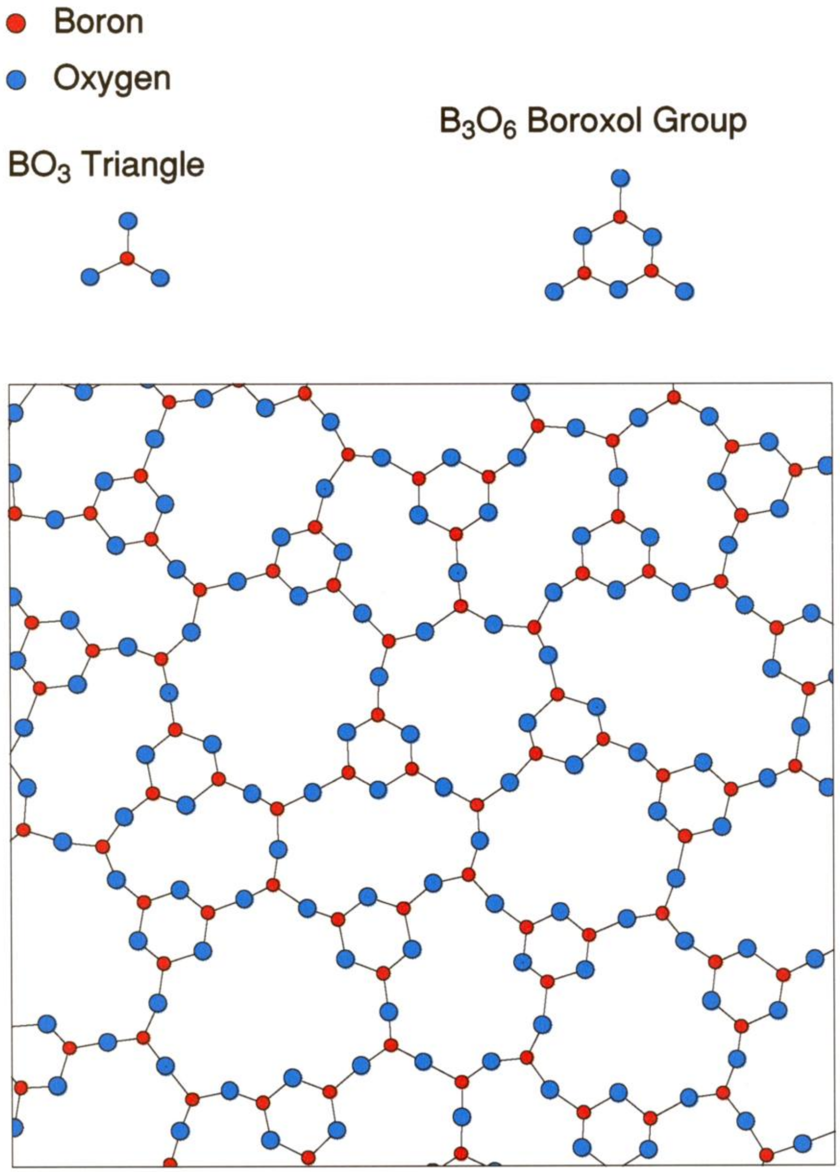


The amount of structure in the correlation function can vary considerably, as may be seen for amorphous and liquid Ge. In general, network materials yield more structure in T(r) than random packed structures.

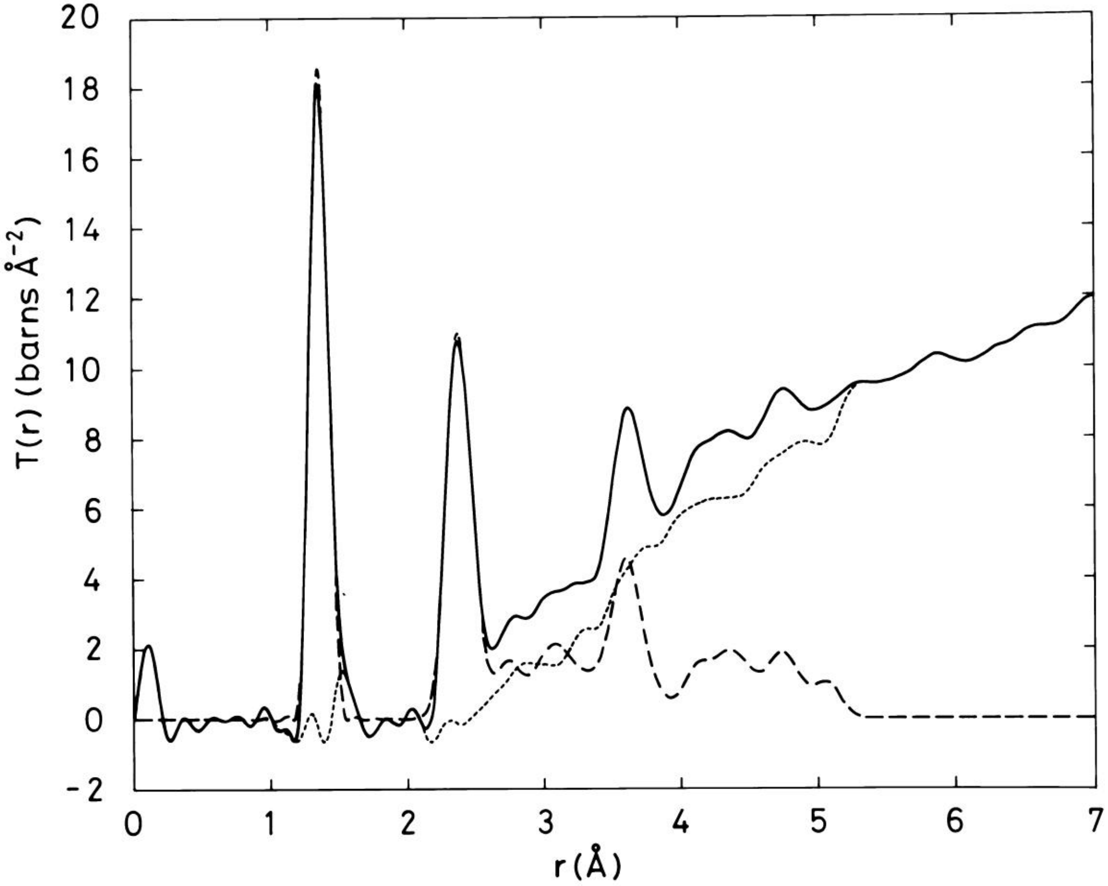
Structure of Vitreous Boron Oxide

The structure of vitreous B_2O_3 thus comprises a mixture of $B\O_3$ triangles and $B_3\O_6$ boroxol groups. Neutron diffraction and NMR data indicate that 70-80% of the boron atoms are in boroxol groups [Figure: A.C. Hannon].

The presence of boroxol groups explains both the low density of the glass (71% of crystal density) and the fact that a crystal seeded into the anhydrous supercooled melt does not grow, even over a period of several months.



Vitreous Boron Oxide

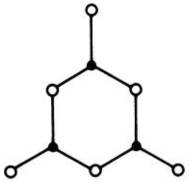


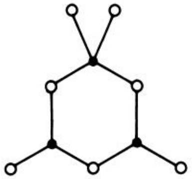
The correlation function for vitreous B_2O_3. A fit to the first two peaks indicates that the basic structural units are $BØ_3$ triangles (Ø represents a non-bridging oxygen atom). However, the sharp peak at 3.6 Å reveals the presence of boroxol groups. A fit to extract the fraction of the boron atoms, *f*, in boroxol groups yields *f* = 0.8 ± 0.05. Solid line, experiment; dashed line, fit and dotted line, residual.

Superstructural Units

The structure of glasses containing boron oxide is further complicated by the presence of superstructural units, which comprise rigidly-defined combinations of the basic structural units:

A: Boroxol
B: Triborate
C: Di-triborate
D: Metaborate
E: Diborate
F: Pentaborate
G: Di-pentaborate
H: Tri-pentaborate


(A)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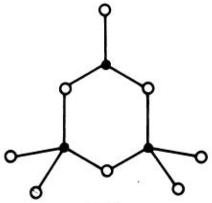
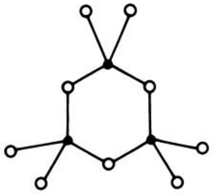
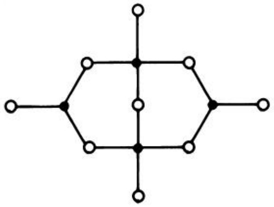
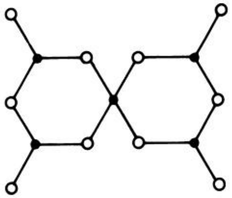
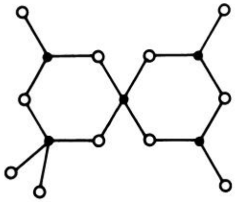
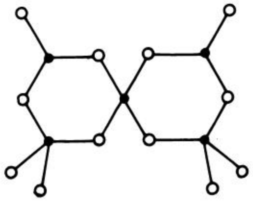

(C)


(D)

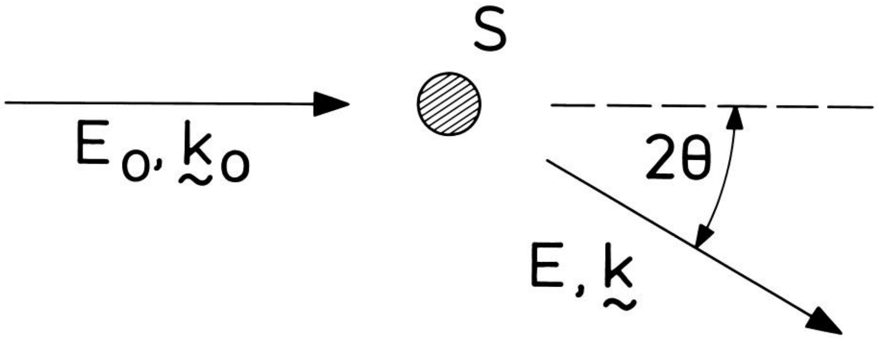

(E)


