

larly dominant were two sets of internal fracture planes at 90° to each other. These are likely to be due to parting on {110} owing to the sudden release of pressure after passage of the shock wave; this type of parting occurs occasionally in natural garnets. Apparently, very little, if any, of the garnet material had been retained in the high-pressure phase. This observation was verified by X ray examination.

Initially, a standard Debye-Scherrer photograph was obtained for unshocked Salida garnet to be used as a basis for comparison with the shocked specimens. A 73-hour exposure produced 48 lines, all of which could be indexed as almandine-garnet except for two, which proved to represent two dominant ilmenite (FeTiO₃) lines when they were compared with American Standard Testing Material data. This exposure confirmed the presence of ilmenite inclusions within the Salida sample and indicated the necessity for this consideration in the analyses of the shocked sample X ray data. Several Debye-Scherrer photographs were then taken of two shocked Salida garnet specimens at various exposure times. Examination of these data, which involved exposure times of up to 100 hours, indicated the presence of several 'extra lines,' which did not appear on the Salida garnet standard and/or could not be indexed as garnet or ilmenite (FeTiO₃). It should be pointed out that all these lines were rated as <1 by a visual intensity estimate (maximum of 10); because the lines were so vaguely defined, no relative intensity differences could be estimated. As a result of the ilmenite (FeTiO₃) inclusions noted in the Salida garnet sample, a shock recovery experiment was also made on the garnet sample from Brazil. Several extra lines also were recovered in the analysis of the X ray data from this sample. However, only three lines out of eight appeared to be consistent between the two sets of photographs.

The paucity of data, the large uncertainties, and the lack of relative intensities preclude a unique structural interpretation in terms of a single high-pressure phase. In addition, it is not clear that the indicated lines even represent a single phase. Indeed, the subsequent heating effect associated with the passage of a shock wave suggests the possibility of the formation of phases unrelated to the phase observed in

the Hugoniot data. Therefore the powder diffraction data for a number of iron-silicate minerals and oxides were compared with the observed extra lines. These materials include α and β quartz, coesite, stishovite, fayalite, Fe₂SiO₄ (spinel), orthoferrosilite, clinoferrosilite, corundum, wustite, and hematite. In no instance could a consistent pattern be associated with any one mineral or any combination of these minerals in relation to the eight extra lines.

If the assumption is made that the observed extra lines do represent the remnants of a single high-pressure phase as defined by the basic Hugoniot data, an effort may be made to index the X ray data. In view of the results of the investigation into possible ABO₃ structures, a preliminary effort was made to index the lines as hexagonal with a and c lattice parameters appropriate for the corundum or ilmenite structures. However, the d spacing data could not be satisfied with such an interpretation. The data appear to require a structure with lower symmetry and therefore have been indexed tentatively as orthorhombic by *Ahrens and Graham* [1972]. Although the relation between the orthorhombic interpretation and the ilmenitelike inference from crystal chemical arguments is not clear, it is not unreasonable to envisage a 'distorted' modification of the basic ilmenite structure under shock conditions. Unfortunately, the quality of data does not warrant an accurate crystal structure determination. The density determined from the orthorhombic indexing is 4.44 ± 0.06 g/cm³, which is consistent with the determinations based on crystal chemical systematics discussed previously. Moreover, because this value is a representative average of the density estimates, it is adopted as the zero pressure density of the garnet hpp and used in all the subsequent Hugoniot data reduction.

HUGONIOT DATA REDUCTION

The pressure-density relation for a material that undergoes a shock-induced phase transformation has been described by *McQueen et al.* [1967] and *Ahrens et al.* [1969]. It is convenient to first reduce the experimental Hugoniot data for the high-pressure phase to a metastable Hugoniot, which represents the shock wave data

centered on the zero pressure density of the new phase. From the metastable Hugoniot data, it is then possible to derive, by using an appropriate equation of state, the isentrope and the isotherms of the high-pressure phase. The material properties are specified in accordance with the equation of state selected to represent the data. In the present analysis we use the fact that shock wave data are approximately linear in the shock velocity-particle velocity ($U_s - u_p$) plane within experimental error. The parameters of the linear $U_s - u_p$ relation, when they are combined with the Murnaghan equation of state, yield directly the appropriate compression of the high-pressure phase.

