theory. Lattice dynamics in the fourth-order approximation lead, under certain assumptions, to the Mie-Grüneisen equation [*Leibfried and Ludwig*, 1961], and *Thomsen* [1970] derived an expansion of this equation into the domain of finite strain. His equation thus describes both compressional and thermal effects. It is written in terms of a particular Lagrangian strain and involves six adjustable parameters. Subsequently it has been shown (G. F. Davies, unpublished manuscript, 1972) that analogous equations can be derived in terms of other strains and that the resulting form of the Mie-Grüneisen equation can be written in the form of a conventional finite strain equation.

In accord with these results, the 300°K isotherm will be represented in this study by the fourth-order Eulerian finite strain equation

$$P(V) = -3K_0(1-2\epsilon)^{5/2}\{\epsilon - \tfrac{3}{2}(K_0' - 4)\epsilon^2 + \tfrac{3}{2}[K_0K_0'' + K_0'(K_0' - 7) + \tfrac{143}{9}]\epsilon^3\} \quad (3)$$

where K_0 is the bulk modulus at zero pressure and 300°K, a prime denotes an isothermal pressure derivative, and

$$\epsilon = \tfrac{1}{2}[1 - (V/V_0)^{-2/3}] \quad (4)$$

is the Eulerian strain parameter. Neglecting the last term in (3) reduces it to the familiar Birch-Murnaghan equation [e.g., *Birch*, 1952].

The particular expression for γ to be used here is derived (G. F. Davies, unpublished manuscript, 1972) by expanding to second order the squared eigenfrequencies of the lattice in terms of displacements of the atoms from their mean lattice positions and substituting the result in the usual definition of γ:

$$\gamma = -\frac{d \ln \omega}{d \ln V} = -\frac{(1+e)(g+he)}{6(1+ge+\tfrac{1}{2}he^2)} \quad (5)$$

Here e is another strain parameter defined as

$$e = (V/V_0)^{1/3} - 1 \quad (6)$$

The strain e is linear in atomic displacements, so that a second-order expansion in terms of e is identical to a second-order expansion in terms of atomic displacements. This result, in turn, is consistent with the expansion of the lattice potential energy to fourth order in terms of atomic displacements on which the fourth-order theory of lattice dynamics is based [*Leibfried and Ludwig*, 1961]. The quantity ω in (5) can be regarded as a characteristic eigenfrequency of the lattice.

The constants g and h in (5) are parameters to be determined. They are related to measured quantities by the following series of equations (G. F. Davies, unpublished manuscript, 1972).

$$g = -6\gamma_0 \quad (7)$$

$$h = g\left[3\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_{T,0} + g - 1\right] \quad (8)$$

$$\gamma = V\alpha K_T/C_v \quad (9)$$

$$\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T = 1 + \delta_T - K_T' - \left(\frac{\partial \ln C_v}{\partial \ln V}\right)_T \quad (10)$$

$$\delta_T = -|/\alpha K_T|(\partial K_T/\partial T)_P \quad (11)$$

Here C_v is the specific heat at constant volume and the subscript T denotes isothermal derivatives. Equations 9 and 10 are thermodynamic identities [*Bassett et al.*, 1968].

An equation for Hugoniot pressure can be derived by combining the Mie-Grüneisen equation with the Rankine-Hugoniot conservation equations. In this way the Hugoniot pressure can be related to any other thermodynamic locus, such as an isentrope or an isotherm. An equation relating the Hugoniot pressure to an isentrope has been given by *Ahrens et al.* [1969]. Another equation relating Hugoniot pressure to the isotherm of the static lattice has been given by *Thomsen* [1970]. This equation has been generalized to include the effects of a phase change and initial porosity (G. F. Davies, unpublished manuscript, 1972); the result is

$$P_h\left(\frac{V_0'}{2} - \frac{V}{2} - \frac{V}{\gamma}\right) = \phi(V) - \phi(V_0) + \frac{V}{\gamma}\frac{d\phi}{dV} - U(V_0) + E_t \quad (12)$$

where P_h is the Hugoniot pressure, V_0' is the initial density of the sample, V_0 is the zero pressure density of the phase in question, U is the thermal energy, E_t is the zero pressure phase transformation energy, and ϕ is the potential energy of the static lattice. The quantity ϕ can be related to the expansion of the isotherm (equation 3) through the constants g and h (G. F. Davies, unpublished manuscript, 1972).