(F)


(G)


(H)

Inelastic Neutron Scattering



Neutrons may also be scattered inelastically, by exchanging energy and momentum with the atomic and magnetic excitations within the sample (phonons and magnons in the case of a crystalline material). The scattering is characterised by the energy transfer

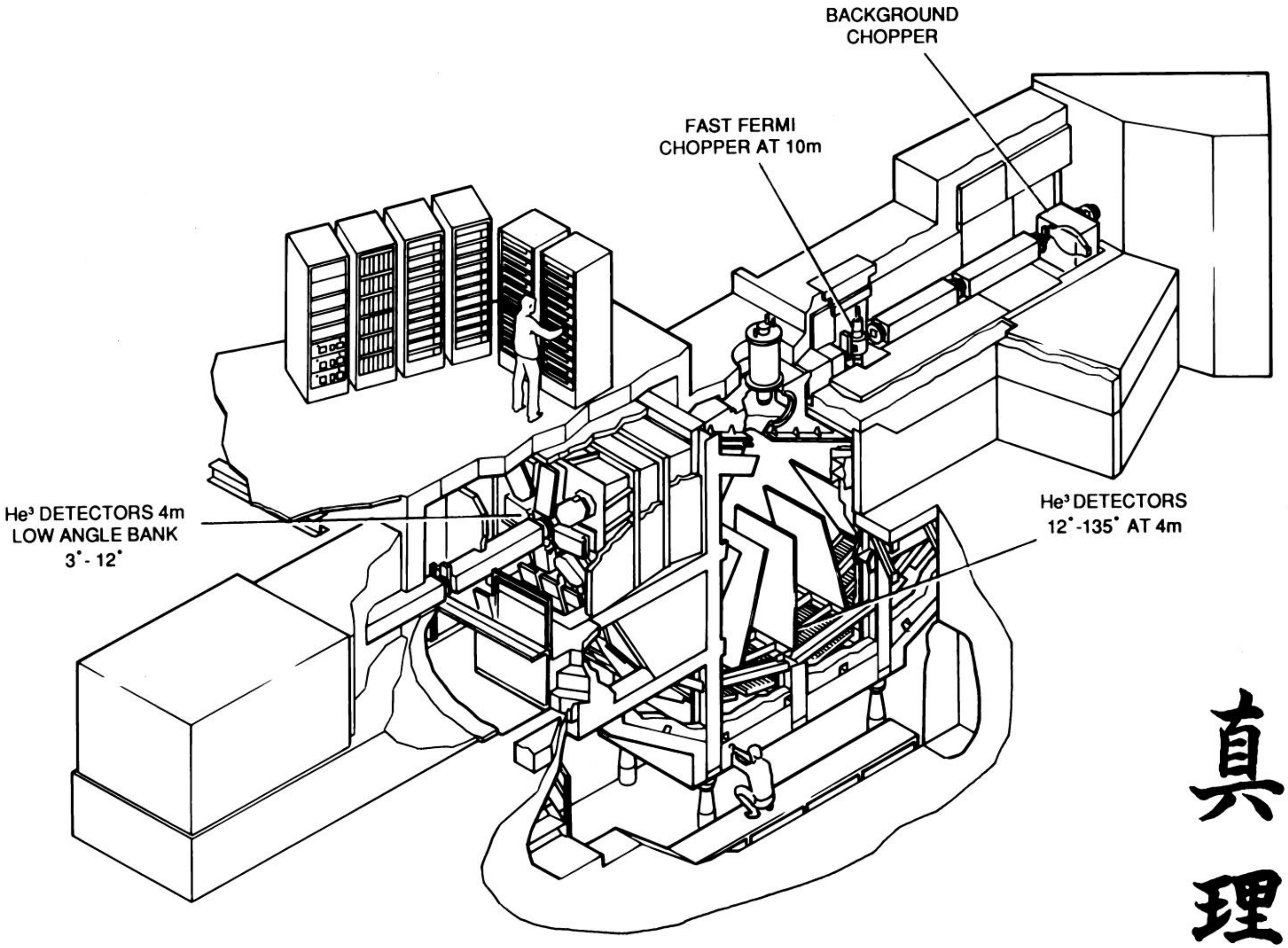
$$\hbar\omega = E_0 - E,$$

and the momentum transfer

$$\hbar Q = \hbar k_0 - \hbar k.$$

For scattering to occur, it is also necessary for an excitation to be possible with the appropriate combination of energy and momentum.

The MARI Spectrometer



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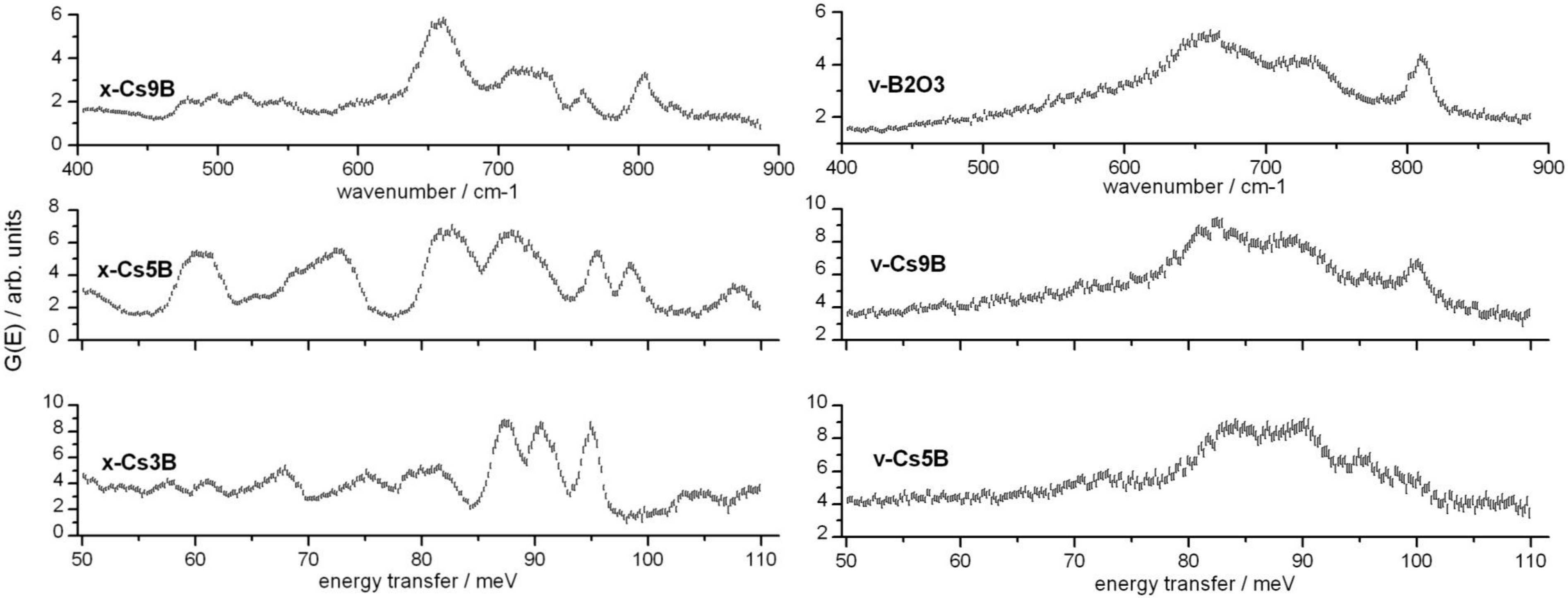
Pulsed, monochromatic neutrons are produced by a chopper, and the energy and momentum of the scattered neutrons are obtained by time-of-flight analysis.

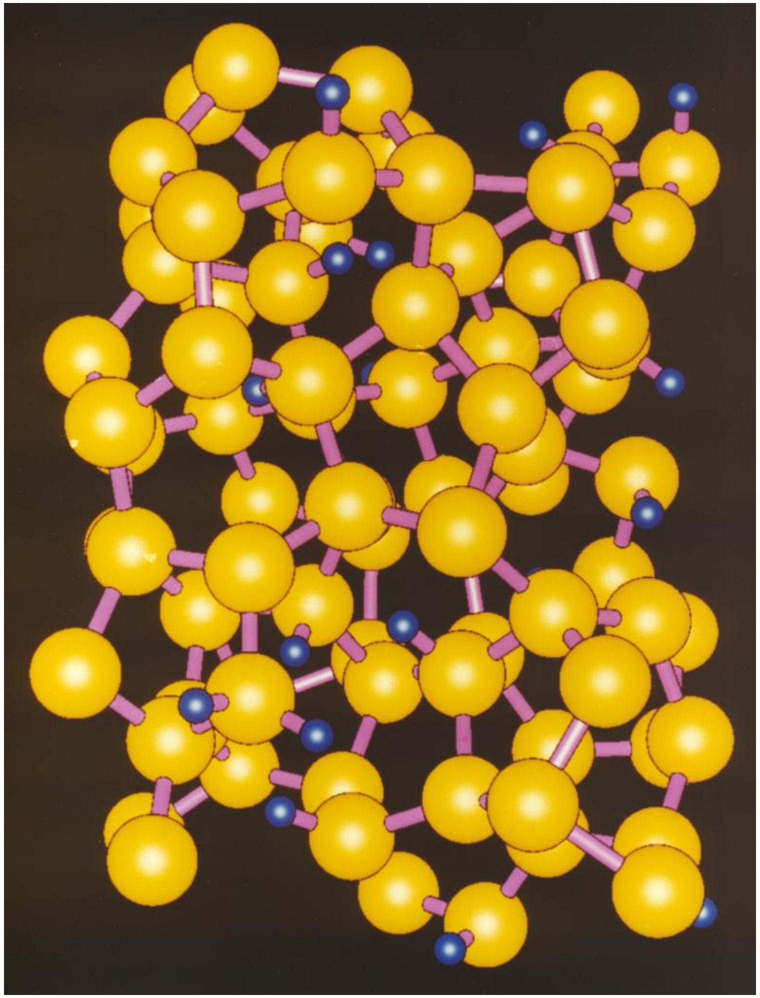
Superstructural Units in Cæsium Borates



The structure of binary and multi-component borate glasses may be extremely complex, due to the presence of a range of superstructural units, which lead to many overlapping peaks in the correlation function. One method of distinguishing between superstructural units is by the energy of the breathing mode of the 3-membered rings of borate structural units on which they are based. The energies of these breathing modes may be obtained by studying crystalline borates with known superstructural unit contents.

