Neutron Scattering from Amorphous, Disordered and Nanocrystalline Materials

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Neutron scattering from disordered materials is invaluable for obtaining two types of microscopic information: the *atomic structure*, obtained from diffraction measurements, and the *atomic dynamics*, obtained from inelastic scattering measurements. A *diffraction* experiment is designed to measure the total scattering as a function of scattering vector Q:

$$Q = k_0 - k_1 \qquad (1)$$

where k_0 and k_1 are the wave vectors of the incident and scattered neutrons:
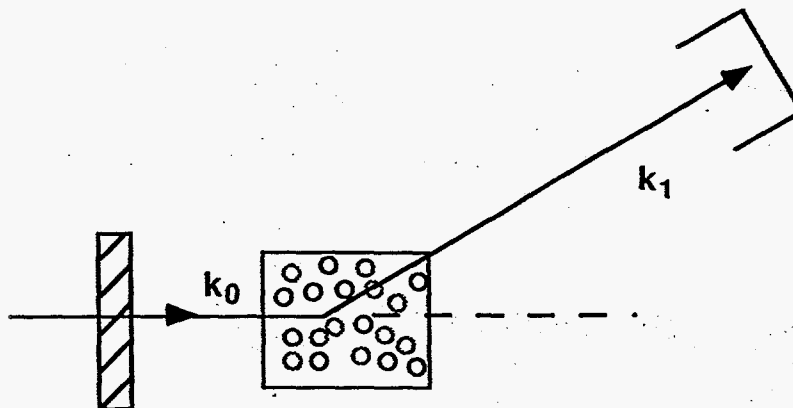
In a diffraction experiment, it is usual to fix the directions of k_0 and k_1 by means of appropriate collimators, detector placement, etc., but to fix only the magnitude of one of the two, generally k_0. Then Q is evaluated from Eq. (1) under the assumption that the scattering is elastic, i.e., there is no energy exchange between the neutron and the sample and so the incident and scattered neutrons have the same energy and thus

$$|k_0| = |k_1|. \qquad (2)$$

In practice this not quite correct since some of the scattering is inelastic, i.e., energy exchange does take place (see below). However, the experiments are usually designed to minimize this error and, if it is important, it can usually be taken care of by appropriate inelasticity (or "Placzek") corrections.

After taking into account appropriate factors such as beam intensity, number of atoms in the sample, and detector efficiency, and making corrections for absorption and multiple scattering in the sample, the scattering intensity measured in the detector is reduced to a fundamental quantity, the *differential cross section* per atom [1]:

$$\frac{d\sigma(\mathbf{Q})}{d\Omega} = \sum_{\alpha\beta} \frac{\sqrt{n_\alpha n_\beta}}{n} \bar{b}_\alpha \bar{b}_\beta S_{\alpha\beta}(\mathbf{Q})$$

(3)

where n_α is the number of atoms of type α in the sample and $S_{\alpha\beta}(\mathbf{Q})$ is the partial structure factor for the atom pair (α,β). In isotropic systems such as liquids and glasses, the structure factors only depend on the scalar variable Q. (In crystalline systems, isotropic structure factors derived from measurements on a powder can be defined by averaging all crystal orientations). The structure factors are related to the structure in real space through a Fourier transform:

$$S_{\alpha\beta}(Q) = \delta_{\alpha\beta} + \frac{4\pi}{Q}\sqrt{n_\alpha n_\beta} \int_0^\infty \left[g_{\alpha\beta}(r) - 1 \right] \sin Qr . r dr$$

(4)

where $g_{\alpha\beta}(r)$ is the partial pair distribution function in real space [2]. The latter quantity has the direct physical interpretation that

$$4\pi r^2 n_\beta g_{\alpha\beta}(r)\Delta r$$

(5)

is the average number of β atoms in a range $(r, r + \Delta r)$ from an α atom.

In a one-component system, the indices α,β obviously disappear and only a single structure factor $S(Q)$ and a single pair distribution function exist. In a system with more than one component, it is clear from Eq. (3) that a weighted average of the partial structure factors is all that can be obtained from a single measurement. This can be defined as:

$$S(Q) = \frac{1}{\langle \bar{b} \rangle^2} \sum_{\alpha\beta} \frac{\sqrt{n_\alpha n_\beta}}{n} \bar{b}_\alpha \bar{b}_\beta S_{\alpha\beta}(Q)$$

(6)

where

$$\langle \bar{b} \rangle = \sum_\alpha \frac{n_\alpha}{n} \bar{b}_\alpha ,$$

(7)

along with the corresponding neutron-weighted pair distribution function

$$g(r) = \frac{1}{\langle \bar{b} \rangle^2} \sum_{\alpha\beta} \frac{\sqrt{n_\alpha n_\beta}}{n} \bar{b}_\alpha \bar{b}_\beta g_{\alpha\beta}(r)$$

