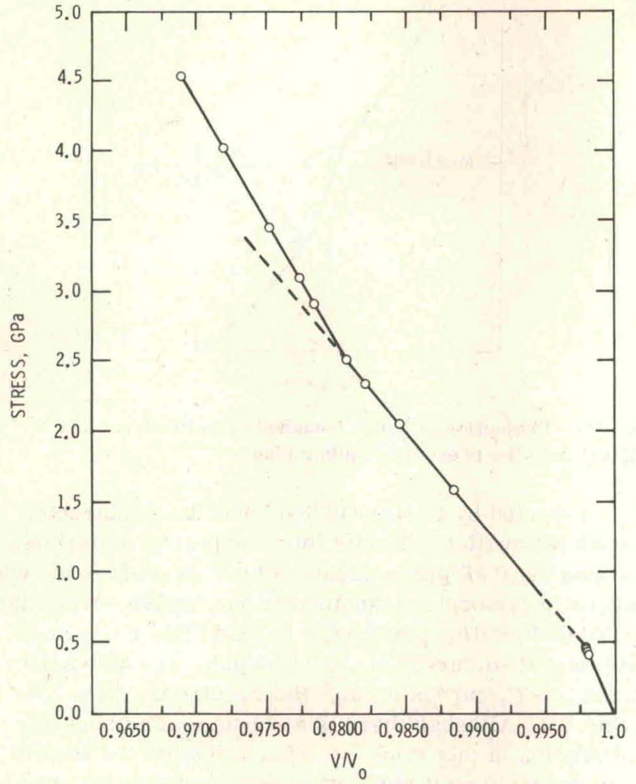

FIG. 30. The stress versus volume relation for a low carbon 28.4 at.% Ni–Fe alloy in the fcc phase shows a second-order phase transition indicated by a large decrease in compressibility at stress of 2.50 GPa. The dashed line indicates an extension of the compressibility of the lower stress data. When a correction for shear strength is applied to the shock data to account for the 0.45 GPa Hugoniot elastic limit, excellent agreement is noted between shock and static loading determinations of the dependence of Curie temperature on pressure. After Graham *et al.* (1967).

shown in Fig. 29 along with the other static pressure measurements. The measured shock loading coefficient is found to be in excellent agreement with static pressure measurements. Wayne (1969) performed static and shock loading measurements of the change in magnetization with pressure or stress in a 31.4 at.% alloy and found reasonable agreement between the two measurements. His data are also shown in Fig. 29.

Theories of the pressure dependence of Curie temperature and static pressure experiments have been extended to ternary iron alloys by Edwards and Bartel (1974). Edwards (1976) has performed shock loading experiments similar to those above on the change in magnetization on several cobalt substituted alloys, $Fe_{0.65}(Ni_{1-x}Co_x)_{0.35}$ with $x = 0.06$ and 0.08, and finds good agreement between static and shock loading results.

Results of this work indicate that static and shock loading measurements of changes in Curie temperature and magnetization with pressure are comparable insofar as their effect on magnetization is concerned. It appears that theory and static pressure experiments provide a basis for quantitative prediction of details of second-order ferromagnetic-to-paramagnetic transitions in ferromagnetic solids under shock loading. The shock loading experiments may in turn be used to provide additional information on changes in compressibility accompanying these transitions.

VI. SHOCK-INDUCED MELTING AND FREEZING

Melting is a first-order transition for which $\Delta V = V_{\text{liq}} - V_{\text{solid}}$ is normally positive, ΔS is normally positive, and therefore $dP/dT > 0$. Transitions are known for which $\Delta V < 0$ and $dP/dT < 0$. Melting of bismuth is an example of this type which is discussed in the latter part of this section.

A hypothetical P–V–T surface for a normal liquid and solid is shown in Fig. 31. Solid and liquid surfaces are labeled and the mixed phase region is the cylindrical surface *NMPR*. The dotted line *QW* is the projection of this surface on the P–T plane. *FGH* is an isotherm originating in the liquid, passing into the mixed phase region and then into the solid. Two cases can be distinguished which depend upon the magnitude of dP/dT:

1. A pressure–volume R–H curve, starting at a point, say *A*, in the solid, intersects the phase boundary *MR* at *B*. It may then proceed through it into the liquid, as shown by the curve *ABCD*, stay within the mixed phase region, or return to the solid. The essential point is that it intersects the boundary.

2. The R–H curve may stay within the solid, in which case no shock-induced melting is possible.

In the second case it may be possible to freeze the liquid by initiating a shock in the liquid phase. Such a case is discussed at the end of this section.

If $dP/dT < 0$, $\Delta V_1 > 0$, $\Delta S < 0$, which seems unlikely, the R–H curve originating in the solid will always intersect the phase boundary. A detailed discussion of the geometry of melting thermodynamics as it relates to shock waves is given by Horie (1967).

