INELASTIC SCATTERING FROM AMORPHOUS SOLIDS*

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ABSTRACT

The potential of inelastic neutron scattering techniques for surveying various aspects of the dynamics of amorphous solids is briefly reviewed. The recent use of the Intense Pulsed Neutron Source to provide detailed information on the optical vibrations of glasses is discussed in more detail. The density of states represents an averaged quantity which gives information about the general characteristics of the structure and bonding. More extensive information can be obtained by studying the detailed wavevector dependence of the dynamic structure factor.

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1. INTRODUCTION

Although the first inelastic neutron scattering measurement on a glass was made over twenty years ago [1], the field has not been a very crowded one. A recent review was able to discuss most of the experiments done up to this time comfortably in the space of a 40-minute talk [2]. Recently, however, there has been a surge of interest, partly because of the increased interest in the field of disordered solids, and in the generality of the phenomena they exhibit, and probably also because of the development of neutron techniques toward new ranges of energy and momentum.

Fig. 1 is a frequency-wavevector plot showing schematically some of the excitations that occur. Typically, $Q_0 \sim 2\text{\AA}^{-1}$ and the acoustic modes extend to ~ 30 meV. Of long-standing interest in the amorphous state are the two-level systems and "excess" vibrational modes which have been postulated to explain the anomalous T and T^3 contributions to the low-temperature specific heat of most amorphous solids [3]. The two-level systems have not so far been observed with neutron techniques but an interesting observation of "excess" vibrational modes in SiO_2 has been made by Buchenau, Dianoux, et al. reported further at this conference [4]. At the Intense Pulsed Neutron Source, experiments by a number of investigators have

up to now concentrated mainly on the higher energy part of Fig. 1, measuring modes labeled "optical" in Fig. 1 because neighboring atoms are moving partly out of phase. The interest here is not so much in the states peculiar to amorphous systems, like the low-lying modes just discussed, but in the possible insight that may be obtained about the structure and dynamics of specific systems, especially oxide and chalcogenide glasses. In particular, it is hoped that measurements in this region will provide information about the intermediate-range order in these glasses, which remains a controversial topic despite the large body of diffraction, optical and other data [5,6].

2. DENSITY OF STATES

The simplest inelastic neutron scattering measurement in a glass is that of the neutron-weighted one-phonon density of states $g(\omega)$. By averaging the scattering intensity over an extended range of wavevector Q , the interference effects caused by coherent scattering can be washed out; furthermore, data from a large detector array can be summed to give high statistical accuracy. As an example, Fig. 2 shows the density of states measured in the chalcogenide glass SiSe_2 [7], an analogous system to SiO_2 except that the SiX_4 tetrahedral structural units are believed to be generally edge-sharing as opposed

to corner-sharing as in SiO_2 [8]. A comparison of Fig. 2 with the density of states in SiO_2 [9] shows significant differences in the prominent features of the spectrum. In particular, the features at 17, 30 and 59 meV correlate precisely with the $\nu_4(\text{F}_2)$, $\nu_1(\text{A}_1)$ and $\nu_3(\text{F}_2)$ modes of an isolated tetrahedral molecule. This can be understood in terms of a simple nearest-neighbor central-force model [10], which predicts strong coupling between molecular modes for Si-X-Si bonds angles greater than $\theta_c = \cos^{-1}(-2m_X/3m_{\text{Si}})$. For SiSe_2 , $2m_X/3m_{\text{Si}} = 1.87$ and θ_c is not defined. For SiO_2 , however, $2m_X/3m_{\text{Si}} = 0.38$ and $\theta_c = 112^\circ$, less than the observed bond angle, and the characteristics of the vibrational modes are determined more by the Si-O-Si bonds than by the SiO_4 tetrahedra.

To extract more subtle information, for example about the packing of tetrahedral units, it is necessary to invoke either detailed computer models, data from additional spectroscopies such as Raman or infrared, further analysis of the detailed neutron scattering data, or perhaps a combination of all of these.

At this point it may be asked to what extent neutrons provide information about the density of states beyond what can be obtained easily and much less expensively with optical spectroscopy. In fact, the matrix elements for the different probes are so

different that a single spectroscopy may lead to misleading results. A dramatic example of this is B_2O_3 , where the Raman spectrum is dominated by a gigantic peak at 100.8 meV (813 cm^{-1}) generally associated with breathing modes of boroxyl rings. On the other hand, the recent neutron data of Hannon et al. [11] show a barely perceptible peak in this region (Fig. 3), even though the higher resolution spectrometer at IPNS was used for this measurement. It is clear that the Raman scattering matrix element is enormously enhanced for this mode, and at least suggestive that the population of boroxyl rings may be less than previous believed.

