SYNOPSIS

The accurate determination of the elastic constants of a solid is possible by the measurement of ultrasonic wave velocities in the solid. These measurements can also be carried out under truly hydrostatic conditions of pressure to obtain the pressure derivatives of the elastic constants. The ultrasonic methods can detect velocity changes of one part in $10^6$. This precision is adequate to measure small changes in elastic constants which occur on application of a few hundred bar pressures. Glasses are isotropic and their elastic constants can be conveniently determined by measuring only the longitudinal and transverse wave velocities. Elements of the elasticity theory, the stiffness property versus velocity relations and the various ultrasonic methods used for the determination of the transit time are given in Chapter 1. The various high pressure techniques used for the measurement of ultrasonic velocities as a function of pressure are also described.

The properties of amorphous solids are determined by the electronic configuration and chemical bonding of the adjacent atoms, in contrast to crystalline solids which
are characterised by the long range order of their constituent atoms. This permits a wide range of material compositions which exhibit a variety of properties. Some of the amorphous solids which are of commercial interest are the chalcogenide glasses. These contain one or more of the chalcogen elements (sulphur, selenium and tellurium) often combined with arsenic, antimony and germanium. The ease of formation and the stability of an amorphous solid may be expressed in terms of the average coordination number \( Z \), which corresponds to the number of bonds a typical atom makes with its neighbours. By equating the number of operating constraints to the number of degrees of freedom, it has been shown that \( Z \) of the most stable glass is around 2.40. Glassy networks with \( Z < 2.40 \) are elastically 'floppy' and those with \( Z > 2.40 \) are elastically 'rigid'. At \( Z = 2.40 \), the network moves from an elastically 'floppy' type to an elastically 'rigid' type. By considering medium range structure, it has been shown that at \( Z \approx 2.67 \) features are seen which are due to the change over from an essentially layer like arrangement in the network to a three dimensional arrangement. The properties of glasses as a function of composition and the various models proposed to account for
their variation are reviewed in Chapter 2. A survey of the elastic properties of chalcogenide glasses under pressure is also presented in Chapter 2.

Chapter 3 deals with the experimental methods used in the present study. A pulse echo overlap technique has been set up for the measurement of ultrasonic velocities. A gas pressure system has been used to pressurize the specimens up to 0.2 GPa. The performance of the ultrasonic measuring system and the gas pressure system has been evaluated by determining the elastic constants and their pressure derivatives of selenium and arsenic selenide glasses. The results have been compared with the values reported in the literature.

The pulse echo methods for the determination of the ultrasonic transit time require sophisticated electronic circuitry. A computer aided technique developed for the determination of the transit time using digital data has been described in Chapter 4. The analysis of the digital data has been performed by digital signal processing techniques. The results obtained by the digital technique on the variation of transit time with pressure on some glass samples have been compared with those obtained from the
pulse echo overlap method.

The current interest in chalcogenide glasses is due to the wide range of applications and anomalous behaviour in physical properties of these materials at specific compositions. The elastic properties of chalcogenide glasses exhibit anomalous variations at the stoichiometric compositions. In the tetrahedrally bonded network glasses, the stoichiometric composition has a Z value which is close to 2.67 predicted by the topological theories. Hence, the effects of chemical ordering and topological considerations cannot be separated. Features may be expected at $Z \approx 2.4$ (from constraints theory) which is far separated from the chemical and the second mechanical threshold. However, no anomaly has been observed at $Z \approx 2.4$. The glasses chosen in the present study are those of the Ge-Sb-Se system. The pressure variation of the ultrasonic velocities has been measured, and the pressure derivatives of the bulk and shear moduli have been obtained with a view to observing whether features are exhibited at $Z \approx 2.4$. The results of such studies on Ge-Sb-Se glass system with varying antimony content have been presented in Chapter 5.

The data on the variation of the elastic moduli and
their pressure derivatives have been analysed using Ge content, Sb content and average coordination number.

In Appendix A, are given the elements of interpolation and the computer program used for the Lagrange interpolation formula. The programs for auto correlation, cepstrum and generation of simulated data used in the digital technique (Chapter 4) are also presented.

In Appendix B, the pulse echo overlap frequency versus pressure data for the several glass samples studied are presented.