structed by means of the mixed triplet and strengthened quartet relationships (Schenk, 1973) on the basis of the same 7 reflexions with an acceptance criterion LIM = 5·5.

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The Elastic Properties of Beryl

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Using the pulse-superposition method, the second-order elastic stiffnesses of aquamarine were determined to be $C_{11}=3\cdot085$, $C_{33}=2\cdot834$, $C_{12}=1\cdot289$, $C_{13}=1\cdot185$, $C_{44}=0\cdot661$ Mbar. Results for goshenite beryl are very similar. Initial pressure derivatives were also determined.

The second-order adiabatic elastic stiffnesses of beryl and their initial pressure derivatives at 25 °C have been measured by the pulse-superposition method. Previous measurements (Voigt, 1887; Madelung & Fuchs, 1921; Bridgman, 1928; Sundara Rao, 1948) are not in agreement: bulk moduli measurements, for instance, differ by 20%. Chung & Buessem (1968) have questioned the validity of the elastic constants of beryl for a different reason. The compression anisotropy calculated from the elastic coefficients appears inconsistent with anisotropies observed in other hexagonal crystals.

Two Brazilian specimens were used in the investigation, a pale-blue aquamarine and a colorless goshenite beryl. The chemical compositions determined by wet chemical and spectroscopic analyses are presented in Table 1. As expected, the aquamarine is richer in iron, but the goshenite specimen contains more alkali ions. Densities were determined by the hydrostatic weighing method described by Smakula & Sils (1955). The goshenite specimen was slightly denser (2·7238 ± 0·0003 g cm^{-3}) than the aquamarine (2·6976 ± 0·0003 g cm^{-3}) because of the higher concentration of alkali ions and water molecules trapped in the structure. Both densities are significantly larger than the X-ray density of 2·640 g cm^{-3} calculated for a hexagonal unit cell measuring $a=9\cdot215$, $c=9\cdot192$ Å, and containing two ideal formula-units, 2 $Be_3Al_2Si_6O_{18}$ (Swanson, Cook, Isaacs & Evans, 1960).

Table 1. *Chemical analyses of two Brazilian beryls*

Analysts: J. DeVine, J. Bodkin and R. Raver.

	Ideal $Be_3Al_2Si_6O_{18}$	Pale blue aquamarine	Colorless goshenite
BeO	13·96 wt. %	13·60 %	12·66
Al_2O_3	18·97	18·20	18·24
SiO_2	67·07	65·92	65·18
Fe_2O_3		0·167	0·006
FeO		0·11	0·08
TiO_2		0·020	0·011
Li_2O		0·03	0·69
Na_2O		0·13	0·79
K_2O		0·013	0·05
Rb_2O		0·001	0·021
Cs_2O		0·075	0·16
H_2O^+		1·36	1·68
H_2O^-		0·02	0·02

Not detected: MnO, CaO, MgO, Cr_2O_3, Nb_2O_5, ZrO_2, SnO_2, Sc_2O_3.

Flawless rectangular prisms about 1 cm on edge were cut from the two large hexagonal crystals using the natural prism and pinacoid faces as a guide. After orientation by the back-reflection Laue method, the crystals were ground and polished with silicon carbide powders and diamond paste. Using specially-designed holders, orientations of better than 10 minutes of arc and flatnesses of 3×10^{-5} cm were achieved. Dimensions were measured with a Lufkin micrometer prior to the determination of the elastic constants from acoustic velocities.

