STRUCTURE AND DYNAMICS OF DISORDERED SYSTEMS

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Introduction

Neutron scattering has proved to be a powerful tool in the study of glasses and liquids: structures are investigated by <u>neutron diffraction</u>, and dynamics by <u>inelastic neutron scattering</u>. Evidence of current interest in this field is provided by the new instruments for diffraction from amorphous systems being constructed at IPNS[1], ISIS[2] and the R2-reactor at Studsvik[3], in addition to existing instruments such as the D4B diffractometer at ILL[4].

Structure

This is the simpler case and we discuss it first. A typical diffraction measurement is shown schematically in Fig.1. We describe an incident neutron by $\underline{k}_0$, a vector in the direction of the beam with magnitude $2\pi/\lambda_0$ where λ_0 is the mean wavelength, and a scattered neutron by a wave vector $\underline{k}_1$. A typical scattering event is described by the scattering vector

$$\underline{Q} = \underline{k}_0 - \underline{k}_1. \tag{1}$$

The count rate in the detector is given by the differential cross section $d\sigma/d\Omega$ multiplied by some trivial experimental factors. For neutron diffraction, $d\sigma/d\Omega$ is very simply related to the <u>static structure factor</u> $S(Q)$ which is a fundamental property of the sample, independent of the details of the scattering experiment:

$$\frac{d\sigma}{d\Omega} = \overline{b}^2 \, S(Q) + (\overline{b^2} - \overline{b}^2), \tag{2}$$

where $\overline{b}$ and $\overline{b^2}$ are the mean and mean square scattering amplitudes of the nuclei comprising the sample. We generally assume that the scattering is mainly elastic, $k_1 \sim k_0$, and so only one quantity, k_0 or k_1 or some combination of the two, needs to be measured. In practice this is only an

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and "Placzek corrections" have to be applied to take care of this fact[5], especially when light atoms are involved.

S(Q) can be written simply in terms of the particle density operators in reciprocal space

$$\rho(Q,t) = \sum_i e^{i\,\underline{Q}\cdot\underline{R}_i\,(t)}$$

(3)

where $\underline{R}_i(t)$ is the position of particle i at time t:

$$S(Q) = \frac{1}{N} < \rho(-Q,0)\rho(Q,0) >$$

(4)

where < > represents a thermal average,

$$= \frac{1}{N} \sum_{i,j} e^{i\,\underline{Q}\,.(\underline{R}_j\,(0)\,-\,\underline{R}_i\,(0))} .$$

(5)

Thus, S(Q) represents the instantaneous correlations in particle density, averaged over the system.

A convenient starting point for considering the structure of disordered systems is the concept of dense random packing of hard spheres (DRPHS)[6]. The structure factor describing the arrangement of spheres of diameter σ is uniquely determined by the packing fraction

$$\eta = \left(\frac{\sigma}{d_s}\right)^3$$

(6)

where $\rho_0^{-1} = (\pi/6)d_s^3$ is the volume per particle. Dense random packing corresponds to the maximum value η=0.637, or d_s = 1.162 σ. S(Q) can be evaluated by numerical methods, or analytical approximations such as the Percus-Yevick method, for such a system, and turns out to be an excellent approximation for most simple liquids, including rare gases and metals, as well as many metallic glasses. As an example, Fig. 2 compares the S(Q) measured for liquid Rb with the DRPHS model[7]: σ=4.3 Å was chosen to give the best fit, while η corresponds to the measured value of the number density ρ_0 through Eq. (6). The main peak is seen to be at Q σ = 6.5, a typical value for a hard sphere close to the dense random packing limit.

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Most glasses have two or more components, which introduces a complication in that an n-component system is described by $n(n+1)/2$ partial structure factors S_{ab} given by