Hydrogenated Amorphous Silicon

Hydrogenated amorphous silicon is a very important material, due to its use in solar cells, liquid crystal displays, *etc*. However, its structure is extremely complex and poorly understood. This structure is certainly two-phase, and may be envisaged as an amorphous silicon random network, with the broken bonds saturated by hydrogen. (Pure amorphous silicon is not a useful electronic material, due to the presence of broken bonds, as characterised by ESR.)



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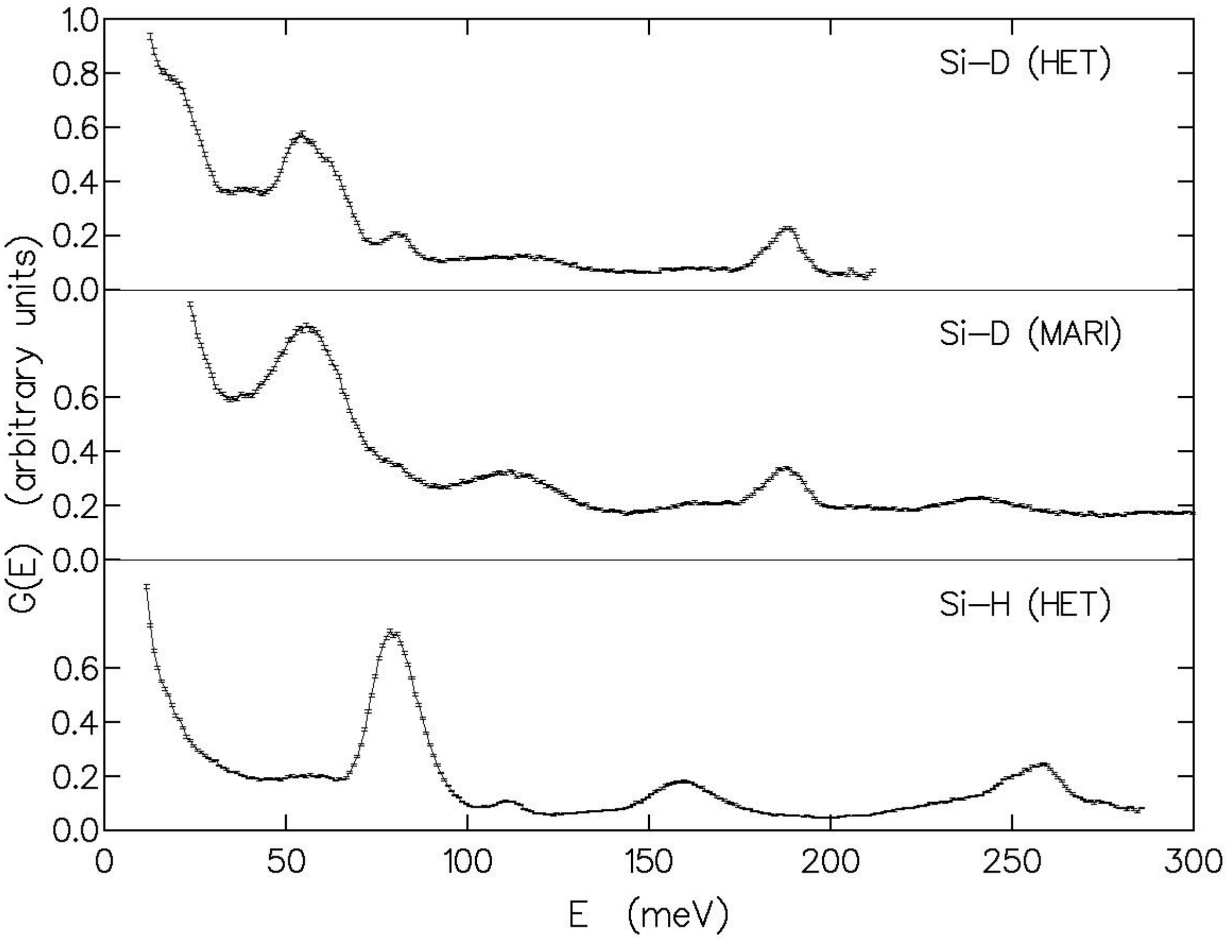
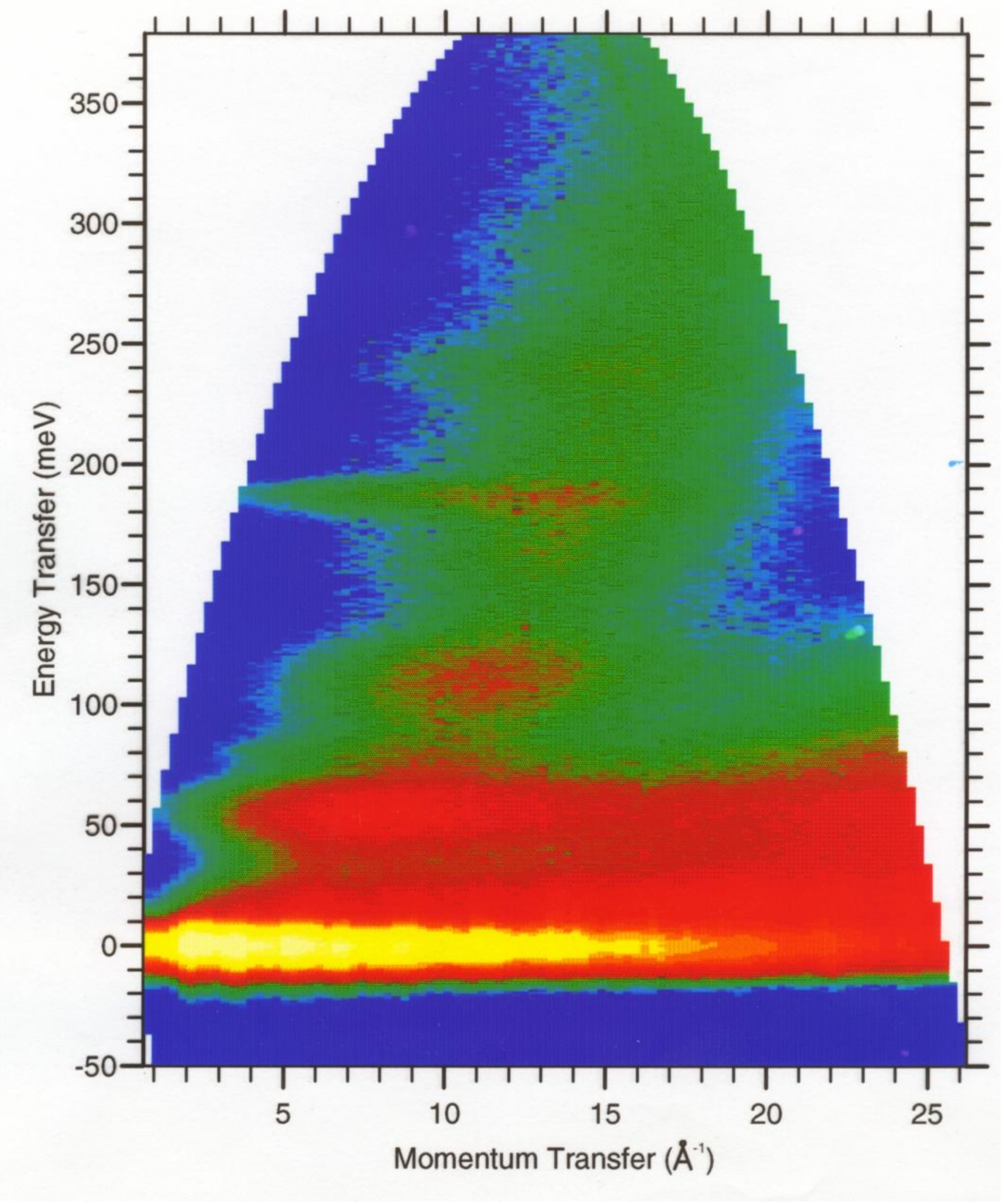
Vibrational Density of States (VDOS)



The (neutron-weighted) VDOS for hydrogenated and deuterated amorphous silicon, obtained with the ISIS MARI and HET spectrometers. The Si-H bending mode is at ~75 meV and the corresponding stretching vibration is at 250-260 meV. The energies of the modes for deuterated amorphous silicon are reduced by a factor of √2.