In the pulse-superposition method (McSkimin & Andreatch, 1962; McSkimin, 1965) a high-frequency

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quartz tranducer is cemented to the specimen and an electrical signal is applied to the transducer, which in turn initiates an acoustic pulse in the sample. After traveling through the crystal, the acoustic pulse is reflected from the opposite face and returns to the transducer as an echo. There it excites an electrical signal which is detected and displayed on an oscilloscope. Ultrasonic velocities are calculated from the delay time and specimen length with small corrections for the bonding materials, salol (phenyl salicylate, m.p. 43 °C) and nonaq stopcock grease. A short series of pulses spaced approximately by the round-trip delay time are applied to enchance the echo by multiple reflection. *X*- and *AC*-cut quartz plates with resonant frequencies near 20 MHz are used to generate longitudinal and transverse pulses respectively. The ultrasonic interferometer and high-pressure equipment used here are the same instruments employed previously in measurements on corundum (Gieske & Barsch, 1968) and forsterite (Graham & Barsch, 1969).

Beryl belongs to crystal class 6/*mmm* for which there are five independent stiffness coefficients relating stress to strain. In matrix form the moduli for the hexagonal system are

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$

where $C_{66}=\frac{1}{2}(C_{11}-C_{12})$. Measurements are referred to right-handed orthogonal axes X_1, X_2, X_3 parallel to crystallographic directions [100], [120] and [001]. Hexagonal materials are transversely degenerate so that all directions in (00.1) are equivalent.

Pure mode directions for the hexagonal system have been derived by Brugger (1965). Three coefficients are determined from the density ϱ, and the longitudinal and two transverse wave velocities along X_1: $\varrho v_L^2=C_{11}$, $\varrho v_T^2=C_{66}$ and $\varrho v_t^2=C_{44}$. Measurements along X_3 give $\varrho v_L^2=C_{33}$ and $\varrho v_T^2=\varrho v_t^2=C_{44}$. A specimen cut at 45° to X_3 gives one pure mode $\varrho v_T^2-\frac{1}{2}(C_{44}+C_{66})$, and two mixed modes from which the remaining constant C_{13} is obtained:

$$C_{13}=[(C_{11}+C_{44}-2\varrho v^2)\,(C_{33}+C_{44}-2\varrho v^2)]^{1/2}-C_{44}\ .$$

Table 2 lists the experimental sound-wave velocities from which the elastic constants in Table 3 are computed. Each velocity was measured twice and all observations were weighted equally in the analysis. The eight independent velocity measurements provide cross-checks on C_{44}, C_{66} and C_{13}, differing by 0·09, 0·26 and 0·04% respectively for goshenite. Corresponding cross-checks for the aquamarine specimen were 0·03, 0·08 and 0·15%. The stiffness coefficients of Brazilian goshenite and aquamarine differ only slightly, but are significantly larger than those reported by Sundara Rao (1948) and Voigt (1887). The bulk moduli measured by Bridgman (1928) and by Madelung & Fuchs (1921) agree well with our measurements. The elastic constants of beryl are comparable to those of other silicates (Newnham & Yoon, 1973). With C_{11} exceeding C_{33}, the mineral is stiffer parallel to Si_6O_{18} rings and the strong Si–O bonds.

Initial values of the first pressure derivatives of the second-order elastic constants of beryl were measured at 25 °C. These pressure derivatives are the isothermal pressure derivatives of the effective elastic coefficients which are, in general, different from those of thermodynamic coefficients (Thurston, 1965, 1967). Measurements were made at pressures up to about 10 kbars (~ 145 000 p.s.i.), using argon as the pressure medium. The pressure vessel was a 37 in-long cylinder of Vasco 1000 alloy with a 10 in outer diameter and a 2 in inner diameter. Closure at the pressure-vessel heads was maintained with modified Bridgman seals in a succession of soft and hard neoprene, lead, brass and mild steel. To the first head was attached the brass specimen holder, along with two chromel–alumel thermocouples and electrical leads to the quartz transducer. The wires were sheathed in $\frac{1}{16}$ in stainless steel tubing filled with compressed magnesium oxide powder for insulation, and sealed with Silastic 891 to prevent argon leakage. Pressures were measured with a manganin pressure cell and a Carey–Foster bridge. The cell was located near a second pressure vessel head connected to a two-stage Harwood gas compressor. The first stage compresses the argon gas to 50 000 psi, and the second up to 200 000. Temperature inside the vessel was maintained near 25 °C by circulating cooling water through copper tubing wound externally around the pressure vessel (Bogardus, 1965).