(8)

As a simple example, we show in Fig. 1 the neutron-weighted average structure factor $S(Q)$ for the archetypal glass vitreous silica (SiO_2), measured at three temperatures [3]. This type of structure factor is characteristic for an oxide or chalcogenide glass and has three pronounced peaks at small Q [4]. The first peak at $Q \sim 1.6$ Å^{-1} is the famous "sharp diffraction peak" representing the intermediate-range order in the glass [5]. The second peak at $Q \sim 3$ Å^{-1} represents the chemical short-range order, in this case the alternation of Si and O atoms; this peak is seen when two or more chemically ordered elements have different scattering lengths, as in the case with SiO_2, and is a dominant feature in the scattering from molten salts and liquid alloys which exhibit chemical ordering. The third peak at $Q \sim 5$ Å^{-1} and the strcutre at higher Q represents the topological short-range order resulting from the need for the atoms to keep a certain distance apart as a result of short-range repulsive forces, a feature of all condensed systems.

In real space, the topological short-range order shows up in the low-r part of the pair correlation function $T(r) = 4\pi\rho r g(r)$ (where ρ is the mean number density), which is plotted in Fig. 2 (again as the neutron-weighted average) for the same three temperatures. The pair correlation function is dominated by two strong peaks representing Si-O and O-O correlations, respectively. The intensity and good definition of these peaks reflects the uniformity and rigidity of the SiO_4 building blocks which make up the network of the glass. The third small peak corresponds to Si-Si correlations; it is smaller because the scattering length of Si is smaller than that of O, and less well defined since there is a greater variation in the bonding angles between adjacent SiO_4 tetrahedra at a common O vertex than in the structure of the tetrahedra themselves. The structure at larger r reflects the details of the intermediate-range structure discussed above.

The dynamics of a system can be measured in an *inelastic neutron scattering* experiment. In this case, the energy transfer given by

$$E = \frac{\hbar^2 k_0^2}{2m} - \frac{\hbar^2 k_1^2}{2m}$$

(9)

is measured in addition to the scattering vector defined in Eq. (1). To accomplish this, both the magnitude and direction of both k_0 and k_1 must be defined in the design of the scattering apparatus. Schematically, this can be represented as:
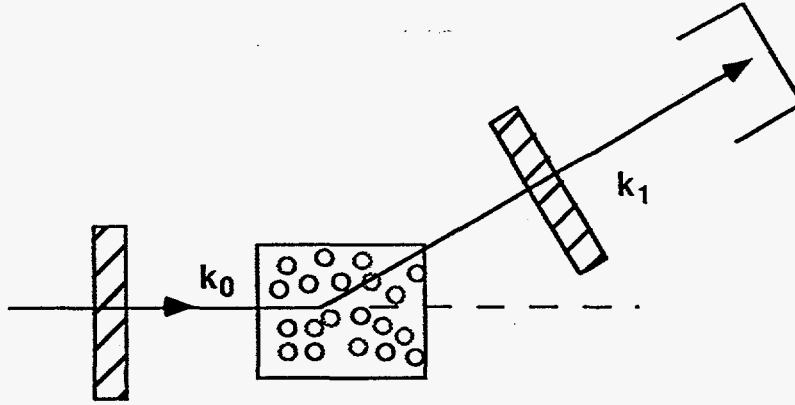
The intensity of this scattering process is reduced to a *double differential cross section*:

$$\frac{d^2\sigma(\mathbf{Q},E)}{d\Omega dE} = \frac{k_1}{k_0}\sum_{\alpha\beta}\frac{\sqrt{n_\alpha n_\beta}}{n}\bar{b}_\alpha\bar{b}_\beta S_{\alpha\beta}(\mathbf{Q},E) \tag{10}$$

where the $S_{\alpha\beta}(\mathbf{Q},E)$ are partial scattering functions (sometimes called *dynamical structure factors*) defined by:

$$S_{\alpha\beta}(\mathbf{Q},E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} I_{\alpha\beta}(\mathbf{Q},t)\exp(-iEt/\hbar)dt \tag{11}$$

where

$$I_{\alpha\beta}(\mathbf{Q},t) = \left\langle \rho_\alpha^*(\mathbf{Q},0)\rho_\beta(\mathbf{Q},t)\right\rangle \tag{12}$$

represents the correlation in space and time between two density fluctuations of the form

$$\rho_\alpha(\mathbf{Q},t) = \frac{1}{\sqrt{n_\alpha}}\sum_{i\in\alpha}\exp(i\mathbf{Q}\bullet\mathbf{R}_i(t)). \tag{13}$$

Through the sum rule

$$\int_{-\infty}^{\infty} S_{\alpha\beta}(\mathbf{Q},E)\,dE = I_{\alpha\beta}(\mathbf{Q},t=0) = S_{\alpha\beta}(\mathbf{Q}) \tag{14}$$

the scattering functions measured in an inelastic scattering experiment can be related to the structure factors measured in a diffraction measurement of the kind described above. In an isotropic system such as a liquid or a glass, the vector quantity $\mathbf{Q}$ is again replaced by its scalar magnitude Q.