To summarize, expressions for the 300°K isotherm and for the Hugoniots are given by (3) and (12) in terms of the six parameters V_0, K_0, K_0', K_0'', g, and h. The only essentially new thing in this analysis is the equation for γ (equation 5). It should be noted that this equation gives a volume dependence of γ qualitatively similar to, for instance, (1). In the present application the volume dependence of γ is constrained by the Hugoniot data, and so the quantitative differences between (1) and (5), for instance, will be absorbed by their parameters. Thus with (5) the value of δ_T will be determined in this way (see equations 10 and 11; all other quantities in (7)–(11) are constrained by other aspects of the data). Because δ_T is otherwise unknown, the only doubt resulting from this procedure concerns the specific value of δ_T.

The specific heat at constant volume has been approximated in these calculations by the Debye model. A discussion of the inadequacy of the Debye model for a number of minerals has been given by *Kieffer and Kamb* [1972]. Their results indicate that, for the purposes of this discussion, the Debye model is not too inadequate for stishovite. It is less appropriate for coesite, but, in view of the other uncertainties of the coesite equation of state (see below), it is an acceptable approximation.

Hugoniot temperatures are calculated according to a method given by *Ahrens et al.* [1969]. For this calculation the volume dependence of the Debye temperature θ_D is required. The Debye temperature is proportional to the Debye cutoff frequency. Thus, for consistency with the treatment of lattice dynamics discussed earlier, the square of θ_D may be expanded to second order in e. Thus

$$\theta_D(V) = \theta_D(V_0)(1 + ge + \tfrac{1}{2}he^2)^{1/2} \qquad (13)$$

EQUATIONS OF STATE

General. The procedure used here to determine the equation of state was to calculate, according to the last section, all relevant quantities, such as Hugoniots, isotherms, bulk modulus, and so forth, and to adjust the equation-of-state parameters to obtain a weighted least-squares fit to the data. The weighting basically was done according to the estimated standard error of the data, but it was also adjusted in some cases, as will be seen, to preferentially fit some of the data.

Some general features of the silica Hugoniot data and a representative set of calculated Hugoniots and isotherms are illustrated in Figure 1. Most of the Hugoniot data radiate from one of two points: the coesite or sitishovite zero pressure densities. The apparent zero pressure density of the data is the basis of the identification by *Trunin et al.* [1971*b*] of the Hugoniots of the two most porous silica samples as being in the coesite phase. This identification will be discussed subsequently; in the meantime the phase will be referred to as 'coesite.'

The Hugoniots of successively more porous silica, which start at zero porosity, become successively steeper up to the initial density ρ_0' of 1.77 g/cm^3, whose Hugoniot is nearly vertical on this plot. The 1.55-g/cm^3 initial density Hugoniot data are at densities lower than but fairly close to the zero pressure 300°K stishovite density, whereas the 1.35- and 1.15-g/cm^3 initial density Hugoniots are less steep and centered about the coesite density. The $\rho_0' = 1.55$ g/cm^3 Hugoniot may represent a mixture of 'coesite' and stishovite [*Trunin et al.*, 1971*b*]. This point will be discussed further below.

The calculated Hugoniots shown in Figure 1 (stishovite case 2 and 'coesite' case 1, discussed below) reproduce these features fairly well. However, the coesite-stishovite transition is not predicted by these calculations. Thus stishovite Hugoniots corresponding to all seven initial porosities are shown. The three most porous Hugoniots are notable for having negative slopes; there is a critical initial density for which the Hugoniot is vertical. The two most porous Hugoniots are shown as dashed lines, since they clearly fail to represent the corresponding data. The $\rho_0' = 1.55$ Hugoniot data approach but do not agree very well with the corresponding calculated stishovite curve shown in Figure 1. Only the two most porous 'coesite' Hugoniots are shown. The other Hugoniots will lie between these Hugoniots and the 300°K isotherm (shown as a short-dashed line) and clearly will not coincide with the corresponding data.