3. DYNAMIC STRUCTURE FACTOR

The full potential of the neutron technique is realized by the measurement of Q - as well as ω -dependence. In crystalline solids, it is the measurement of phonon dispersion curves $\omega_j(q)$ with coherent inelastic neutron scattering which really established the field of lattice dynamics. In amorphous solids the wavevector q is not defined for a particular mode because of the lack of long-range order. Nevertheless, the coherent scattering intensity associated with a particular mode depends on the wavevector Q because of correlations in the motions of neighboring atoms [12]. This intensity is

conveniently represented by the one-phonon dynamic structure factor $S^{(1)}(Q, \omega)$ which in the harmonic approximation takes the form

$$S^{(1)}(Q, \omega) = \frac{1}{2N} \sum_{i,j} \frac{b_i b_j}{\langle b^2 \rangle} \exp [-(W_i + W_j)] \\ \times \exp [iQ \cdot (R_i - R_j)] \\ \times \sum_{\lambda} \hbar \frac{(Q \cdot \underline{e}_i^{\lambda})(Q \cdot \underline{e}_j^{\lambda})}{(M_i M_j)^{1/2} \omega_{\lambda}} \langle n_{\lambda} + 1 \rangle \delta(\omega - \omega_{\lambda})$$

where $\underline{e}_i^{\lambda}$, ω_j and $\langle n_{\lambda} \rangle = [\exp(\hbar\omega_{\lambda}/kT) - 1]^{-1}$ are the displacement vector, frequency and population factor of the normal mode λ . The calculation of $S(Q, \omega)$ for a realistic model of adequate size represents a substantial computational problem, and only limited results are available at this time [13].

Qualitative predictions for AX_2 -type glasses can be obtained from the nearest-neighbor central-force model discussed previously [10]. Figure 4 shows the predicted Q dependence of $S(Q, \omega)$ for the two delta-function modes which arise in this simple model, correspond to symmetric-stretch (ω_3) and antisymmetric-stretch (ω_4) distributions in SiO_2 . These predictions may be compared with the experimental Q dependence [9] shown in Fig. 5 for the three prominent peaks in the density of states of SiO_2 . Despite the apparent qualitative similarity, there are important differences in the detailed

behavior. In particular, the periods of the oscillations in this simple model are given essentially by the distance between second-nearest-neighbor silicon atoms-- $2\pi/R_{\text{Si}(1)\text{Si}(2)} \approx 2.15 \text{ \AA}^{-1}$ -- while the experimental dynamic structures have periods as low as $1.6 \text{ \AA}^{-1}$, suggesting correlations that extend beyond the second-neighbor distance.

Extensive model calculations have also been carried out for the amorphous semiconductors Si and Ge. Alben, Weaire et al. [14] were among the first authors to make detailed calculations of $S^{(1)}(Q, \omega)$ for an amorphous semiconductor. Fig. 6 reproduces one of their more dramatic results showing the Q dependence of the ratio of the intensities of the upper and lower principal peaks in the density of states for amorphous Ge. (These are labeled TA and TO by loose analogy with crystalline germanium.) The ratio exhibits a significant oscillation with period $2\pi/R_{12}$ given by the distance between nearest neighbors, reflecting the fact that the displacements projected along the bonds are in phase and out of phase respectively for the two modes. Very recently amorphous Ge prepared by triode magnetron sputtering was measured at IPNS by Maley et al. [15] In addition to a precise measurement of the one-phonon density of states, Q -dependent information was obtained by interpolating the constant-angle data onto constant

Q. The ratio of the "TO" and "TA" intensities as a function of Q is shown in Fig. 7. It reveals a qualitative similarity to the model prediction. Again, a detailed comparison shows quantitative discrepancies which must be referred to more realistic calculations of $S(Q, \omega)$.

4. CONCLUSIONS

Inelastic neutron scattering can reveal significant information about the structure and bonding in an amorphous solid. The one-phonon density of states reveals general features that, in conjunction with optical spectroscopy and other experimental probes, yield qualitative information about a particular system. More extensive information is provided by the full Q-dependent dynamical structure factor. While general features in the Q-dependence can be compared with the prediction of simple models, calculations with large systems (~ 1000 atoms) using realistic potentials are needed to make full use of the neutron data.

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FIGURE CAPTIONS

- Figure 1 Plot of frequency-wavevector space showing various types of excitations in glasses.
- Figure 2 Neutron-weighted density of states in SiSe_2 glass [7]
- Figure 3 Section of the neutron-weighted density of states in B_2O_3 [11]. The arrow shows the position of the boroxyl ring breathing mode which dominates the Raman spectrum in this region.
- Figure 4 Dynamic structure factors for the two delta-function modes in the model of Sen and Thorpe for SiO_2 [10].
- Figure 5 Experimental dynamic structure factors for SiO_2 [9].
- Figure 6 Ratio of the dynamic structure factors for the upper and lower peaks in the density of states of amorphous Ge, calculated for an 35-atom cluster [14].
- Figure 7 Experimental ratio of the dynamic structure factors for the lower and upper peaks in the density of states of magnetron sputtered amorphous Ge [15].

EXCITATIONS IN AMORPHOUS SOLIDS

SiO₂ Ω -3 & -4

STRUCTURE FACTOR

ω_3 (99.6 meV)

ω_4 (146.1 meV)

WAVE VECTOR

a-SiO₂