In a multi-component system, as in the diffraction case, several measurements, for example with separated isotopes, are needed to define the full set of partial scattering functions. In a single measurement, a neutron-weighted average scattering function

$$S(Q,E) = \frac{1}{\langle \overline{b} \rangle^2} \sum_{\alpha\beta} \frac{\sqrt{n_\alpha n_\beta}}{n} \overline{b}_\alpha \overline{b}_\beta S_{\alpha\beta}(Q,E)$$

(15)

is obtained. However, in many cases of practical interest, this may already contain much useful information.

In the case of a solid sample, it is often convenient to decompose the scattering function into components representing different physical processes, for example, elastic scattering (in which there is no appreciable energy transfer between neutron and sample), one-phonon scattering (in which one quantum of vibrational energy is transferred), and multiphonon processes:

$$S(\mathbf{Q},E) = S_{el}(\mathbf{Q})\delta(E) + S_1(\mathbf{Q},E) + S_m(\mathbf{Q},E)$$

(16)

The one-phonon scattering function $S_1(\mathbf{Q},E)$ contains a wealth of detail about the vibrational dynamics, and is the basis of the well-known method for determining the phonon dispersion relation $E_\lambda(\mathbf{Q})$ in a crystalline material with triple-axis spectrometry [6]. What is not so well known is the fact that, in a system without long range-order like a glass or amorphous solid where $\mathbf{Q}$ is no longer a good quantum number, $S_1(\mathbf{Q},E)$ nevertheless contains considerable information about the normal modes of vibration, in particular the correlated motions of nearby atoms:

$$S_{1,\alpha\beta}(\mathbf{Q},E) = \frac{1}{2n} \sum_{i\in\alpha, j\in\beta} \exp-\left[W_i(\mathbf{Q}) + W_j(\mathbf{Q})\right] \times$$

$$\times \sum_{\lambda} \frac{\hbar(\mathbf{Q}\cdot\mathbf{e}_i^\lambda)^*(\mathbf{Q}\cdot\mathbf{e}_j^\lambda)}{(M_i M_j)^{1/2} \omega_\lambda}(n_\lambda + 1)\exp\left[i\mathbf{Q}\cdot(\mathbf{R}_i - \mathbf{R}_j)\right]\delta(E - \hbar\omega_\lambda)$$

(17)

where

$$W_i(\mathbf{Q}) = 1/2\left\langle\left[\mathbf{Q}\cdot\mathbf{u}_i\right]^2\right\rangle \tag{18}$$

is the Debye-Waller exponent representing the decrease in scattering intensity due to vibrations, $\mathbf{u}_i$ being the vibrational amplitude of atom i at mean position $\mathbf{R}_i$, and n_λ, e_i^λ, and ω_λ are the Bose-Einstein thermal population factor, polarization vectors and frequency of the mode λ.

In an average sense, the dynamics is sometimes described in terms of a *generalized density of vibrational states G(Q,E)* defined as

$$S(Q,E) = \left(\frac{\hbar Q^2}{2\overline{M}}\right)\exp\left(-2\overline{W(Q)}\right)\frac{\langle n(E)+1\rangle}{E}G(Q,E) \tag{19}$$

where $\overline{M}$ is an average mass of atoms in the sample and $\overline{W(Q)}$ is an average Debye-Waller exponent. $G(Q,E)$ defined in this way reverts to the true density of states $G(E)$ in a system where all the scattering is incoherent. Fig. 3 shows the form of $G(E)$, corresponding to $G(Q,E)$ averaged over the full Q range of the measurement, for vitreous silica [7]. This is seen to have several peaks which can be identified with the normal modes of vibration of the local SiO_4 structural units. In this respect the average generalized density of states measured with inelastic neutron scattering gives information comparable to that which can be obtained from Raman spectroscopy.

