

TABLE 1

Single-crystal elastic moduli, c_{ij} (Mbars), and their pressure derivatives c'_{ij} , of rutile-structure compounds, (bulk moduli, K , and shear moduli, μ , of isotropic aggregates are estimated from the Hashin-Shtrikman bounds [26,27])

	c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	c_{66}	c_s^*	K	μ	Reference
GeO ₂	3.372	5.994	1.882	1.874	1.615	2.584	0.745	2.58	1.51	[33]
TiO ₂	2.714	4.840	1.780	1.496	1.244	1.948	0.467	2.15	1.14	[34]
	2.701	4.819	1.766	1.480	1.239	1.930	0.468	2.13	1.13	[30]
SnO ₂	2.617	4.496	1.772	1.555	1.031	2.074	0.423	2.12	1.02	[35]
MnF ₂	1.030	1.628	0.816	0.709	0.300	0.677	0.107	0.893	0.30	[22]
CoF ₂	1.023	1.704	0.730	0.610	0.373	0.952	0.147	0.836	0.39	[36]
MgF ₂	1.237	1.770	0.732	0.536	0.552	0.978	0.253	0.868	0.52	[25]
	1.395	2.041	0.897	0.625	0.564	0.951	0.250	1.010	0.54	[23]
	1.399	2.042	0.893	0.637	0.570	0.954	0.253	1.014	0.55	[22]
	1.408	2.053	0.900	0.635	0.567	0.957	0.254	1.019	0.55	[24]
	1.427	2.040	0.922	0.641	0.567	0.935	0.253	1.028	0.55	this paper **
	±0.003	±0.005	±0.005	±0.010	±0.002	±0.015	±0.001	±0.010	±0.01	
	c'_{11}	c'_{33}	c'_{12}	c'_{13}	c'_{44}	c'_{66}	c'_s	K'	μ'	Reference
GeO ₂	6.65	6.63	8.05	4.10	1.78	4.10	-0.70	6.1	1.13-1.59	[33]
TiO ₂	6.47	8.34	9.10	5.02	1.10	6.43	-1.32	6.8	0.50-1.34	[34]
	6.29	8.13	9.02	5.57	1.08	5.91	-1.37	6.9	0.35-1.16	[30]
SnO ₂	5.25	6.10	6.73	4.65	0.89	3.18	-0.74	5.5	0.28-0.76	[35]
MgF ₂	5.0	5.7	6.4	4.2	0.8	2.9	-0.7	5.1	0.38-0.72	this paper ***
	±0.1	±0.1	±0.2	±0.3	±0.1	±0.2	±0.1	±0.2		
	-	-	-	-	-	-	-	5.1 †	0.7 †	[12]
	(3.31)	(3.96)	(5.21)	(3.31)	(-0.31)	(2.94)	(-0.95)	(3.84)	(-0.25-0.11)	[31] ††

* $c_s = 1/2(c_{11} - c_{12})$.

** Uncertainties derived from deviations from internal consistency (Table 3).

*** Uncertainties derived from scatter in data.

† Measurements on polycrystalline aggregates.

†† Values in parentheses are theoretical.

provide more information on the nature of the interatomic forces, and because the reliability of measurements on polycrystals has been questioned (e.g. [13]). This paper reports the results of ultrasonic measurements of the elastic moduli of single-crystal MgF₂ under pressures up to 7 kbars. These results are less accurate than is commonly achieved (or claimed) in ultrasonic measurements, but they are nevertheless accurate enough to be useful.

2. Specimens

Five crystals of MgF₂, with the orientations listed in Table 2, were purchased from Optovac Inc., North Brookfield, Mass., each being about 1 cm long and 1 cm in diameter. One pair of faces, flat and parallel

to within about 1 μ m, was polished on each crystal by Valpey-Fisher Corporation. The orientations of the faces were checked by Laue X-ray back-reflection, and found to be within 1° of those listed, except for specimen 5, which was misaligned by 6°. A rough estimate indicates that this error will not affect the results within the accuracy reported here. The final lengths of the samples are listed in Table 2.

