

stress record at the triple point, about 1.7 GPa, that melting had indeed occurred.

Asay (1974) undertook a more extensive experimental program in which both initial temperature and final pressure were varied, the former to 523 K, which is only 21 K below the melting temperature. His measurements confirmed the Johnson *et al.* (1974) results. Moreover, since the transition (triple point) pressure did not vary with propagation distance between two and six millimeters, he inferred that the rate dependence of melting may be small within the range of his experiments, i.e., the characteristic time for melting is appreciably less than about 10^{-6} s.

Hayes (1975) modified the constitutive relation given by Johnson *et al.* to include a Maxwell-like relation for melting. This was incorporated in one-dimensional wave propagation calculations, and the Asay experiments were simulated for various values of the melting time. His results show that experimental profiles can be reproduced reasonably well for an inverse transformation rate of 2.5×10^{-8} s, which is in accord with Asay's observation that amplitude of the melting shock is independent of propagation distance beyond 2 mm. [Asay (1977) has recently reported additional evidence for melting in bismuth.]

The case thus made for shock-induced melting in bismuth is very strong. The results show that sound and useful work in this field is possible if theory, experiments, and computations are carefully done.

C. Heterogeneous melting

The case for heterogeneous melting upon yielding in shock-loaded quartz has recently been made in three papers which appeared almost simultaneously. Graham (1974) studied the compressibility of x-cut quartz above the HEL and noted a substantial reduction in shear strength and poor agreement with pressure derivatives of bulk modulus determined in other static experiments. Anan'in *et al.* (1974) recovered crystalline quartz samples shock-loaded just above the HEL and found "blocks" of α -quartz surrounded by layers of quartz glass. Grady *et al.* (1975) measured unloading velocities in the mixed phase region of polycrystalline quartz rocks and found a loss of shear strength indicated by bulk wave speeds. The independent interpretation of all three authors associated the loss of shear strength upon yielding with formation of localized regions of planar features in which high temperatures would be expected due to the dissipation of large amounts of energy stored as shear strain. This behavior comes about in material of low thermal conductivity whose shear strength approaches the theoretical strength of the lattice. The large shear strength and apparent loss of shear strength had been observed in quartz by Wackerle (1962) and Fowles (1962, 1967). The latest interpretations associating the loss of shear strength with heterogeneous melting were guided to a large extent by studies of quartz rocks in meteorite craters which show shock-induced planar features and formation of glass [see Chao, (1967) and Stofler (1972)]. The geophysical literature apparently failed to make the connection between localized planar features of glass and the substantial reduction of shear

strength upon yielding.

Grady *et al.* (1975) calculated temperature profiles for heterogeneous melting and pointed out that such inhomogeneities in temperature would be expected to lead to complex conditions far from equilibrium which could lead to melting and formation of dense polymorphs of quartz all within distances of a few microns. The calculations of Walsh (1969) show that the liquid inclusions lead to bulk behavior in solids as indicated by the shock compression data. The combined data on a loss or substantial reduction of shear strength (Wackerle, 1962; Fowles, 1967; Graham, 1974), poor agreement with other measurements on pressure derivatives of bulk modulus (Graham, 1974), recovery of planar quartz glass regions just above the HEL (Anan'in *et al.*, 1974), calculations showing high local temperatures (Grady *et al.*, 1975), and calculations of the effect of liquid inclusions in solids (Walsh, 1969) make a strong case for heterogeneous melting in quartz upon yielding.

Similar reductions of shear strength upon yielding have been observed in crystalline Al_2O_3 (Graham and Brooks, 1971), and behavior such as this is anticipated in quartz and other oxide rocks and minerals. The observations of heterogeneous melting are cause for serious concern that interpretation of data on high-pressure dense phases of rocks and minerals obtained under shock loading may be significantly in error since they are based on assumptions of homogeneous response in thermodynamic equilibrium. Grady (1977) has recently extended the heterogeneous melting model to predict characteristics of transitions in silicates.

D. Freezing

Bridgman noted that pressure-induced freezing occurred in most of the liquids he compressed statically. Speculations about the possibility of shock-induced freezing were natural consequences of this experience. Schardin (1941) fired bullets into CCl_4 and water at speeds varying from 800 to 1800 m/s and photographed them. He found the region surrounding the bullet to be opaque in CCl_4 at 1200 m/s and in water at 1800 m/s, whereas water was transparent at 800 m/s. Snay and Rosenbaum (1952) assembled thermodynamic data on water and calculated R-H curves. For initial conditions at room temperature and atmospheric pressure their R-H curve passed into the mixed phase region between liquid and ice VII at about 2.7 GPa and back into the liquid phase at about 10 GPa. The maximum solid content occurred at about 5 GPa with $\Delta V/V_0 \approx 0.025$. In a refinement of this calculation using new shock data, Rice and Walsh (1957) found essentially the same result, except that the excursion into the mixed phase region was limited to 3 to 4.5 GPa.

Walsh and Rice (1957) did the first carefully controlled experiments to detect freezing. They used a framing camera to photograph light reflected from a metal plate used to drive a plane shock into the liquid under study. The plate was provided with a contrasting grid and reductions in transparency were equated to freezing. The duration of their experiments was about 20 μsec . They looked at benzene, CCl_4 , water, and ethanol with the results shown in Table VIII. Only CCl_4 showed evidence

TABLE VIII. Freezing experiments in liquids.