MARI Data for Hydrogenated Amorphous Silicon

The primary data from an inelastic scattering experiment comprise the scattered intensity as a function of energy and momentum transfer. The elastic diffraction pattern corresponds to the cut with ħω = 0, and the (neutron-weighted) vibrational density of states (VDOS) is obtained by averaging over ħQ for each value of ħω.



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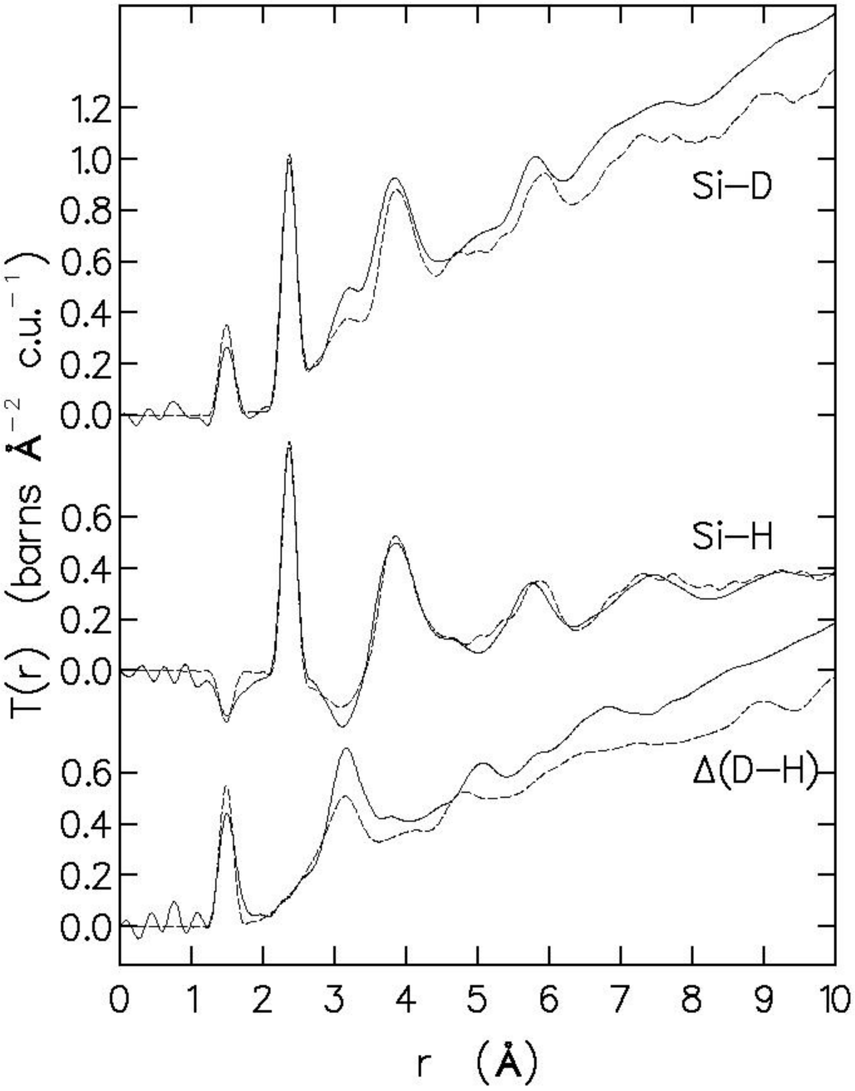
Correlation Functions for Amorphous Si-H/D

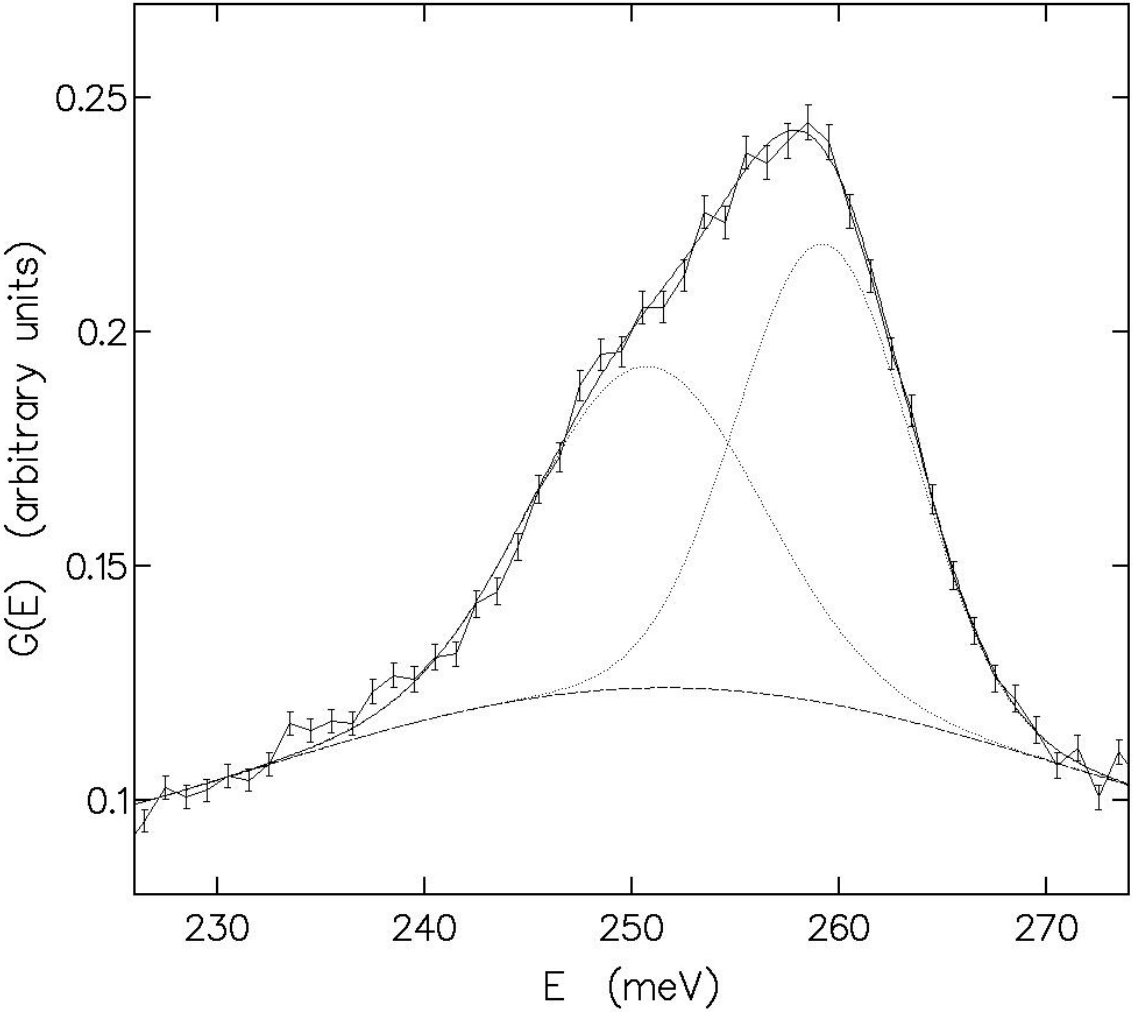
Correlation functions for hydrogenated and deuterated amorphous silicon, together with the isotopic difference. Note that H has a negative neutron scattering length ($b_H = -0.37406 \times 10^{-14}$ m) and so Si-H peaks are negative. (D has a positive scattering length; $b_D = 0.6671 \times 10^{-14}$ m.) The experimental data (solid line) are compared to the random network cluster model of Weaire et al.* (dashed line).



* D. Weaire, N. Higgins, P. Moore and I. Marshall, *Philos. Mag.* **40** (1979), 243.

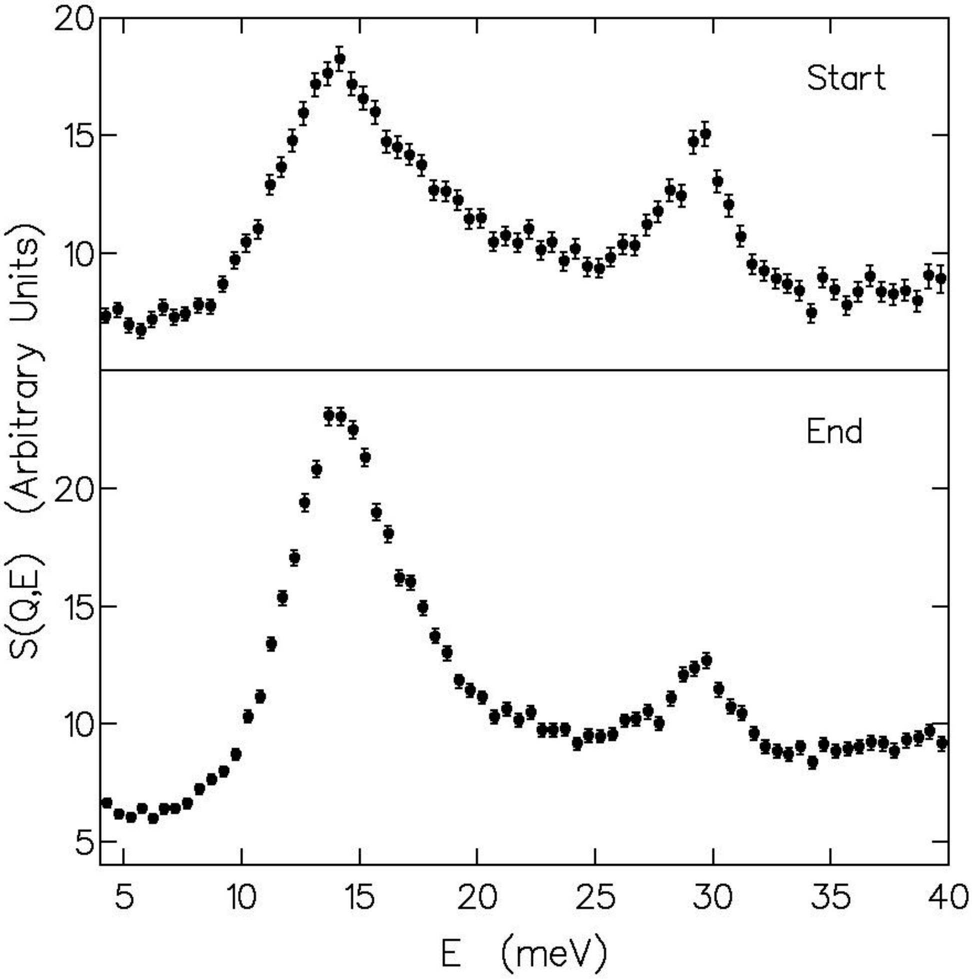
Fit to ≡SiH and =SiH_2 Stretching Modes

A fit to the ≡SiH and =SiH_2 stretching modes, at 251 and 259 meV respectively, indicates that approximately equal numbers of H atoms are involved in ≡SiH and =SiH_2 units.



