

reason to expect that it would also be appropriate for noncubic solids. In a following section it is shown that all the parameters appearing in (4) can be satisfactorily estimated for garnet hpp.

In addition to (4), several other expressions for the Grüneisen parameter have been in common use by previous investigators in reducing shock Hugoniot data [Slater, 1963; Dugdale and MacDonald, 1953]. These relations for γ have been based on particular assumptions involving the vibrational modes of lattice dynamic models. However, it has been pointed out by Knopoff and Shapiro [1969] that the results for $\gamma(x)$ calculated by these expressions are not mutually consistent and do not yield the thermodynamic value for γ at ambient conditions. Equation 4 avoids these difficulties and reduces the number of approximations required to a minimum [O'Keefe, 1970], because $\gamma(x)$ has been determined directly from the thermodynamic definition $\gamma = V(\partial P/\partial E)_v$, where V is the specific volume, rather than from a lattice dynamic model. Equation 4 has been used by O'Keefe [1970] to evaluate accurate pressure, volume, and temperature relations for copper from Hugoniot data.

The quantities α , C_p , and δ , which appear in (4), are not available for garnet hpp and therefore must be estimated from ancillary data. The thermal expansion α is an anharmonic parameter and as such is difficult to model theoretically unless higher-order terms in the potential function are defined. It is assumed for the present problem that the thermal expansion of a complex oxide compound can be represented by the weighted volumetric average of the individual component oxides, provided valence and coordination are consistent. That is,

$$\alpha = \sum_i \alpha_i V_i / \sum_i V_i \quad (6)$$

where V_i and α_i are the molar volume and the thermal expansion of the i th component oxide, respectively. From several estimates of the thermal expansion of known silicates using (6), it appears that such estimates should be accurate to within $\pm 20\%$. The specific heat at constant pressure is estimated according to

$$C_p = \sum_i C_{p_i} M_i / \sum_i M_i \quad (7)$$

where C_{p_i} and M_i are the specific heat and the gram formula weight of the i th component oxide, respectively. Specific heats estimated from (7) should be accurate to within $\pm 2\%$ on the basis of the results of several calculated examples. The appropriate quantities calculated for garnet hpp by using (6) and (7) are $\alpha = 23(10^{-6})/^\circ\text{K}$ and $C_p = 7.37(10^6)\text{ergs/g } ^\circ\text{K}$. Appropriate data for FeO (wustite), MgO, Al_2O_3 , and SiO_2 (stishovite), all of which involve sixfold coordinated cations, were used in the calculations.

Anderson *et al.* [1968] have compiled values of the Anderson-Grüneisen parameter δ for a number of oxides and silicates. Although there appears to be some correlation between δ and γ_0 , the relation is not clear. Examination of the data indicates that most of the values for δ fall between 2.0 and 8.0. For garnet hpp a value of 6.0 ± 2.0 is used; it will later be shown that uncertainty in this parameter has little effect on the calculated high-pressure phase material properties.

In addition to $\gamma(x)$ in (3), it is necessary to know the energy of transition $\Delta E_{tr} = E_0^h - E_0^l$, the difference between the specific internal energies of the low- and high-pressure phases at ambient conditions. A method of approximating this quantity by using the fact that the Gibbs free energy is constant across a phase transition has been given by McQueen *et al.* [1963]. Assuming that the change in entropy results in a negligible specific internal energy change in relation to the $P\Delta V$ term, we can write

$$\Delta E_{tr} = E_0^h - E_0^l = \{[(\rho_p^h - \rho_p)/\rho_p^h \rho_p] + [(\rho_0^h - \rho_0)/\rho_0^h \rho_0]\} P/2 \quad (8)$$

where the subscript p indicates density to be taken at the transformation pressure P . The transformation pressure has been estimated from the basic Hugoniot compression data and is indicated as point A in Figure 4; this point corresponds to density ρ_p in (8). Point B, estimated by extrapolating the garnet hpp Hugoniot data to the transformation pressure P , represents ρ_p^h . Substituting these values into (8), together with the ambient densities of the garnet and garnet hpp phases, yields an energy of transition of $\Delta E_{tr} = 2.13 \text{ kb/g/cm}^3$. Using point B rather than the garnet hpp isotherm

leads to a slight underestimate of ΔE_{tr} ; however, the difference is not significant, as will be obvious later.