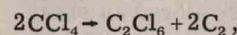
| Material | Pressure range, GPa | Phase transitions | | Comment | References |
|---------------------|---------------------------|-------------------|---------|---|------------------------------------|
| | | Press., GPa | Temp. | | |
| Benzene | 8-11 | ... | ... | Transparent | Walsh <i>et al.</i> (1957) |
| Benzene | 0.48-0.78 | ... | ... | R-H measurement | Cook <i>et al.</i> (1963) |
| Benzene | 1.9-43 $\Delta V = 17\%$ | 13.3-19.4 | 2300 K | Discont. in U_s-U_p ; probably not freezing | Dick (1970) |
| Ethanol | 7-10 | ... | ... | Transparent | Walsh <i>et al.</i> (1957) |
| CCl ₄ | 1-17 | 7-13 | ... | Increasing opacity with p | Walsh <i>et al.</i> (1957) |
| CCl ₄ | 1.2-12.9 | ... | ... | R-H measurement | Cook <i>et al.</i> (1963) |
| CCl ₄ | 0-1.6 | ... | ... | R-H measurement | Lysne (1971) |
| CCl ₄ | 8-20 | ... | ... | Brightness measurement | Voskoboinikov <i>et al.</i> (1968) |
| CCl ₄ | 2.7-63.3 | 16.5 | ~2500 K | Probably not freezing | Dick (1970) |
| H ₂ O | 3-10 | ... | ... | Transparent | Walsh <i>et al.</i> (1957) |
| H ₂ O | | 11.5 | ... | Discontinuity in U_s-U_p | Al'tshuler <i>et al.</i> (1958) |
| H ₂ O | 4-30 | ... | ... | Transparent | Zeldovich <i>et al.</i> (1961) |
| H ₂ O | 1.8-11 | Double shock | | Freezing occurred, see text | Kormer <i>et al.</i> (1968) |
| CS ₂ | 0.4-6.2 $\Delta V = 16\%$ | ... | ... | R-H measurement | Cook <i>et al.</i> (1963) |
| CS ₂ | 2.3-52.6 | 6.2-8.0 | ... | Discontinuity in U_s-U_p | Dick (1970) |
| Methanol | 9.6-10.7 | ... | ... | R-H measurement | Cook <i>et al.</i> (1963) |
| Liq. N ₂ | 1.9-39.1 | 13.5 | 3400 K | Slight discontinuity in U_s-U_p ; probably not freezing | Dick (1970) |

of transition.

Al'tshuler *et al.* (1958) reported detailed shock measurements in water, including a phase transition at 11.5 GPa. The shock data had a slope discontinuity in the $U_s - U_p$ plane, and there was a change in reflectivity in accompanying optical experiments. Zeldovich *et al.* (1961) explored the region from 4 to 30 GPa using optical transparency measurements and did not find evidence of freezing of water. Kormer *et al.* (1968) reported still more experiments on water. They confirmed the reliability of the Rice and Walsh (1957) equation of state and did reflectivity, index of refraction, and opacity experiments in a system designed to send a double shock into water. They found that if the amplitude of the first shock was between 2 and 3.5 GPa and the second between 4 and 10 GPa, reflection turned to intense diffuse scattering after the second shock entered the water. They interpreted this as formation of ice VII and inferred a time to freeze of the order of 10^{-7} to 10^{-6} s. It seems likely at this time that the Al'tshuler *et al.* (1958) observation was an artifact of their experiment, and that the equation of state of Rice and Walsh (1957) represents a good approximation to the equation of state of water in shock and static loading, provided the requisite time for transformation is available. An interesting sidelight of this is a comment by A. H. Jones (1975) that shock experiments in some water-saturated porous rocks are compatible with the formation of ice VII. In such cases the compression path of the water is apt to be one of multiple shocks, and the results of Kormer *et al.* (1968) accordingly apply.

Following Walsh and Rice's observation that shocked regions in CCl₄ became opaque above about 13.0 GPa, Doran and Ahrens (1963) and Dick (1964) both reported that its electrical conductivity increased rapidly with shock pressure above 12 GPa. Dick (1970), who made shock measurements from 2.7 to 63.3 GPa, also reported a slight bend in the $U_s - U_p$ curve for CCl₄ at 16.5 GPa,

corresponding to a weak cusp in the R-H curve. Brightness temperature measurements made by Voskoboinikov and Bogomolov (1968) gave temperatures ranging from 1400 to 2900 K for shocks between 8 and 20 GPa in CCl₄. These were somewhat lower than Dick's calculated temperatures, but of comparable magnitude. Equilibrium calculations show that the R-H curve for CCl₄ from room temperature crosses into the mixed phase region of the solid at about 1 GPa and may reenter the liquid phase at about 16 GPa (Dick, 1970). Lysne (1971) reported shock measurements made below 1.6 GPa at initial temperatures of 254, 264, and 297 K in an attempt to identify this low-pressure phase boundary. There was no positive evidence of freezing in this pressure region, though he notes that calculated temperatures on his R-H curve centered at room temperature are about 40 C greater than those on R-H curves extrapolated from earlier work to low pressures. He suggests that this difference might result from partial freezing, but concludes that none of the experiments on CCl₄ give positive evidence of total freezing or the lack of it. This seems a fair statement. It is unlikely that the 16.5 GPa break noted by Dick is freezing. He suggests, following C. Mader, that it might be due to a chemical reaction



but again there is no positive evidence that this is the case.

Several other liquid measurements are listed in Table VIII, only some of which show evidences of phase change. Dick (1970) notes that the $U_s - U_p$ slope discontinuity in benzene is compatible with similar observations by Warnes (1968) on anthracene, 18 GPa, phenanthrene, 20 GPa, pyrene, 24 GPa. All are hydrocarbons and the pressure of the discontinuity increases with molecular complexity. He suggests that the effect may be due to polymerization.

Dick (1970) also notes that A. Kusobov of Lawrence