Ortho-Para H_2 Conversion

Hydrogenated amorphous silicon also contains hydrogen molecules, trapped under high pressure (~2 kbar) in the voids within the amorphous network. The presence of molecular hydrogen is demonstrated unambiguously by the observation of the ortho to para conversion at low temperature (~15 K), via molecular rotation modes at 14.5 and 29.4 meV. SANS data indicate that there are on average ~60 H_2 molecules in each void.



The rotational modes for ortho and para hydrogen immediately after cooling to ~15 K and after 2 days.

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Stay Awake Question

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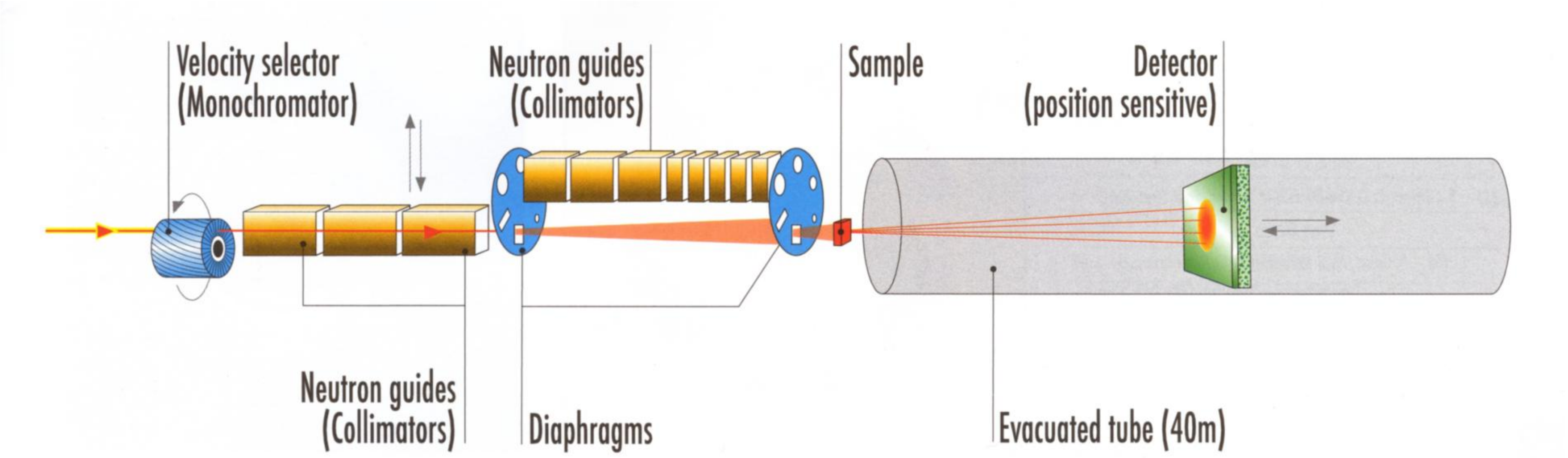
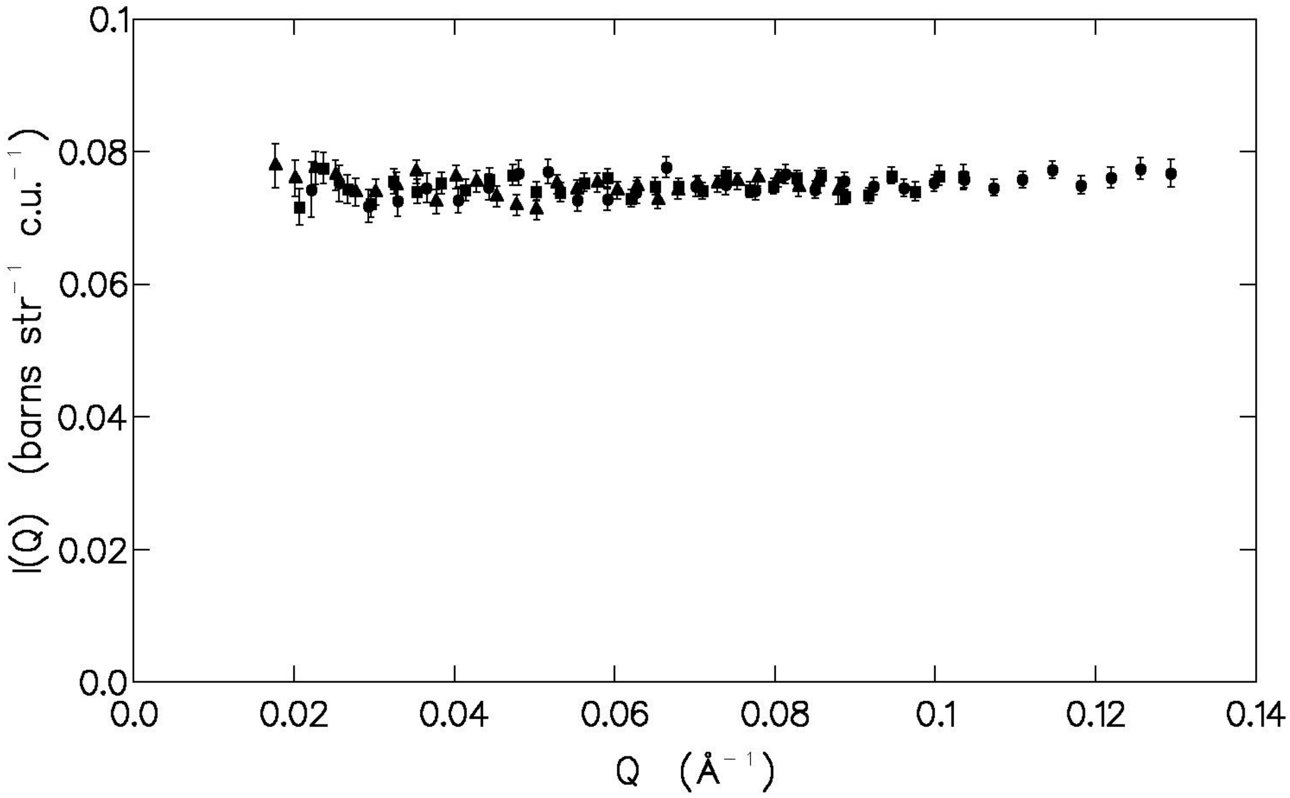
Range IV



The D11 Small Angle Neutron Scattering (SANS) instrument
at the Institut Laue-Langevin, Grenoble, France.

Long range density and composition fluctuations in glasses can be studied by Small Angle Neutron and X-ray Scattering (SAXS and SANS). Density fluctuations occur in all glasses, and even single-phase binary and multi-component glasses are chemically nanoheterogeneous. Phase separated glasses can also be studied by electron microscopy and AFM.

SANS from Vitreous Silica

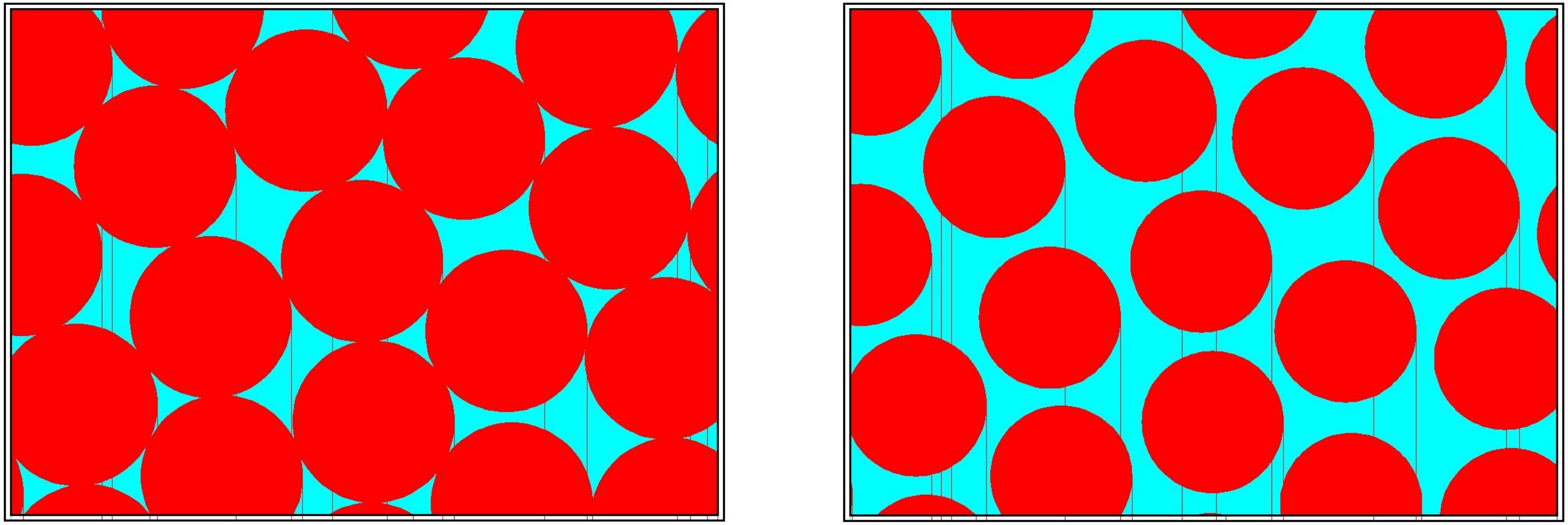


The SANS from vitreous silica is of the form

$$I(Q) = I(0) + cQ^2,$$

where c is a constant, and is characteristic of the thermodynamic fluctuations in the melt at the fictive temperature, T_f. For the melt, the zero-Q limit, $I(0)$, is related to the isothermal compressibility.

