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PRESSURE DERIVATIVES OF THE ELASTIC PROPERTIES OF POLYCRYSTALLINE QUARTZ AND RUTILE

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Ultrasonic measurements at 298°K as a function of hydrostatic pressure to 7 kb for polycrystalline quartz and rutile yield the following values of pressure coefficients of the velocities of compressional (P) and shear (S) waves, the adiabatic bulk modulus (K_S), and its isothermal pressure derivative:

Property	Units	Quartz	Rutile	
$(\partial \ln V_{\rm P}/\partial P)_{\rm T, P=0}$	mbar ⁻¹	2.34 (±0.04)	0.83 (±0.05)	
$(\partial \ln V_{\rm S}/\partial P)_{\rm T, P=0}$	$mbar^{-1}$	-0.80 (±0.03)	0.18 (±0.03)	
KS	mbar	0.378 (±0.010)	2.105 (± 0.043)	
$(\partial K_{\rm S}/\partial P)_{\rm T, P=0}$		6.5 (±0.04)	6.4 (±0.08)	

These data are discussed in relation to the structure and the phase instability at high pressure. The relatively small values of $(\partial \ln V_S / \partial P)_T$ may indicate that neither high thermal gradient nor partial melting is required to account for the low velocity layer in the earth.

Transformation of the elasticity of the earth into parameters of composition, pressure, and temperature depends, in large part, on the use of equations of state. Parameters for the appropriate equations of state may be obtained for pressure above a few hundred kilobars from shock-wave experiments and for lower pressures from static or dynamic measurements in the laboratory. Because the chemical and mineralogical composition of the interior of the earth is still largely unknown, the parameters used in the equations of state may be based on those of model materials, or on some form of a universal equation of state (believed valid by some authors for suitably restricted materials). The universal equations of state were discussed recently by Simmons and England [1]. Better understanding of the equations of state is most likely to arise from careful measurements on specific materials. In this note, we report data on the elastic properties of hotpressed polycrystalline quartz and rutile as a function of pressure.

Our measurements of the elastic properties were made on polycrystalline specimens produced by means of the resistance hot-pressing method described by Crandall et al. [2]. The shape of the specimens was a rectangular prism. The microstructural characteristics of the rutile specimen have been described earlier, and this specimen was cut from one of several specimens used in the earlier study of room-temperature elastic properties of this material [3]. Specific information about each specimen follows:

- Quartz: density at 298°K, 2.645 g/cm³ (0.2% porosity); size, $1.2338 \times 1.2329 \times 0.6122$ cm; 99.9% SiO₂ with traces of Al, Mg, Ti, Fe, and Zr (each less than 0.01%).
- *Rutile (I)*: density at 298°K, 3.189 g/cm³ (25% porosity); size, 1.0127 × 0.9943 × 0.4877 cm; 99.9% TiO₂ with 0.03% Pb, 0.02% Fe, and 0.01% Zn.

Rutile (II): density at 298° K, 4.212 g/cm^{3} (0.9% porosity); size, $1.0424 \times 0.9848 \times 0.8878 \text{ cm}$; 99.9% TiO₂ with 0.03% Pb, 0.02% Fe, and 0.01% Zn.

The measurement of sound velocities at room conditions and as a function of hydrostatic pressure to about 7 kb were made with the pulse-echo-overlap method [4] as modified by Chung et al. [5]. We used the pressure system described in detail by Brace [6] with the exceptions that we used reagent grade petroleum ether as the pressure medium, and the pressure was read directly from a precalibrated, 7500-bar Heise gauge. The readability of this gauge is better than 0.2%. X-cut and AC-cut quartz transducers with resonance frequencies of 20 MHz were used for generation of compressional (P) and shear (S) waves, respectively. The material used for acoustic bonding between specimen and transducer was a 50% (by volume) mixture of phthalic anhydride and glycerine.

The primary data determined in our ultrasonic experiments were (1) P and S velocities in each specimen at 25°C and 1 bar, and (2) pulse-repetition frequencies corresponding to these velocities as a function of pressure to about 7 kb. The first derivative of an elastic modulus with respect to pressure was calculated from

$$\begin{pmatrix} \frac{\mathrm{d}M_j}{\mathrm{d}P} \end{pmatrix}_{P=0} = \left(\frac{M_j}{3K_{\mathrm{T}}} \right)_{P=0} + \\ + \left(M_j \frac{\mathrm{d}}{\mathrm{d}P} \left(F_{jp} / F_{jo} \right)^2 \right)_{P=0}, \quad (1)$$

where F_{jo} and F_{jp} are the corrected pulse-repetition frequency at zero-pressure and at pressure P, respectively. $K_{\rm T}$ is the isothermal bulk modulus calculated from the adiabatic bulk modulus $K_{\rm S}$ by the relation $K_{\rm T} = K_{\rm S}(1 + \alpha T \gamma)^{-1}$, where the quantity $(1 + \alpha T \gamma)$ is 1.0078 for quartz and 1.0116 for rutile at 300°K. M_j is an elastic modulus, and the subscript (j) refers to either the longitudinal or transverse elastic mode. From the values of $\{dM_j/dP\}_{P=0}$ we calculated values of the first pressure derivatives of P and S velocities from

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$$\left(\left(\frac{\partial V_j}{\partial P}\right)_{\mathrm{T}}\right)_{P=0} = \left(\frac{1}{2\rho_0 V_j} \left[\left(\frac{\partial M_j}{\partial P}\right)_{\mathrm{T}} - -\frac{\rho_0}{K_{\mathrm{T}}}(V_j)^2\right]\right)_{P=0}, \qquad (2)$$

where ρ_0 is the initial density of the specimen.

