

single crystal Zn between 200 and 400 kbar (Walsh, et al., 1957).

The P - V - E results along the Hugoniot or shock hydrostat can be converted to P - V results along other lines in the pressure-volume plane by employing an equation of state. Generally the Mie-Gruneisen equation is used. This equation was discussed in section 4 and arguments presented to show that it is quite reliable at temperatures above the characteristic Debye temperature of the material. The most critical term in this equation of state is the volume dependence of the Gruneisen parameter, $\gamma(V)$ (Duvall and Fowles, 1963). In general, this expression is estimated from Slater's formula for the Debye theory extended for an isotropic continuum (Slater, 1939).

$$\gamma = -\frac{V}{2} \left(\frac{d^2 P/dV^2}{dP/dV} \right) - 2/3 \quad (6)$$

Dugdale and MacDonald (1953) have modified this formula for cubic lattices to read

$$\gamma = -\frac{V}{2} \left(\frac{d^2(PV^{2/3})/dV^2}{d(PV^{2/3})/dV} \right) - 1/3 \quad (7)$$

The Dugdale-MacDonald formula seems to give better results (Rice, et al., 1958; Chang, 1967) than the Slater formula, in spite of the fact that one of the assumptions in its derivation has been shown false. The usual approach is to transform the P - V relations along the Hugoniot to the isotherm passing through the initial value P_0 , V_0 , by assuming $(\partial P/\partial T)_V$ is independent of pressure or equivalently that $\gamma C_v/V$ is a constant (Birch, 1968). C_v is the specific heat at constant volume. This relation is very likely inexact but for small enough changes in V , i.e., low energy shocks, it should be a satisfactory approximation.

In order to interpret dynamic shock measurements of phase changes, one must know the temperature as well as P and V at the transition. Again, for relatively low energy shocks, it is sufficient to approximate the temperature from the relation along an isentropic compression (Walsh and Christian, 1955).

$$T = T_0 \exp \left[- \left(\frac{\partial P}{\partial T} \right)_V \frac{(V - V_0)}{C_v} \right] \quad (8)$$

where C_v and $(\partial P/\partial T)_V$ are assumed independent of pressure. This equation gives the temperature for isentropic compression but neglects the extra rise in temperature due to the shock. The temperature along the Hugoniot can also be calculated in a more elaborate manner by using the Mie-Gruneisen equation of state (Goranson, et al., 1955).

Even with all the above assumptions, one would expect the P - V relations along an isotherm to be correct to within a few percent if the work is done carefully. There still remains the question as to whether these results, after transforming to the isotherm, should

be expected to compare with static pressure measurements. Work hardening and strain rate effects may alter the pressure distribution, especially in the low pressure region. Since there is a disparity between dynamic and static yield strength (Duvall and Fowles, 1963), one might also expect a difference in the static and dynamic equations of state. Recently there have been some comparisons between static and dynamic measurements in the low pressure range with very good agreement (Lundergan and Herrmann, 1963; Munson and Barker, 1966). Munson and Barker compared their results with static measurements by calculating best fit a and b coefficients along their isotherm using Bridgman's equation. (Equation (1) section 4.) They compared these with the same coefficients determined from static compression and ultrasonic measurements. Ruoff (1967) shows that the agreement with the ultrasonic work is very satisfactory especially if the a and b for the ultrasonic data are not taken from B_0 and B'_0 but rather determined again from a least squares fit to the ultrasonic measurements. This is necessary because the two-coefficient Bridgman equation is not a good representation of an equation of state.

The shock measurements give values of $P(V, T)$ along the Hugoniot which agree, to within the uncertainty of the measurement, with Decker's (1965, 1966, 1971) equation of state for NaCl; this in turn agrees with static measurements along the room temperature isotherm to better than 2 percent in pressure for a given volume.

5.2. Phase Transitions Via Shock Measurements

There are a few phase transitions that have been observed both in the static and dynamic measurements. Since the pressure in the dynamic case can be determined experimentally with an accuracy of 2 to 3 percent, this could help establish the pressure at these transitions. A number of problems arise, however. The temperature at the dynamic measurement is greater than the initial starting temperature. Thus, the measured transition pressure must be corrected to the same temperatures as that of the static measurement. This requires a knowledge of dP/dT along the phase line. A more difficult problem is centered in the question of rates of transition and possible nucleation problems. In general, there will be a tendency to exceed the equilibrium pressure before a new phase can nucleate, and then one wonders if the rapid changes in pressure in the shock front might not tend to overshoot the phase transition pressure. In fact, if the transition is not rapid enough, it may not even occur at all. This is the case for melting of bismuth (Duff and Minshall, 1957). Duvall and Fowles (1963) claim that melting is a slow transition. One must also consider the slow nature of many solid state reactions (Roy and Dachille, 1967). In determining the pressure at the transitions, a correction for the strength of material must be applied before com-

paring with static data. There is also the question as to whether the plastic shear strain in the shock might not alter the transition pressure.