Once the appropriate thermal properties of the high-pressure phase are estimated, it is possible to calculate the metastable Hugoniot data by using (3). Because values for C_0 and s appearing in (4) are unknowns to be evaluated, an iteration procedure is followed. Initially, values for C_0 and s are arbitrarily defined for use in the expression to calculate the Grüneisen parameter. The basic experimental Hugoniot data points are then reduced to the equivalent data points on the metastable Hugoniot. The data on the metastable Hugoniot are then indicated in the shock velocity-particle velocity plane by using (1) and (2). It has been shown by *Ruoff* [1967] that, if data in the $U_s - u_p$ plane can be represented by

$$U_s = C_0 + su_p + s'u_p^2 + \dots \quad (9)$$

and if an equation of state is assumed that is based on a bulk modulus variation with pressure of the form

$$K^S = K_0^S + K_0^{S'}P + \frac{1}{2}K_0^{S''}P^2 \quad (10)$$

the parameters in (9) take the form

$$C_0 = (K_0^S/\rho_0)^{1/2} \quad (11)$$

$$s = (K_0^{S'} + 1)/4 \quad (12)$$

$$s' = (24C_0)^{-1}$$

$$\cdot [s(7 - K_0^{S'} + 4\gamma) + 2K_0^S K_0^{S''}] \quad (13)$$

where

$$K_0^{S'} = (\partial K^S/\partial P)_S|_{P=0}$$

$$K_0^{S''} = (\partial^2 K^S/\partial^2 P)_S|_{P=0}$$

In most cases the uncertainty in the shock data precludes inclusion of s' and therefore of $K_0^{S''}$ in the data reduction. Note that, if $K_0^{S''} = 0$ in (10), the familiar *Murnaghan* [1944] equation of state results. When the second-order parameters are neglected, the elastic properties of the material may be determined from the relations

$$K_0^S = \rho_0 C_0^2 \quad (14)$$

$$(\partial K^S/\partial P)_S = 4s - 1 \quad (15)$$

where C_0 and s may be evaluated by a linear

least-squares fit to the metastable Hugoniot $U_s - u_p$ data. In addition, $(\partial K^S/\partial P)_S$ may be converted to the familiar mixed derivative by

$$(\partial K^S/\partial P)_T = (\partial K^S/\partial P)_S + \alpha T \gamma_0 \delta \quad (16)$$

where T is the absolute temperature. In the iteration scheme used in this analysis, new values of C_0 and s are generated for each successive repetition. These values are used in turn to evaluate $\gamma(x)$ in the following iteration. The procedure is simply repeated until convergence is attained, generally after only two or three iterations.

The results for garnet hpp are indicated in Table 3, which examines the effects of varying each significant input parameter. The first column indicates the basic set of input data estimated by using the methods discussed previously. The remaining columns indicate the effects of varying each individual factor on the final calculated K_0^S and $(\partial K^S/\partial P)_T$ values for garnet hpp. Generally, each parameter was altered by an amount in excess of its estimated uncertainty. For the present problem it is apparent that the uncertainties in the estimated input parameters have little effect on the calculated elastic properties. However, a significant difference is indicated when the initial density of the high-pressure phase is varied, as is evident from data sets *a* and *b*. A 20% uncertainty in the calculated K_0^S value results from a 1.5% estimated error in initial density. Clearly, the initial density is a very sensitive parameter in shock wave high-pressure phase data reduction, and the accuracy of the final results is closely related to the uncertainty in this factor.

ELASTIC PRECURSOR ANALYSIS

It has been shown by *Ahrens et al.* [1968] and *Graham* [1971] that, when the shock wave data for Al_2O_3 are corrected for residual stress differences in the high-pressure shock state, the resulting calculated values of the bulk modulus and its first pressure derivative are more consistent with published values determined by using ultrasonic methods. The 'strength effect' occurs when the material is shocked to a state along the deformational Hugoniot and is still able to support a shear stress of magnitude τ . The Hugoniot is offset above the 'hydrostatic' Hugoniot by a pressure of $\Delta P_H = \frac{4}{3}\tau$ [e.g., *Ahrens et al.*, 1969]. The