Random Network vs Crystallites



B.E. Warren rejected the crystallite theory on the basis of the absence of small angle scattering. This is incorrect in that, if the crystallites are closely packed, the small angle scattering is very much reduced, as may be seen from the simple modern-crystallite model above.

The crystallite radius is taken as 5 Å and the interconnecting material is shown in cyan.

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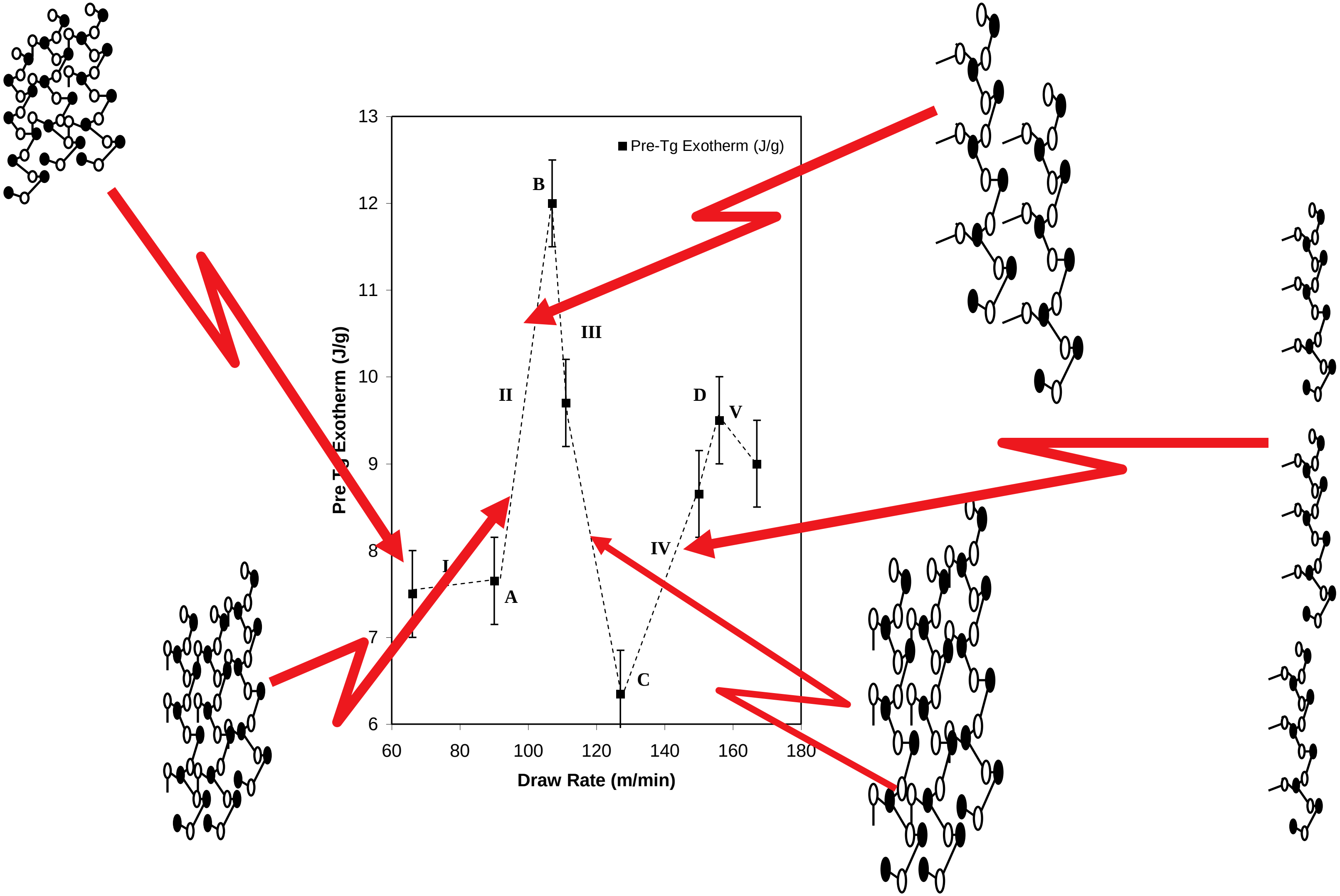
Energy Storage/Relaxation Sequence



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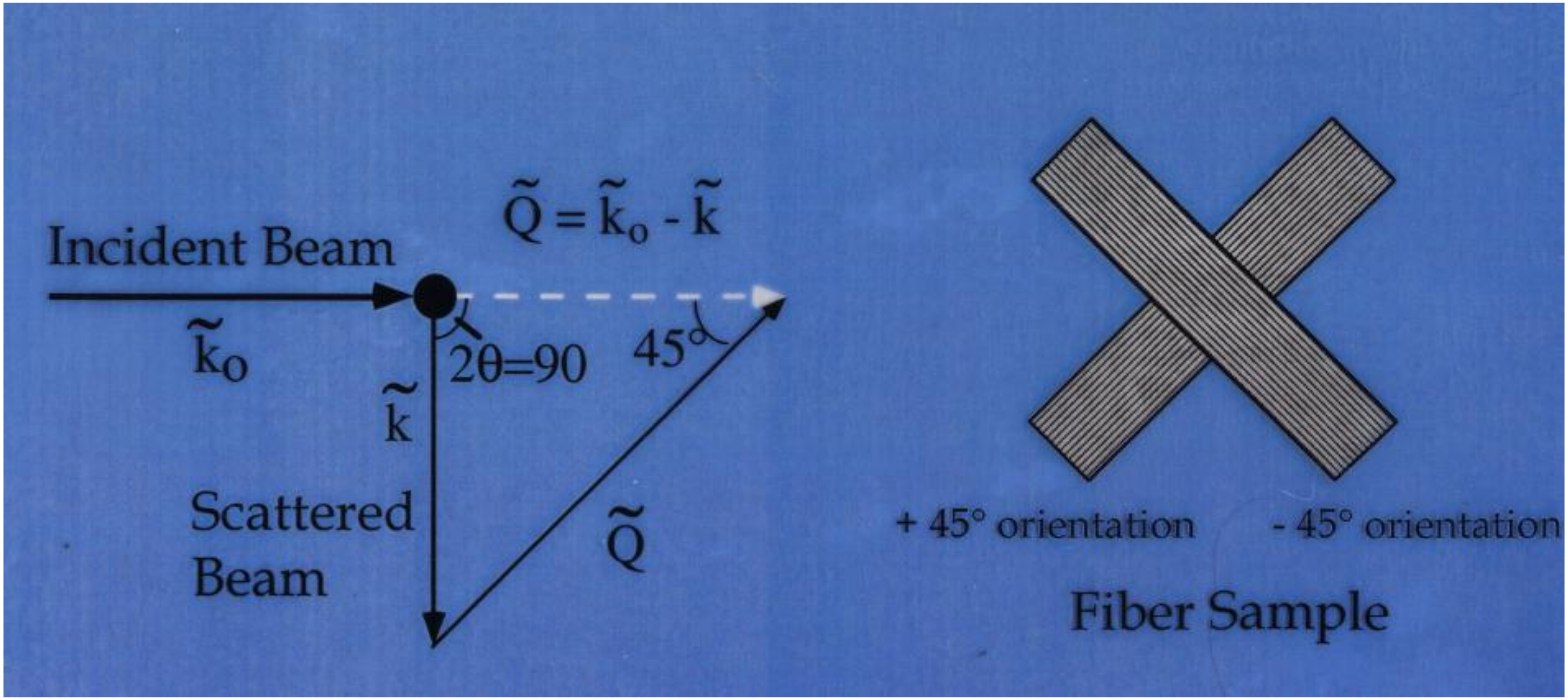
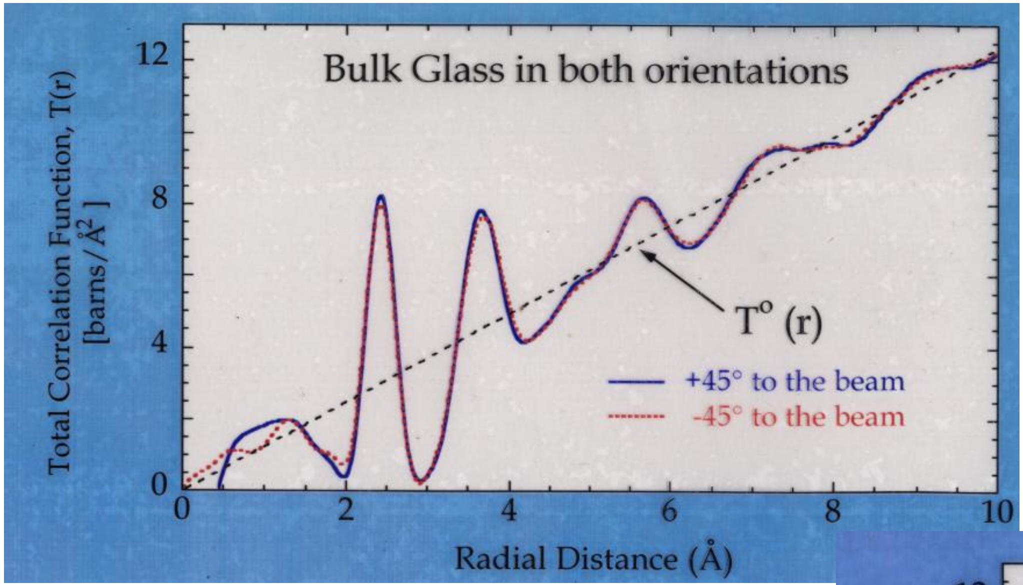
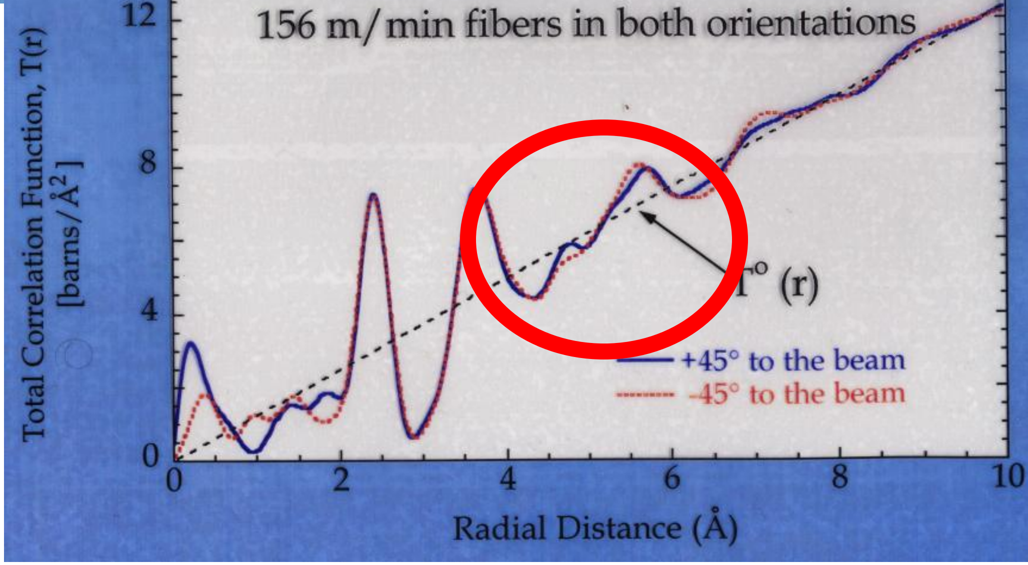
Neutron Scattering



