



Fig. 8. Principal stretches λ_i and lattice parameters a_i of bronzite versus pressure from ultrasonic elastic data according to Thurston's equation of state. Here $a_0 = 18.262$ Å, $b_0 = 8.870$ Å, and $c_0 = 5.203$ Å.

axes differ by only 30%, at higher compressions the linear compressibility of the c axis appears to be reduced by the greater stiffness of the SiO_4 chains against further compression.

Debye temperature and Grueneisen parameter. The isotropic elastic constant data (Table 12) can be used to calculate the elastic Debye temperature θ according to [Anderson, 1965]

$$\theta = h/k[(3p/4\pi)(N\rho/M)]^{1/3}v_m \quad (13)$$

where h and k are Planck's constant and Boltzmann's constant, respectively, p is the number of ions per primitive unit cell (5 for enstatite), N is Avogadro's number, and M is the molecular weight. The mean sound velocity v_m is given by [Anderson, 1965]

$$v_m = [(v_p^{-3} + 2v_s^{-3})/3]^{-1/3} \quad (14)$$

and v_p and v_s are the longitudinal and shear velocities, respectively (Table 13). The low- and high-temperature limits γ_0 and γ_∞ of the elastic Grueneisen parameter can be calculated approximately from [Anderson et al., 1968]

$$\gamma_0 = (\Delta^3\gamma_P + 2\gamma_S)/(\Delta^3 + 2) \quad (15a)$$

$$\gamma_\infty = (\gamma_P + 2\gamma_S)/3 \quad (15b)$$

where $\Delta = v_s/v_p$ and γ_P and γ_S are the average

Grueneisen parameters of the longitudinal and shear modes, respectively [Anderson et al., 1968]:

$$\gamma_P = \frac{1}{3} + (K_T/v_P)(\partial v_P/\partial P)_T \quad (16a)$$

$$\gamma_S = \frac{1}{3} + (K_T/v_S)(\partial v_S/\partial P)_T \quad (16b)$$

where $(\partial v_P/\partial P)_T$ and $(\partial v_S/\partial P)_T$ are the pressure gradients of the velocities listed in Table 13.

The quantities calculated according to (13), (15), and (16) are $\theta = 724^\circ\text{K}$, $\gamma_P = 3.09$, $\gamma_S = 1.48$, $\gamma_0 = 1.65$, and $\gamma_\infty = 2.02$. Because no experimental specific heat data of bronzite are available, the elastic Debye temperature cannot be compared with its thermal value.

The room temperature value of the thermal Grueneisen parameter

$$\gamma = \beta K_T/\rho c_V \quad (17)$$

is 1.56, calculated from the experimental value of the volume thermal expansion coefficient $\beta = 4.70 \cdot 10^{-5} \text{ }^\circ\text{K}^{-1}$ [Frisillo and Buljan, 1972] and from a value of $c_V = 94.50 \text{ joule mole}^{-1} \text{ }^\circ\text{K}^{-1}$, which was calculated from the elastic Debye temperature on the basis of the Debye function [Beattie, 1926]. As has been observed for numerous other (but not all) solids, the elastic and

thermal Grueneisen parameters γ_z and γ agree surprisingly well. This agreement shows that bronzite belongs to that large class of materials for which the average over all vibrational modes of the crystal required for the calculation of the Grueneisen parameter in the quasi-harmonic approximation [Barron, 1955] can be successfully approximated by the directional average of the elastic modes, the dispersion and the contributions from the optical branches thereby being neglected.

Because γ_0 is only 18% smaller than γ_z , it appears that the temperature variation of the Grueneisen parameter is small. A small temperature dependence of γ has been observed for many (but not all) oxide compounds [Anderson *et al.*, 1968].

SUMMARY AND CONCLUSIONS

The dependence of the nine single-crystal elastic constants of bronzite on pressure and temperature was measured and showed several unusual features. The first pressure derivative and the temperature derivative of the longitudinal modulus in the crystallographic c axis and the first pressure derivative of the bulk modulus are anomalously large. These results are consistent with earlier polycrystal data and compression measurements of Bridgman. The linear compressibility of the c axis decreases much more rapidly with increasing pressure than the linear compressibilities of the other two axes. All these phenomena seem to arise from the more rapid stiffening upon compression of the SiO₄ chains parallel to the c axis and constituting the crystal structure of enstatite. In addition, the pressure dependence of the shear velocities along the three crystallographic axes, of the velocities of the quasi-shear modes along directions forming angles of approximately 45° with these directions, and of the associated shear moduli were found to be noticeably non-linear below 10 kb. This phenomenon is attributed to the decreasing stability of the enstatite structure with increasing pressure, which results in a phase transformation or in disproportionation into spinel and stishovite. On the other hand, other properties, such as the magnitude and the temperature dependence of the thermal Grueneisen parameter and its agreement with the elastic Grueneisen parameter, are entirely normal.

APPENDIX: LEAST-SQUARES FIT OF $\rho_0 W^2$ TO A POLYNOMIAL OF DEGREE N IN PRESSURE

The pressure derivatives of the effective elastic constants were determined from the expansion coefficients A_n^N of the quantity $\rho_0 W^2$ as defined by

$$\rho_0 W^2 = \rho_0 \sum_{n=0}^N A_n^N (P^n/n!) \quad (\text{A1})$$

The degree N of the polynomial to which a given set of data points for a particular mode was fitted was determined on the basis of three criteria.

First, the total sum of the least-squares deviation $[vv]$ for a fit of $\rho_0 W^2$ to a polynomial of degree N must be significantly smaller (say, at least 3 times) than that of a polynomial of degree $N - 1$ and not significantly larger (say, at most 3 times) than that of a polynomial of degree $N + 1$.

Second, the coefficients $t_n^N = A_n^N/\Delta A_n^N$, where ΔA_n^N denotes the standard error of the n th-order expansion coefficient for a fit to a polynomial of degree N , must obey the standard Student t test [Draper and Smith, 1966] for a probability of 0.95. Because all runs consist of 16–18 data points of $\rho_0 W^2$ (with the exception of one run consisting of only 11 data points), the degrees of freedom for $N = 1, 2$, and 3 range from 13 to 17, and the coefficient t_n^N for a probability of 0.95, according to the tables for the standard t test [Draper and Smith, 1966], must be larger than about 2.1–2.2.

Third, the coefficients A_n^N and especially the highest-order coefficients A_N^N obtained from independent measurements and representing different modes belonging to the same elastic modulus must be consistent within their joint standard error.

The application of these criteria is illustrated for the shear and quasi-shear modes. As can be seen from Table A1, the total sum of the least-squares deviation $[vv]$ is, for the fit to a quadratic relation ($N = 2$), 2.6–4.6 times smaller than that for the fit to a linear relation ($N = 1$), whereas, for the fit to a third-order polynomial ($N = 3$) $[vv]$ is reduced by only a small amount ranging from 1 to 70%. Thus the first criterion, with the exception of one mode, is satisfied for a fit to a quadratic relation.

In Table A2 the quantities t_n^N (for the coefficient of P^2 for the fit to a quadratic relation