$$S_{ab}(Q) = \frac{1}{\sqrt{N_a N_b}} < \rho_a(-Q,0)\rho_b(Q,0) > .$$

$$(7)$$

The measured differential cross section is then an average of the S_{ab} weighted by the appropriate products of scattering lengths. In many cases, it turns out that the DRPHS model is still a good description if the hard sphere diameters are chosen appropriately for the two components. In some cases, however, an additional peak in the structure is observed at smaller Q, especially when there is an appreciable difference in the scattering lengths of the two components. Fig. 3 shows an example of this case for glassy TiZr (ref. 8), where there is a peak in the structure factor $S_{CC}(Q)/c_1 c_2$ ($=c_2 S_{11} + c_1 S_{22} - 2(c_1 c_2)^{1/2} S_{12}$) at $Q=2.0$ Å in contrast with the main peak in the structure factor $S_{NN}(Q)$ ($=c_1 S_{11} + c_2 S_{22} + 2(c_1 c_2)^{1/2} S_{12}$) at $Q=3.0$ Å which represents the DRPHS peak. The peak at lower Q represents the effects of chemical short-range order (CSRO) and has a similar origin to the first peak observed in liquid alkali halides, for example, when the two scattering lengths are appreciably different. Typically, the pre-peak is observed at Q values given by $Q r_1 \sim 5$, where r_1 is the nearest neighbour distance ($\sim \sigma$ for the DRPHS model).

In many glasses and liquids we observe a peak at still smaller Q. An example is given in Fig. 4 where the structure factors for both glassy and liquid $GeSe_2$[9] reveal a peak at $Q \sim 1$ Å^{-1}, or $Q r_1 \sim 2.5$. This "first sharp diffraction peak" (FSDP) is observed in many glasses and complex liquids, usually at very similar values of $Q r_1$.[10] It is characterized by anomalous behavior in several properties, compared with the remainder of the structure factor, including dependence on temperature, pressure, components and thermal treatment[11]. Fig. 5 shows the Q values for significant peaks in the structure factors of several glasses and liquids scaled with respect to r_1 and d_s. The figure shows the grouping into the three classes of peaks discussed above, namely DRPHS, CSRO and FSDP.[10]

The physical origin of the FSDP raises interesting questions. In molecular glasses and liquids, it can be understood in terms of the random packing of

molecules or other structural units, for which the structure factor is given by[12]

$$S(Q) = f_1(Q) + f_2(Q) [S_c(Q) - 1]$$
(8)

where $S_c(Q)$ is the DRPHS solution for spheres circumscribing the structural units and f_1, f_2 are form factors for the units themselves. Usually $S_c(Q)$ is rising sharply and the $f(Q)$'s falling sharply where the two functions cross, giving rise to a sharp peak in $S(Q)$ that is very sensitive to small changes in structure. For network glasses, such as $GeSe_2$ and SiO_2, the interpretation is not so clear. It is possible that the same picture holds with regard to inter-mediate-range structural entities such as large rings in the network. Support for this view comes from Molecular Dynamics (MD) computer simulation[13] of $GeSe_2$, where it is found that Ge-Ge correlations in the range of 10 Å are primarily responsible for the peak. The MD results also explain the anomalous temperature dependence, namely that the decrease in available volume in cooling frustrates the formation of intermediate-range order and leads to a decrease in the peak height.

Dynamics

We now investigate whether dynamic properties, measured for example by inelastic neutron scattering, can shed light on the problem of intermediate-range order and other aspects of glass and liquid structure. In inelastic scattering measurements we no longer assume that $k_1 \sim k_0$ but measure directly the energy transfer

$$E = \frac{h^2 k_0^2}{2m} - \frac{h^2 k_1^2}{2m} .$$
(9)

In this case the count rate is measured as a function of two variables, Q and E, and is given by the double differential cross section

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_1}{k_0} \left[\overline{b}^2 S_c(Q,E) + \left(\overline{b^2} - \overline{b}^2 \right) S_i(Q,E) \right] ,$$
(10)

where $S_c(Q,E)$ and $S_i(Q,E)$ are the coherent and incoherent scattering functions. Here we are interested in the coherent function, which tells us about the time development of the correlations in particle density:

$$S_c (Q,E) = \frac{1}{2\pi hN} \int < \rho(-Q,0) \; \rho(Q,t) > e^{-i \, E \, t/h} \, dt \; . \tag{11}$$

For solids, whether crystalline or amorphous, S(Q,E) is dominated by elastic scattering in which the neutron recoils from the sample as a whole, without measurable loss of energy. For a harmonic solid, this is given by

$$S_{c,el} (Q,E) = S_{el}(Q) \; \delta(E) \tag{12}$$

where the elastic structure factor is

$$S_{el} (Q) = \frac{1}{N} \sum_{i,j} e^{-(W_i + W_j)} \; e^{i \, Q \cdot (j - i)} \tag{13}$$

and i, j represent the equilibrium positions of particles i and j. The first factor after the summation sign in Eq. (13) is the Debye-Waller factor, a slowly varying function of Q, expressing the effects of thermal displacements about the equilibrium positions. We see that the total and elastic structure factor, Eqs. (5) and (13), are similar in form but mean different things. Sometimes this difference can be exploited[14].

