samples prepared by hot-pressing or sintering method contain residual pores along the interstices of adjacent mineral grains; the porosity may frequently be as high as 5 to 10%, although values of a few percent or less are more common. When acoustic measurements are made on porous polycrystalline samples, the values must be corrected before being used to predict the intrinsic behavior of material deep in the Earth, which undoubtedly is pore-free.

Effects of porosity upon pressure derivatives of the elastic moduli are complicated not only by the manner in which the porosity-sensitive moduli change with pressure, but also by the change of porosity with pressure. In an earlier discussion of this problem, Chung and Simmons [17, p. 5318] suggested that for porosity less than 1% $(\mathrm{d} \ln M/\mathrm{d}p) = (\mathrm{d} \ln M^{o}/\mathrm{d}p)$ is a good approximation (where M is a modulus and the superscript (^{o}) refers to the value at zero-porosity. Based on Mackenzie's work [18], Anderson et al. [19, p. 507] found (by differentiating Mackenzie's expression for the bulk modulus) an expression for $\mathrm{d}K_S{}^{o}/\mathrm{d}p$ in terms of $\mathrm{d}K_S/\mathrm{d}p$ measured on a porous sample. Walsh [20] in his recent analysis on the same problem pointed out that Mackenzie [18] developed his theory using linear elasticity in which $K_S{}^{o}$ and μ^{o} are independent of stress and that a simple differentiation of Mackenzie's expression as was done in [19] could not result in a correct expression for $\mathrm{d}K_S{}^{o}/\mathrm{d}p$. Walsh [20] then used Murnaghan's theory of finite strains to find expressions for $\mathrm{d}K_S{}^{o}/\mathrm{d}p$ in terms of the second and third-order elastic constants of the solid material. Use of Walsh's expressions for porous materials requires these high-order elastic constants of solid under discussion; frequent unavailability of these constants limits further application.

In this paper, the writer suggests a practical method for correcting porosity effects on pressure coefficients of the elastic parameters of porous materials. The present scheme has been successfully tested with two independent sets of porous forsterite samples having different porosities. The scheme was also tested with porous corundum and rutile samples successfully. The scheme described here may be a useful tool for experimentalists working with polycrystalline materials.

2. Scheme

The quantity of interest in the acoustic experiments, in which pressure is a variable, is the first derivative of an isotropic elastic modulus M with respect to hydrostatic pressure evaluated at zero-pressure; this will be denoted here after as $\{\mathrm{d}M/\mathrm{d}p\}_{p=0}$. This derivative is an isothermal one, 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 or shear mode, we have

$$M_j = 4\rho\, \ell^2\, (f_j)^2 \qquad (1)$$

where ρ and l are the density and length of the specimen at the initial condition, respectively, and f_j is the corrected pulse repetition frequency in the jth mode. Taking logarithms and differentiating both sides with respect to pressure,

$$\frac{\mathrm{d} \ln M_j}{\mathrm{d}p} = \frac{\mathrm{d} \ln \rho}{\mathrm{d}p} + 2\left(\frac{\mathrm{d} \ln \ell}{\mathrm{d}p}\right) + \frac{\mathrm{d} \ln (f_j)^2}{\mathrm{d}p} \qquad (2)$$

Since $(\mathrm{d} \ln \ell/\mathrm{d}p) = (\mathrm{d} \ln V/\mathrm{d}p)/3$ for the isotropic medium and $(\mathrm{d} \ln \rho/\mathrm{d}p) = -(\mathrm{d} \ln V/\mathrm{d}p) \equiv 1/K_T$, where V is the volume, and after evaluating the derivatives at zero-pressure, we have

$$\left\{\frac{\mathrm{d}M_j}{\mathrm{d}p}\right\}_{p=0} = \left\{\frac{M_j}{3K_T}\right\}_{p=0} + \{M_j R_j\}_{p=0} \qquad (3)$$

where $R_j = \mathrm{d}(f_{jp}/f_{j0})^2/\mathrm{d}p$ and this is obtained by fitting $(f_{jp}/f_{j0})^2$ versus pressure data to a straight line by the method of least squares. K_T is the isothermal bulk modulus and it is related to the adiabatic bulk modulus K_S by $K_T = K_S/(1 + \alpha T \gamma_G)$, where α is the coefficient of volume expansion, γ_G is Grüneisen's ratio, and T is temperature in °K. Thus it is clear from eq. (3) that the measurements of isotropic compressional and shear velocities of sound at a reference temperature and ultrasonic pulse-repetition-frequencies 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 eq. (3) for porous materials involves a two-step correction:

