PHONONS IN AMORPHOUS MATERIALS

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Abstract.- A brief review is given of phonons in amorphous materials as seen in Raman scattering, infrared absorption and inelastic neutron scattering. It is shown that phonons (i.e. quantised harmonic vibrations) are well defined in network structures and a description is given of the standard theoretical technique which is to build a finite model and then use one of a number of numerical techniques to obtain the eigenvalue spectrum of the dynamical matrix. Particular emphasis is given to newer theoretical techniques that do not require the building of a model. The results are illustrated with reference to experiments in elemental semiconductors like Si and Ge and two component glasses like SiO₂, GeS₂, etc.

1. Introduction.- The vibrational spectra of amorphous solids and glasses have been extensively studied particularly in the last decade. The principle experimental techniques used are inelastic neutron scattering, Raman scattering and infra-red absorption. Although there is no one theoretical approach that can explain all aspects of these vibrational spectra, the main features are now understood. However, many significant details remain to be put in place.

We will try to briefly review the most important theoretical techniques that are available to calculate the phonon spectra of glasses. The results are illustrated mainly with a. Si and a. SiO₂ on which most work has been done. More exotic types of glasses have also been studied but less theoretical progress has been made on these.

2. Model Building and Numerical Methods.- The standard and most successful calculations of phonon spectra have involved numerical methods on particular models. It is of course essential to know the structure of a glass before proceeding to calculate the vibrational spectrum.

The earliest of these models were hand built ball and stick models of a. SiO₂(1). These were based on the known local bonding arrangements and typically contained ≈ 300 atoms in a roughly spherical cluster. Bell and Dean(1) used these models to set up a dynamical matrix using the Born model which has nearest neighbor central and non-central forces. The eigenvalue spectrum was obtained as a histogram using the negative eigenvalue theorem.
In figure 1 we show a recent comparison between theory and an inelastic neutron scattering experiment\(^{(2)}\) for SiO\(_{2}\). The experiment is done at large wave vector transfer so that essentially the density of states is measured. This has the disadvantage that the multiphonon background has to be subtracted. This is indicated in the figure by the dashed line\(^{(2)}\). The theory is the density of states weighted by the appropriate neutron scattering lengths for Si and O. The agreement overall is impressive.

Similar calculations\(^{(3)}\) have been performed for the Raman and I.R. spectra. Again reasonably good agreement is obtained. However, the matrix elements are difficult to put in as they are not simple as in neutron scattering. Usually some local bond polarisabilities are introduced which have the correct symmetry. This introduces a major theoretical uncertainty that is not present in inelastic neutron scattering.

Similar work has also been done on a. Si. Hand built models have been constructed by many groups. While the hand construction fixes the topology of the network, the positions of the atoms can be refined by relaxing according to a suitably chosen potential.\(^{(5)}\) The equation of motion method has been used by Alben and collaborators to determine all quantities of interest [density of states, Raman scattering, I.R. absorption and the neutron scattering law \(S(q,\omega)\)]. The method tracks the behavior of the displacements with time and then Fourier transforms. It can be used in any harmonic system that is disordered. Good overall agreement is achieved between theory and experiment using this method\(^{(6)}\).\(^{(6)}\)

The negative eigenvalue theorem was used to construct histograms for the density of states\(^{(1)}\) for SiO\(_{2}\) type glasses. To calculate other quantities, sample eigenvectors must be obtained. This method could also be applied to a. Si as could the equation of motion method be applied to SiO\(_{2}\) type glasses. It is an accident of history that this
has not happened.

It is particularly difficult to calculate the I.R. absorption in elemental glasses because there is no I.R. absorption in the corresponding crystal usually. A new mechanism must be invoked. Two have been suggested; dipole moments associated with three near neighbor atoms \(^4\) or fluctuating dynamic charges on all the atoms. \(^7\)

Direct diagonalisation of the dynamical matrix for a finite model is now rarely used as it is inefficient.

These numerical techniques may be regarded as providing a solution to the problem - although some effects such as those produced by the long range Coulomb forces have yet to be included. However, they do not often provide a great deal of insight and calculations must be repeated every time a change is made in the model - such as increasing the local distortions or changing the masses. For this reason, more analytic approaches are now being persued.

3. Beyond Numerical Methods. - Some progress has been made in two directions. The phonon spectrum of a Bethe lattice \(^8\) can be obtained using Born forces for a. Si. This shows many features in common with the density of states of crystalline Si although the van Hone singularities and some other features are absent. (see fig. 2)

![Graph](image)

Fig. 2: Showing the density of states for crystalline Si in the diamond structure (solid line) and the Bethe lattice (dashed line). [From reference 8.]

This or other Bethe lattices can be tied onto small pieces of network and used as a convenient boundary condition in the "Cluster - Bethe - lattice" method. This avoids the large effects that the free surfaces of small clusters can produce. A review of this method contains many of the results obtained to date \(^7\). Good agreement with experiment is obtained in many cases.

The other approach is to keep only the central forces and completely neglect the non-central forces. This is not an unreasonable starting point as the non-central forces are typically only \(\sim 20\%) of the nearest neighbor central force. Within this scheme the problem is essentially
soluble and very simple expressions are obtained for the positions and widths of the main peaks in the density of states. These are particularly valuable when the network is modified in some simple way. For example $O^{18}$ can be substituted for $O^{16}$ and the Raman spectra of the two glasses compared. It may be possible eventually to include non-central forces and Coulomb forces in this model using perturbation theory.

4. Future Prospects. Although many Raman and I.R. experiments have been performed on many glasses whose structure is known, progress has been hampered by the absence of a good knowledge of the optical matrix elements. Recent work by Martin and Galeener has shown that these matrix element effects are extremely important and can produce peaks in the optical spectra where non exist in the density of states (see figure 3).

![Graphs showing Raman scattering, density of states in the central force model, and measured weighted density of states from neutron scattering.][1]

The clearest measurements to interpret theoretically are from inelastic neutron scattering. However, the measurements at large $Q$ have problems with multiphonon scattering. It may be that measurements at smaller $Q$ will give the most information. These can be obtained theoretically using the equation of motion technique.
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References.

1. See P. Dean, Rev. Mod. Phys. 44, 127 (1972) and R. J. Bell, Reports of Prog. in Phys. 35, T215 (1972).