In Fig. 6 we show an example of $S_c(Q,E)$, measured for a-GeSe$_2$[14]. The scattering is clearly dominated by the elastic scattering, which has a somewhat similar profile to the S(Q) shown in Fig. 4.

The inelastic scattering for an amorphous system described by a continuous and in general slowly varying function of Q and E. For most solids it is dominated by the one-phonon scattering

$$S_{c,\pm 1} (Q,E) = \sum_{\lambda} S_{c,\lambda} (Q) \; \delta(E \pm h\omega_\lambda) \; . \tag{14}$$

The coherent one-phonon structure factor for the mode λ is given by

$$S_{c,\lambda} (Q) = \frac{1}{2N} \sum_{i,j} (\text{same factors as } S_{el}) \frac{h \left(Q \cdot e_i^\lambda \right)^* \left(Q \cdot e_j^\lambda \right) < n_\lambda + 1>}{(M_i M_j)^{1/2} \, \omega_\lambda} \tag{15}$$

where ω_λ, $\underline{e}_i^\lambda$ and n_λ represent frequency, displacement vectors and thermal population for the mode λ. The phase factor (see Eq. (13)) and scalar products in Eq. (15) give $S_{c,\lambda}(Q)$ a characteristic Q variation for a given λ.

Fig. 7 shows the inelastic scattering measured for a-GeSe$_2$[14]. Structure can be observed, varying with both E and Q. To investigate this in detail, we investigate the scattering over a range in Q (2.0 - 7.5 Å^{-1}) to obtain the effective <u>one-phonon density of states</u> shown in Fig. 8. The symbols v_λ identify the vibrational modes of the Ge(Se$_{1/2}$)$_4$ tetrahedron which is the basic building block of this glass. The identification of each mode λ can be confirmed by calculating $S_{c,\lambda}(Q)$ for that mode and comparing it with the variation in Q of the scattering observed at $E = \hbar\omega_\lambda$. This is done in Fig. 9 for the breathing mode at $E = 26$ meV (v_1) and excellent agreement is seen to be obtained. We should like to proceed further to identify the two components in this mode resolved by recent Raman scattering and ascribed to intermediate range order[15]: at present this appears extremely difficult to do.

Conclusions

Neutron diffraction is a powerful tool for investigating the atomic structure of amorphous systems. In particular, the various types of ordering - hard-sphere packing, chemical short-range order and intermediate-range order caused by the presence of structural units, can be identified. The origin of the intermediate-range order in certain amorphous solids, for example oxide and chalcogenide glasses, is a controversial question. The measurement of phonon densities of states and structure factors with inelastic neutron scattering may shed some light on this problem, coupled with computer simulation techniques such as molecular dynamics.

Acknowledgements

Figure Captions

1. Schematic diagram of a neutron scattering measurement.

2. DRPHS model (line) fitted to experimental data (points) for $S(Q)$ of liquid Rb at 40°C (from Ref. 7).

3. Partial structure factors S_{NN}, S_{CC} and S_{NC} for $Ni_{40}Ti_{60}$ alloy glass (Ref. 8).

4. Structure factors $S(Q)$ for glassy and liquid $GeSe_2$ (Ref. 9).

5. Wavevectors Q_1 of peaks in the structure factors of some liquids and glasses, scaled by nearest-neighbor distance r_1 and mean atomic spacing d_s. The full line represents the limit for dense random packing, $d_s = 1.162\ r_1$ (from Ref. 10).

6. Scattering function $S(Q,E)$ for a-$GeSe_2$ at 13K (Ref. 14).

7. Scattering function $S(Q,E)$ for a-$GeSe_2$, with the elastic region suppressed to highlight the inelastic scattering (Ref. 14).

8. One-phonon effective density of states for a-$GeSe_2$. The labels attached to various features give the frequency in cm^{-1}; the symbols v_λ, $\lambda=1-4$, give assignments in terms of a $Ge(Se_{1/2})_4$ tetrahedron (Ref. 14).

9. One-phonon structure factor $S_{c,\lambda}(Q)$ for the breathing mode v_1 in a-$GeSe_2$. Circles: measurement at $E=25.91$ meV; solid line: cubic spline fit to measured data; dashed line: calculation for an isolated $Ge(Se_{1/2})_4$ tetrahedron (Ref. 14).

