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# Dynamic Compression of Quartz

# RICHARD FOWLES

Shock Dynamics Laboratory, Physics Department Washington State University, Pullman, Washington 99163

Measurements of the stress-density states achieved during shock compression of X-, Y-, and Z-cut crystalline quartz are presented. For the elastic shocks comparison is made with predictions based on acoustic measurements of the second- and third-order elastic coefficients, and observed differences, which are substantial, are used to calculate two of the fourth-order coefficients. The values of  $c_{\rm HH}$  and  $c_{\rm sess}$  are found to be  $159.3 \pm 20\% \times 10^{12}$  and  $184.9 \pm 20\% \times 10^{12}$  dynes/cm<sup>2</sup>, respectively. This procedure, employing the difference between acoustic measurements and shock wave measurements to evaluate higher-order elastic coefficients, should be generally applicable to solids that sustain large-amplitude elastic waves.

# INTRODUCTION

The shock compression of quartz is of particular interest because of its importance to geophysics, its widespread use in shock wave studies as a pressure transducer, and its representation of a different class of materials than the more thoroughly studied metals. In this paper we describe measurements similar to those reported by *Wackerle* [1962]. The data are in substantial agreement; however, the recording techniques were somewhat different, so that the present results provide independent corroboration, in most respects, of Wackerle's data. (The present data were reported originally in *Fowles* [1961a].)

As in Wackerle's experiments double shock fronts were observed. The first is identified as the elastic shock; the second is the 'plastic' shock in which permanent deformation occurs. The separation into a fast and slow front is thus attributed to instability of the initial shock caused by yielding at the elastic limit [Duvall and Fowles, 1963]. For X- and Y-cut crystals the elastic amplitudes are in the range 55-85 kb; for Z-cut crystals elastic amplitudes are observed in the range 100-150 kb. The maximum pressure in these experiments (230 kb) was not high enough to show clearly the phase transition to stishovite.

In addition to describing the experiments and the results, we examine the agreement between the uniaxial stress-strain data derived from shock experiments and predictions based on finite strain theory and the second- and third-order elastic constants measured by Mc-Skimin et al. [1965] and Thurston et al. [1966]. From this comparison it is clear that shock wave measurements and low-pressure acoustic measurements are complementary methods for evaluating higher-order elastic coefficients.

#### EXPERIMENTS

Experimental method. In the experiments shock propagation velocities and associated free surface velocities were measured in  $\alpha$  quartz crystals oriented as X, Y, or Z cuts. (Synthetic crystals were supplied by Valpey Corporation.) Shock waves of varying intensity were generated by plane-wave explosive lenses with or without additional explosive pads.

The experimental arrangement is shown schematically in Figure 1. A 4-inch-diameter explosive lens (and in some cases an explosive pad) was cemented to one surface of a  $\frac{1}{2}$ inch-thick, 5-inch-diameter Dural plate. The quartz specimens (usually two) were cemented to the opposite lapped surface of the plate. The specimens were accurately flat and polished; the tolerance on crystallographic orientation was  $\pm 1^{\circ}$ . The faces of the specimens in contact with the plate were vapor-plated with aluminum to yield a reflecting surface. Lucite mirrors, also aluminized on their inside faces, were cemented to the outer surfaces of the specimens at angles of 3° to 8°. The edge of the lucite mirror in contact with the specimen was, in each case, set back from the edge



Fig. 1. Diagram of experimental assembly.

of the specimen at least one specimen thickness to avoid interference from edge effects. The X, Y, or Z orientation refers to the smallest linear dimension and also designates the direction of shock propagation. The X-cut crystals were measured in both the plus and minus orientations because of the large differences observed in electrical experiments [Neilson et al., 1961].

In some of the experiments an inclined lucite mirror was cemented directly to the aluminum plate. Its function was to measure the freesurface velocity of the aluminum to permit impedance-match solution to the final shocked states [Duvall and Fowles, 1963].

The angles of the inclined mirrors with respect to the quartz surfaces were measured after assembly by mounting the assembly on a mill table and observing with a telescope the superposition of a cross-hair and its image reflected alternately in the quartz and lucite surfaces. The angles could thus be measured to a precision of 0.1%. Some difficulty was encountered in keeping the lucite mirrors extremely flat. It was necessary to allow angular deviations of up to  $\pm 1$  min of arc. In each case this amounted to less than  $\frac{1}{2}$ % of the total angle.

To obtain the desired accuracy in shock velocity,  $\pm 1\%$ , good contact (0.0002 inch) between the inside edge of the inclined mirror and the outer quartz surface was required. A contact in which no transmitted light was visible was considered satisfactory.

To avoid complications due to air shocks the

assembly was evacuated before firing to a pressure of less than 0.05 torr. A hemicylindrical section of lucite tubing cemented to the aluminum plate served as a vacuum chamber. (A photograph of an assembly, without explosive, before firing is shown in Figure 2.)

The assembly was viewed through a slit of a rotating-mirror streak camera aligned along the centers of the inclined mirrors in the direction of maximum inclination (i.e., the direction in which the mirror angles were previously measured). The camera was focused on the reflecting surfaces. The slit width was 0.05 mm; the time resolution, determined from the slit width and the camera writing speed (3.81 mm/ $\mu$ sec), was approximately 0.01  $\mu$ sec.

Illumination was provided by an explosive argon light source consisting of a 4-inch-diameter, 18-inch-long cardboard tube with a 1inch pad of composition C-3 explosive at one end. A ground glass diffusing screen was placed over the other end, and argon flowed continously through the tube. The light source explosive was initiated simultaneously with the plane-wave lens of the experimental assembly. The resulting strongly luminous shock in the argon produced a bright reflection from the aluminized surfaces a few microseconds before the first arrival to be recorded in the quartz.

