The shock-wave propagation velocity through the sample may be detected by optical techniques,[27] Sandia quartz gauge techniques,[28] charged pins,[29] or electrical response measurements from the shock-loaded samples.[23] An accuracy of about ±1% is normally achieved. For impact experiments utilizing impacts produced by a quartz gauge[28] and shock arrival times indicated by quartz gauges, shock-velocity accuracies of ±0.5% are achieved. Shock-velocity measurements with the Sandia velocity interferometer[30] can achieve accuracies of a few tenths of 1%. These experimental capabilities indicate that the best precision of shock-velocity measurements approach those achieved ultrasonically. However, the nominal accuracy of ±1% achieved in most shock experiments is suitable to establish accurate (2%–6%) high-order constants when large compressions are achieved.

### B. High-Order Elastic Constants

Fowles[1] has expressed the finite elastic strain theory, as developed by Thurston,[31] in terms of the one-dimensional compressions achieved in the shock-compression experiment. An expansion of strain energy in a power series in finite strain, $P_x$, gives the result that:

$$\sigma_x=(V/V_0)[C_{xx}P_x+\tfrac{1}{2}C_{xxx}P_x^2+\tfrac{1}{6}C_{xxxx}P_x^3], \qquad (3)$$

when the expansion is arbitrarily terminated at the cubic term. In Eq. 3, $\sigma_x$ is the longitudinal component of stress in the shock propagation direction taken to be the $x$ axis, $C_{xx}$ is the usual adiabatic second-order elastic constant for uniaxial compression in the shock direction, $C_{xxx}$ is the longitudinal third-order elastic constant, $C_{xxxx}$ is the longitudinal fourth-order elastic constant, and $P_x\equiv\eta[(\eta/2)-1]$.

The shock-compression experiments provide values for $\sigma_x$ and $\eta$ that can be used in Eq. 3 to evaluate those longitudinal elastic constants that contribute significantly to the magnitude of the stress. The magnitude of the contribution of a given constant depends very strongly upon the magnitude of the compression; high-order contributions at typical static compressions of less than 0.1% are negligible, whereas high-order contributions for typical elastic shock compressions of a few percent are pronounced. It is apparent from Eqs. 1–3 that the shock-compression measurements determine only those longitudinal constants in the direction of shock propagation.

Because of the somewhat arbitrary definition of strain utilized in Thurston's finite strain development, it is possible that alternate formulations[32,33] may give a better representation to compression data. In any event, however, it is useful to determine the extent to which the data can be represented by these constants.

Unlike the static compression measurements that provide isothermal derivatives of adiabatic constants, the elastic shock compression measurements provide adiabatic derivatives of adiabatic constants. However, the difference between the two thermodynamic conditions is not significant for the present accuracies achieved in the third-order constant measurements.

## II. DATA ANALYSIS

Examination of Eq. 3 indicates that a single $\sigma_x$, $\eta$ measurement cannot be used to calculate a high-order constant unless all lower-order constants are known. Even though a single experiment cannot distinguish between various high-order elastic constants, the best fit to data obtained over a wide range of compressions must accommodate the various high-order contributions that are significant in different compression ranges. The principal contribution to the stress in the elastic compression range is the second-order constant, which is frequently known to a precision of ±0.1%. Thus, it is appropriate to assume that the second-order contribution can always be calculated and proceed to determine third- and fourth-order constants.

At compressions of less than a few tenths of 1%, the third- and fourth-order contribution to the magnitude of the stress is too small to influence the data. As compressions become larger, third-order contributions become significant, whereas the fourth-order contribution is too small to influence the data. If elastic compressions of a few percent are achieved, the fourth-order contributions may become significant.

Although a cubic polynomial can be fit to the $\sigma_xV_0/V$ vs $P_x$ relation, the iterative procedure given below has the feature of taking full advantage of the precisely known second-order constant before proceeding to successively less well characterized constants. Consider calculating an elastic constant, $C_{xxx}^+$, representing all contributions greater than second order, from observed $\sigma_x$ vs $\eta$ data. In this case, it follows from Eq. 3 that

$$C_{xxx}^+\equiv(2/P_x^2)[\sigma_xV_0/V-C_{xx}P_x], \qquad (4)$$

where $C_{xx}$ is taken to be the value obtained from ultrasonic measurements. If $C_{xxxx}$ is zero, or the contribution of $C_{xxxx}P^3$ is negligible at the compression in question, $C_{xxx}^+=C_{xxx}$ and the third-order constant is determined. In all cases, however, $C_{xxx}^+$ can serve as the first approximation to $C_{xxx}$. Based on the shock-compression data, an iterative procedure can then be followed to give the best set of $C_{xxx}$ and $C_{xxxx}$ constants over the entire compression range. If data exist over a sufficiently large pressure range, the high-order longitudinal constants can be independently determined.

The iterative procedure follows a perturbation technique as follows:

(1) Calculate $C_{xxx}^+$ from Eq. 4 for all data.

(2) Compute a $\sigma_x$ vs $\eta$ relation from $C_{xxx}^+$ and $C_{xx}$ and compare it to the observed $\sigma_x$ vs $\eta$ data.