The full power of the neutron method comes when the Q dependence of the scattering corresponding to a particular feature in $G(E)$ is examined. As stated above, this provides detailed information about the correlated motions of nearby vibrating atoms. Fig. 4 shows $S(Q,E)$ as a function of Q for several different values of E corresponding to peaks in the $G(E)$ shown in Fig. 3. The solid lines through the data show model fits based on the identification of these peaks with specific vibrational modes and validates the mode assignments of the model. The correlated motions involved in the mode at $E = 133$ meV are shown in Fig. 5.

We have described the power of neutron diffraction and inelastic scattering techniques for determining the structure and dynamics of disordered systems, using the archetypal glass SiO_2 as a detailed example. Of course the field of amorphous and disordered systems contains a much greater variety of types of materials exhibiting a wide range of possible types of disorder. In the context of a short review, it is only possible to list some of these and give references which the interested reader can pursue in greater depth:

1. *Glasses* (like the SiO_2 described above), where the atoms vibrate about static equilibrium positions which have no long-range order [8].

2. *Liquids,* where there are no such equilibrium positions and the atoms are in complete state of motion on the time scale of neutron scattering (~ 1 ps) [9]; two important classes of liquid for which the structures have recently been reviewed are *liquid alloys* [10] and *molten salts* [11].

3. Solid phases which are *liquid-like in one or two dimensions*, following a ferroelastic phase transition [12].

4. *Liquid crystals*, which are dynamically disordered but retain a high degree of translational and/or orientational order [13].

5. *Quasicrystalline materials*, which have a static long-range orientational order but no long-range translational order [14].

6 *Rotor phases* (some of which are called *plastic crystals*) which have a long-range translational order but dynamic orientational disorder [15]; at low temperatures the orientational order may become frozen in, leading to what is called an *orientational glass*.

7. *Fast-ion phases* (some of which are called *solid electrolytes*) in which one component is rapidly moving or liquid-like, while the others remain static; the static components can be either crystalline or glassy [16].

8. *Disordered alloys* in which all atoms lie in sites with crystalline order but with chemical disorder between different types of atom [17].

9. More generally, various kinds of *disordered crystalline materials* where the positions or occupancies of specific atoms or sites do not fall on a regular crystalline lattice [18]; in a literal sense of course, all real crystalline materials fall into this category.

10. *Nanocrystalline materials*, where the size of crystalline grains is within one or two orders of magnitude of the length scale of neutron diffraction (~ 0.1 nm) so that the structure appears partially disordered [19].

Fig. 6 shows a schematic plot of these various types of materials in two dimensions corresponding to translational order (positions of particular atoms) and orientational order (orientations of particular groups of atoms).

Many other types of parameter describing disorder of course exist and should be taken into account in a really comprehensive treatment, for example the arrangement of blocks in copolymers, atomic configurations in complex molecules, etc. It is hoped that, nevertheless, this brief review gives the reader a flavor of the richness of the varieties of order and disorder exhibited by condensed matter and of the power of neutron scattering techniques to unravel some of their mysteries.