The possibility of shock-induced melting has often been questioned because of the short times involved. If

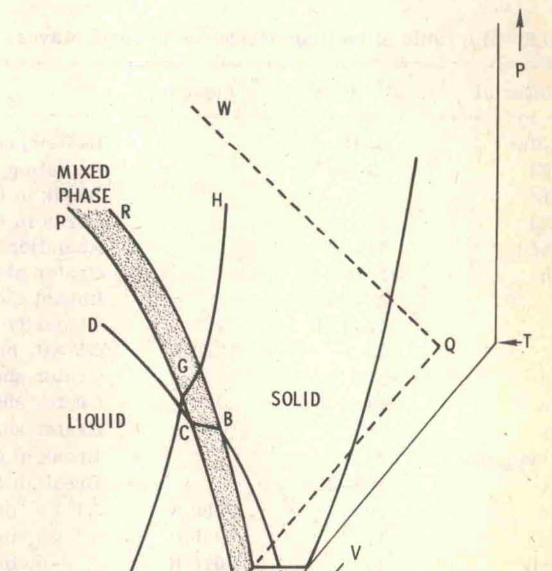

FIG. 31. P–V–T surface for a normal liquid and solid. The mixed phase region is bounded by *RPNM*.

melting did not occur in the time available in a shock experiment, the R–H curve, AB of Fig. 31, would continue on the metastable surface of the solid lying behind the liquid surface and, on release of pressure, would once again return to the stability field of the solid state unless irreversible shock heating were great enough to produce a terminal liquid state at zero pressure. No significant attempt has been made to answer this question theoretically, and there have been persistent efforts to determine melting in shock experiments. The first of these was by Duff and Minshall (1957), who failed to find evidence of melting when shock pressure extended into the liquid region.

A. Homogeneous melting of normal materials

In a report of shock measurements at pressures up to 200 GPa, McQueen and Marsh (1960) expressed the opinion that materials, such as lead and thallium, with low melting points had probably melted in some of their experiments. This belief was based on the observation that thermodynamic paths of the shocked material intersected the melt region in such cases. In such cases, also, it was sometimes observed that the $U_s - U_p$ graph showed a discontinuity in slope at the calculated melting point.

That such a slope discontinuity might result from melting is readily seen from Eq. (33). At point B of the R–H curve of Fig. 31, its slope changes discontinuously. This is shown more clearly in Fig. 32, where phase boundaries and the R–H curve starting at A are projected onto the P–V plane. The points labeled $A'B'C'D'$ are projections of $ABCD$ in Fig. 31. Since dP/dV changes discontinuously at B' and C', R of Eq. (33) also changes discontinuously, producing a discontinuity in dU_s/dU_p. Whether the total change is large enough to be detected in a $U_s - U_p$ plot cannot be determined in advance.

The most extensive investigation of this possibility has been reported by Carter (1973a), who has constructed complete equations of state for a number of materials, mapped the P–T phase planes, which sometimes include several polymorphic transformations, and shown that the calculated melting curves for Pb, Gd, Eu, Er, and Ce intersect R–H curves close to the point at which a break in the $U_s - U_p$ curves occur. His results are listed in Table VII. Although there is a substantial amount of speculation in this work, it is hard to label the results coincidental, and it must be taken as substantive evidence that equilibrium melting can occur in the short time available in shock experiments.

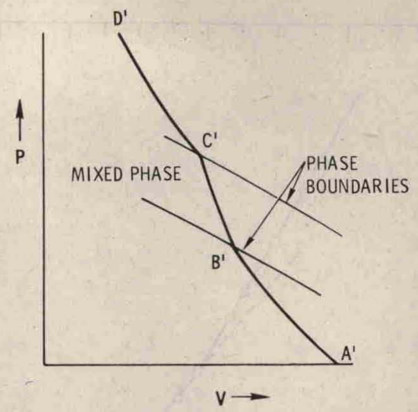

FIG. 32. Projection of phase boundaries and R–H curves of Fig. 31 onto the pressure–volume plane.

Kormer *et al.* (1965a), in experiments with KCl and KBr, reported discontinuities in dU_s/dU_p as indicating melting. Hauver and Melani (1964) found breaks in $U_s - U_p$ slope for Plexiglas and polystyrene which may be related to melting. Abrupt changes in the character of polarization signals were also found in the pressure ranges of transition. McQueen *et al.* (1971) have reported solid–liquid phase line calculations in Cu and experiments in porous Cu in which melting is thought to occur.

TABLE VII. Table of melting pressures in shock waves.

Material	P^T, GPa	T(est.)	Method	References
Sulfur[b]	6–10		Resistance change, break in U_s-U_p curve	Berger *et al.* (1960, 1962)
KCl	33–48[a]		Radiation temperature	Kormer *et al.* (1965b)
KBr			Break in U_s-U_p curve	Kormer *et al.* (1965a)
KCl			Break in U_s-U_p curve	Kormer *et al.* (1965a)
NaCl	54–70[a]		Radiation temperature, break in U_s-U_p curve	Kormer *et al.* (1965b, 1965a)
Pb	~22		Crater shape	Belyakov *et al.* (1965)
	23–25		Impact ejecta, spall, $\Delta t = 3 \times 10^{-7}$ s	Belyakov *et al.* (1967)
	41–124		Viscosity measurement	Mineev and Savinov (1967)
	28	1210 K	$\Delta V > 0$, break in U_s-U_p curve	Carter (1973a)
Cd	~31		Crater shape	Belyakov *et al.* (1965)
Zn	~44		Crater shape	Belyakov *et al.* (1965)
Sn	~28		Crater shape	Belyakov *et al.* (1965)
Plexiglas	28		Break in U_s-U_p curve	Hauver (1966b)
Al	105–202		Break in U_s-U_p curve	Mineev and Savinov (1967)
Gd	70	3500 K	$\Delta V > 0$, break in U_s-U_p curve	Carter (1973a)
Eu	11	950 K	< 0, break in U_s-U_p curve	Carter (1973a)
Erb	44	2070 K	~ 0, break in U_s-U_p curve	Carter (1973a)
Cerium	43	3600 K	> 0	Carter (1973a)
Fe	>184			Hord (1975)

[a]Melting region extends from first to second temperature.
[b]David and Hamman (1958) suggested that this pressure is transformation to a metallic solid.