This is four orders of magnitude less than c_{333}. Hence, although the above calculation is hardly accurate for the cases under consideration, only pathological behavior of some of the thermodynamic variables, α, C_p or $(\frac{\partial c^S_{33}}{\partial T})$ 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 Eq.(2.16) to terms of third-order is 2.5×10^9 erg/gm. The internal energy on the Hugoniot is 2.8×10^9 erg/gm. Taking Gruneisen's ratio, Γ, to be approximately 1*, the stress difference due to this difference in thermal energy is less than 1 kbar--very much less than the observed stress difference, and within the experimental scatter.

C. 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 II. The procedure followed was to fit differences between the data and the third-order predictions 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 Figs. 2.6, 2.7, and 2.9. Note that for X-cut crystals the slope of the curve in the shock velocity-particle-velocity plane (Fig. 2.6) is always negative when constants only up to and including third-order are used. This would imply

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*ANDERSON (44) gives a value of 0.746 for hydrostatic compression. Calculated for the individual components with the assumption $C_p = C_v$ gives $\Gamma_{11} = \Gamma_{22} = 1.17$; $\Gamma_{33} = 0.53$.

that a shock wave in this direction is unstable and spreads as it travels. With the addition of the fourth-order constant, however, the slope is always slightly positive. Thus, the addition of the fourth-order term results in a qualitative difference in predicted behavior.

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 Z direction.

It is also easily shown that the Murnaghan form of equation of state, when fitted to the correct slope and curvature of the σ - 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 σ, in Eq. 2.20 in terms of γ yields:

$$\sigma = c_{11}\,\gamma[1 - 1/2\,(3 + \frac{c_{111}}{c_{11}})\gamma + 1/6\,(3 + 6\,\frac{c_{111}}{c_{11}})\gamma^2 + \ldots] \quad (2.21)$$

A linear relation between shock and particle velocity of the form

$$V_s = a + b\,u_p$$

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

$$\sigma = \rho_o \frac{a^2\,\gamma}{(1 - b\gamma)^2} \ ,$$

where ρ_o is initial density, and can be expanded to give

$$\sigma = \rho_o a^2\,\gamma[1 + 2b\gamma + 3b^2\,\gamma^2 + \ldots] \quad (2.22)$$