A drawing of the complete arrangement as it appeared before firing is shown as Figure 3.

An abrupt change in intensity of the light reflected from the aluminized surfaces of the assembly showed arrival times of the shock fronts and free surfaces on impact with the mirrors.

A streak camera photograph taken in this



Fig. 2. Photograph of experimental assembly.

# DYNAMIC COMPRESSION OF QUARTZ



SLIT DIRECTION

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Fig. 3. Diagram showing relation of experimental assembly, light source, and camera.

manner is shown in Figure 4. The two specimens in this shot were Z-cut; the upper one was 1/8-inch thick and the lower one was 1/4inch thick. The final pressure was approximately 200 kb. At time  $T_0$  the reflection from the rear (aluminized) face of the quartz extinguishes abruptly as the shock arrives at the quartzaluminum interface. At time  $T_1$  the first shock arrives at the quartz free surface. The traces are relatively smooth until the change in slope caused by the arrival of a second shock at time  $T_2$ ; thereafter the traces are slightly irregular. A slight curvature to the trace of the first shock can be detected. This slowing up of the free surface is due to stress-relaxation effects, as was pointed out by Wackerle [1962].

The reason for the loss of reflectivity at the quartz-aluminum interface is not understood; however, it served as a distinct marker of the shock arrival time. That this trace does indeed occur at the proper time is shown by the experiments in which inclined mirrors were also placed on the aluminum surface. In those experiments the time of the first motion of the surface coincides with the traces due to loss of reflectivity.

The free-surface traces, as the free surfaces impact the lucite mirrors, are due in part to rotation of the mirrors resulting from the impact. This rotation changes the angle at which the mirrors view the light source. Note that between times  $T_1$  and  $T_2$  (Figure 4) the freesurface traces are evident because of brightening of the light intensity as the mirrors view the light source more nearly along its axis. The ground glass diffusing screen on the face of the light source is somewhat directional in its transmission. Distinct free-surface traces were obtained by adjusting the light source so that the line of sight from the free-surface mirrors initially intersected the side of the argon tube and did not intersect the shock in the argon (Figure 3). On rotation the free-surface mirrors directly view the argon shock, with consequent increase in intensity. The loss of reflected light as the second shock arrives at time  $T_2$  is reproducible and, together with the change in smoothness of the trace, evidently signifies a change in character of the surface. These observations are consistent with the conclusion based on the data that the first shock causes



Fig. 4. Streak camera photograph showing shock arrival times and free-surface traces for shot 7394.

an irreversible change in the material—perhaps to a fractured state.

For reliable results the point of collision of the quartz free surface with the inside surface of the mirror must travel with supersonic velocity with respect to both quartz and lucite (non-jetting configuration). Consequently, the initial mirror angle must be less than approximately

$$\alpha_{\max} = \sin^{-1} \left( u_f / U_s \right)$$

where  $u_t$  is the quartz free-surface velocity and  $U_s$  is the larger of the two shock wave velocities in quartz and lucite. This criterion restricted the usable mirror angles to less than about 8°.

Data reduction. The shock velocities were determined from distances measured on the film and the known writing speed of the camera. The velocity of the second shock requires corrections because of the motion of the free surface and because of the interaction of the second shock with the reflection of the first shock. The first of these corrections is straightforward, and a simple derivation gives

$$U_2 = \frac{d + u_{f1}(T_2 - T_1)}{T_2 - T_0}$$
(1)

where d is the initial specimen thickness,  $u_{t1}$  is the free-surface velocity due to the first shock, and  $T_0$ ,  $T_1$ , and  $T_2$  are the arrival times of the shock fronts as shown in Figure 4.

The correction required by the interaction of the second shock with the reflection of the first requires knowledge of the state (and constitutive relation) of the quartz in the region between the two fronts and cannot be made unequivocally. The assumption that the material is stressed and relieved only elastically by the first wave leads, however, to a large correction and unreasonably high compression for the state behind the second shock in shot 7394 (Table 1). The results from that shot are the most sensitive to this correction because the second shock was relatively slow with respect to the first. For the other experiments the correction is smaller and does not appreciably affect the conclusions.

It should be emphasized, however, that the result for shot 7394 implies that an irreversible change in the material properties occurs between the two shock fronts. This conclusion is consistent with the observed relaxation of the state of the first shock and with the photographic observations just mentioned. It is not consistent with an assumption of elastic-plastic behavior as exhibited, for example, by aluminum [Fowles, 1961b].

Because of the arbitrariness of the interaction correction the data are here reported without such a correction. The correction used by *Wackerle* [1962] is plausible but does not significantly change the data of this paper.

The free-surface velocities were calculated from the measured slopes of the traces by means of the relation

$$u_f = \tan \alpha' / MF \tan \gamma' \tag{2}$$

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where  $\alpha'$  is the effective angle of the inclined mirror with respect to the quartz surface,  $\gamma'$  is the angle of the trace on the film with respect to the space axis, M is the magnification or the ratio of the distance on the film to the corresponding distance on the shot, and F is the writing speed of the camera. The parameters  $\alpha'$  and  $\gamma'$  of this relation are not identical to their nominal values  $\alpha$  and  $\gamma$  because of tilt of the incident shock and slight departures from orthogonality of the slit and sweep directions. The corrections are given by

$$\tan \alpha' = \tan \alpha (1 + \theta' / \tan \gamma)$$

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$$\gamma' = \tan \gamma \sec \delta (1 - \tan \gamma \tan \delta)$$

where  $\alpha$  is the angle of the inclined mirror with respect to the quartz surface,  $\theta'$  is the angle of shock tilt as measured on the film,  $\delta$  is the angle of the slit with respect to the normal to the sweep direction, and  $\gamma$  is the angle of the trace with respect to the slit direction (Figure 5).