MgF₂ (rutile) has tetragonal symmetry (space group $D_{4h}^{14}-P4/mmm$), and consequently has six independent second-order elastic moduli [14]. The combinations of these moduli which control the velocities of compressional and shear waves in the crystallographic orientations of the above specimens are listed in Table 2. The eleven modes of propagation are sufficient to determine all six independent moduli with some redundancy.

TABLE 2

Crystal lengths, wave modes and corresponding combinations of elastic moduli for MgF₂ samples

Length (cm)	Mode	Mode *	Modulus
<i>Crystals 1 and 2</i>			
1.0797	1	[001]L	c_{33}
	2	[001]T any	c_{44}
<i>Crystal 3</i>			
0.9639	3	[100]L	c_{11}
	4	[100]T[010]	c_{66}
	5	[100]T[001]	c_{44}
<i>Crystal 4</i>			
1.0797	6	[110]L	$c_L = \frac{1}{2}(c_{11} + c_{12} + 2c_{66})$
	7	[110]T[110]	$c_T = \frac{1}{2}(c_{11} - c_{12})$
	8	[110]T[001]	c_{44}
<i>Crystal 5</i>			
0.9639	9	45° L **	$c_{QL} = \frac{1}{4}(A + B) ***$
	10	45° T45° **	$c_{QT} = \frac{1}{4}(A - B) ***$
	11	45° T[010] **	$\frac{1}{2}(c_{44} + c_{66})$

* Wave normal direction, type (longitudinal, L, or transverse, T) and polarization.

** Wave normal 45° to [100] and [001].

*** $A = c_{11} + c_{33} + 2c_{44}$, $B = [(c_{11} - c_{33})^2 + 4(c_{13} + c_{44})^2]^{1/2}$. Modes 9 and 10 are not purely longitudinal and transverse, respectively.

3. Experimental methods

Ultrasonic measurements were made using an interferometer system, described in detail by R.J. O'Connell et al. (in preparation) and basically similar to that described by Spetzler [15]. Two high-frequency phase coherent ultrasonic pulses are generated in the sample via quartz transducers, the second pulse superimposed on the echo of the first. Variation of the ultrasonic frequency produces alternate constructive and destructive interference, which is monitored via the amplitude of a selected echo combination. The phase of the interference cycle is directly related to the phase difference between the pulses, and hence to the sound velocity, and is determined as a function

of frequency via a series of Fourier transform algorithms. An on-line mini-computer controls the data acquisition and performs the initial data processing. Pressure derivatives were here calculated from a determination of the variation of phase with pressure at a fixed frequency. Used in this way, the method is therefore equivalent to the widely used pulse superposition method described by McSkimin and Andreatch [16].

Pressures up to 7 kbars were generated with a Bridgman piston-cylinder apparatus with a kerosene pressure medium. Pressure was determined to within 1% with a Heise gauge.

Measurements of zero-pressure velocities were made with a steel buffer rod between the transducer and sample. The buffer rod and sample were bonded with phenyl salicylate, which melts at 44°C, and hence can easily be made to form a thin bond. 20 MHz transducers were used, and phase was measured between about 10 and 30 MHz. The phase difference between successive echoes is:

$$\phi = \frac{4\pi fL}{v} + \phi_r \quad (1)$$

where f is the ultrasonic frequency, L is the sample length, v is the wave velocity and ϕ_r is the phase shift due to reflections at the ends of the sample. A constant phase shift of π occurs at the free end. The buffer-sample bond causes a phase shift at the buffer end of the sample which depends on frequency. This type of phase shift has been investigated theoretically and experimentally by McSkimin [17,18] and Davies and O'Connell [19]. The results of Davies and O'Connell indicate that $d\phi_r/df$ is likely to be less than about 0.1% of $d\phi/df$. The effects of the bond phase shift can thus be ignored to this accuracy. In terms of the frequency step $\Delta f = 2\pi/(d\phi/df)$ between successive constructive interferences, the velocity is, from equation (1):

$$v = \frac{4\pi L}{d\phi/df} = 2L\Delta f \quad (2)$$

Δf is the reciprocal of the round-trip travel time of the wave through the sample.

Measurements under pressure were made with transducer bonded directly onto the sample with Dow Chemical resin 276-V9. Both the transducer and the bond cause a phase shift upon reflection from that face of the sample. The bond phase shift is very small at the