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Figure Captions

1. Structure factor of vitreous SiO_2 measured at three temperatures (ref. 3).

2. Pair correlation function of vitreous SiO_2 measured at three temperatures (ref. 3).

3. Average generalized density of vibrational states for vitreous SiO_2 (ref. 7).

4. Wave-vector dependence of the dynamic structure factor of vitreous SiO_2 for three different energies (ref. 7).

5. Correlated motions derived from fitting to the peak at $E = 133$ meV for vitreous SiO_2 (ref. 7).

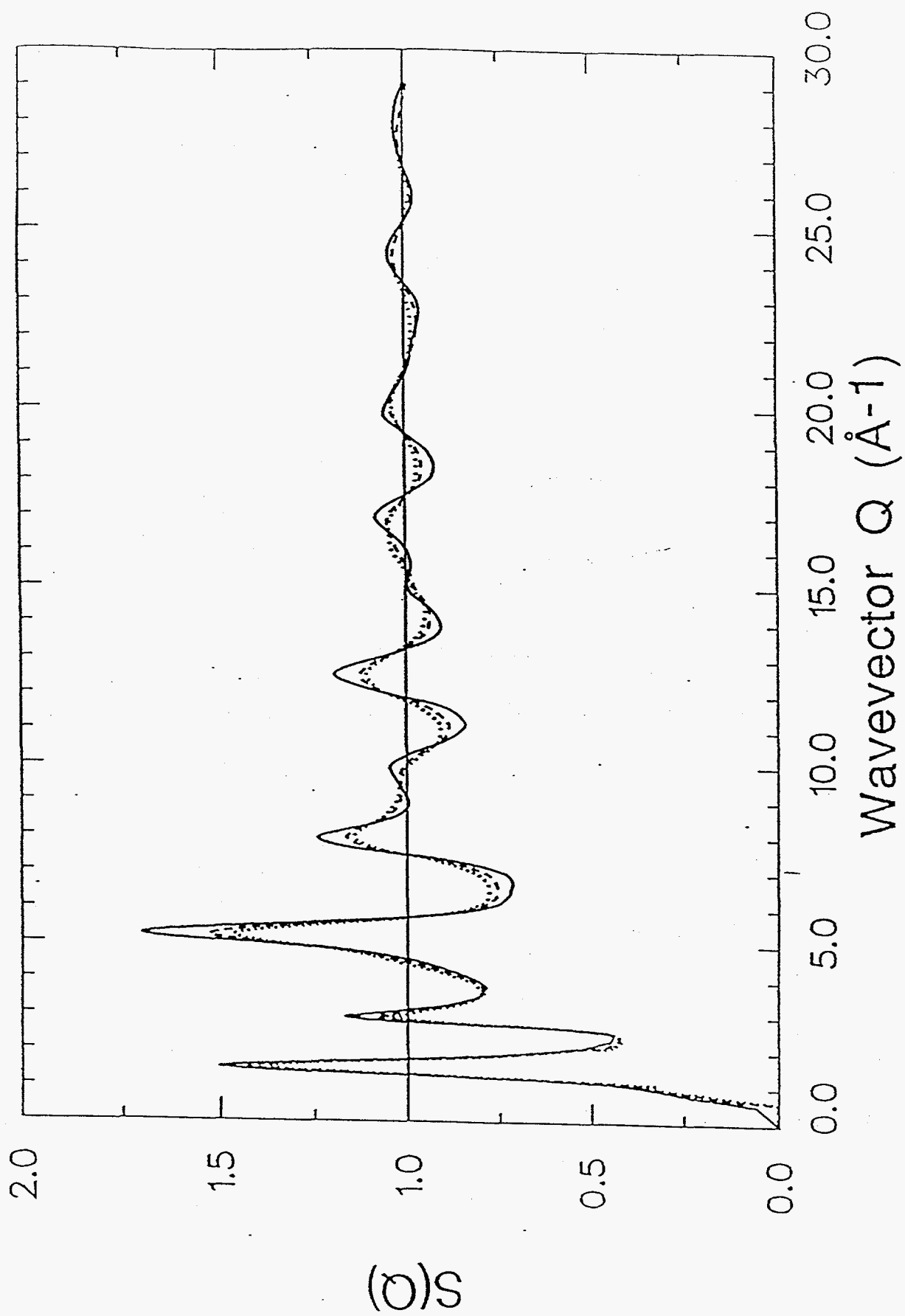6. Schematic plot of types of order and disorder in condensed matter.
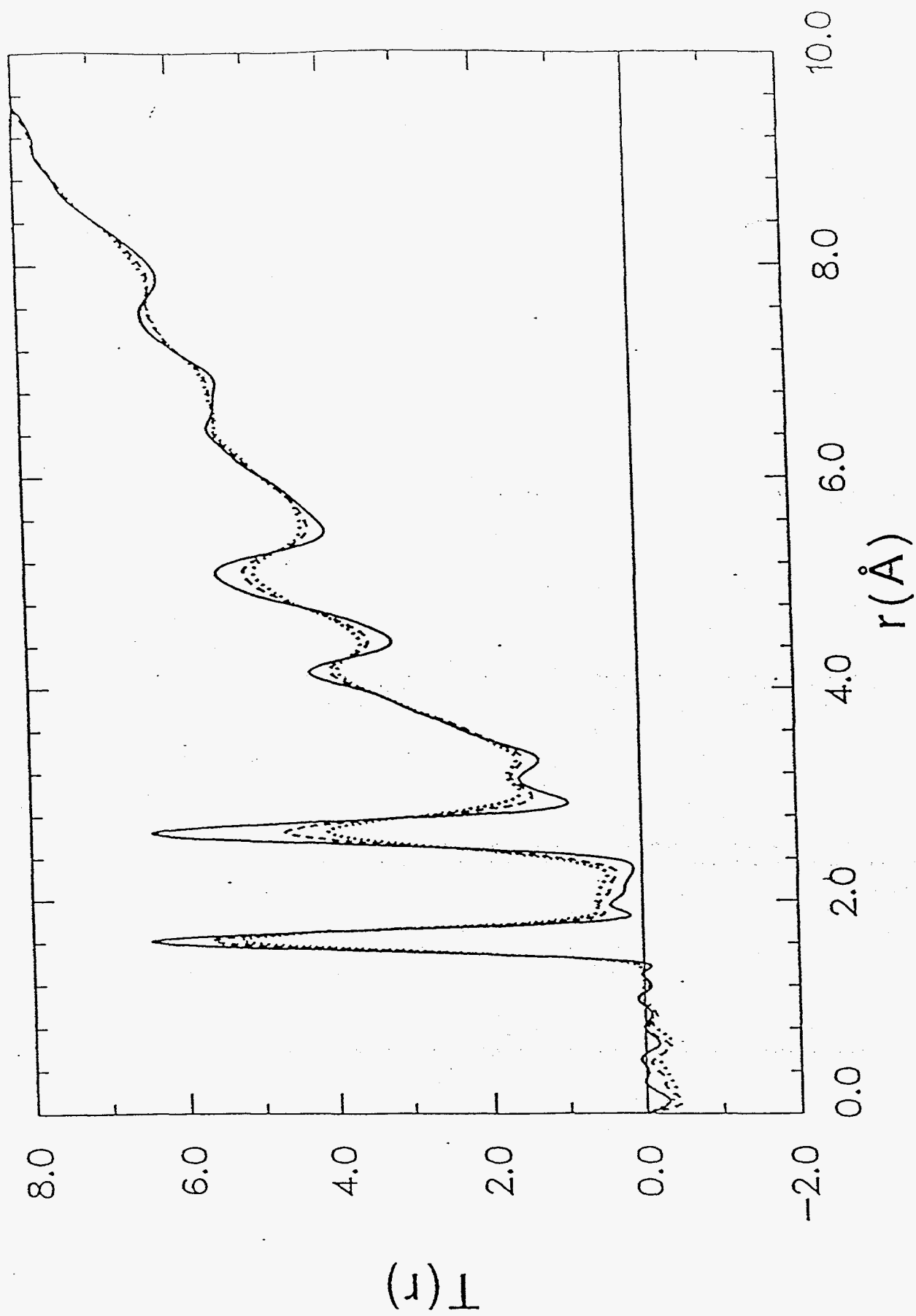
Fig. 1, Susman, Phys. Rev. B.

