



FIG. 16. The observed shock velocity versus particle velocity for NaCl, as reported by Fritz *et al.* (1971). The larger symbols indicate more than one datum point. The ultrasonic bulk sound speed determined by Haussühl (1960) is shown at the lower extension of the shock data. The data in the vicinity of $U_s = 6$ km/s indicate that a phase transition is occurring. However, the behavior is different from that expected in the idealized case, for which a horizontal line in the U_s vs U_p relation would be observed.

mentioned earlier. The post mortem technique of metallurgical examination has provided surprisingly good information in several instances. Of particular note is the work of Johnson *et al.* (1962) which provided the first experimental evidence for a triple point in iron at 11.5 GPa and 775 K by metallurgical examination.

Of the other detectors, the electromagnetic gauge, the Manganin gauge, and the sapphire gauge are capable of wave profile measurements. The first two of these have been used extensively. The flash radiograph provides measurement of locations of shocks at various times and has been used to observe kinetic effects in the antimony transition in a configuration of steady two-dimensional plane flow.

X-ray diffraction measurements under static high pressure are valuable for determining characteristics of high-pressure polymorphic phase transitions (Banus, 1969). X-ray diffraction measurements are a recent addition to the probes available for shock-induced phase transition measurements. The success so far enjoyed by these measurements is the result of a substantial effort and it is not clear how widely applicable the technique will be. Nevertheless the measurements have shown that shock-loaded crystals retain order at the microscopic level in spite of gross plastic deformation (Johnson *et al.*, 1970, 1971, 1972). The technique has

been successfully used to identify a high-pressure BN phase (Johnson and Mitchell, 1972). A similar flash x-ray device has been constructed in Japan (Kondo *et al.* 1975). For further descriptions of the technique see Mitchell *et al.* (1973a, 1973b).

IV. EXPERIMENTAL OBSERVATIONS OF POLYMORPHIC PHASE TRANSITIONS

A. Summary of shock-induced polymorphic phase transition measurements

Results of a comprehensive search to document measurements of shock-induced polymorphic phase transformations are shown in Table AI in the Appendix. The summary is too extensive to fully discuss in the text; however, Table AI gives considerable information on each measurement and a reference to the original article. Except in special cases no attempt has been made to document measurements on geologic materials since this work has been reviewed by Ahrens *et al.* (1969) and Ahrens (1972). Second-order and melt transitions are not included in Table AI. They are treated separately in Sec. V and VI, respectively.

Entries in the table give a description of the sample and its original condition and give observed values of p_x^{TL} and η_{TL} for the transition.⁵ The table also includes information on loading method and measurement technique and special remarks. If kinetic effects are associated with the transition, sample thickness is an important variable; hence, thickness or range of thicknesses is included under remarks.

Examination of the entries in Table AI shows that iron is the most extensively investigated material. The transition stresses of iron alloys have also been widely investigated but are typically single measurements. Of the measurements on elements, the antimony results are especially interesting because of large kinetic effects. Bismuth has been well investigated and its importance to static pressure calibrations makes the work of particular importance. Germanium and silicon are interesting because of their large HEL values. The graphite-to-diamond transition has been investigated by a number of authors. Among the alkali halides, NaCl is of interest and KCl has shown interesting crystallographic orientation effects. Among the oxides both vitreous silica and crystalline quartz show features not found in other solids.

In the remainder of this section individual materials will be separately discussed in an attempt to bring the observations into perspective.

B. The $\alpha \leftrightarrow \epsilon$ transformation in iron

The 13 GPa $\alpha \rightarrow \epsilon$ transformation in iron is the most widely studied shock-induced phase transition. Progress from a newly discovered transition to a well-characterized $\alpha \rightleftharpoons \epsilon$ transition illustrates the important role that various static high-pressure and shock loading techniques can play in characterizing a transition. Further-

⁵ p_x^{TL} is transition pressure observed in shock loading; $\eta_{TL} = 1 - V_{TL}/V_0$ is the corresponding volume compression.

more, the shock investigations cover a period of 20 years and afford an opportunity to check consistency of measurements and to assess the roles of different instrumentation.

Minshall reported results from shock measurements on iron at the Berkeley meeting of the American Physical Society in 1954 (Minshall, 1955a). His pin technique records of free surface motion showed the arrival of three distinct shocks, which he identified as an elastic wave of 0.67 GPa amplitude, a Plastic I wave, commensurate with a phase transformation at 13.0 GPa, and a Plastic II wave representing driving pressure. This information was incorporated with other measurements and reported by Bancroft *et al.* (1956). Following this discovery, considerable effort was directed toward reconciling shock and static loading experiments and identifying the high-pressure phase. In 1956 Bridgman attempted, without success, to detect the transition with resistance measurements in static high-pressure experiments. Subsequent measurements of the well-known Bi I \rightarrow Bi II transition by Duff and Minshall (1957) gave confidence in comparisons of shock and static experiments. Katz *et al.* (1959) and Curran *et al.* (1959), with oblique shock measurements, found qualitative agreement with the observations of Bancroft *et al.* The gross difference between static and shock measurements was finally reconciled by resistance measurements of Balchan and Drickamer (1961), who observed the transition in static experiments. This measurement at 13 GPa emphasized that Bridgman's failure to observe the transition was the result of an incorrect calibration for the high-pressure scale with the Bridgman anvil apparatus.

The new high-pressure phase was first thought to be the fcc (γ) phase. Claussen (1961) determined the $\alpha \rightarrow \gamma$ phase boundary with a high-pressure belt apparatus to

about 8 GPa. [The original data were corrected for the new pressure scale by Kaufman (1961).] Kennedy and Newton (1963) used a piston-cylinder apparatus for similar studies to 5 GPa. When Kaufman (1961) extended his $\alpha \rightarrow \gamma$ phase stability calculations to 17 GPa, disagreement between static experiments, calculations, and shock observations was apparent. Minshall (1961) reported further studies of the shock-induced transition in iron and in low carbon steels, including some in which the initial temperature of the sample was varied, and determined that the slope of the phase boundary in the vicinity of the 13 GPa transition was in substantial disagreement with Kaufman's calculations.

The gross discrepancy between shock measurements and combined results of thermodynamics and static measurements on the $\alpha \rightarrow \gamma$ transitions was resolved by experiments of Johnson *et al.* (1962), who used a shock loading technique with samples at temperatures from 78 to 1158 K to suggest the existence of a triple point at 775 K and 11.5 GPa. It is significant that these measurements, which were crude by shock loading standards, were instrumental in establishing correct overall features of the phase diagram and have not been greatly altered to date. It is likely, however, that important quantitative features determined by Johnson *et al.*, such as the location of the triple point, are in error due to the experimental method. Their experiments did not use plane-wave loading. Transition pressures were determined from observations of the locations of dark-etching zones within sectioned samples, earlier identified as transformed regions by Smith (1958) and Katz (1955). Locations of zone boundaries were correlated with transformation pressure by reference to Bancroft *et al.* (1956) at room temperature and calibration of the pressure field using a pellet momentum technique de-

FIG. 17. The temperature-pressure phase diagram of iron as determined by shock and static loading experiments and calculation of the triple point. The shock loading data do not include a shear strength correction. The data of Barker *et al.* (1974) include the temperature increase due to shock loading, while the other shock data are plotted at the initial sample temperature. Data on the α - γ phase line by Leger *et al.* (1971) under static loading agree with the other static loading investigations but are not shown owing to a lack of space. The dotted line connects the calculated triple point of Blackburn *et al.* (1965) to the equilibrium stress or pressure determined as the mean value between loading and unloading in both static and shock loading investigations.