Orientation Glasses in IV





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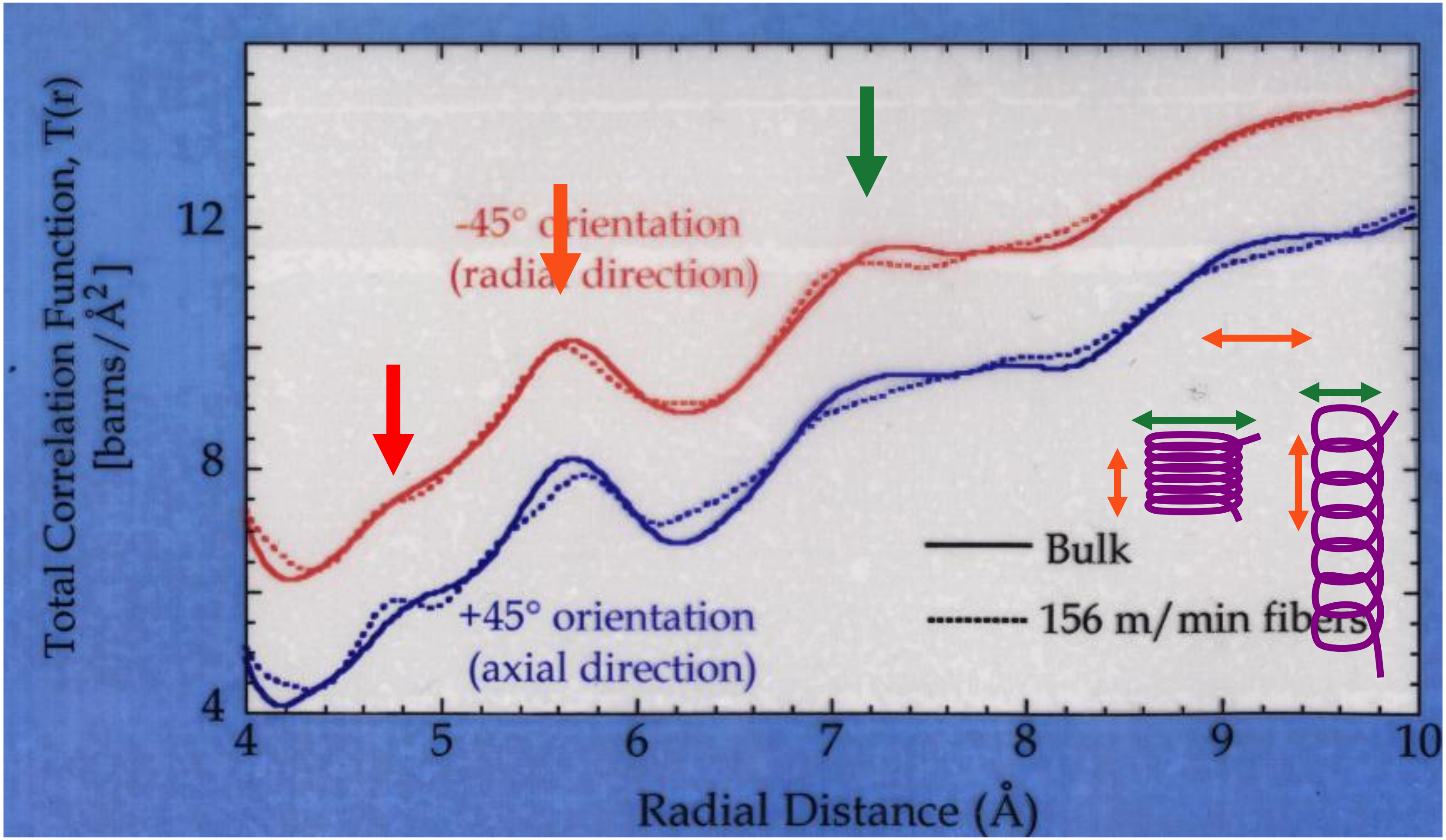
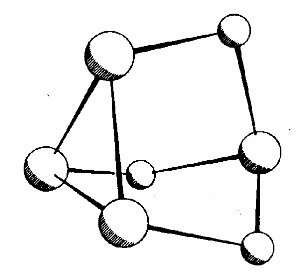
A Closer Look….



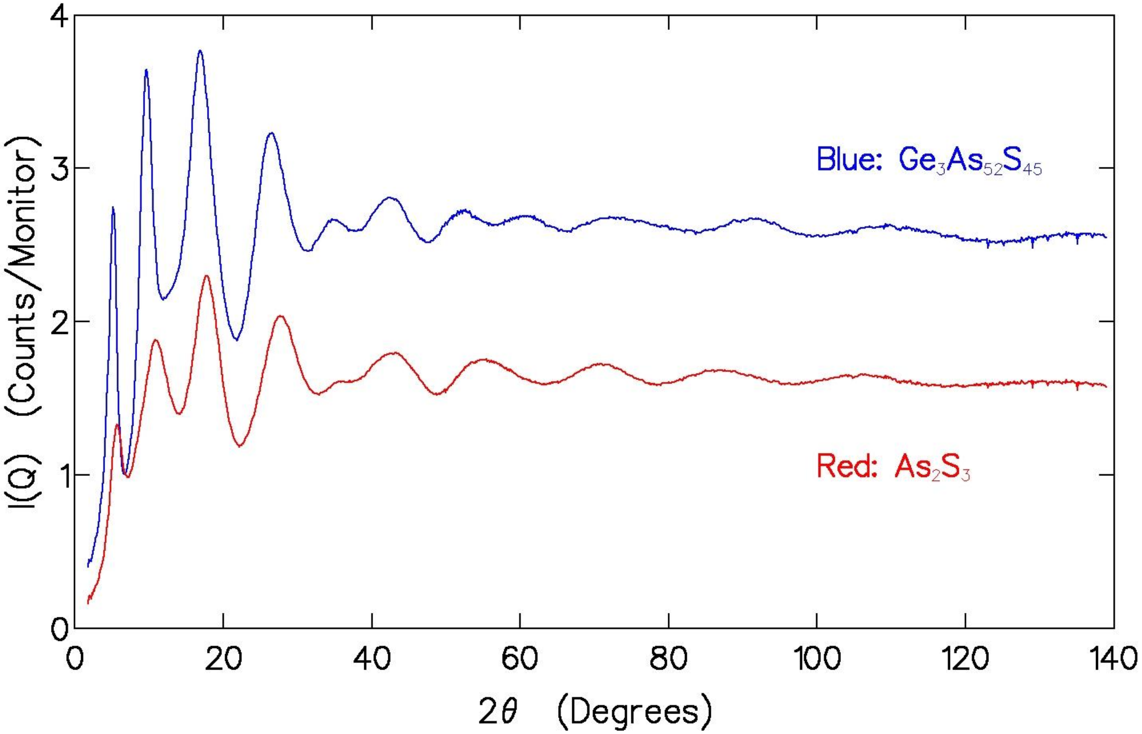
Vitreous $Ge_3As_{52}S_{45}$ – A Plastic Glass!