The initial problem is to correct the basic experimental Hugoniot data of the high-pressure phase to corresponding points consistent with the metastable Hugoniot. This procedure amounts to making a small pressure correction for a given (ρ, P_H) Hugoniot data point. It has been shown by *McQueen et al.* [1963] that it is possible to calculate a particular Hugoniot from a known Hugoniot centered at different initial conditions. The appropriate relation, which follows from the basic definition of the volume-dependent Grüneisen parameter γ and the Rankine-Hugoniot relations, may be written as

$$P_M = \frac{P_H \{1 - \gamma/2[(\rho/\rho_0) - 1]\} - \gamma\rho(E_0 - E_0^h)}{1 - \gamma/2[(\rho/\rho_0^h) - 1]} \quad (3)$$

Here ρ_0 and E_0 and ρ_0^h and E_0^h refer to initial conditions for the low- and high-pressure phases, respectively, where E represents specific internal energy. To apply (3) and calculate pressure on the metastable Hugoniot P_M , it is necessary to know $\gamma(\rho)$ for the high-pressure phase and the energy of transition $\Delta E_{tr} = E_0 - E_0^h$ (evaluated at ambient conditions).

A relation for calculating the volume dependence of the quasi-harmonic Grüneisen parameter $\gamma(\rho)$ in the classical temperature region has been derived by *Pastine and Forbes* [1968]. This relation is exact, provided that U_s is given rigorously by $U_s = C_0 + su_p$ along each individual Hugoniot. We assume this to be the case in the present analysis. The Pastine-Forbes relation is given by

$$\begin{aligned} \gamma(x) = & 2x(1-x)\{\delta[s(1-x) - 1] \\ & + 2sx\} + 2x^2[1 - s(1-x)] \\ & + 4x(1-x)^2\nu \cdot \{2(1-x)^3\nu \\ & + (1-x)^2[\delta(s(1-x) - 1) + 2sx] \\ & + (1-x)(1+x)[1 - s(1-x)] \\ & + (2C_p/\alpha C_0^2)[1 - s(1-x)]^3\}^{-1} \quad (4) \end{aligned}$$

where $x \equiv \rho_0/\rho$, C_0 , and s are the parameters in the linear $U_s - u_p$ relation, C_p is the specific heat at constant pressure, and α is the volume thermal expansion. The parameter δ appearing in (4) is the Anderson-Grüneisen parameter and is defined as

$$\delta = \frac{1}{\alpha K^s} \left(\frac{\partial K^s}{\partial T} \right) \Big|_{p=0}$$

where K^s is the adiabatic bulk modulus. In addition, the parameter ν is given by

$$\nu = \frac{1}{\alpha} \left(\frac{\partial s}{\partial T} \right) \Big|_{p=0}$$

The preceding expression for $\gamma(x)$ may be used in (3) to calculate the metastable Hugoniot.

The use of (4) is dependent on whether the various parameters appearing in the relation can be evaluated. The quantities C_p and α are

generally available in the literature for most oxides and silicates; however, for high-pressure phases these properties must be calculated or estimated. In addition, the quantity $(\partial K^s/\partial T)_p$, available from ultrasonic data for many low-pressure phase materials, must be evaluated to define the parameter δ . In some cases, δ may be evaluated by using the Wachtman-Anderson relation [*Anderson*, 1966]. The quantity ν is difficult to evaluate; however, an approximation has been provided by *Pastine* [1970]:

$$\nu \simeq s/4(\gamma_0 + 2 - s) \quad (5)$$

where γ_0 is the Grüneisen parameter evaluated at ambient conditions. Equation 5 was originally determined for cubic solids; however, there is