



FIG. 26. Determinations of the phase diagram of bismuth I, bismuth II, and liquid by static and shock loading are found to be in good agreement. Earlier discrepancies reported by Duff and Minshall (1957) were apparently caused by a lack of time resolution of their detectors.

loading because there is uncertainty in the correct assignment of transition stress for wave profiles in which pressure changes slowly with time.

As is the case with transitions in other solids, lack of thermodynamic equilibrium in the mixed phase region is indicated in the measurements of Duff and Minshall by the differences between the calculated and observed Hugoniot curve in the mixed phase region above the solid I–solid II transition pressure.

Johnson *et al.* (1974) have reported a complete solid I–solid II–liquid equation of state for bismuth from which equilibrium calculations can be readily made. Differences between calculated and observed rise times indicate that equilibrium calculations do not correctly describe details of the material response. This work was extended to a more complete and elegant treatment incorporating transformation rates by Hayes (1975). This work is described in more detail in Sec. VI.B.

F. Graphite-to-diamond transformation

Parsons (1920) subjected graphite to explosive shock waves and produced what he believed to be diamond in the recovered residue, but positive identification was not possible at that time. Riabinin (1956) attempted unsuccessfully to identify diamond in graphite recovered from shock loading experiments. DeCarli and Jamieson (1961) subjected shock-loaded graphite to chemical separation, followed by x-ray diffraction analysis, and produced positive evidence of the existence of diamond particles in the residue. Alder and Christian (1961) reported an abrupt change in slope of the R–H curve for graphite of 95% theoretical density at about 40 GPa; this they identified with formation of the diamond phase.

This result was confirmed by Pavlovskii and Drakin (1966) and by Trunin *et al.* (1969). An apparent second transformation reported by Alder and Christian at about 60 GPa was attributed to experimental error by Pavlovskii and Drakin and Trunin *et al.*

Doran (1963b) reported measurements of the R–H curve for pyrolytic graphite to about 30 GPa, and Coleburn (1964) reported measurements to 49 GPa. Both authors found compressibility decreasing substantially above about 10 GPa, in contrast with measurements mentioned in the preceding paragraph; in those cases compressibility was essentially constant below 40 GPa. Coleburn found no evidence for a transition at 40 GPa. McQueen (1964) and McQueen and Marsh (1968) reported a multitude of measurements on diamond and graphite of various densities for pressures between 2.4 and 90 GPa. Their data on pyrolytic graphite agree with the Doran and Coleburn values in the same pressure ranges and show a break in slope of the $U_s - U_p$ curve at 40 GPa which they interpreted as the transition to diamond. Their measurements show no evidence of a transition above 40 GPa, in agreement with Trunin *et al.* (1969). Pavlovskii (1971) has reported shock compression data on single-crystal diamond between 50 and 580 GPa and finds no evidence for a high-pressure phase transition. McQueen and Marsh (1968) also reported data on pressed powder diamonds between 43 and 128 GPa and found no evidence for a transition.

McQueen and Marsh fitted their $U_s - U_p$ data on pyrolytic graphite below 40 GPa with two straight lines having a break in slope at about 6 GPa. They attribute this break to a second-order phase transition associated with buckling of basal planes. They were able to fit R–H curves for all the various graphite densities by assuming them to respond to pressure according to the equation of state of pyrolytic graphite above 6 GPa with a Grüneisen parameter, Γ chosen so that $\Gamma\rho = \text{const}$.

Both Dremin and Pershin (1968) and McQueen and Marsh (1968) found that graphites of densities lower than 2.2 Mg/m³ exhibit a break in their $P-V$ curves around 23 GPa. These observations indicate that the graphite-to-diamond transition is lowered in samples of lower initial density.

It appears fairly certain that graphite does indeed transform to diamond at a shock pressure of the order of 40 GPa with a mixed phase region extending to 60 GPa. It is equally certain that there is no metallic transition of the kind reported by Alder and Christian for $P < 300$ GPa (Trunin *et al.*, 1969). The second-order transition at 6 GPa in pyrolytic graphite suggested by McQueen and Marsh (1968) is speculative. To place it on firmer ground appears to be a formidable task. Increasing porosity appears to decrease the transition pressure possibly due to the effect of temperature.

Alder and Christian (1961), Pavlovskii and Drakin (1966), and Dremin and Pershin (1968) reported that measurements below 40 GPa were sensitive to sample thickness. This observation is consistent with a finite transformation rate for the transition to diamond. McQueen and Marsh (1968) did not see thickness effects, but the possibility does not appear to be excluded by their data.

In related work on recovered samples, Trueb (1968,

1970) has identified both hexagonal and cubic forms of carbon and has identified a "hard" graphite, which apparently resulted from conversion of diamond formed during shock loading. Only the cubic form of diamond is found in recovered shock-loaded graphite in a copper matrix (Trueb, 1971). In examination of Madagascar graphite compressed to a density of 2.05 Mg/m^3 and shock loaded to 45 GPa for a duration of 300 ns, Pujols and Boisard (1970) found a well-defined region within the sample which had apparently transformed to diamond and reverted to graphite on unloading. Fournier and Oberlin (1971) have examined recovered samples of shock-loaded graphite with an electron microscope and found diamond as well as other disordered forms of graphite.