Fig. 2, Susman, Phys. Rev. B
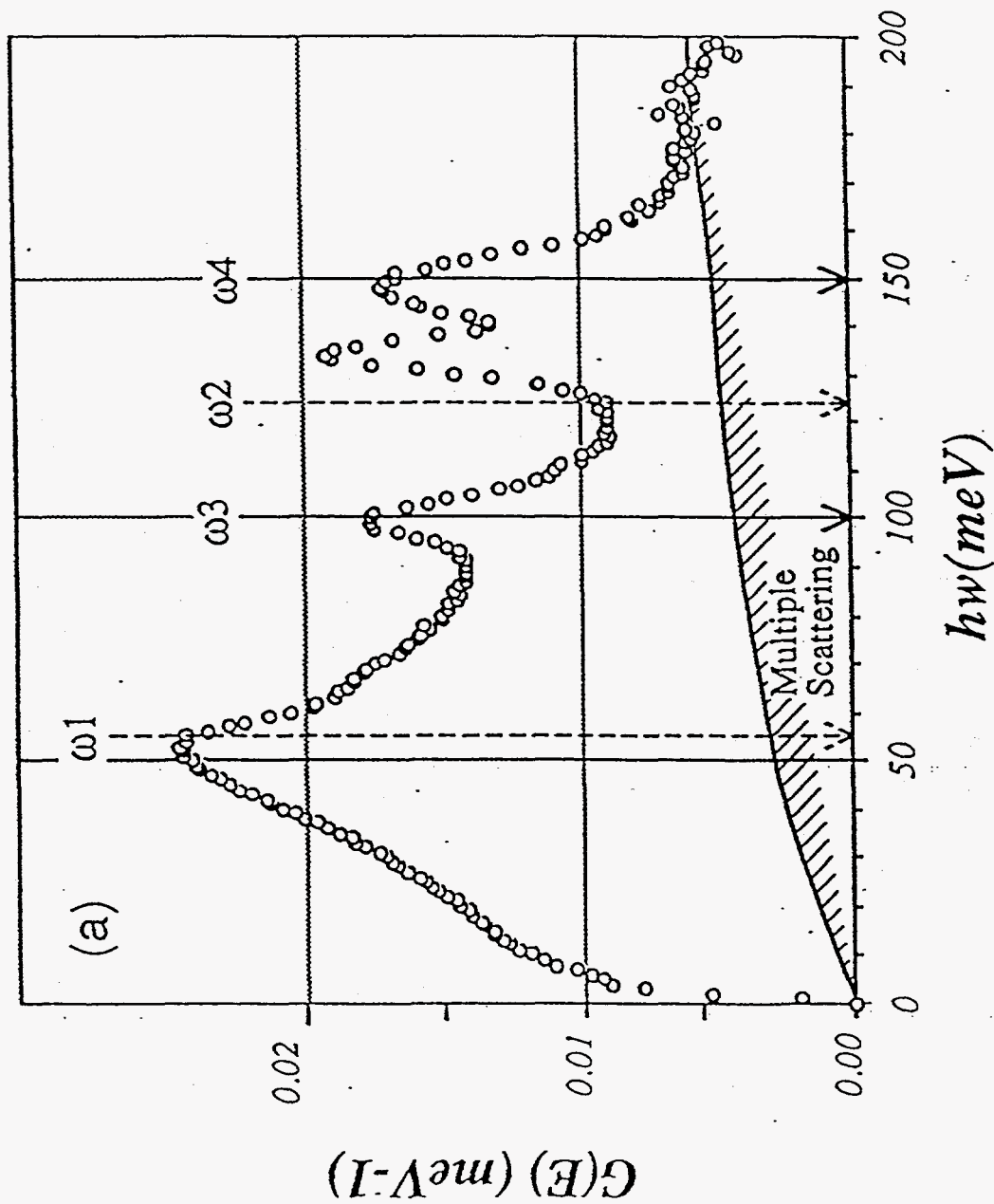
Vibrational Density of States of SiO2