The observed shock wave velocities and associated free-surface velocities are given in Table 1 with the initial conditions for each experiment and other quantities derived from the measured velocities.

The experimental precision based on assembly tolerances, camera resolution, and film reading errors is estimated to be  $\pm 1\%$  in shock velocity and  $\pm 5\%$  in free-surface velocity. Most of the

			Pellet					First Shock				Second Shock					
				Arrival Times		Free Surface Velocities		Shock	Particle	Stress		Internal	Shock	Particle	Stress		Internal
Shot No.	Explosive System	Orienta- tion	ness, mm	$t_1 - t_0,$ µsec	t <sub>2</sub> - t <sub>0</sub> , μsec	$u_{f_1}, mm/\mu sec$	$u_{f_3},$ mm/ $\mu$ sec	$U_{1},$ mm/ $\mu$ sec	$u_{1},$ mm/ $\mu$ sec	σı, kb	$V_{1}/V_{0}$	$E_1 - E_0,$ cal/g	$U_{2},$ mm/ $\mu$ sec	u <sub>2</sub> , mm/μsec	σ <sub>2</sub> , kb	$V_2/V_0$	$E_2 - E_0,$ cal/g
5648	P-40 lens	X (-) to (+)	6.378	1.057	1.296	0.692	1.62	6.03	0.346	55.5	0.9426	14.3	5.05	0.810	117.0	0.8495	86.6
		X (-) to (+)	6.388	1.075	1.308	0.807	1.62	5.94	0.403	63.7	0.9320	19.5	5.03	0.810	117.4	0.8500	86.4
5807	P-40	X (+) to (-)	6.388	1.079	1.320	0.836	1.52	5.92	0.418	65.7	0.9294	20.9	4.99	0.758	110.1	0.8603	75.6
		Z	6.383	0.876		1.02		7.28	0.508	98.4	0.9302	30.9		N	lot observ	ed	
5880	P-40	(+) to $(-)$	6.391	1.078	1.322	0.754	(1.66)	5.93	0.377	59.4	0.9364	17.0	4.97	(0.828)	118.1	0.8444	90.5
		Initial state in Al			1.47												
5921	P-40 + 1 in. comp B	X (+) to (-)	6.380	1.079	1.146	(0.786)	2.630	5.91	0.393	(61.8)	(0.9335)	18.5	5.61	1.315	198.8	0.7686	212.0
		Y	6.347	1.020	1.144	0.994	2.56	6.22	0.497	82.2	0.9201	29.6	5.66	1.281	199.0	0.7803	206 6
5920	P-40 + 1 in. comp B	X (-) to (+)	6.391	1.069	1.139	(0.687)	2.63	5.98	0.344	(54.6)	(0.9426)	14.1	5.65	1.315	199.9	0.7702	211.7
		Z	6.380	0.876		1.40		7.28	0.698	135.1	0.9041	58.3		I	Not observ	ed	
6009	P-40	Y Z	6.358 6.388	1.058	1.363	0.819	1.43	6.01 7.15	0.410	65.3 106.6	0.9320	20.0	4.85	0.713	103.7	0.8684	68.4
5997	P-40 + 2 in. comp B	Y	6.360	1.011	1.158	1.03	3.00	6.29	0.515	86.2	0.9180	58.5	5.62	1.50	231.9	0.7411	311.9
		Z	6.386	0.871	1.201	1.40	(2.63)	7.33	0.700	136.1	0.9046	34.0	5.70	(1, 32)	(227.2)	(0, 7924)	217 6
7363	P-40	Z	6.599	0.914	1.824	1.04	1.58	7.22	0.520	99.8	0.9280	32.4	4.14	0.79	127.4	0.8598	102.2
		Z	3.396	0.469	0.958	1.09	1.65	7.24	0.545	104.8	0.9247	35.5	4.10	0.82	133.4	0.8519	113.6
7394	P-40 + 1 in. comp B	Z	6.607	0.899	1.336	1.27	2.32	7.35	0.635	123.6	0.9139	47.9	5.36	1.16	195.8	0.8124	193.9
		Z	3.411	0.462	0.681	1.51	2.47	7.38	0.751	147.6	0.8981	67.7	5.49	1.23	215.3	0.8066	217.2
7395	P-40	Y. Y	6.601 3.399	$1.088 \\ 0.562$	1.448 0.745	0.836 0.862	1.60 1.58	6.07 6.05	0.418	67.7 69.3	0.9308 0.9287	22.2 22.2	4.77 4.77	0.800	114.9 113.9	0.8495 0.8519	85.3 85.5

# TABLE 1. Summary of Experimental Data

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Initial density,  $\rho_0 = 2.6485$  g/cm<sup>3</sup>. Points in parentheses are less reliable.

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DYNAMIC COMPRESSION OF QUARTZ

# RICHARD FOWLES



Fig. 5. Definition of parameters used in adjusting streak camera data.

error in free-surface velocity is due to uncertainty in reading the angle  $\gamma'$  ( $\pm 1^{\circ}$ ).