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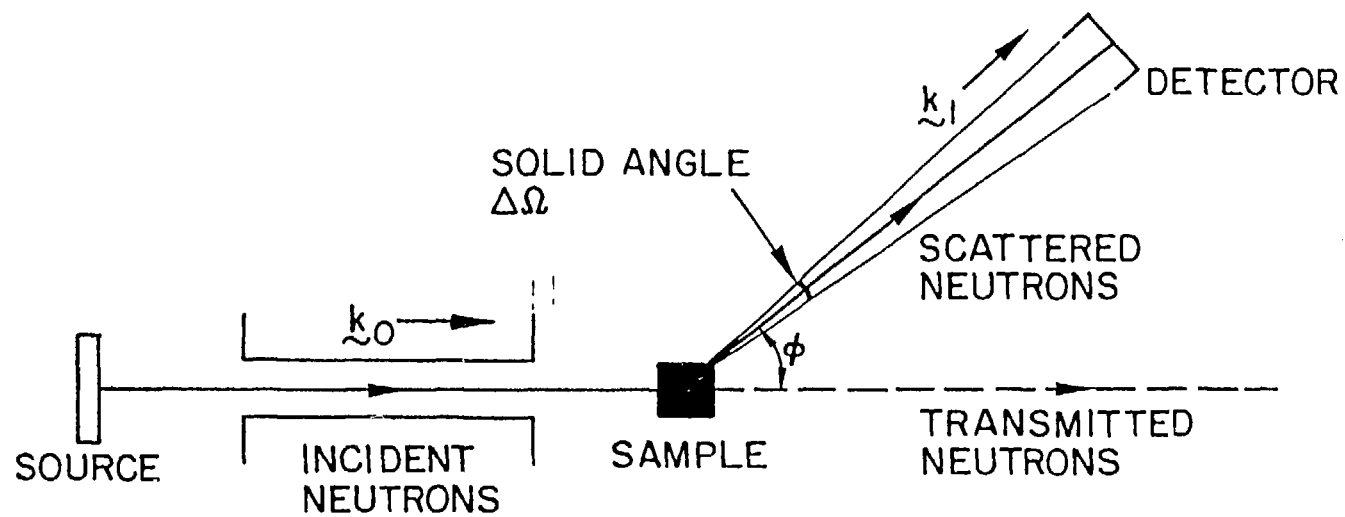
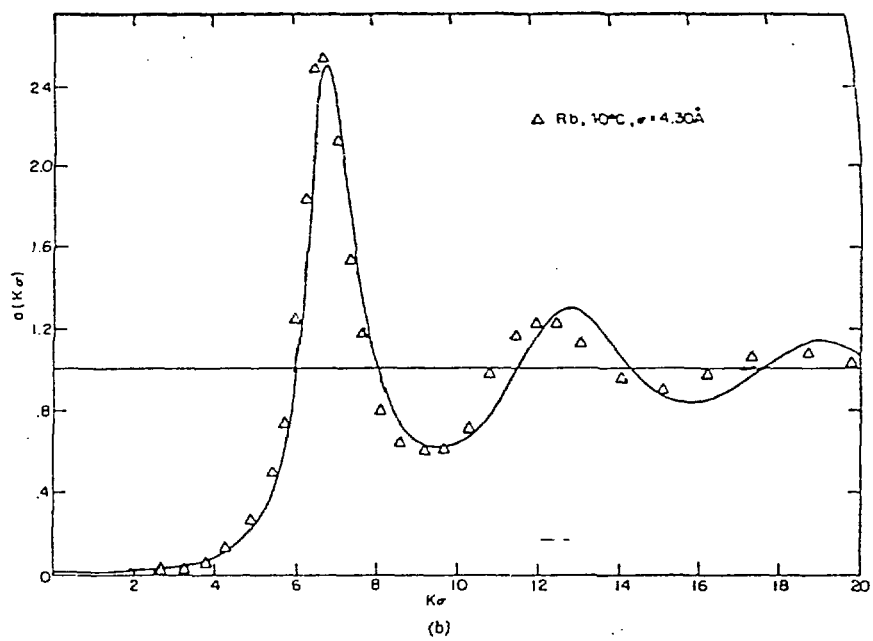