(a)

$\omega 1$ $\omega 3$ $\omega 2$ $\omega 4$

Multiple Scattering

$G(E)$ (meV-1)

0.02 0.01 0.00

0 50 100 150 200

$hw(meV)$

Fig. 3

(b)

S(Q,E=50meV) (45~55meV)

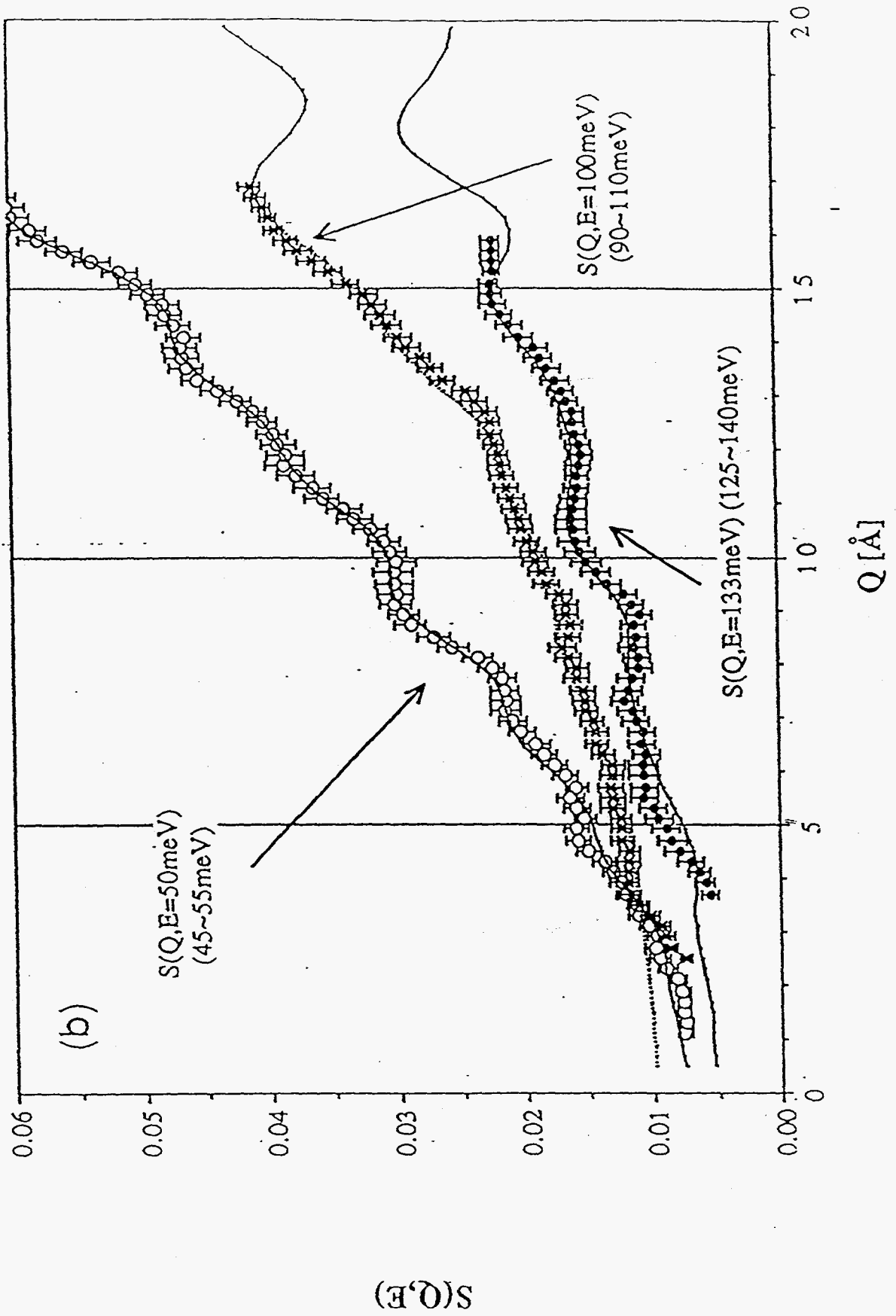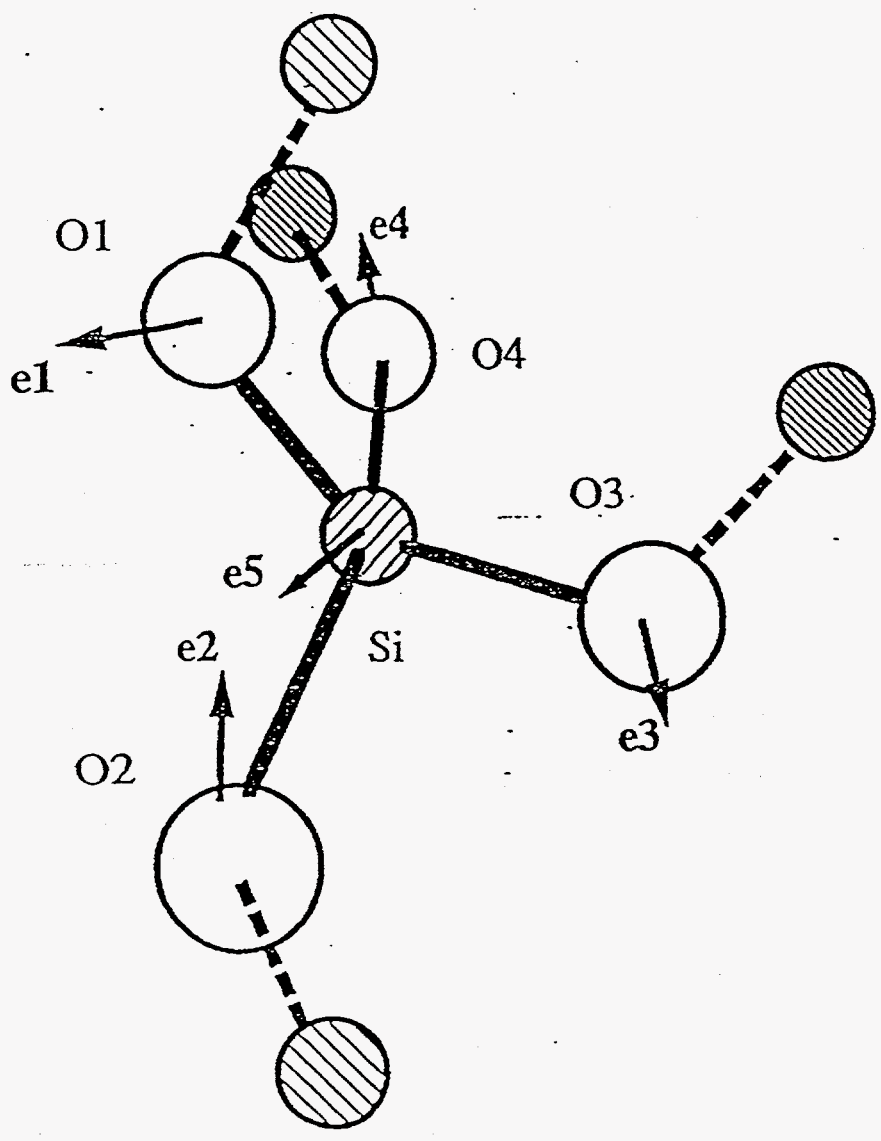S(Q,E=100meV) (90~110meV)

S(Q,E=133meV) (125~140meV)

Q [Å]

S(Q,E)

Fig. 1

Fig. 5

TYPES OF ORDER AND DISORDER

Fig. 6

Plastic crystals

Dense gases

Liquids

Orientational glasses

Glasses

Fast-ion conductors

Liquid crystals

Defects

Oriented block copolymers

Perfect crystals

Quasicrystals

SRO

LRO

LRO ⟷ SRO

Orientational disorder →

Translational disorder →