Experimental results. The observed shock velocities are plotted as functions of the shock particle velocities (taken to be one-half the free-surface velocities) in Figure 6. Data from Wackerle [1962] and V. Gregson (personal communication, 1963) are also shown. The data of Wackerle are his 'average'' values, shown for comparison because they were determined on the same basis as the present results. The solid curves are predicted from finite strain theory. The agreement among the experimental data is seen to be generally satisfactory.

The stress-compression states were calculated from the measured velocities by means of the Rankine-Hugoniot jump conditions [Duvall and Fowles, 1963]:

$$V/V_0 = 1 - [(u_I - u_0)/U_I - u_0]$$
  

$$\sigma_I - \sigma_0 = \rho_0(U_I - u_0)(u_I - u_0)$$
(3)

Fig. 6. Shock velocity as function of particle velocity. Curves labeled 3rd, 4th, are fits based on zero-pressure elastic constants up to third- and fourth-order, respectively, for X- and Z-cut crystals.



Fig. 7. Stress-volume states resulting from shock compression of X-cut quartz. Solid curve is Bridgman's hydrostatic data. Curves labeled 3rd, 4th are fits based on zero-pressure elastic constants to third- and fourth-order.

In these equations, V is specific volume, u is particle velocity, U is shock velocity,  $\sigma$  is stress normal to the shock front, and  $\rho$  is density. Subscripts 0 refer to the state ahead of the shock; subscripts I refer to the state behind the shock. Velocities are with respect to laboratory coordinates. Figures 7, 8, and 9 show the results in the stress specific-volume plane for X, Y, and Z crystals, respectively. Bridgman's [1947] hydrostatic curve based on measurements to 98 kb is shown for comparison. The curves labeled 3rd, 4th, are fits based on lowpressure acoustic measurements and finite elastic strain theory.

These plots show clearly the following important features of the compression: (1) extremely high-amplitude elastic waves, up to 150 kb in Z-cut quartz, (2) loss of rigidity above the elastic limit, as shown by the agreement of the higher-pressure shock data with extrapolation of the hydrostatic data, and (3) lack of a unique value for the Hugoniot elastic limit.

This behavior implies that yielding is not due to dislocation motion, as in a metal, but is analogous (or identical) to fracture. It is shown below that the shear stresses behind the elastic shocks approach the theoretical shear strength of the crystal lattice.

The range of the present data is not sufficient to show clearly the transformation to stishovite, as indicated by Wackerle's higherpressure measurements.

# FINITE ELASTIC STRAIN THEORY

Because the strains behind the elastic shocks are relatively large, it is of interest to examine the agreement of the data with predictions of finite strain theory. Predictions are made possible by the work of *Thurston et al.* [1966] and  $McSkimin \ et \ al.$  [1965] on the third-order elastic constants of quartz. Such comparisons should indicate the extent to which third-order constants are sufficient to describe the stressstrain behavior at strains of the order of 5-10%. The constants are determined from precise acoustic measurements at strains of less



Fig. 8. Stress-volume states resulting from shock compression of Y-cut quartz. Solid curve is Bridgman's hydrostatic data.



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Fig. 9. Stress-volume states resulting from shock compression of Z-cut quartz. Solid curve is Bridgman's hydrostatic data. Dashed curves labeled 3rd, 4th, are fits based on zero-pressure elastic constants to third- and fourth-order. The curve labeled X represents the tangential stresses, calculated from constants up to and including third order.

than 0.1%. Anderson [1966] has already shown that the second- and third-order constants alone give reasonably good predictions for hydrostatic compressions of up to about 15% in quartz, provided that the constants are used in the Murnaghan logarithmic equation or the Birch equation of state.

Discrepancies between the observed and predicted stress-strain curves can be used alternatively to evaluate fourth- and higher-order constants or to guide the formulating of improved or more convenient constitutive assumptions. Finally, to the extent that the thirdorder constants give adequate predictions, the normal stresses parallel to the shock fronts can be calculated from the observed stresses normal to the fronts; hence, the shear stresses sustained (momentarily) by the crystal can be deduced.

*Finite strain fundamentals.* (This section is a summary of parts of the theory presented by

Thurston [1964].) Denote the coordinates of a mass element in an initial (unstrained) coordinate system by  $a_i$ , and the coordinates in a final (strained) system by  $x_i$ , with the transformation given by

$$x_i = x_i(t, a_1, a_2, a_3)$$
  $i = 1, 2, 3$  (4)  
where

$$a_i = x_i(t_0, a_1, a_2, a_3)$$

 $t_0$  being a reference time. The  $x_i$  are thus Eulerian, or spatial, coordinates and the  $a_i$  Lagrangian, or material, coordinates.

For this transformation one can derive an expression for the ratio of specific volumes

$$V/V_0 = J = \left| \frac{\partial x_i}{\partial a_s} \right| \tag{5}$$

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J is thus the determinant of the Jacobian of the transformation or the 'functional determinant.'

The strain  $N_{jk}$  is defined, somewhat arbitrarily, from the difference in the squares of the lengths of line elements by

$$N_{ik} da_i da_k = dx_i dx_i - da_i da_i$$

$$N_{ik} = \frac{1}{2} \left( \frac{\partial x_i}{\partial a_i} \frac{\partial x_i}{\partial a_k} - \delta_{ik} \right)$$
(6)

Here and in the following the Einstein summation convention for repeated subscripts applies.  $\delta_{IE}$  is the Kronecker delta.

