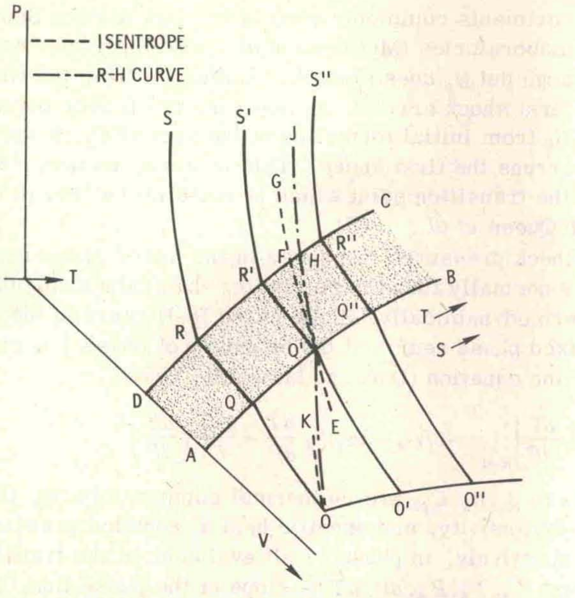

FIG. 9. P–V–T surface for a normal polymorphic transition. $\Delta S<0$, $\Delta V<0$, $dP/dT>0$. $O'Q'R'S'$, etc., are isotherms; OK and $EQ'FG$ are isentropes. $OQ'HJ$ is an R–H curve centered at 0.

conform to the rule that on an isotherm the high-pressure phase has the lesser volume, and on an isobar the high-temperature phase has the greater entropy.

In Fig. 9, where $dP/dT>0$, $ABCD$ is the mixed phase region; $OQRS, O'Q'R'S', O''Q''R''S''$ are isotherms that start in phase 1 at $P=0$, cross the mixed phase region at constant pressure, and rise again in phase 2. $EQ'FG$ is an isentrope which experiences a break in slope at boundaries of the mixed phase region; $OQ'HJ$ is the R–H curve centered at O and recentered at Q'. It has a second-order contact with the isentrope OK at O; it intersects the phase boundary at Q', starts again with a second-order contact with $EQ'F$ at Q', continues on to intersect the second phase boundary at H, and turns sharply up in phase 2. Relative positions of phase boundaries, isotherm, isentropes, and R–H curve in the P–V plane are indicated in Fig. 10.

The discontinuity in slope of isentropes at the mixed

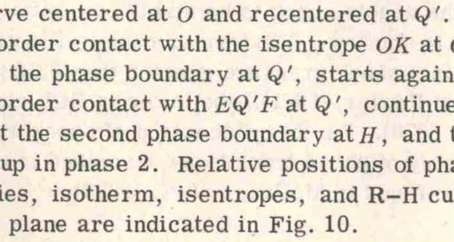

FIG. 10. Configuration of isentropes, isotherm, and R–H curves in the pressure–volume plane for a solid shock loaded through a normal polymorphic phase transition. Equation of state surface as in Fig. 9.

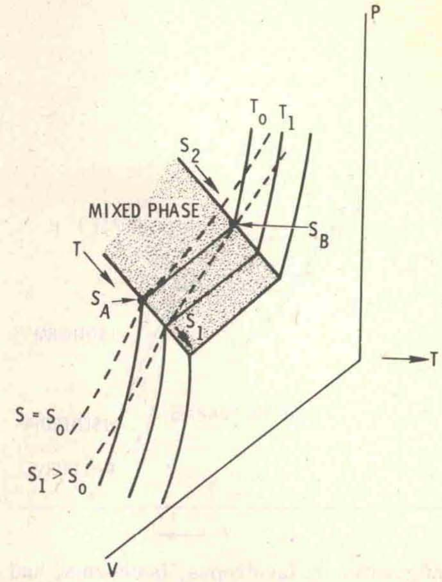

FIG. 11. Equation of state surface for $\Delta V<0$, $\Delta S>0$, $dP/dT<0$.