(3) If $C_{xxx}^+$ gives a good fit to the data over the entire compression range, $C_{xxxx}$ has a smaller value than can be observed and $C_{xxx}^+=C_{xxx}$.

TABLE I. Comparison of high-order elastic constants of sapphire.[a]

| Method | Present work,[b] shock | Present work,[c] shock | Hankey *et al.*,[d] static ultrasonic | Gieske,[e] static ultrasonic | Carr,[f] 4.2°K, microwave |
|---|---|---|---|---|---|
| Maximum strain | 4.0% | 2.2% | 0.1% | 0.5% | $\sim 10^{-7}$ |
| $C_{111}$ | $-3.3\pm0.3$ | ... | $-3.87\pm0.07$ | $-3.9\pm0.03$ | $-3.8\pm0.3$ |
| $C_{333}$ | $-3.3\pm0.3$ | $-3.25\pm0.1$ | $-3.34\pm0.1$ | $-3.1\pm0.03$ | $-2.1\pm0.1$ |
| $C_{1111}$ | $50\pm15$ | ... | ... | ... | ... |
| $C_{3333}$ | $50\pm15$ | ... | ... | ... | ... |

[a] Units are $10^4$ kbar, temperatures are 25°C except for the work of Carr.
[b] Data from Ref. 19.
[c] Data from Ref. 20.
[d] Ref. 8.
[e] Ref. 36.
[f] Ref. 11.

(4) If systematic differences are observed, the $C_{xxx}^+$ value includes contributions from $C_{xxxx}$. Compute a value of $C_{xxxx}$ from $C_{xxx}^+$ used in Eq. 3.

(5) Iterate with assumed values of $C_{xxx}$ and $C_{xxxx}$ until a good fit is obtained over the entire compression range.

(6) Express errors in the constants in terms of the range of values of constants which give an equally good fit to the observed experimental data.

For successful application of this technique, shock-compression data are required over a large compression range. Unfortunately, most elastic shock-compression data are limited to Hugoniot elastic limit points; however, the sapphire data of Graham and Brooks[19] extend from 0.3% to 4% compression and the sapphire data of Barker and Hollenbach[20] extend from 0.5% to 2.2%, while their fused quartz data extend from 0.2% to 10%. These data are used to compute third- and fourth-order longitudinal elastic constants for sapphire and fused quartz in Secs. III-A and III-B.

## III. RESULTS

### A. Sapphire

Before proceeding with detailed analysis of the sapphire data, several general features of the elastic shock-compression data on sapphire of Graham and Brooks[19] should be noted. The data were obtained from experiments in three crystallographic orientations, 0°, 90°, and 60°. The 0° and 90° orientations are "specific" crystallographic directions and purely longitudinal compression modes are achieved.[34] The $C_{11}$ and $C_{33}$ values differ by only 0.9%.[35] Thus, even though sapphire has trigonal symmetry, the longitudinal elastic constants do not vary significantly with orientation. This is an important consideration, since a number of experiments were also performed on natural-growth 60°-orientation samples. These samples are more readily available in large diameters required for shock-compression experiments. Since this orientation is not a specific direction, these samples would not be expected to exhibit pure longitudinal motion. However, since the longitudinal constants do not vary strongly with orientation, it might be expected that the nonlongitudinal contribution is small. A special experiment reported in Ref. 19 found that these 60° samples responded in a purely longitudinal mode within the experimental error. The data have the feature that, within the observed experimental scatter, all data from the three orientations fall on a common compression curve. Thus, to a good approximation, the high-order constants are independent of orientation for the three orientations investigated.

To analyze the data of Graham and Brooks, the stress-versus-compression data are smoothed by fitting to a quadratic polynomial with no restraints applied to the data. Following this, a mean value of $C_{xx}=4990$ kbar is chosen for all orientations[35] such that the second-order contribution is computed from the ultrasonic data. The analysis shows that $C_{xxx}^+=-3.6\times10^4$ kbar but that a good fit is not obtained over the entire compression range. Upon iteration, the high-order longitudinal constants are found to be $C_{111}\approx C_{333}=-(3.3\pm0.3)\times10^4$ kbar and $C_{1111}\approx C_{3333}=(5\pm1.5)\times10^5$ kbar. The errors are established by observing the range of values that give an equally good fit to the data within one standard deviation of the raw fit to the data. Because the second-order contribution dominates at smaller compressions, the high-order constants are determined by data in the range from 100 to 200 kbar.

The sapphire data of Barker and Hollenbach were obtained on 0° samples. Even though their shock-velocity measurements are more precise than those of Graham and Brooks, the compression range that they utilized is too small for significant contributions from the fourth-order constants. Analysis of their data gives: $C_{333}^+=C_{333}=-(3.25\pm0.1)\times10^4$ kbar.

The data are compared to third-order constants as determined by static stress and microwave techniques in Table I. The data at 25°C from all sources are found to be in reasonable agreement. The fourth-order constants of sapphire are obtained for the first time. It appears that the accuracy of the third-order constants obtained from the shock-compression data is comparable with that achieved in the static experiments. The low-temperature microwave second-harmonic-generation measurements of Carr[11] cannot be directly compared to