Expanding the internal (strain) energy in a power series in the strains, one obtains (at constant entropy)

$$\rho_0[E(N, S) - E(0, S)]$$

$$= (1/2)c_{ijkl}^* N_{ij} N_{kl} + (1/6)c_{ijklmn} N_{ij} N_{kl} N_{mn}$$

$$+ (1/24)c_{ijklmnpa}^* N_{ij} N_{kl} N_{mn} N_{pq} + \cdots (7)$$

In this expression the  $c_{ijk} \cdot \cdot \cdot$ , represent the second- and higher-order isentropic elastic stiffness coefficients. The first-order term is missing because the reference state is considered to be zero stress and strain.

We now define quantities, called thermodynamic tensions, by

$$t_{ij} = \rho_0 (\partial E / \partial N_{ij})_s \tag{8}$$

In terms of these quantities the elastic constants are

$$c_{ijkl}^{s} = \left(\frac{\partial t_{ij}}{\partial N_{kl}}\right)_{s} = \frac{\partial^{2} E}{\partial N_{ij} \partial N_{kl}}$$

and similarly for the higher-order coefficients. Consequently,

$$\rho_0 dE = t_{ij} dN_{ij} \qquad (dS = 0)$$

Finally, the equilibrium (nondissipative) components of the stress are obtained from the thermodynamic tensions by the relation

$$\sigma_{km} = \frac{1}{J} \frac{\partial x_k}{\partial a_i} \frac{\partial x_m}{\partial a_i} t_{ij} \tag{9}$$

The above formulas provide isentropic constitutive relations in terms of the elastic stiffness coefficients. Other forms of constitutive relations can, of course, be derived in a similar fashion.

Low-pressure acoustic measurements yield a mixed third-order constant of the form

$$C_{ijkmpq} = (\partial c_{ijkm}^{*} / \partial N_{pq})_{T}$$

where the subscript T means the derivative is taken at constant temperature. The corresponding purely isentropic constant is given by

$$c_{ijkmpq}^{*} = C_{ijkmpq} + (T/\rho_0 \ C_t)c_{uvpq}^{*}\alpha_{uv}$$
$$\cdot [C_{ijkmrs}\alpha_{rs} - (\partial c_{ijkm}^{*}/\partial T)_t] \qquad (10)$$

[Brugger, 1964] where  $C_t$  is the specific heat at constant tension and the  $\alpha_{uv}$  are thermal expansion coefficients,

$$\alpha_{uv} = (\partial N_{uv} / \partial T)_t$$

In view of the symmetry of the stress and strain tensors, the number of subscripts can be reduced by adopting the following convention:

$$\begin{array}{ccc} 11 \rightarrow 1 & & 32 \rightarrow 4 \\ 22 \rightarrow 2 & & 31 \rightarrow 5 \\ 33 \rightarrow 3 & & 21 \rightarrow 6 \end{array}$$

This convention is employed in the following.

Application to uniaxial strain in quartz. We assume the deformation to occur in the X direction only. The coordinate transformation is accordingly

$$x_1 = (1 - \gamma)a_1$$

 $x_2 = a_2 \qquad x_3 = a_3$ 

Formulas 5 through 9 then give

$$J = V/V_0 = 1 - \gamma$$
$$N_1 = \gamma(\gamma/2 - 1)$$
$$\rho_0(E - E_0) = \frac{1}{2}c_{11}N_1^2 + \frac{1}{6}c_{111}N_1^3$$

$$+ \frac{1}{24} c_{1111} N_1^4 + \cdots$$

$$t_k = c_{1k} N_1 + \frac{1}{2} c_{11k} N_1^2$$

$$+ \frac{1}{6} c_{111k} N_1^3 + \cdots$$

$$(k = 1, 2, \cdots 6)$$

or writing out the components

$$t_{1} = c_{11}N_{1} + \frac{1}{2}c_{111}N_{1}^{2} + \frac{1}{6}c_{1111}N_{1}^{3} + \cdots$$

$$t_{2} = c_{12}N_{1} + \frac{1}{2}c_{112}N_{1}^{2} + \cdots$$

$$t_{3} = c_{13}N_{1} + \frac{1}{2}c_{113}N_{1}^{2} + \cdots$$

$$t_{4} = c_{14}N_{1} + \frac{1}{2}c_{114}N_{1}^{2} + \cdots$$

$$t_{5} = c_{15}N_{1} + \frac{1}{2}c_{115}N_{1}^{2} + \cdots$$

$$t_{6} = c_{16}N_{1} + \frac{1}{2}c_{116}N_{1}^{2} + \cdots$$

The stress components are then

$$\sigma_{1} = (1 - \gamma)t_{1} \qquad \sigma_{4} = (1 - \gamma)^{-1}t_{4}$$
  

$$\sigma_{2} = (1 - \gamma)^{-1}t_{2} \qquad \sigma_{5} = t_{5} \qquad (11)$$
  

$$\sigma_{3} = (1 - \gamma)^{-1}t_{3} \qquad \sigma_{6} = t_{6}$$

For  $\alpha$  quartz compressed in the X direction the above formulas are correct as they stand. For compression in other directions the proper translation of subscripts must, of course, be made to indicate the correct constants.

The above formulas have been applied to uniaxial compression of X- and Z-cut quartz, using the second- and third-order constants determined by *McSkimin et al.* [1965] and *Thurston et al.* [1966]. Values of these constants are shown in Table 2.