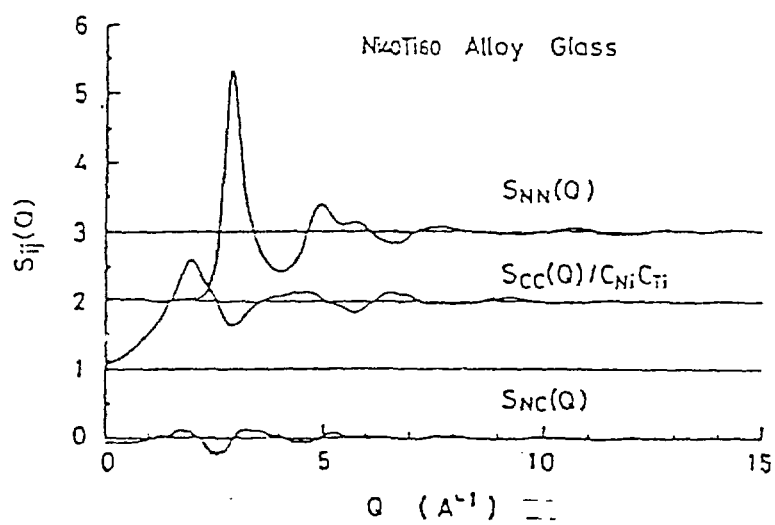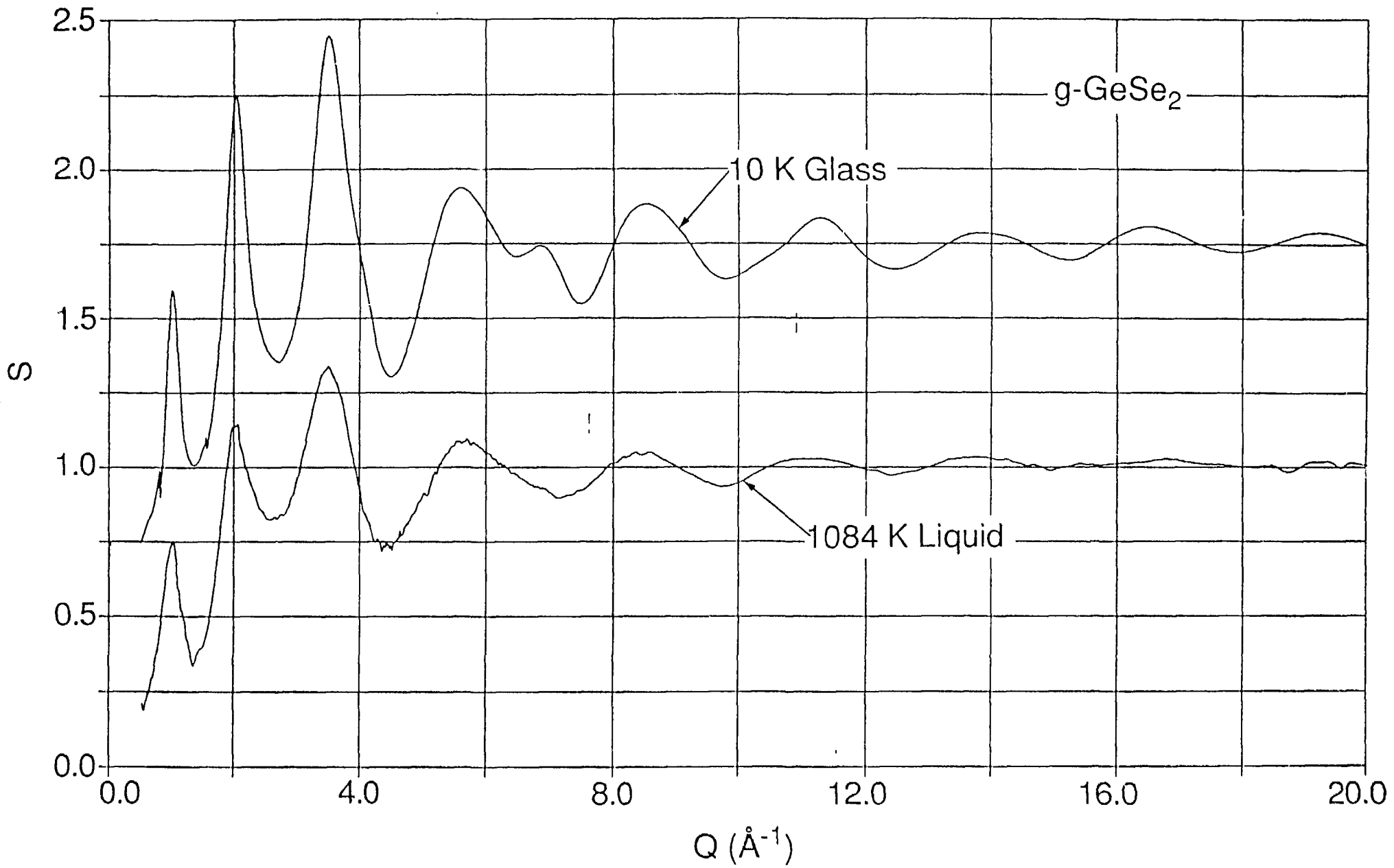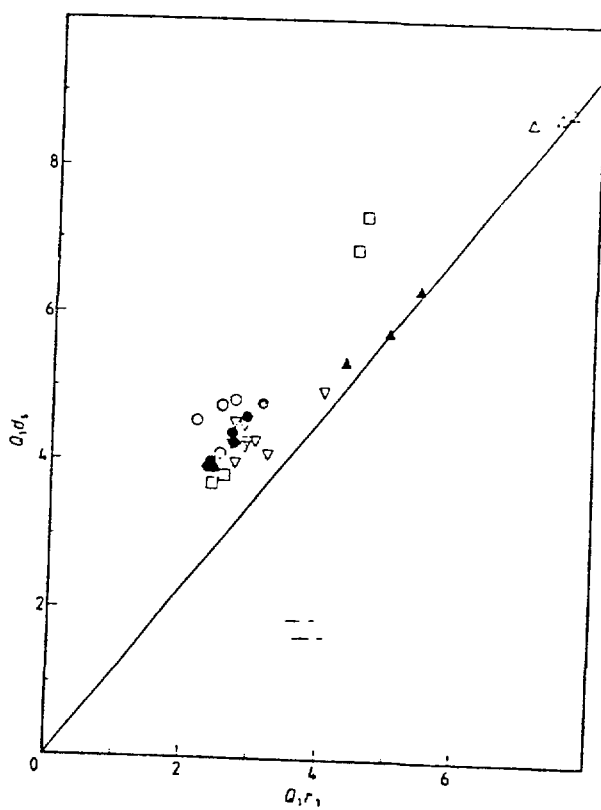