that the elastic properties of zero-porosity material estimated from measurements made on highly porous material are inaccurate but also that even the sign of the derivatives with respect to pressure may be incorrect.

The reliability of measurements made on materials

of low porosity (less than 1%, say) for the estimation

of our data on the quartz sample with the correspond-

of the intrinsic properties is shown by a comparison

ł.

ing values predicted from single crystal data. The single crystal elastic constants of quartz were determined as a function of hydrostatic pressure to 3 kb by McSkimin et al. [11]. To compute the isotropic elastic parameters from these data, we followed the Voigt-Reuss-Hill (VRH) approximation and the variational methods (VM) of Hashin and Shtrikman (see, for example, Lowrie [12]). The general expressions for the pressure derivatives of the isotropic VRH moduli for trigonal crystals have been given earlier in terms of the single crystal elastic constants and their pressure derivatives [13]. Similar expressions may be found for the VM bounds from equations derived by Peselnick and Meister [14]. The values for the pressure derivatives of the velocities can then be calculated from eq. (2). The result of these calculations shows that pressure derivatives of the shear and bulk moduli are 0.44 and 6.42, respectively, from the VRH scheme whereas the VM scheme yields 0.44 and 6.41 for the same properties. Soga [15] used the single crystal data of McSkimin et al. [11] to estimate the pressure coefficients of the isotropic wave velocities and the bulk modulus on the basis of the VRH approximation. Comparison of the calculated isotropic values with the experimental data shown in table 2 reveals good agreement between the measured polycrystalline data of quartz and the isotropic VRH and VM moduli calculated from the single crystal data. Similar comparisons cannot be made for rutile because the single-crystal elastic constants, as a function of pressure, are not yet available. Tables published by

Simmons [16] list the maximum and minimum limits of isotropic compressional and shear velocities in units of (km/sec) as 9.607 and 9.071 for  $V_{\rm P}$  and 5.474 and 4.909 for  $V_{\rm S}$  for rutile. The present values of  $V_{\rm P}$  and  $V_{\rm S}$  are within these limits and they are in good agreement with velocities calculated from the polycrystalline elastic constants [3] reported earlier.

Commenting on a negative pressure dependence of

the isotropic shear modulus for some oxides, Anderson [17] predicted the value of the first pressure derivative of the shear modulus for rutile to be "negative but close to zero". As seen from table 2, our experimental value determined on a dense polycrystalline rutile specimen is  $(\partial \mu / \partial P) = +0.91$ ; this value does not support the prediction made by Anderson.

Quartz has an unusually small value of Poisson's ratio. Its rate of change with pressure is greater than that of any other oxide or silicate yet measured; compare the value of 4.9 per mbar for quartz with 0.18 for periclase. This fact is an obvious consequence of the large change in  $K_s$  with pressure compared with the change in  $\mu$ . The high value of  $(\partial \sigma_s / \partial P)_T$  for quartz may be an indication of the phase instability of the crystal lattices at high pressures. At room temperature, SiO<sub>2</sub> undergoes a change of phase from  $\alpha$ -quartz to coesite at a pressure of about 20 kb and from coesite to stishovite at a pressure of about 100 kb. We speculate that the high value of  $(\partial \sigma / \partial P)_T$  of polycrystalline quartz may be associated with the phase change to coesite.

Consideration of the values in table 2 shows that rutile possesses some of the common properties of oxides: a low value of compressibility, high value of  $\Phi = K_s/\rho$ , high wave velocities, and an intermediate value of  $(\partial \ln K_s/\partial P)_T$ . The value of  $(\partial \ln K_s/\partial P)_T$  of 3.1 mb<sup>-1</sup> for rutile may be compared with 2.6 for periclase and 1.7 for corundum. The properties of quartz, on the other hand, are *not* typical of other closely packed oxides: its value of compressibility is high,  $\Phi$  is low, wave velocities are low, and  $(\partial \ln K_s/\partial P)_T$  is 17 mb<sup>-1</sup>.

A final observation of importance to geophysicists is that  $(\partial V_S / \partial P)_T$  is a small negative quantity for quartz but a small positive quantity for rutile. The small values of  $(\partial V_S / \partial P)_T$  for these two materials *may* imply that excessive thermal gradients are not required to produce a low velocity layer in the earth's mantle.

## Acknowledgements

We thank W.F.Brace for the use of his pressure system and also for his valuable comments on the manuscript. N.H.Suhr is acknowledged for the spectrochemical analysis of our specimens. Financial support of this work was provided by the National Aeronautics and Space Administration under Grant NGR-22-009-176.

## REFERENCES

- G.Simmons and A.W.England, Universal equations of state for oxides and silicates, Phys. Earth Planet. Interiors (1969), in press.
- [2] W.B.Crandall, D.H.Chung and T.J.Gray, in: Mechanical Properties of Engineering Ceramics, eds. W.Kriegel and H.Palmour, Vol. III (Interscience, New York, 1961) p. 349.
- [3] D.H.Chung and W.R.Buessem, The VRH approximation and the elastic moduli of polycrystalline ZnO, TiO<sub>2</sub> (rutile), and α-Al<sub>2</sub>O<sub>3</sub>, J. Appl. Phys. 39 (1968) 2777.
- [4] E.P.Papadakis, Ultrasonic phase velocity by the pulseecho-overlap method incorporating diffraction phase corrections, J. Acoust. Soc. Am. 42 (1967) 1045.
- [5] D.H.Chung, D.J.Silversmith and B.B.Chick, A modified ultrasonic pulse-echo-overlap method for determining sound velocities and attenuation of solids, Rev. Sci. Inst. 40 (1969), in press.
- [6] W.F.Brace, Some new measurements of linear compressibility of rocks, J. Geophys. Res. 70 (1965) 391.
- [7] J.B.Walsh, The effect of cracks on the compressibility of rock. J. Geophys. Res. 70 (1965) 381.
- [8] N.A.Weil, in: High temperature technology, eds. N.K. Hiester (Butterworths, Washington, D.C., 1964) p. 217.

- [9] D.H.Chung and G.Simmons, Pressure and temperature dependences of the isotropic elastic moduli of polycrystalline alumina, J. Appl. Phys. 39 (1968) 5316.
- [10] O.L.Anderson, E.Schreiber, R.C.Liebermann and N. Soga, Some elastic constant data on minerals relevant to geophysics, Rev. Geophys. 6 (1968) 491.
- [11] H.J.McSkimin, P.Andreatch Jr. and R.N.Thurston, Elastic moduli of quartz versus hydrostatic pressure at 25° and -195.8°C, J. Appl. Phys. 36 (1965) 1624.
- [12] R.Lowrie, Elastic constants of polycrystalline MgO, Phil. Mag. 8 (1963) 1965.
- [13] D.H.Chung, First pressure derivatives of polycrystalline elastic moduli: their relation to single-crystal acoustic data and thermodynamic relations, J. Appl. Phys. 38 (1967) 5104.
- [14] L.Peselnick and R.Meister, Variational methods of determining effective moduli of polycrystals: (A) Hexagonal symmetry, (B) Trigonal symmetry, J. Appl. Phys. 36 (1965) 2879.
- [15] N.Soga, Temperature and pressure derivatives of isotropic sound velocities of α-quartz, J. Geophys. Res. 73 (1968) 827.
- [16] G.Simmons, Single crystal elastic constants and calculated aggregate properties, J. Grad. Res. Ctr. 34 (1965) 240.
- [17] O.L.Anderson, Comments on the negative pressure dependence of the shear modulus found in some oxides, J. Geophys. Res. 73 (1968) 7707.