The resulting curves are plotted in Figures 6, 7, and 9. The values of shock velocity  $U_s$  and particle velocity  $u_p$  of Figure 6 were obtained from the Hugoniot relations

 $U_{s} = V_{0} (\sigma/V_{0} - V)^{1/2}$ 

and

$$u_n = [\sigma(V_0 - V)]^{1/2}$$

The predictions are seen to fall outside the estimated error of the shock data, indicating that the fourth-order term contributes sig-

#### TABLE 2. Elastic Moduli of Quartz\*

The second-order constants are isentropic, the third-order are mixed isothermal, isentropic constants, and the fourthorder are Hugoniot constants (see text).

Modulus	Value (10 <sup>11</sup> dynes/cm <sup>2</sup> )	Reference						
Value         Value           Modulus         (10 <sup>11</sup> dynes/cm <sup>3</sup> )         Reference           Gecond-Order         Ci1 <sup>4</sup> 8.757         McSkimin et al. [1965]           Ci12         0.704         McSkimin et al. [1965]         Ci13           Ci13         1.191         McSkimin et al. [1965]         Ci14         -1.804         McSkimin et al. [1965]           Ci14         -1.804         McSkimin et al. [1965]         Ci14         -16.575         McSkimin et al. [1966]         Ci1966]           Chird-Order         Ci11         -21.0         Thurston et al. [1966]         Ci166]         Ci1966]           Chird         -34.5         Thurston et al. [1966]         Ci15         1.2         Thurston et al. [1966]         Ci166]           Ci13         1.2         Thurston et al. [1966]         Ci13         Ci1966]         Ci13         Ci1966]         Ci13         Ci1966]         Ci13         Ci1966]         Ci13         Ci1966]         Ci1966]								
C11*	8.757	McSkimin et al. [1965]						
C12	0.704	McSkimin et al. [1965]						
C13	1.191	McSkimin et al. [1965]						
C14	-1.804	McSkimin et al. [1965]						
C33	10.575	McSkimin et al. [1965]						
Third-Order								
C111	-21.0	Thurston, et al. [1966]						
C112	-34.5	Thurston et al. [1966]						
C113	1.2	Thurston et al. [1966]						
C114	-16.3	Thurston et al. [1966]						
C133	-31.2	Thurston et al. [1966]						
C233	-81.5	Thurston et al. [1966]						
Fourth-Order								
C1111	1593	Present work						
C3833	1849	Present work						

\* The  $c_{11}$  constant used is appropriate for open circuit compression, i.e., at constant electric displacement, D.

nificantly to the energy (and the stress) at larger values of strain. Although it might be thought that the discrepancy is due in part to the use of isentropic second-order moduli and mixed isentropic-isothermal third-order moduli to predict Hugoniot states, for which internal energy is greater than for isentropic compression, a straightforward calculation shows that the errors thus produced are negligible.

The differences between the purely isentropic third-order moduli and the mixed moduli given in Table 2 can be calculated from (10).

The temperature coefficients of expansion, as given by *Mason* [1950] are

$$\alpha_3 = 7.8 \times 10^{-6}$$

$$\alpha_1 = \alpha_2 = 14.3 \times 10^{-6}$$

and the expression, from Westrum, reported by *McSkimin et al.* [1965] for the specific heat is

$$C_{p}(T) = C_{p}(T_{c}) + (T - T_{c})C_{1}$$
  
+  $(T - T_{c})^{2}C_{2} + (T - T_{c})^{3}C_{3} \cdots$   
 $(77.4^{\circ}K < T < 298^{\circ}K)$ 

where

 $T_{o} = 190^{\circ} \text{K}.$ 

$$C_p(T_c) = 5.189 \times 10^6 \text{ ergs/g °K.}$$
  
 $C_1 = 2.444 \times 10^4 \text{ ergs/g °K.}$   
 $C_2 = -4.126 \times 10^1 \text{ ergs/g °K.}$   
 $C_3 = 5.327 \times 10^{-2} \text{ ergs/g °K.}$ 

Taking  $T = 25^{\circ}$ C,  $\rho_0 = 2.6485$  g/cm<sup>3</sup>,  $C_p = 7.42 \times 10^{\circ}$  ergs/g °K and estimating  $(\partial C_{ss}^{\circ}/\partial T)$  from McSkimin's data taken at 25° and  $-195.8^{\circ}$ C to be of the order of  $-1 \times 10^{\circ}$  dynes/cm<sup>2</sup> °K, we find the difference given by (10) for the  $c_{stst}$  constant, for example, to be of the order of  $5 \times 10^{\circ}$  dynes/cm<sup>2</sup>. This value is four orders of magnitude less than  $c_{stst}$ . Hence, although the above calculation is hardly accurate for the cases under consideration, only erratic behavior of some of the thermodynamic variables,  $\alpha$ ,  $C_p$ , or  $(\partial c_{st}^{\circ}/\partial T)$ , could significantly influence the results.

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The difference between Hugoniot and isentropic compressions can also be shown to be negligible. For compression in the Z direction to a relative volume of 0.9 the strain energy given by (7) to terms of third-order is 2.5  $\times$ 10° ergs/g. The internal energy on the Hugoniot is 2.8  $\times$  10° ergs/g. By taking Gruneisen's ratio, Γ, to be approximately 1\*, the stress difference due to this difference in thermal energy is less than 1 kb-very much less than the observed stress difference, and within the experimental scatter. (Anderson [1966] gives a value of 0.746 for hydrostatic compression. Calculations for the individual components with the assumption  $C_p = C_v$  gives  $\Gamma_{11} = \Gamma_{22} = 1.17$ ;  $\Gamma_{ss} = 0.53.)$ 

Fourth-order constants. The discrepancies between the observed data and the predictions based on low-pressure data can be used to evaluate fourth-order coefficients. This was done for X- and Z-cut crystals to yield the values of  $c_{nn}$  and  $c_{ssss}$  shown in Table 2. Differences between the data and the third-order predictions were fitted with a straight line. Because of the large differences in pressure range and experimental precision, this method proved to give an adequate fit to both the high- and lowpressure data. No adjustment of the second- or third-order constants was necessary.

