Measurement of Single-Crystal Elastic Constants of Bronzite as a Function of Pressure and Temperature

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The nine single-crystal elastic constants of orthopyroxene, $Mg_{0.8}Fe_{0.2}SiO_3$, have been measured as a function of temperature from 25° to 350°C and at 25°C as a function of pressure to 10 kb by means of the ultrasonic pulse superposition technique. It was found that the shear constants exhibited a distinctly nonlinear pressure dependence in addition to the usual linear terms. Owing to the difficulty in obtaining precise data for the longitudinal modes above approximately 4.5 kb, where curvature might be observed, only a linear pressure dependence was found for the on-diagonal longitudinal constants. Because the second pressure derivatives of the on-diagonal longitudinal constants (c_{11}, c_{22}, and c_{33}) enter the expressions required for the evaluation of the second pressure derivatives of the off-diagonal constants (c_{12}, c_{23}, and c_{13}), the second derivatives of the off-diagonal constants are probably considerably in error. The second pressure derivatives of the on-diagonal shear constants and of the unprocessed data for the cross-coupling moduli, however, have been precisely and consistently measured and represent the first observations of curvature for noncubic oxide materials. The dimensionless quantities $K(\partial c_{\mu\nu}/\partial P^2)$ (where K denotes the bulk modulus, $c_{\mu\nu}$ denotes the elastic constants, and P denotes the pressure) for the on-diagonal shear moduli are about ten times larger than the corresponding quantities for the eight alkali halides for which these quantities are known. The isotropic bulk and shear moduli and their pressure and temperature derivatives calculated from the single-crystal data by means of the Voigt-Reuss-Hill (VRH) approximation are $K^s = 1.035$ Mb, $G = 0.749$ Mb, $(\partial K^s/\partial P)_T = 9.59$, $(\partial G/\partial P)_T = 2.38$, $(\partial K^s/\partial T)_p = -0.268$ kb°C^{-1}, and $(\partial G/\partial T)_p = -0.119$ kb°C^{-1}. Owing to the large values of the pressure derivatives of the longitudinal elastic constants c_{11}, c_{22}, and especially c_{33}, the pressure derivative of the bulk modulus of orthopyroxene is approximately twice as large as that for most other materials normally considered to be of importance in the earth's mantle. The ultrasonic equation of state calculated from the first-order Birch equation agrees well with static-compression data and, below about 150 kb, with shock-wave data. The elastic Grueneisen parameter calculated from the VRH approximation is found to be 30% larger than the thermal Grueneisen parameter.

The single-crystal elastic constants of many geophysically relevant materials have been ultrasonically measured by several authors as a function of temperature and pressure (see, for example, the compilations by *Hearmon* [1969] and *Bechmann* [1969] and, in addition, those by *Graham and Barsch* [1969] and *Kumazawa and Anderson* [1969]). Available single-crystal elastic data on pyroxenes, however, have been limited by the paucity of suitable specimens of sufficient size and quality on which to perform ultrasonic measurements. Single-crystal data have been reported for six clinopyroxenes [*Alexandrov and Ryzhova*, 1961; *Alexandrov et al.*, 1963] and two orthopyroxenes of the bronzite variety [*Ryzhova et al.*, 1966; *Kumazawa*, 1969]. In none of these studies, however, were the effects of elevated temperature and pressure included. For orthopyroxene the temperature and pressure dependence of compressional- and shear-wave velocities has been measured [*Birch*, 1960; *Simmons*, 1964; *Hughes and Nishitake*, 1963]. These measurements, however, have been made on natural rock specimens in which the problems of porosity, cracks, heterogeneity, and large grain size reduce the precision of the measurements, particularly those of the temperature and pressure derivatives. In addition, compressional- and shear-wave velocity

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TABLE 1. Quantitative Analysis of Bronzite Specimens by Atomic Absorption
(All values in wt %.)

Element	Sample 1	Sample 2	Sample 3	Sample 4	Maximum Difference
MgO	30.10	28.80	30.30	30.80	2.0
SiO_2	54.80	53.80	54.00	54.00	1.0
Fe_2O_3*	13.60	13.90	14.90	14.40	1.3
Al_2O_3	0.60	0.68	1.00	0.79	0.4
CaO	0.18	0.29	0.50	0.50	0.04
MnO	0.24	0.28	0.25	0.24	0.04
Na_2O	0.00	0.00	0.43	0.09	0.43
BaO	0.00	0.00	0.04	0.04	0.04
NiO	0.06	0.00	0.00	0.00	0.06
Total	99.58	97.75	101.42	100.86	

Detected spectrographically in trace amounts for all samples: Cr, V, Zn, Zr, Co, Cu, Ti.
*All iron expressed as ferrous iron.

data as well as temperature and pressure dependence were obtained from different specimens with varying compositions by several investigators. Therefore, for a more complete understanding of materials thought to be of importance in the earth's mantle, it is necessary to obtain elasticity data for members of the pyroxene family as a function of temperature and pressure. The purpose of this paper is to present precise data for the single-crystal elastic constants of natural orthopyroxene and their temperature and pressure derivatives.

EXPERIMENTAL PROCEDURE

Four natural single-crystal orthopyroxene samples from India (purchased from the Commercial Mineral Company, New York) were used in this investigation. A quantitative analysis using atomic absorption was performed by R. E. Raver of the Pennsylvania State University Mineral Constitution Laboratory (Table 1). The mean molecular formula as determined from these data is approximately $Mg_{0.8}Fe_{0.2}SiO_3$. The specimens are therefore of the bronzite variety.

Orthopyroxene belongs to the orthorhombic space group Pbca [Wyckoff, 1968]. Therefore nine second-order elastic constants are necessary to describe the elastic behavior of the crystal. In the Voigt notation they are c_{11}, c_{22}, c_{33}, c_{44}, c_{55}, c_{66}, c_{12}, c_{13}, and c_{23}. All the on-diagonal moduli $c_{\mu\mu}$ (no summation convention) can be deter-

mined from ultrasonic velocity measurements in pure-mode directions parallel to the crystallographic a, b, and c axes, which also provide cross checks on c_{44}, c_{55}, and c_{66}. The three cross-coupling moduli (c_{12}, c_{13}, and c_{23}) can be determined from three different propagation directions perpendicular to one of the orthogonal crystallographic axes and oblique to the remaining two. Therefore three different orientations are necessary to determine the cross-coupling moduli in addition to the pure-mode orientations. The equations used for the calculation of the elastic constants and their first and second pressure derivatives for these orientations can be determined from the Christoffel equations and have been given by Fisher and McSkimin [1958], Graham [1969], and Barsch and Frisillo [1973]. Because no single specimen was large enough to determine all nine of the elastic constants and because the specimens have approximately the same chemical composition, it was decided to use all four specimens.

Figure 1 illustrates the orientation of the four samples. Specimen 1 was used for determining the on-diagonal moduli, and specimens 2, 3, and 4 were used for determining the cross-coupling moduli. In addition, propagation directions parallel to the x axis for specimens 2, 3, and 4 (Figure 1) were also used to measure the respective on-diagonal moduli, which could then be compared with data from specimen 1. In this way the results from the four different