Chalcogenide glasses are of interest due to their infrared transmission. In the case of the Ge-As-S system, an anomalous thermal expansion coefficient at an average co-ordination number, <*n*>, of ~2.6 has been ascribed to the presence of As_4S_3 molecules.



As_4S_3

The existence of a molecular structure is demonstrated by the very intense, sharp first diffraction peak, compared to vitreous As_4S_3 which has a network structure.



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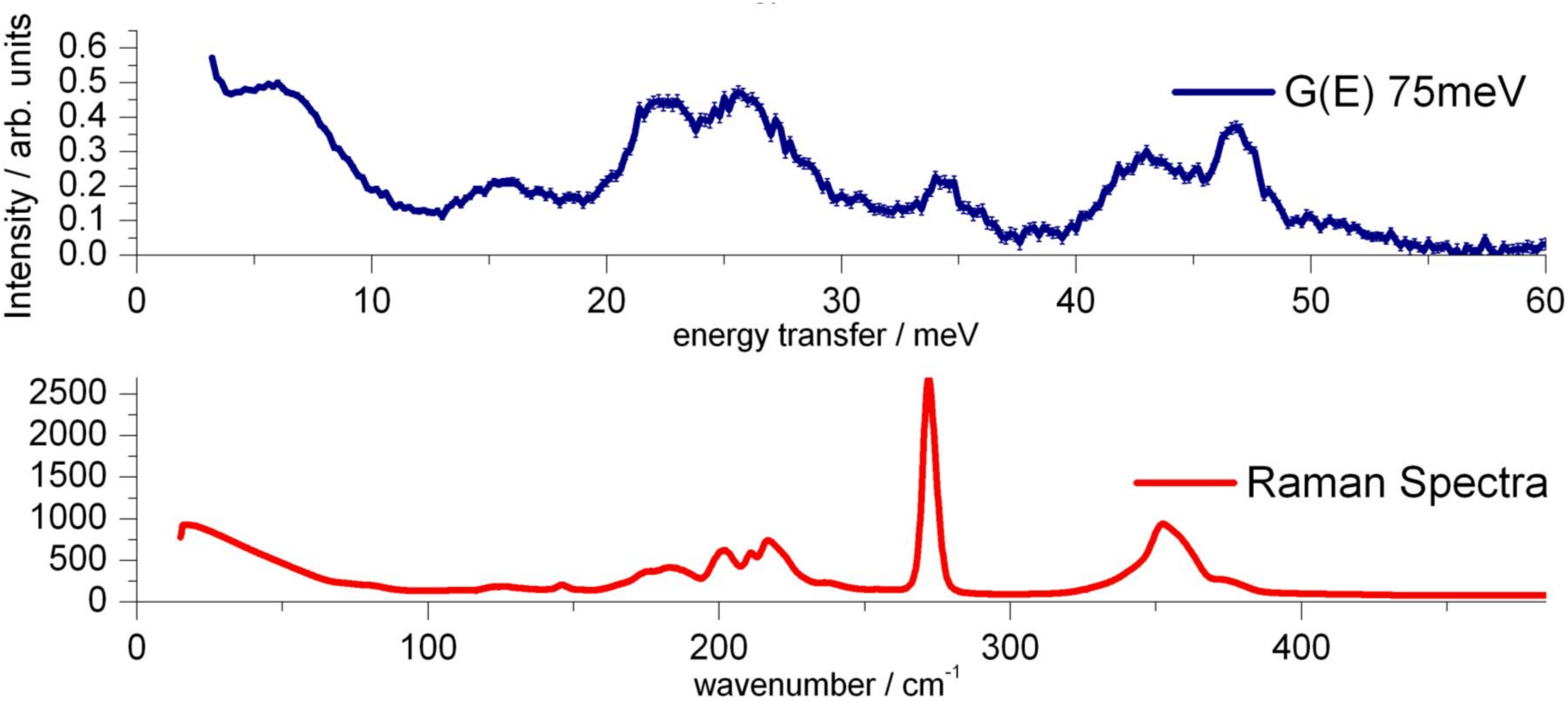
Vibrational Density of States



The presence of As_4S_3 molecules is also shown by the strong, sharp Raman line at ~270 cm^{-1} (34 meV), due to the symmetric stretching mode of the three As-atom ring. Top, neutron VDOS and bottom, Raman spectrum.

Quasi-Elastic Scattering

Vitreous $Ge_3As_{52}S_{45}$ also exhibits quasi-elastic scattering (a broadening of the elastic peak), which shows that the As_4S_3 molecules are freely rotating at ambient temperature. On cooling to 5 K, there is no indication of a sharp rotational-freezing transition, but the data yield a rotational activation energy of ~14 meV, corresponding to a temperature of ~160 K.

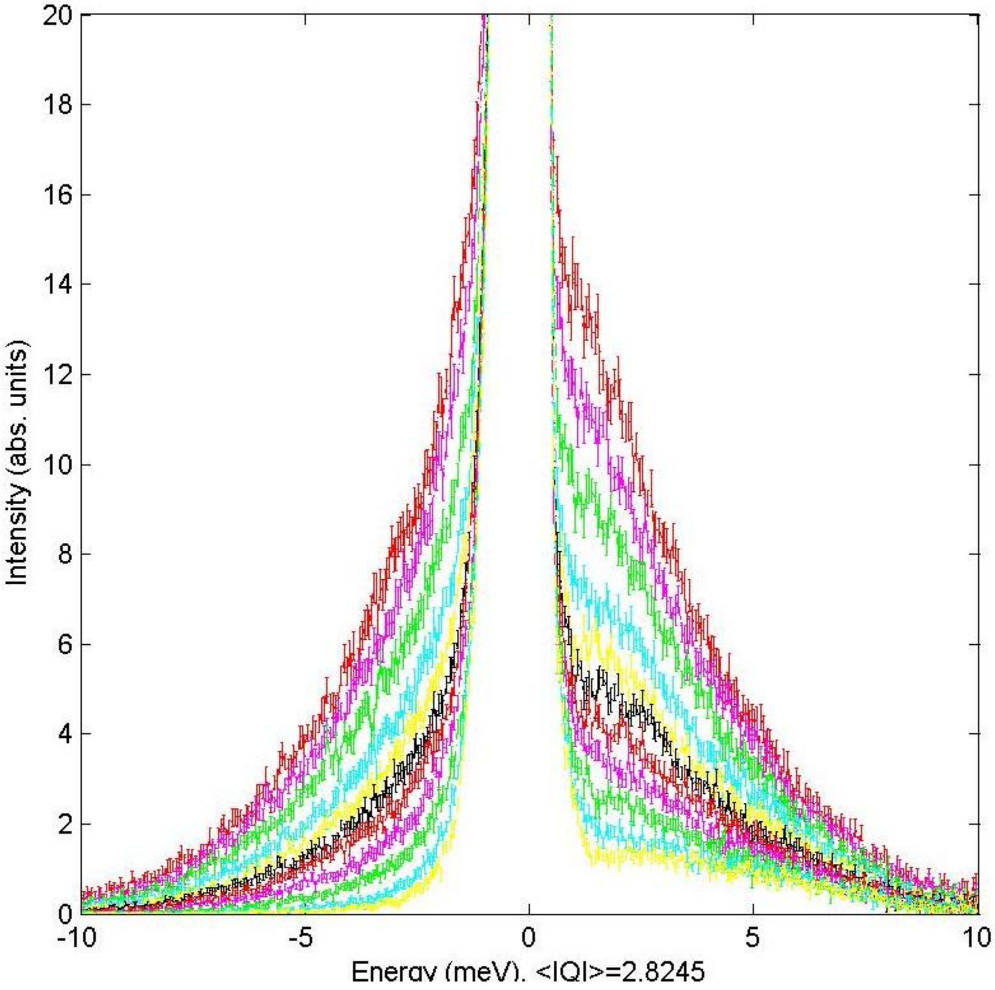


Fig. 1 Quasi-elastic scattering from $Ge_3As_{52}S_{45}$, at different temperatures: 290K (top, red), 250K, 200K, 150K, 120K, 100K, 80K, 60K, 40K, 20K & 5K (bottom, yellow).

Some of the Practicalitites of Doing X-ray and neutron experiments

- Lab X-ray amorphous diffractometers are few and far between. There are no lab neutron diffractometers.
- Synchotron or Reactor/Accelerator
- http://www.isis.rl.ac.uk/
- http://www.nsls.bnl.gov/
- http://www.sns.gov/
- http://www.anl.gov/Science_and_Technology/facilities.html
- http://www.chess.cornell.edu/
- http://www.spring8.or.jp/en/
- http://lansce.lanl.gov/

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Practicalities continued:

- Samples:
  - For x-ray about the same as powder diffraction
  - For neutron usually need several grams
  - Can be powder or solid but if solid need to be defect free
  - For neutrons can be a powder in thin-walled can (need to measure empty can background)
  - For neutrons you must limit the OH or the Placzek corrections will not work well
  - If you can’t get rid of the OH then try to deuterate (incoherent scattering length for deuterium is five times lower than for hydrogen)

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Practicalities continued:

- Getting Beam Time
  - Write a proposal (most of the websites have help for writing proposals)
  - Attend an education workshop at the user facility
  - Be patient
  - Start early

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