The fits obtained using the constants up to fourth-order are shown in Figures 6, 7, and 9. Note that for X-cut crystals the slope of the curve in the shock-velocity-particle-velocity plane (Figure 6) is always negative when con-

stants only up to and including third-order are used. This would imply that a shock wave in this direction is unstable and spreads as it travels. With the addition of the fourth-order constant the curve has a minimum at a value of  $u = 0.032 \text{ mm}/\mu\text{sec}$ . The minimum sound speed occurs at a compression ratio  $V/V_{o} =$ 0.9830 and a stress  $\sigma_x = 15.4$  kb. Its value there is 5.6889  $\times$  10<sup>5</sup> cm/sec. The critical shock strength above which a single shock is stable occurs at  $u = 0.063 \text{ mm}/\mu\text{sec}, V/V_0 = 0.9890$ , and  $\sigma_x = 9.6$  kb. The lack of a unique shock speed below the critical value probably does not influence the operation of quartz shock transducers appreciably, because the variation in speed is small (<1%).

The  $U_s$ - $U_p$  plot for Z-cut crystals is nearly a straight line; however, it is easily shown that a straight line does not accurately fit the slope at zero particle velocity. Thus, the straight line relation often assumed in shock studies is only an approximation for quartz shocked in either the X or the Z direction.

It is also easily shown that the Murnaghan form of the equation of state, when fitted to the correct slope and curvature of the  $\sigma$ -V curve (utilizing second-and third-order constants), does not accurately fit the higher-pressure data and is therefore an approximation only.

These statements can be illustrated by examining the derivatives of each function. Expanding the relation for  $\sigma$  in (11) in terms of  $\gamma$  yields

$$-\sigma_{1} = c_{11}\gamma \left[1 - \frac{1}{2}\left(3 + \frac{c_{111}}{c_{11}}\right)\gamma + \frac{1}{6}\left(3 + 6\frac{c_{111}}{c_{11}} + \frac{c_{1111}}{c_{11}}\right)\gamma^{2} + \cdots\right] (12)$$

A linear relation between shock and particle velocity of the form

$$V_s = a + bu_p$$

can be written, by means of the Rankine-Hugoniot jump conditions, as

$$-\sigma = \rho_0 [a^2 \gamma / (1 - b\gamma)^2]$$

where  $\rho_o$  is initial density, and the relation can be expanded to give

$$-\sigma = \rho_0 a^2 \gamma [1 + 2b\gamma + 3b^2 \gamma^2 + \cdots] \quad (13)$$

Finally, the one-dimensional strain analog of the Murnaghan equation

$$-\sigma_1 = (A/B)[(V_0/V)^B - 1]$$

can be expanded to give

$$-\sigma = A\gamma [1 + \frac{1}{2}(B+1)\gamma + \frac{1}{6}(B+1)(B+2)\gamma^2 + \cdots]$$
(14)

Equating the derivatives up to second-order, we have

$$c_{11} = \rho_0 a^2 = A$$
 (1st order)  
 $-\left(3 + \frac{c_{111}}{c_{11}}\right) = 4b = (B + 1)$  (2nd order)

Evaluating the parameters A, b, and B from these equations, we have

X cut

$$A = \rho_0 a^2 = c_{11} = 8.757 \times 10^{11}$$
  

$$b = -0.15 \qquad B = -1.6$$

Z cut

$$A = \rho_0 a^2 = c_{33} = 10.575 \times 10^{11}$$
$$b = 1.177 \qquad B = 3.71$$

With these values all three expressions have the same slope and curvature at zero stress. The predicted stresses for various compressions are shown in Table 3.

That the closed form expressions are approximate is hardly surprising inasmuch as they are both empirical with no known physical basis. They are of value because they both are twoparameter functions that have physically reasonable shapes and they are, therefore, convenient for interpolation and extrapolation when experimental information is lacking.

The close agreement of the Murnaghan and linear  $U_s \cdot u_p$  fits is somewhat curious. It presumably results from the fact that the thirdand higher-order coefficients in the expansions of these formulas are relatively small; they must agree exactly, of course, to terms of second order. Direct calculation shows that the coefficient of the third-order term in (12) is, for each crystal orientation, a factor of 5 or more greater than the corresponding term in (13) and (14).

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		X		Z				
V/Vo	Murnaghan	Linear $U_s - U_p$	Finite Strain	Murnaghan	Linear $U_s - U_p$	Finite Strain		
0.99	8.7	8.8	8.7	10.7	10.8	10.8		
0.98	17.4	17.5	17.5	21.8	22.2	22.3		
0.97	26.1	26.3	26.5	32.0	34.0	34.5		
0.96	34.7	35.0	35.9	47.1	46.5	47.6		
0.95	43.1	43.7	45.7	60.3	59.7	61.6		
0.94	51.7	52.5	56.1	73.9	73.5	76.5		
0.93	59.9	61.3	67.1	87.9	88.0	92.6		
0.92	68.6	70.0	78.9	103.4	103.0	109.7		
0.91	77.0	78.8	91.4	119.6	119.0	127.9		
0.90	85.2	87.6	104.7	136.4	135.8	147.3		

Knopoff's [1963] suggestion that because of the arbitrariness in the definition of strain alternative definitions may prove more suitable for representing constitutive relations would seem to be worthy of further consideration. Some guidance from physical reasoning is necessary, however, to provide any degree of generality to a given definition.