Commercial shock processes presently being used for production of commercial diamond yield crystallites ranging from 500 Å to 30 μm in size (DeCarli, 1966; Trueb, 1971).

DeCarli (1967, 1976) has identified diamonds in graphite shock-loaded to pressures less than 15 and as great as 150 GPa, using more porous samples at the lower pressures. He attributes diamond formation to nucleation and growth processes, followed by immediate quenching in heterogeneously heated samples. It has also been suggested that diamond is formed by direct compression of rhombohedral graphite, but this seems unlikely since amounts of recovered diamond appear to be independent of starting material (DeCarli, 1967).

Diamonds found in meteorites are believed to result from shocks produced in terrestrial or extraterrestrial impact (Lipschutz, 1964; DeCarli, 1967), and the presence of diamonds in certain minerals is considered as evidence of meteoritic origin (Lipschutz, 1968). Vdovykin *et al.* (1973) have shock-loaded samples of carbonaceous matter from two meteorites and produced diamonds.

G. Germanium and silicon

Germanium and silicon exhibit particularly interesting transitions because their HEL values are a substantial fraction of their transition pressures. For example, [111] orientation Ge crystals have HELs of about 4.5 GPa compared to the transition pressure of about 14 GPa, and [111] orientation Si crystals have HELs of about 5.0 GPa compared to transition pressure of about 10 GPa. Thus, these crystals offer an excellent test of the equivalence of shock and static loading transition pressure measurements in the presence of large shear stresses resulting from shear strength.

Minomura and Drickamer (1962) reported a decrease in resistance of six orders of magnitude in Ge at static high pressures between 12.0 and 12.5 GPa; the large change in resistance and other considerations indicated that the transition was to a metallic phase. With x-ray diffraction techniques, Jamieson (1963a) determined that both Si and Ge go to the white Sn phase when pressure is increasing; both revert to a still different structure when pressure is subsequently decreased (Kasper and Richards, 1964). Jamieson also measured volume compression required to initiate the transition and volume change between the two phases.

In the first shock loading work on Ge, McQueen (1964) reported a multiple wave structure with an HEL of about 4.0 GPa and a transition stress of about 12.5 GPa.

Graham *et al.* (1966) used resistance measurements of impact-loaded [111] Ge to give a measure of the HEL and the transition pressure. Pavlovskii (1968) used the electromagnetic gauge in explosive loading experiments to measure wave profiles in [111] samples. He derived values for the HEL and p_x^{TL} that were in good agreement with Graham *et al.*; however, measured particle velocity and shock velocity values show considerable disagreement with other measurements and with the shock velocity predicted from ultrasonic measurements. Hence, Pavlovskii's measurements apparently contain two compensating errors and raise questions about problems with the electromagnetic gauge technique.

Jacquesson *et al.* (1970) reported thermoelectric emf measurements on [111] Ge which confirmed shock velocity measurements of Graham *et al.* for the elastic and transition waves. Gust and Royce (1972) reported wave profile measurements on [111], [100], and [110] Ge and determined HEL and transition pressure values. Their p_x^{TL} values are somewhat lower than the value reported by Graham *et al.*, but the stated errors appear to bring the measurements into agreement within experimental error.

A comparison of shock and static loading transition values in Table V shows reasonable agreement, after shear strength correction, between shock and static pressures and between volume compressions required to initiate the transition. No significant discrepancies are indicated between shock and static loading measurements even though shock loading pressures are subject to large shear stress corrections.

In the mixed phase region above the transition, Graham *et al.* reported a value of compressibility in agreement with that calculated from the equilibrium phase line, whereas the more numerous measurements of Gust and Royce disagree with the equilibrium calculation. Since the investigation of Graham *et al.* included only a single measurement in that region, it is likely that their result is incorrect because of misinterpretation of the resistance record. If this is true, the mixed phase region of shock-loaded Ge exhibits nonequilibrium behavior, as do other materials which have been examined.

The situation with silicon is less well-defined than with germanium. Minomura and Drickamer (1962) reported a five to six order-of-magnitude change in the resistance of silicon samples between 19.5 and 20 GPa when shear stresses were low. A resistance drop was observed between 13.5 and 15 GPa when shear stresses were high, even though there was no indication of intermediate transitions when shear stresses in their apparatus were low. Jamieson's (1963a) x-ray diffraction measurements in an apparatus with large shear stress showed the transition at a volume compression of 9.2%, which corresponds to approximately 16 GPa. Thus Jamieson's measurements confirm the sensitivity of the transition to shear. Wentorf and Kasper (1963) found the transition to be sensitive to shear, temperature, and time of pressure and found a bcc structure from samples recovered after release of pressure.