a. Bismuth I-II Transition

Duff and Minshall (1957), Hughes, et al. (1961) and Larson (1967) have all measured the Bi I-II transition by shock techniques. The observed break in the Hugoniot was identified as the Bi I-II transition by Duff and Minshall who measured the temperature dependence of the phase transition and found excellent agreement with the slope of the static phase line. Duff and Minshall observed the dynamic transition pressure to be about 2.7 kbar above the accepted static equilibrium value. They assumed that u_p was half the measured free surface velocity when the plastic wave reflected from the free surface. They observed no elastic wave and made no strength of material correction to account for non-hydrostatic compression. Hughes, et al., used the same assumption concerning the particle velocity but their technique, which was quite different, had too much scatter from sample to sample. Their best estimate of the transition pressure would be 26 ± 3 kbar after correcting to 25 °C and for strength of material (Larson, 1967). Larson measured the pressure using an impedance matching technique between Bi and a piezoelectric quartz gauge. After the appropriate corrections, Larson's value for pressed Bi is 25.4 ± 0.8 kbar and for cast Bi is 25.9 ± 1.2 kbar, in good agreement with static equilibrium measurements. (The values given in table 18 are uncorrected.) None of these measurements showed any variation of the transition pressure for shock transit times between 10^{-6} to 10^{-9} seconds.

A comparison of these three measurements is given in table 18. P_{HY} is the pressure in the elastic wave, U_{21} , u_{p2} , P_2 , and V_2/V_0 are the shock velocity, particle velocity, pressure and relative volume in the first plastic wave. T is the temperature behind the first plastic shock. The particle velocity of Duff and Minshall is probably too large which could be due to experimental error as discussed by Larson. The following paragraph shows that generally the appropriate particle velocity is less than half the free surface velocity when an elastic wave precedes the plastic wave. This also would indicate that the first two values of u_{p2} in the table may be large.

TABLE 18. Bi transition by shock measurements

P_{HY}	U_{21}	u_{p2}	P_2 (kbar)	V_2/V_0	T	Reference
	2.049	0.135	27.15	0.943	42 °C	Duff & Minshall (1957)
	2.054	.128	25.7	.938		Hughes, et al. (1961)
2.0	2.060	.126	25.55	.939		Larson (1967) cast
2.4	2.060	.125	25.2	.941		Larson (1967) pressed

This would increase his measured pressure by 0.7 kbar.

Let us consider the corrections mentioned in the above paragraph. From (1) and (2)

$$u_{p1} = \sqrt{P_1(V_0 - V_1)} \quad (9)$$

for the elastic precursor wave and for the following plastic shock

$$u_{p2} = \sqrt{(P_2 - P_1)(V_1 - V_2)} + u_{p1}. \quad (10)$$

Now assume an elastic decompression wave reflects from the free surface and moves back into the material, with essentially the same velocity as the initial elastic wave. This decompression wave interacts with the plastic shock before it strikes the surface, slightly lowering the density behind the shock giving:

$$u'_{p2} = \sqrt{(P_2 - P_1)(V_0 - V'_2)} > u_{p2}. \quad (11)$$

The appropriate specific volumes in the above equation are pictured in figure 6. In fact, from the interaction

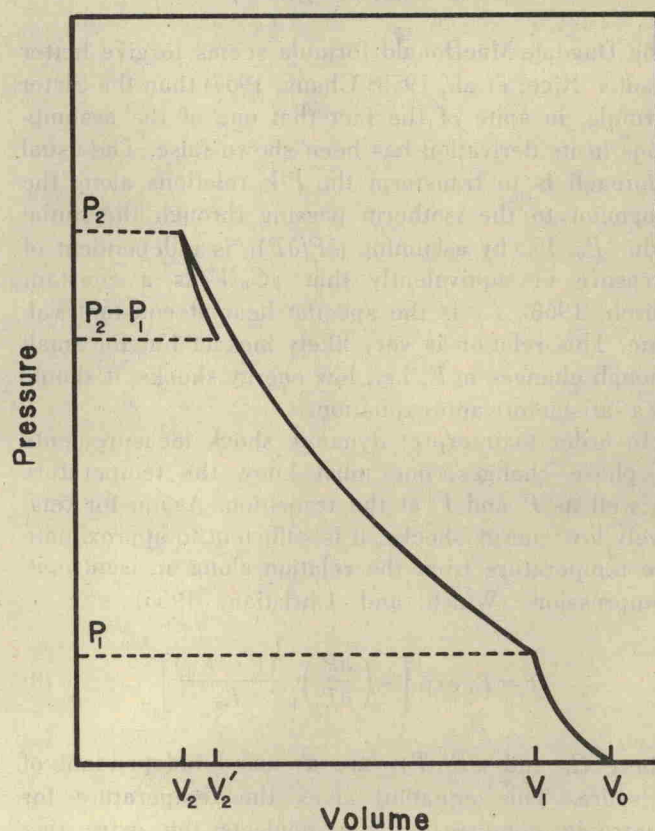


FIGURE 6. The elastic and plastic Hugoniot showing the effect of the returning elastic wave on the forward plastic compression wave.

$$u'_{p2} = u_{p2} + \sqrt{P_1(V'_2 - V_2)}. \quad (12)$$

$V_0 - V'_2 > V_1 - V_2$ because the elastic wave Hugoniot is steeper than the plastic wave Hugoniot and the volume change for a given pressure change is less at higher