*Error analysis.* The precision of the fourthorder constants is determined by the precision of the shock data and by the precision of the second- and third-order constants. Of these the error in the shock data has the largest effect.

Differentiation of the stress-strain relation shows that the error in  $c_{nn}$  due to an error in  $c_n$  is

$$\frac{dc_{1111}}{c_{1111}} = \left(-\frac{6c_{11}}{c_{1111}N_1^2}\right)\frac{dc_{11}}{c_{11}}$$

and for strains  $N_1 = 6 \times 10^{-2}$  the coefficient is approximately -10. Thus, a 0.1% error in  $c_{11}$  results in a 1% error in  $c_{111}$ . Similarly, an error in the third-order constant  $c_{111}$  is equivalent to an error in  $c_{1111}$  of

$$\frac{dc_{1111}}{c_{1111}} = \left(-\frac{3c_{111}}{c_{1111}N_1}\right)\frac{dc_{111}}{c_{1111}}$$

and the coefficient for strains of approximately  $6 \times 10^{-2}$  is 0.5. For Z-cut crystals the corresponding coefficients are approximately 5 and 2.

Taking the precision of the second- and thirdorder constants to be approximately  $\pm 0.1$ and  $\pm 5\%$ , respectively [*McSkimin et al.*, 1965; *Thurston et al.*, 1966], the error in the fourthorder constants from these sources is approximately  $\pm 3$  and  $\pm 10\%$  for X- and Z-cut crystals, respectively.

The error due to inaccuracies in the shock data is evaluated as follows. From the jump conditions (equation 3) we have

$$1 - (V/V_0) = u/U$$

 $\sigma = \rho_0 U u$ 

 $-\frac{\delta V}{V_0} = \frac{u}{U} \left( \frac{\delta u}{u} - \frac{\delta U}{U} \right)$ 

Hence,

and

and

$$\delta\sigma/\sigma = \delta u/u + \delta U/U$$

We are interested, however, not in the total error in the measured state but in the error in the Hugoniot stress-strain curve. That is, we wish to know the error in stress at a given specific volume.

If the true slope of the Hugoniot is  $d\sigma/dV$ , the quantity of interest is

$$\frac{\Delta\sigma}{\sigma} = \left(\frac{d\sigma}{dV} - \frac{\delta\sigma}{\delta V}\right)\frac{\delta V}{\sigma}$$

This can be reduced to

$$\frac{\Delta\sigma}{\sigma} = \frac{\delta U}{U} \left[ \frac{d\sigma/d V}{\sigma/(V_0 - V)} - 1 \right] - \frac{\delta u}{u} \left[ \frac{d\sigma/d V}{\sigma/(V_0 - V)} + 1 \right]$$

Note that, if the Hugoniot stress-strain relation is a straight line,  $-d\sigma/dV = \sigma/(V_o - V)$ , then errors in particle velocity do not produce errors in the stress-strain curve.

In the present experiments the curves are nearly straight and, approximately,

$$\Delta\sigma/\sigma = 2 \ \delta U/U$$

The error in stress at a given volume is thus twice the error in shock velocity at a given particle velocity. The corresponding error in the fourth-order elastic coefficient is

$$\frac{dc_{1111}}{c_{1111}} = \left[\frac{6c_{11}}{c_{1111}N_1^2} + \frac{3c_{111}}{c_{1111}N_1} + 1\right]\frac{d\sigma}{\sigma}$$

Taking the error in shock velocity to be  $\pm 1\%$ , we find the corresponding fractional change in  $c_{\min}$  to be

$$dc_{1111}/c_{1111} = 9 \ d\sigma/\sigma = \pm 18\%$$

For Z-cut crystals the result is

$$dc_{3333}/c_{3333} = \pm 10\%$$

The total precision of the fourth-order constants from all sources is, therefore, estimated to be

$$dc_{1111}/c_{1111} = \pm 20\%$$

and

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$$dc_{3333}/c_{3333} = \pm 20\%$$

### CONCLUSIONS

The behavior of quartz under shock loading conditions is very much different from that of metals, as was pointed out by Wackerle. The elastic precursor waves are an order of magnitude higher and, correspondingly, so are the shear stresses. The curve labelled X in Figure 9 is the normal stress component (based on constants to third-order) across a plane perpendicular to the shock front when the shock propagates in the Z direction. The maximum stress difference is seen to exceed 100 kb. This is of the same order of magnitude as the effective shear modulus; consequently, it appears that quartz momentarily exhibits theoretical yield strength under dynamic conditions.

That cohesion of the material is destroyed upon yielding is indicated by the close agreement of the second shocked states with Bridgman's hydrostatic data. There is no indication of a residual shear stress, in contrast to the case for metals [*Fowles*, 1961a].

The pronounced stress relaxation shown by the observed variation in amplitude of the elastic waves and the apparent dependence on the final pressure is quantitatively larger than for metals, although it is similar qualitatively.

Evidently, shock wave methods provide a valuable supplement to low-pressure acoustic measurements in determining higher-order elastic constants, as least for ceramic type materials that sustain large-amplitude elastic waves. Shock waves are inherently more suitable for higher-pressure measurements than acoustic methods are, but they are less suitable for the high-precision, low-pressure measurements required to evaluate second-order constants. To what extent shock wave techniques are capable of measuring coefficients other than the principal coefficients, i.e., the directions for which the elastic wave is purely longitudinal, requires additional study.

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