phase boundary is given by (Duvall and Horie, 1965)

$$(\partial V/\partial P)_{S1}-(\partial V/\partial P)_{SM}=(T/C_p)(dS/dP)^2>0. \tag{31}$$

Subscript SM refers to the isentropic condition in the mixed phase region. All quantities are evaluated at the boundary between phase 1 and the mixed phase. The sign of the inequality in Eq. (31) insures that the isentrope in phase 1 is always steeper than that in the mixed phase. This implies that Inequality (28) is satisfied for some P_0, V_0 and $p_x^{(2)}, V_2$; i.e., under some conditions a double shock-wave structure will result from the cusp at A in Fig. 10. An analogous argument shows that the discontinuity in slope at B cannot produce a double wave. These statements apply only for $\Delta V<0$.

Some anomalous transitions exist for which $\Delta V<0$, $\Delta S>0$, $dP/dT<0$. The equation of state surface for such cases is illustrated in Fig. 11. For this case, $dS/dT<0$ on the phase boundary, so temperature decreases on the isentrope through the mixed phase region, as shown. Projections in the P–V plane are shown in Fig. 12. Inequality (31) is independent of the sign of dP/dT, so in this case, too, a double wave structure is possible.

There are discontinuities in slope of the R–H curve in the U_s-U_p plane which correspond to those illustrated in Figs. 9–12. Differentiation of Eqs. (9) and (10) yields the relation

$$\eta D'=(R-1)/(R+1), \tag{32}$$

where

$$\eta\equiv 1-V/V_0,$$
$$R\equiv(dP/d\eta)/[(P-P_0)/\eta],$$
$$D'\equiv d(U_s-U_0)/d(U_p-U_0).$$

R is the ratio of slope of the R–H curve at a point (P,V) to the slope of the chord drawn from (P_0,V_0) to (P,V). For a single shock from (P_0,V_0) to (P,V), $R>1$ and $d(U_s-U_0)/d(U_p-U_0)>0$, since $\eta>0$. If the R–H curve crosses a phase boundary at P_A, V_A and a single shock

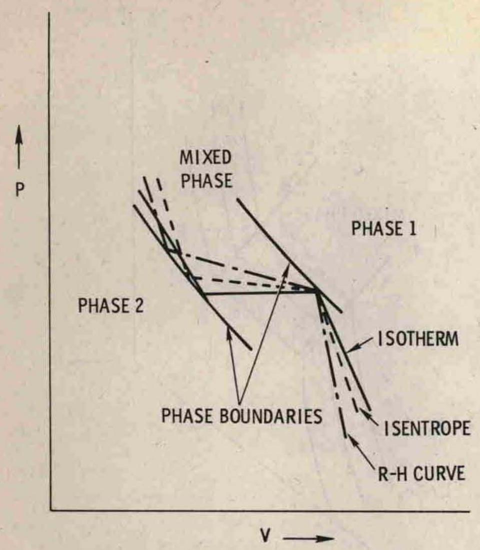

FIG. 12. Configuration of isentropes, isotherms, and R–H curves in the pressure–volume plane for $\Delta V < 0$, $\Delta S > 0$, $dP/dT < 0$.

remains stable, $(P - P_0)/\eta$ is unchanged, but $dP/d\eta$ has a discontinuity which produces a discontinuity ΔR in R. The corresponding discontinuity in D' is

$$\Delta D' = 2\Delta R/[\eta(R+1)(R+1+\Delta R)]. \qquad (33)$$

ΔR can be negative; if it is less than $1 - R$, a single shock is unstable.

If the change in R–H curve slope at the phase boundary is great enough to produce a second shock, two cases must be distinguished: (1) the second shock is perceived as a second shock and data reduction proceeds accordingly; (2) the compression is still perceived as a single shock.

