

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

and similarly for the higher-order coefficients. Consequently,

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

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

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

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

$$C_{ijklmpq} = (\partial c_{ijkl}^* / \partial N_{pq})_T$$

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

$$c_{ijklmpq}^* = C_{ijklmpq} + (T/\rho_0 C_i) c_{uvpq}^* \alpha_{uv} \cdot [C_{ijkhrs} \alpha_{rs} - (\partial c_{ijkl}^* / \partial T)_i] \quad (10)$$

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

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

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

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

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

$$\begin{array}{ll} x_1 = (1 - \gamma)a_1 & \\ x_2 = a_2 & x_3 = a_3 \end{array}$$

Formulas 5 through 9 then give

$$J = V/V_0 = 1 - \gamma$$

$$N_1 = \gamma(\gamma/2 - 1)$$

$$\rho_0(E - E_0) = \frac{1}{2} c_{11} N_1^2 + \frac{1}{6} c_{111} N_1^3 + \frac{1}{24} c_{1111} N_1^4 + \dots$$

$$\begin{aligned} t_k &= c_{1k} N_1 + \frac{1}{2} c_{11k} N_1^2 \\ &+ \frac{1}{6} c_{111k} N_1^3 + \dots \end{aligned} \quad (k = 1, 2, \dots, 6)$$

or writing out the components

$$t_1 = c_{11} N_1 + \frac{1}{2} c_{111} N_1^2 + \frac{1}{6} c_{1111} N_1^3 + \dots$$

$$t_2 = c_{12} N_1 + \frac{1}{2} c_{112} N_1^2 + \dots$$

$$t_3 = c_{13} N_1 + \frac{1}{2} c_{113} N_1^2 + \dots$$

$$t_4 = c_{14} N_1 + \frac{1}{2} c_{114} N_1^2 + \dots$$

$$t_5 = c_{15} N_1 + \frac{1}{2} c_{115} N_1^2 + \dots$$

$$t_6 = c_{16} N_1 + \frac{1}{2} c_{116} N_1^2 + \dots$$

The stress components are then

$$\begin{aligned} \sigma_1 &= (1 - \gamma)t_1 & \sigma_4 &= (1 - \gamma)^{-1}t_4 \\ \sigma_2 &= (1 - \gamma)^{-1}t_2 & \sigma_5 &= t_5 \\ \sigma_3 &= (1 - \gamma)^{-1}t_3 & \sigma_6 &= t_6 \end{aligned} \quad (11)$$

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

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

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 fourth-order are Hugoniot constants (see text).

Modulus	Value ( $10^{11}$ dynes/cm <sup>2</sup> )	Reference
Second-Order		
$c_{11}^*$	8.757	McSkimin et al. [1965]
$c_{12}$	0.704	McSkimin et al. [1965]
$c_{13}$	1.191	McSkimin et al. [1965]
$c_{14}$	-1.804	McSkimin et al. [1965]
$c_{33}$	10.575	McSkimin et al. [1965]
Third-Order		
$c_{111}$	-21.0	Thurston, et al. [1966]
$c_{112}$	-34.5	Thurston et al. [1966]
$c_{113}$	1.2	Thurston et al. [1966]
$c_{114}$	-16.3	Thurston et al. [1966]
$c_{133}$	-31.2	Thurston et al. [1966]
$c_{333}$	-81.5	Thurston et al. [1966]
Fourth-Order		
$c_{1111}$	1593	Present work
$c_{3333}$	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

$$C_p(T) = C_p(T_c) + (T - T_c)C_1 \\ + (T - T_c)^2 C_2 + (T - T_c)^3 C_3 \dots \\ (77.4^\circ\text{K} < T < 298^\circ\text{K})$$

where

$$T_c = 190^\circ\text{K}.$$

$$C_p(T_c) = 5.189 \times 10^6 \text{ ergs/g } ^\circ\text{K}.$$

$$C_1 = 2.444 \times 10^4 \text{ ergs/g } ^\circ\text{K}.$$

$$C_2 = -4.126 \times 10^4 \text{ ergs/g } ^\circ\text{K}.$$

$$C_3 = 5.327 \times 10^{-2} \text{ ergs/g } ^\circ\text{K}.$$

Taking  $T = 25^\circ\text{C}$ ,  $\rho_0 = 2.6485 \text{ g/cm}^3$ ,  $C_p = 7.42 \times 10^6 \text{ ergs/g } ^\circ\text{K}$  and estimating  $(\partial C_{33}^*/\partial T)$  from McSkimin's data taken at  $25^\circ$  and  $-195.8^\circ\text{C}$  to be of the order of  $-1 \times 10^8 \text{ dynes/cm}^2 \text{ } ^\circ\text{K}$ , we find the difference given by (10) for the  $c_{333}$  constant, for example, to be of the order of  $5 \times 10^8 \text{ dynes/cm}^2$ . This value is four orders of magnitude less than  $c_{333}$ . 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  $(\partial C_{33}^*/\partial T)$ , could significantly influence the results.

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  $2.5 \times 10^9 \text{ ergs/g}$ . The internal energy on the Hugoniot is  $2.8 \times 10^9 \text{ ergs/g}$ . By taking Gruneisen's ratio,  $\Gamma$ , 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  $\Gamma_{11} = \Gamma_{22} = 1.17$ ;  $\Gamma_{33} = 0.53$ .)

*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  $c_{1111}$  and  $c_{3333}$  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 low-pressure 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-