

grease (Fisher Chemical Company) for low temperature measurements, and an epoxyphenolic resin (Bloomington Rubber Company) for high temperature measurements.

The following data were determined in our ultrasonic experiments: (a) both  $P$  and  $S$  velocities in each specimen at room conditions, (b) pulse repetition frequencies (PRF) corresponding to these velocities as a function of pressure to about 7.5 kb at 23 °C, and (d) these PRFs corresponding to the velocities at 1 bar in the temperature range of 0 to 200 °C.

The quantity of interest in the ultrasonic experiments, in which pressure is a variable, is the first derivative of an isotropic elastic modulus  $M_j$  with respect to hydrostatic pressure evaluated at zero-pressure; this will be denoted hereafter as  $\{dM_j/dp\}_{p=0}$ . This is an isothermal derivative, although the velocity-of-sound measurements involve an adiabatic process. Thus, the acoustic data resulting from such experiments are *thermodynamically mixed* isothermal pressure derivatives of the adiabatic modulus. For a modulus  $M_j$ , where the subscript  $j$  refers to either compressional ( $P$ ) or shear ( $S$ ) mode, we have

$$\left\{ \frac{dM_j}{dp} \right\}_{p=0} = \left\{ \frac{M_j}{3K_T} \right\}_{p=0} + \{M_j R_j\}_{p=0} \quad (1)$$

where  $R_j = d(f_{jp}/f_{j0})^2/dp$ , and this is obtained by fitting  $(f_{jp}/f_{j0})^2$  versus pressure data to a straight line by the method of least squares, following Bacon (1953).  $K_T$  is the isothermal bulk modulus, and it is related to the adiabatic bulk modulus  $K_s$  by  $K_T = K_s/(1 + \alpha_v T \gamma_G)$ , where  $\alpha_v$  is the coefficient of volume expansion,  $\gamma_G$  is Gruneisen's ratio, and  $T$  is temperature in °K. It is clear from equation (1) that the measurements of isotropic compressional and shear velocities of sound at a reference temperature and ultrasonic pulse-repetition-frequencies  $f_j$  corresponding to these velocities as a function of pressure (also at the reference temperature) yield the values of  $\{dM_j/dp\}_{p=0}$ .

The use of equation (1) for porous materials involves a two-step correction. The first correction is for crack-pores. The elastic properties, if measured on a polycrystalline sample, are the apparent properties of the sample; they may or may not correspond to the intrinsic elastic properties of the sample being studied. Certain hot-pressed samples often contain microcracks. Effects of these microcracks on the elastic properties of the samples should be given careful attention by the investigator. Helpful references to these effects as observed on rocks are Brace (1965) and Walsh (1965). The most practical method for finding the intrinsic elastic properties of such samples is to measure both  $P$  and  $S$  velocities as a function of hydrostatic pressure to about 7 to 10 kb. From these  $V_j(p)$  data, velocities at zero-pressure are found by extrapolating high-pressure results back to the zero-pressure point. These velocities found at the origin present crack-free but not pore-free values; isotropic elastic properties at zero-porosity can be evaluated from these data.

The second correction is concerned with pores in the samples and their rate of change with pressure. It was observed that the quantity  $R_j$  in the second term of equation (1) is to the first order independent of small porosity at a pressure range of 2 to 10 kb, a range of pressure most commonly utilized in ultrasonic experiments. Theoretical justification for this observation is difficult, if not impossible, without making assumptions as to size, shape, and orientations of pores in the polycrystalline aggregate. Furthermore, even for a pore-free aggregate, the task of determining the macroscopic state of stress distribution is hopelessly complicated, due to numerous superimposed effects which originate from the properties of the mineral grains and from the boundaries between them. For these reasons, a satisfactory general model for the elasticity of porous materials has not yet been developed, in spite of numerous investigations (see Walsh & Brace (1966) for a review). In an earlier analysis of

spherical pores, based on the work of Walsh & Brace (1966), the author (Chung 1971a) indicated that the quantity  $(d\eta/dp)$  estimated at the origin is small and is well within the scatter of most experimental data. Thus, with the experimental quantity  $R_j$  determined on a porous sample, one should be able to find the pressure coefficients of compressional ( $L_s$ ), shear ( $\mu$ ), and adiabatic bulk ( $K_s$ ) moduli of the non-porous material from equations (2) and (3) below:

$$\left\{ \frac{dM_j^\circ}{dp} \right\}_{p=0} = \left\{ \frac{M_j^\circ}{3K_T^\circ} \right\}_{p=0} + \left\{ M_j^\circ \frac{d}{dp} (f_{jp}/f_{j0})^2 \right\}_{p=0} \quad (2)$$

$$\left\{ \frac{dK_s^\circ}{dp} \right\}_{p=0} = \left\{ \frac{dL_s^\circ}{dp} \right\}_{p=0} - \frac{4}{3} \left\{ \frac{d\mu^\circ}{dp} \right\}_{p=0} \quad (3)$$

where  $L_s^\circ$ ,  $\mu^\circ$ , and  $K_s^\circ$  are the porosity-corrected values and the superscript ( $^\circ$ ) refers to the zero-porosity.

In the ultrasonic experiments, in which temperature is a variable, we are interested in both  $P$  and  $S$  velocities as a function of temperature and their temperature coefficients evaluated at various temperatures. From these data, we find the temperature derivatives of the elastic constants in the usual way:

$$\frac{dM_j}{dT} = 2\rho V_j \left( \frac{dV_j}{dT} \right) - \alpha_v M_j \quad (4)$$

where  $\rho$  is the density of sample,  $V_j$  is the sound velocity in the  $j$ th mode (either  $P$  or  $S$  mode), and  $\alpha_v$  is the coefficient of volume expansion. We used thermal expansion data of Skinner (1966) and unpublished data of Singh & Simmons (1971) throughout this study.

In the first-order approximation for low porosity, the porosity-sensitive polycrystalline elastic constants  $M_j$  (where  $j = P, S$  as before) can be represented by

$$M_j = M_j^\circ (1 - k\eta) \quad (5)$$

where  $\eta$  is the porosity and  $M_j^\circ$  is the elastic constant of nonporous material given by  $M_j^\circ = \rho_0 (V_j^\circ)^2 = 4\rho_0 l_0^2 f_j^2$ .  $k$  is a constant (see, for example, a review paper by Walsh & Brace 1966). The temperature derivative of the porosity-sensitive elastic constant is then

$$\frac{dM_j}{dT} = \left( \frac{dM_j^\circ}{dT} \right) (1 - k\eta) - M_j^\circ (k) (d\eta/dT). \quad (6)$$

Since  $(d\eta/dT)$  is practically zero, the last term drops out. Thus, from equations (5) and (6), we obtain

$$\frac{d \ln M_j}{dT} = \frac{d \ln M_j^\circ}{dT}. \quad (7)$$

Equation (7) implies that the temperature coefficient of an elastic constant determined on a porous polycrystalline sample can be used to evaluate the elastic constant of the non-porous aggregate (as a function of temperature) simply by interpolating the room-temperature constant of the porous sample to that of the non-porous aggregate.