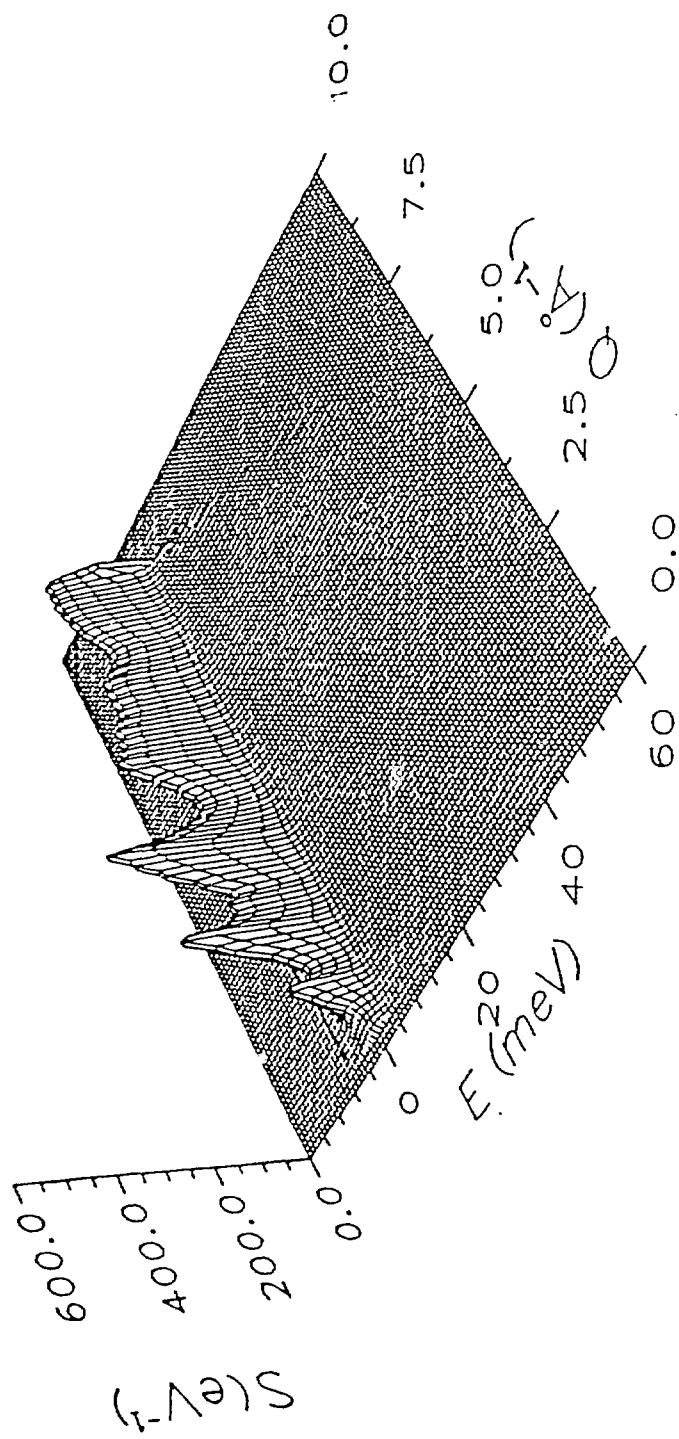14. U. Walter, D.L. Price, S. Susman and K.J. Volin, Phys.Rev.B37, 