In the first case, if intersection with the phase boundary is at (P_A, V_A), Eqs. (9) and (10) still apply with P_0, V_0, U_0 replaced by P_A, V_A, and U_A. Then Eq. (32) is replaced by

$$\eta_A D'_A = (R_A - 1)/(R_A + 1), \qquad (34)$$

where

$$\eta_A = 1 - \frac{V}{V_A} = \frac{V_A - V}{V_0 - V}\,\frac{V_0}{V_A}\,\eta,$$

$$R_A = \frac{(dP/d\eta_A)}{(P - P_A)/\eta_A},$$

$$D'_A = d(U_s^{(2)} - U_A)/d(U_p^{(2)} - U_A),$$

$U_s^{(2)}$ = propagation velocity of second shock,

$U_p^{(2)}$ = particle velocity behind the second shock.

At the intersection, $P = P_A, V = V_A, \eta_A = 0$ and Eq. (34) is indeterminate. Let $P - P_A = C_1\eta_A + C_2\eta_A^2 + \cdots$. Then Eq. (30) gives

$$D'_A = C_2/2C_1. \qquad (35)$$

The change in slope in the $U_s - U_p$ plane is

$$D'_A - D' = \frac{C_2}{2C_1} - \frac{dP/d\eta - [(P_A - P_0)/(V_0 - V_A)]V_A}{dP/d\eta + [(P_A - P_0)/(V_0 - V_A)]V_A}. \qquad (36)$$

In the second case, which describes the "flash gap" experiments commonly used at the Los Alamos Scientific Laboratories (McQueen *et al.*, 1970), U_s does not change but U_p does since U_s is inferred from the time of first shock arrival. In that case $D' = 0$ over the span of U_p from initial formation of the second shock until it overruns the first shock. This produces an uncertainty in the transition point which is noted in the literature (McQueen *et al.*, 1967).

Shock pressures measured in the mixed phase region are normally found to be greater than values calculated thermodynamically. Slope of the R–H curve in the mixed phase region at the boundary of phase 1 is given by the equation (Duff and Minshall, 1957),

$$\left.\frac{dV}{dP}\right|_{\text{R-H}} = -\beta_1 V_A + 2\alpha_1 V_A \frac{dT}{dP} - \frac{C_{p1}}{T_A}\left(\frac{dT}{dP}\right)^2, \qquad (37)$$

where $\beta_1, \alpha_1, C_{p1}$ are isothermal compressibility, thermal expansivity, and specific heat at constant pressure, respectively, in phase 1, all evaluated at the transition point V_A, T_A, P_A; dP/dT is slope of the phase line. Measured values of $|dP/dV|$ are observed to be much greater than values calculated from Eq. (37) for iron and quartz (Duvall and Horie, 1965) and for KCl (Hayes, 1974). The difference is smaller for bismuth and may conform to the equilibrium value (Duff and Minshall, 1957; Duvall and Horie, 1965). Hayes (1972) and Podurets and Trunin (1974) have discussed possible causes for these differences. Both Hayes and Podurets and Trunin suggest surface energy as a cause for larger values of dP/dV, but means for establishing the validity of this proposal do not presently exist.

It is important to note that even though double wave structures are possible, they will not necessarily be found in a given experiment. Final pressure may be too high for the double shock to be stable, or initial pressure may be too low. The former case is illustrated in iron for final shock pressure greater than 33.0 GPa (Zukas and Fowler, 1961),[3] the latter in CCl_4 and liquid N_2 (Dick, 1970). Further discussion of shock waves and the geometry of phase transitions described in this section can be found in McQueen *et al.* (1970).

E. Effects of shear stress on phase transitions

According to Eq. (3) the stress component p_x in a shock wave is composed of mean pressure and a shear stress. No account of shear stress was included in the preceding section, and it is reasonable to suppose that it may complicate comparisons of shock-induced and static transformation parameters. In ductile solids τ is limited by the yielding process; it may be very small in soft metals like pure aluminum; in brittle materials, like sapphire, it may amount to several tens of GPa. The value of p_x at which elastic failure occurs in a shock wave is often called the "Hugoniot Elastic Limit," abbreviated HEL. When the HEL is large, τ may be large at the transition point, and the role of shear stress in transitions intrudes on the simplicity of hydrostatics. Unfortunately, it is not easy to account for the effects of shear.

[3]See also Fig. 18, this paper.