(a) For a polycrystalline sample with a known porosity, V_p and V_S are measured in the usual way. The elastic properties as one measures on a polycrystalline sample, are the *apparent* properties of the sample; they may or may not be corresponding to the *intrinsic* elastic properties of the sample being studied. Certain hot-pressed samples often contain microcracks, for example, and effects of these microcracks on the elastic properties of the samples should receive the careful attention of the investigator. Helpful references to these effects are Brace [21], Walsh [22], and Nur and Simmons [23]. The most commonly practised method of 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, as is frequently done (see, for example [13; 16, p. 2743]); from these $V_j(p)$ data, velocities at zero-pressure are found by extrapolation of high-pressure results back to the zero-pressure point. These velocities found at the origin in this manner correspond to the zero-pressure values for that porous sample; from these data, isotropic elastic properties at zero-porosity can be evaluated. Weil [24, p. 217] and Walsh [22] discussed how elastic properties of non-porous polycrystalline materials can be evaluated from the elastic data obtained on a porous sample. The Weil-Hashin expressions for the shear and bulk moduli with constants k_1 and k_2, which are a function only of Poisson's ratio σ_S, are recommended. Mackenzie's [18] expressions can be used as well. Thus, for $\sigma_S = \sigma_S{}^o$, we obtain μ^o, $K_S{}^o$, $V_p{}^o$, and $V_S{}^o$.

(b) It was observed [17, 26] that the quantity R_j in the second term of eq. (3) is independent to the first order of small porosity at a pressure range of 2 to 10 kb, a range most commonly utilized in acoustic experiments. The 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. In addition, even for a pore-free aggregate, the task of determining the microscopic state of stress distribution is hopelessly difficult, due to numerous superimposed effects which originate from the properties of the constituting mineral grains and from the boundaries between them. For these reasons, no satisfactory general model for the elasticity of porous materials has yet been developed, in spite of numerous investigations (see for a review [24, p. 217; 22]). An earlier analysis [17, p. 5320], based on Walsh's work for the rate of change of pores with pressure, indicates that, for a polycrystalline corundum with a porosity $\theta = 0.3\%$, the quantity $(d\theta/dp)$ estimated at the origin is in the order of -3×10^{-6} per kb. This value is small, and it is well within the scatter of most experimental data; thus, suggesting the observation may be justified for small properties (say θ less than one or two percent).

Additional support for the observation made in the earlier paragraph follows from the work of Walsh [22] and Brace [21]. As shown by Walsh and Brace, the pressure p^* required to close a cavity having the aspect ratio a is

$$p^* = aY \tag{4}$$

where Y is Young's modulus of the solid material surrounding the cavity. The values of Young's modulus for oxides and silicates of interest to geophysics are at least 1000 kb or greater (see Birch [25]). If pores are spherical, as in many polycrystalline samples prepared by sintering or by hot-pressing, the aspect ratio α is one; this means then that the pressure required to close the pores is 1000 kb or higher, depending upon the stiffness of the materials. This is a very high pressure as compared to the range of pressure involved in acoustic experiments. It would appear then that an application of 2 to 10 kb pressure to a sample containing spherical pores is too small a pressure for pore closure to affect the quantity R_j.

Thus, with experimental quantity R_j determined on a porous sample, one should be able to find the pressure coefficients of compressional, shear, and bulk moduli of the non-porous material from eqs. (5) and (6).

$$\left\{\frac{dM_j{}^o}{dp}\right\}_{p=0} = \left\{\frac{M_j{}^o}{3K_T{}^o}\right\} + \left\{M_j{}^o \cdot \frac{d}{dp}(f_{jp}/f_{j0})^2\right\}_{p=0} \tag{5}$$