The dependence of the quantity $(F_{in}/F_{io})^2$ on pressure for both quartz and rutile was linear within experimental precision; the data are given in table 1. Variations with direction in the velocities are due probably to physical inhomogeneities in the specimens and represent the apparent anisotropy of the specimens. The anisotropies are rather small, about the same size as the experimental uncertainties in our measurement of velocities. The values of $(F_{in}/F_{io})^2$ and their dependence on pressure vary slightly with direction in the sample, are probably real, and imply also that the specimens were slightly anisotropic. This dependence on direction of the elastic properties is attributed to the effects of residual porosity. The effects of pores and cracks on the elastic properties have been discussed by Walsh [7].

Various elastic parameters for the specimens are listed in table 2. On the basis of these parameters, the isotropic elastic properties of polycrystalline aggregates at zero-porosity were evaluated. The elastic moduli of non-porous polycrystalline aggregates can be estimated from acoustic measurements made on a porous aggregate (see Weil [8]). The shear modulus is given by the Weil-Hashin relation

$$\mu^{0} = \mu (1 + k_{1} \theta) / (1 - \theta)$$
(3)

and the adiabatic bulk modulus

$$K_{s}^{0} = K_{s}(1 + k_{2}\theta)/(1 - \theta) , \qquad (4)$$

where

$$k_1 = 2(4 - 5\sigma)/(7 - 5\sigma) ,$$

$$k_2 = (1 + \sigma)/2(1 - 2\sigma) ,$$

and θ is the volume fraction of total pores, σ is Poisson's ratio, and the superscript (0) refers to the value at zero-porosity. From these values of μ^0 and K_s^0 all the other isotropic elastic parameters are calculated and these values may be compared with the quantities obtained on the corresponding single crystals. Effects of porosity upon pressure derivatives of the elastic moduli are complicated not only by the manner in which the porosity-sensitive modulus changes with pressure but also by the change of porosity with

Material	Initial density, 00	Compressional velocity, Vp	Shear velocity, Vs	$(F_p/F_{po})^2$	$(F_{\rm s}/F_{\rm so})^2$
add ma th	(g/cm ³)	(km/sec)	(km/sec)	(at 10 kb)	(at 10 kb)
Quartz	2.645	6.062 (±0.007) *	4.106 (±0.005) *	1.06480 (±0.00023) *	1.00170 (±0.00011) *
Rutile I	3.189	8.281 (±0.009) *	4.760 (±0.007) *	1.02075 (±0.00024) *	1.00302 (±0.00017) *
Rutile II	4.212	9.146 (±0.009) *	5.146 (±0.007) *	1.01984 (±0.00020) *	1.00679 (±0.00013) *

 Table 1

 Measured properties of polycrystalline quartz and rutile at 298°K

* These uncertainties are due to observed variations in the property measured for different directions of the specimen.

Quantity Unit		Quartz		Rutile		
	Unit	(measured)	(extrapolated)	(measured)		(extrapolated) *
	ding the second			(I)	(II)	
00	g/cm ³	2.645	2.649	3.189	4.212	4.250
VP	km/sec	6.062	6.066	8.281	9.146	9.193
VS	km/sec	4.106	4.110	4.760	5.102	5.122
$L_{\rm S} (= \rho_0 V_{\rm P}^2)$	109dyn/cm ²	971.8	974.6	2186.7	3523.6	3592
$\mu (= \rho_0 V_{\rm S}^2)$	10 ⁹ dyn/cm ²	446.0	447.4	722.5	1096.3	1115
Ks	10 ⁹ dyn/cm ²	377.2	378.1	1223.4	2061.9	2105
KT	$10^9 dyn/cm^2$	374.3	375.2	1209.3	2038.3	2081
Js	none	0.076	0.076	0.253	0.264	0.274
$\partial V_{\rm P}/\partial P)_{\rm T}$	$10^{-3} (\rm km/sec)/\rm kb$	14.2	14.2	21.0	7.6	7.7
$\partial V_{\rm S}/\partial P)_{\rm T}$	$10^{-3} ({\rm km/sec})/{\rm kb}$	-3.3	-3.3	-0.6	0.9	0.9
$\partial L_{\rm s}/\partial P)_{\rm T}$	none	7.16	7.2	5.14	7.57	7.7
$\partial \mu / \partial P)_{\mathrm{T}}$	none	0.47	0.5	0.42	0.91	0.9
$\partial K_{\rm s}/\partial P)_{\rm T}$	none	6.53	6.5	4.58	6.35	6.4
$\partial K_{\rm T}/\partial P)_{\rm T}$	none	6.54	6.5	4.57	6.33	6.4
$\partial \sigma_s / \partial P)_T$	$10^{-3}/kb$	4.93	4.9	19.6	0.46	0.4

* Extrapolation based on Rutile II data (see text).

pressure. In an earlier discussion [9] of this problem, we suggested that for porosity less than 1%

$$\frac{\mathrm{d}\,\ln M}{\mathrm{d}P} = \frac{\mathrm{d}\,\ln M^0}{\mathrm{d}P} \tag{5}$$

is a good approximation. Our data have been corrected on the basis of eq. (5) and the results are shown in table 2 under the column designated "extrapolated". The data on the highly porous rutile specimen (Rutile I) are included here to illustrate the important result that the intrinsic properties of materials *cannot* be estimated reliably from the properties of highly porous materials. Anderson et al. [10] recently pointed out this difficulty in connection with their earlier measurements of the elastic properties of a polycrystalline sample of forsterite with 6% porosity. Our present set of data on Rutile I shows not only 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

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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 μ . 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, SiO₂ undergoes a change of phase from α -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⁻¹ 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, Φ is low, wave velocities are low, and $(\partial \ln K_s/\partial P)_T$ is 17 mb⁻¹.

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.

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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, TiO₂ (rutile), and α-Al₂O₃, 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.