

Mitzutani *et al.* (1972). Therefore, the present reduction provides an adequate fit to the low to moderate-pressure range data. The calculated errors were based on normal error propagation involving the uncertainties in the elastic properties for stishovite determined from the shock-wave analysis.

The isentrope defined by the 'preferred' solution of Ahrens *et al.* (1970) also has been indicated on Fig. 1. These authors reduced the shock-wave Hugoniot data according to the first-order Birch equation, which may be written in the form

$$P(\rho) = \frac{3}{2} K^S [(\rho/\rho_0)^{7/3} - (\rho/\rho_0)^{5/3}] \left\{ 1 - 3 \left(1 - \frac{\beta^S}{4} \right) [(\rho/\rho_0)^{2/3} - 1] \right\}, \quad (9)$$

in conjunction with an empirical function for the volume dependent Grüneisen parameter

$$\gamma = \gamma_0 (\rho_0/\rho)^A \quad (10)$$

where A is an adjustable parameter. The pertinent results from the Ahrens *et al.* (1970) study are: $K^S = 3.0$ Mbar; $(\partial K^S/\partial P)_S = 6.86$; $(\partial K^S/\partial T)_P = -0.50$ Kbar/ $^\circ$ K; $\gamma_0 = 1.58 \pm 0.35$; and $A = 6$. This particular choice of the A parameter was predicted on the best fit to the Hugoniot data for porous and fused-quartz as indicated in Fig. 2. The physical significance of A in equation (10) may be understood in terms of the relation for γ given by equation (2). Equation (2) may be expanded in a series of the type

$$\gamma(\rho_0/\rho) = \gamma_0 - \gamma_0'(1 - \rho_0/\rho) + 1/2\gamma_0''(1 - \rho_0/\rho)^2 + \dots \quad (11)$$

where

$$\gamma_0 = \alpha K^S / \rho_0 C_p$$

and

$$\gamma_0' = \gamma_0(\gamma_0 + 2 + \delta - 4s)$$

and the other parameters have been defined previously (e.g. Pastine & Forbes 1968). Expressing equation (10) in terms of an exponential expansion and comparing first order coefficients, it can be shown that

$$A \simeq \gamma_0 - \frac{1}{\alpha K^S} \left(\frac{\partial K^S}{\partial T} \right)_P - \left(\frac{\partial K^S}{\partial P} \right)_T + 1 \quad (12)$$

to first-order in compression. Substituting the appropriate values from the results of Ahrens *et al.* (1970) yields a value of $A = 6$.

Comparison of the isentrope of Ahrens *et al.* (1970) with the present results in Fig. 1 indicate equivalence within the indicated errors in the region of the shock Hugoniot data. However, examination of the Ahrens *et al.* (1970) results in comparison with the static-compression data of Liu *et al.* (1971) and the ultrasonic value of Mitzutani *et al.* (1972) suggest marginal discrepancy. The question arises as to whether the differences observed reflect real variation in the functional forms of the equations of state; or if they are simply the result of the use of different relations for the volume dependence of the Grüneisen parameter and/or different shock-wave data sets.

The conclusions of Ahrens *et al.* (1970) were based on the shock-wave Hugoniot data of Wackerle (1962) and Al'tshuler *et al.* (1965). In order to assess the extent to which the differing data sets affect the results, the present method of reduction was applied to the combined data of Wackerle (1962) and Al'tshuler *et al.* (1965) only. The results ($K^S = 3.47 \pm 0.28$ Mbar and $\partial K^S/\partial P = 4.9 \pm 1.1$) clearly are consistent with the previous calculations based on all the available shock-wave data. Fig. 3 graphically illustrates the differences in pressure ΔP between the isentropes calculated from the Wackerle-Al'tshuler (WA) data set and the Wackerle-Al'tshuler-Trunin (WAT) data set, as well as between the Ahrens *et al.* (1970) solution and the WAT

results. In the range of the shock-wave data the isentropes are equivalent within the calculated error; however, in the lower pressure region the WA and WAT Murnaghan isentropes reflect the static-compression data more favourably.

The empirical form of the volume dependent Grüneisen parameter,

$$\gamma = 1.58 (\rho_0/\rho)^6,$$

used by Ahrens *et al.* (1970) is indicated in Fig. 2. It is apparent that the empirical form with the indicated parameters is reasonably consistent with the expression given by equation (2) when $\delta = 7$. Moreover, when the foregoing empirical relation is used in the present reduction scheme, rather than equation (2), the results are equivalent within the estimates of error. Thus, it appears that the discrepancies between the present results and the study by Ahrens *et al.* (1970) are not resolvable in terms of the Grüneisen relation or data sets; rather, the differences seem to reflect inherent dissimilarity in the forms of the equations of state and/or curve fitting procedure.

An isotherm calculated by Davis (1972) also is indicated in Fig. 1. In addition to the data considered in the present study, Davis (1972) included Hugoniot data for porous quartz samples in order to constrain the Grüneisen parameter. His preferred solution, case 2, shown in Fig. 1, involves a fit of the Hugoniot and static compression data to a fourth-order Eulerian equation of state. The results of that study are in agreement with the low-pressure data, but diverge somewhat from the present curve and that of Ahrens *et al.* (1970) in the high-pressure region. As suggested by Davies (1972), the essential differences between the analyses reflects his reliance on the porous Hugoniot data to constrain the Grüneisen parameter, while the present study utilizes Weaver's thermal expansion data. Davies (1972) also carried out an analysis using the latter alternative, the results of which, case 1, are consistent with the present study.

Comparison of the functional forms of the Murnaghan and Birch equations is possible in terms of the implied pressure dependences of the bulk modulus. The first-order Murnaghan equation is based on the assumption that the bulk modulus may be given by a linear function of pressure. In order that such an approximation be valid for a particular material implies that the sum total of the higher order terms be effectively zero over the range of pressure represented by the data. The form of the first-order Birch equation implies a fixed negative value of the quadratic term in the bulk modulus-pressure expansion. The foregoing results imply that for stishovite in the pressure range of zero to 2 Mbar, the linear relation in pressure affords a better approximation for the bulk modulus than a quadratic or higher-order expansion. A similar result was noted by Barsch & Shull (1971) in the case of *NaI* and *KI*; exact lattice-theoretical calculations for these materials indicate that the bulk modulus is more adequately represented by a linear function of pressure than a quadratic expansion over the pressure range 50 Kbar–1 Mbar.

Systematic relations of rutile-structure oxides

The elastic constants of single-crystal rutile-structure GeO_2 and TiO_2 have been measured as a function of pressure and temperature by Wang (1972) and Manghnani (1969). It is of interest to compare the present results for isostructural stishovite with the GeO_2 and TiO_2 data. A compilation of the pertinent measurements is indicated in Table 1. In Table 1 the single-crystal elastic data are represented by the Reuss average calculated by Wang (1972) and Manghnani (1969). It has been pointed out (e.g. Kumazawa 1969) that the Reuss average or single-crystal property, is to be identified with the density equation of state for the single-crystal or polycrystalline aggregate under conditions of high hydrostatic pressure. The elastic constants of polycrystalline TiO_2 have been measured by Chung & Simmons (1969) and are consistent with Manghnani's (1969) averaged values. In addition, the pertinent values for K^S , $(\partial K^S/\partial P)_T$, and $(\partial K^S/\partial T)_P$ have been plotted for stishovite, rutile, and