4232(1988).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6
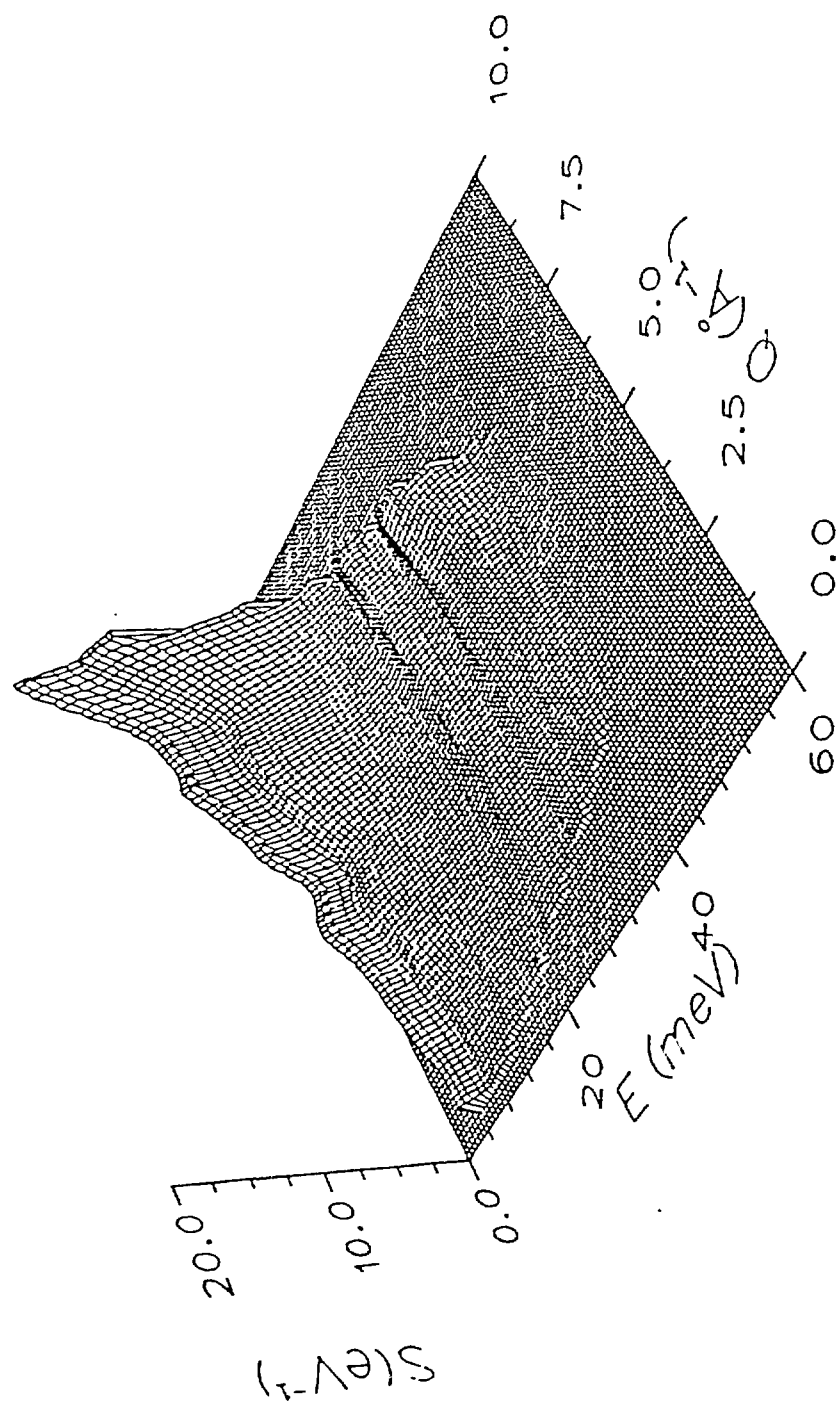