Table 2. *Ultrasonic velocities for transverse and longitudinal waves in beryl*

Propagation direction	Displacement direction	Velocity (km/sec)	
		Goshenite	Aquamarine
X_1	X_1	10·568 (5)	10·696 (5)
	X_2	5·752 (3)	5·772(2)
	X_3	4·899 (2)	4·951 (2)
X_3	X_3	10·097 (5)	10·250 (5)
	X_1	4·901 (3)	4·950 (2)
45° to X_1 and X_3	~45° to X_1 and X_3	9·926 (9)	10·067 (5)
	X_2	5·347 (5)	5·375 (2)
	~45° to X_1 and $-X_3$	5·684 (5)	5·727 (2)

Table 3. *Adiabatic elastic stiffnesses of beryl at* 25 °C

B and C_{ij} are given in Mbar. Initial pressure derivatives $(\partial C_{ij}/\partial P)_{P=0}$ are dimensionless, and represent the isothermal pressure derivatives of the adiabatic elastic constants.

Reference	Voigt (1887)	Madelung & Fuchs (1921)	Bridgman (1928)	Sundara Rao (1948)	Present Work		Pressure derivative
Description	Ural	Brazilian	Transparent Light green	Sea green	Brazilian Goshenite	Brazilian Aquamarine	Brazilian Aquamarine
Temperature	–	0 °C	30 °C	–	25 °C	25 °C	25 °C
Specific Gravity	2·70	2·703	–	2·720	2·7238	2·6976	2·6976
Bulk Modulus, B	1·35	1·75	1·84	1·43	1·76	1·81	3·90 (5)
C_{11}	2·6929	–	–	2·873	3·042 (3)	3·085 (3)	4·47 (2)
C_{33}	2·3624	–	–	2·418	2·776 (4)	2·834 (3)	3·43 (2)
C_{12}	0·9611	–	–	0·991	1·238 (8)	1·289 (4)	3·96 (5)
C_{13}	0·6610	–	–	0·729	1·145 (3)	1·185 (5)	3·78 (5)
C_{44}	0·6531	–	–	0·702	0·653 (1)	0·661 (1)	−0·18 (2)
C_{66}	0·8659	–	–	0·941	0·902 (5)	0·898 (2)	0·25 (2)

Readings of the acoustic delay time were made in steps of about 10 000 p.s.i. Longitudinal-mode measurements showed a greater scatter at high pressures compared with the transverse mode. A better bonding material is needed for the study of longitudinal waves at high pressures. The acoustic damping encountered at high pressures drastically reduces the height of echoes, making identification of the correct echo difficult.

Pressure derivatives of the second-order elastic stiffnesses of the aquamarine specimen (Table 3) at zero pressure and 25 °C were calculated from the pressure dependence of the round-trip delay times by a least-squares polynomial fit (Yoon, 1971) based on Cook's (1957) analysis. Eight independent mode measurements were made for both zero-pressure and high-pressure experiments. Standard deviations were calculated taking account of the errors in specimen thicknesses and transit times, leading to uncertainties in the pressure derivatives of approximately 0·02. Two derived pressure derivatives for C_{13} agreed to within 0·1 %.

Compared with other oxides, the pressure derivatives for beryl are somewhat smaller than those of corundum (Gieske & Barsch, 1968), quartz (McSkimin, Andreatch & Thurston, 1965) and forsterite (Graham & Barsch, 1969). Like quartz, which also has a rather open crystal structure, beryl possesses a negative pressure derivative, $\partial C_{44}/\partial P$. The resistance to shearing stress therefore decreases with pressure, suggesting a structural instability, consistent with the reported phase transition at high pressures (Munson, 1967). Relationships between mineral structures and elastic constants and their pressure dependence have been discussed in a separate paper (Newnham & Yoon, 1973).

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