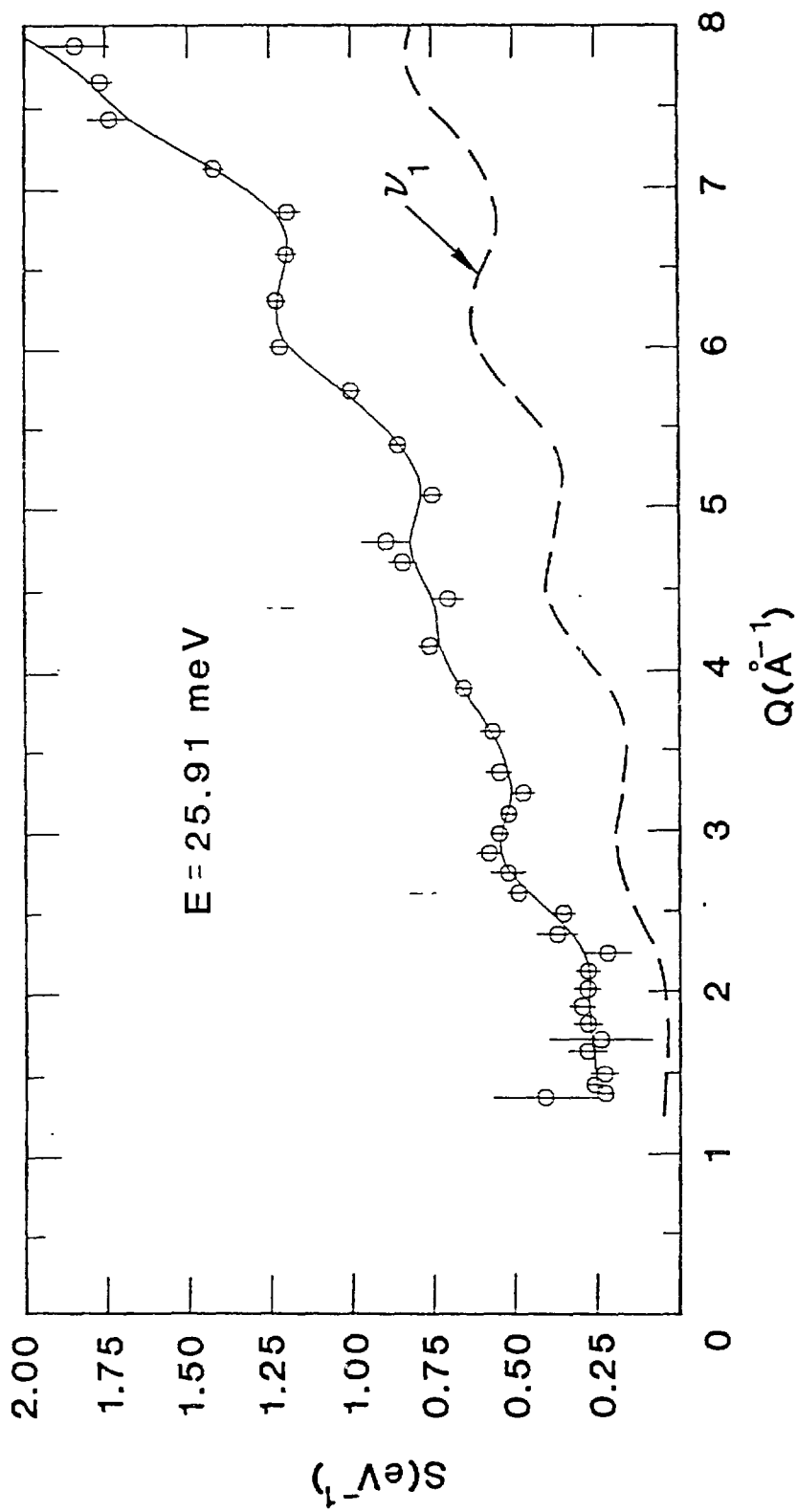
Figure 7

GeSe2 1-phonon DOS

Figure 8

GeSe2 – MS

E = 25.91 meV

ν_1

Figure 9