

others. Multi-anvil apparatus with multi-directional applied forces are expected to produce fewer shears than uniaxial apparatus. One would also expect a Bridgman anvil system with planar-type chambers to fit the hydrostatic approximation less well than systems containing volumes of a more three-dimensional nature.

The shear component in shockwave environments is less certain than in solid-media systems since both acceleration and strength-of-materials forces can operate. Some intercomparison studies have been made between shock and quasi-hydrostatic data, but the calibrations are basically independent. Volumetric intercomparisons through theoretical equations of state indicate a fair consistency between the two techniques. Although the shear stresses in shock waves are large, the pressures are also very high, and the ratio of shear stress to normal stress may not represent as poor an approximation to the hydrostatic condition as a first impression suggests. The actual stress state in the shock front has not yet been fully characterized, but phase transition pressures in single-crystal samples have been shown to exhibit a sizable orientational dependence attributable to shear stresses.

c. Equilibrium Pressure

As discussed in section 3, phase transformations in selected materials are the basis for a fixed-point calibration procedure at high pressure. Such points must be specifically defined in terms of the thermodynamic equilibrium condition between the two phases. We have alluded earlier to the condition of system equilibrium, wherein we mean "a stable state which a system approaches asymptotically within laboratory times." As used, this phrase applies to changes in continuously varying parameters such as pressure, temperature, electrical resistivity, etc. associated with the pressure-generating system. Equilibrium of the total system in this sense does not imply thermodynamic equilibrium of a material sample or calibration specimen within the pressure chamber. We now desire to discuss this more critical equilibrium condition.

Since fixed-point calibrations involving first-order transformations are the dominant technique used by the average high-pressure worker, a thorough characterization of the transformations in various environments should be made. The thermodynamic equilibrium transition pressure for a pure substance is defined for isobaric processes as the pressure (or temperature) at which the Gibbs free energy per atom of the two adjacent phases is equal. Such a point is readily defined in a mathematical symbolism, but for solid-solid transformations the experimental realization of this idealized condition and the determination of the equilibrium pressure and temperature to high precision requires greater insight. Furthermore, in practice many measured transformations are used to calibrate an apparatus-load scale rather than a true sample-pressure scale. An understanding of the non-reversible effects in both

the apparatus and the sample is required to make precise equilibrium determinations.

Upon application of a continuously increasing load, suppose that a material undergoes a first-order transformation from phase I to a phase II (I-II) at an applied load L_{I-II} and an applied sample pressure P_{I-II} . Upon continuously decreasing load the reverse transformation (II-I) will occur at an applied load L_{II-I} and an applied sample pressure P_{II-I} , where $L_{II-I} < L_{I-II}$ and $P_{II-I} < P_{I-II}$. The differences $(L_{I-II} - L_{II-I})$ and $(P_{I-II} - P_{II-I})$ are commonly called hysteresis and even in the most ideal hydrostatic situations are non-zero for solid-solid transformations. The differences $(L_{I-II} - L_{II-I})$ reflect apparatus effects known as apparatus hysteresis as well as non-reversible effects in the sample itself, referred to as sample hysteresis.

Four interrelated phenomena giving rise to this hysteresis have been isolated:

- (1) Mechanical friction in pressure-generation apparatus such as in piston-cylinder apparatus (not the free-piston gage),
- (2) pressure gradients in solid-media systems (both within the pressure-transmitting solid and within the calibration specimen itself),
- (3) nucleation energy (which may differ between hydrostatic and non-hydrostatic conditions), and
- (4) growth energy.

Each of the above has been discussed by various workers, often with differing terminology, but here we attempt to categorize and delineate. In non-hydrostatic media systems all four phenomena are operating during procedures generally used to "calibrate" the press load in terms of pressure using known fixed points. In some cases L_{II-I} may differ from L_{I-II} by as much as 30 percent due to (1) and (2). In such cases values of L_{I-II} only are used as calibration points, but serious uncertainties arise due to unknown hysteresis of types (3) and (4). Items (1) and (2) above are also the source of "smeared out" transitions in which transformations take place over a broad interval of applied load.

The first two items are obviously distinct from each other, but experimentally the two are rather difficult to separate from one another, and the separation is seldom made. Items (1) and (2) combined are spoken of as the apparatus hysteresis, and together can be separated from (3) and (4) by placing pressure sensors at the specimen itself. Jeffery, et al. (1966), using the tetrahedral-anvil press equipped for x-ray diffraction studies, used the lattice parameter of NaCl as the pressure indicator. A calibrant foil (Bi or Ba) was surrounded by NaCl and enclosed in 50-50 wt percent boron-plastic tetrahedron. Pressure was determined from the measured lattice parameter through Decker's (1966) equation of state. Load differences $L_{I-II} - L_{II-I}$ corresponding to differences in calculated pressures of 20 to 30 kbar were measured, whereas the differences $P_{I-II} - P_{II-I}$ associated with nucleation was of the order of two to five kbar.

Time-dependent variations in the pressure gradients in a solid-media hexahedral-anvil apparatus have been studied by Barnett and Bosco (1966). The pressure was indicated by a manganin gage placed inside a liquid chamber, which in turn was embedded in the pyrophyllite cube. Relaxation of the pressure in the pyrophyllite with time was measured as well as magnitudes of the gradients.

The non-reversible nature of transformations at high pressure even in a hydrostatic environment and the interpretation of this effect as a nucleation energy barrier was well understood by Bridgman (1940a) and others working in liquid chambers at the lower pressures but has not been fully appreciated by those working at much higher pressures in non-hydrostatic environments. The phenomenon has been studied rather extensively with regard to temperature-initiated solid-solid phase transformations at one bar (Smoluchowski). Temkin (1966) presents a theoretical discussion on the thermodynamics of the formation of a new phase under hydrostatic pressure.

The fact that the Gibbs free energy of two phases becomes equal as pressure is exerted on a sample of phase I does not imply that the transformation will proceed even though the equilibrium pressure has been reached. The kinetics of the transformation must be considered, and means must be available for the atoms of the specimen to rearrange into the new crystalline structure, at least in a small localized region called an embryo. High temperature is often used to provide energy for the rearrangement (Stark and Jura, 1964). The energy barrier against the rearrangement is so large at room temperature for many strong-bonding materials that the transformation never proceeds at *any* applied pressure, whereas the barrier for some metals is relatively small. Any transformation to be of value as a fixed point must exhibit a small nucleation energy. At high temperatures where the kinetics of reactions are faster, the temperature hysteresis across a phase boundary is generally small, but high pressure often increases this hysteresis by inhibiting the rearrangement. For example, in iron at one bar the temperature hysteresis of the α - γ transition is of the order of a few degrees. At higher pressure (but lower temperature) as one approaches the triple point near 100 kbar, this hysteresis has increased to about 30°.

Smoluchowski (1951) has discussed the statistical creation of embryos of phase II in a phase I matrix near the equilibrium pressure and temperature. There is an increasing probability of nucleating embryos of a given size as pressures or temperatures further into the stability field of II are reached. The fundamental reason for the appearance of such embryos in a homogeneous substance is the existence of transient local fluctuations from the normal state. These deviations may occur in any part of the substance as fluctuation of local energy or density, possibly due to localized regions of strain. The condition for growth of the new

phase, and thus the occurrence of the transformation, is that the Gibbs free energy per atom of the embryo *and its surrounding* be less than the free energy per atom of the original matrix. When an embryo of II is formed in a matrix of I at conditions within the stability region of II, a free energy difference proportional to the volume (cube of the dimension) is available. This difference generally increases as one moves farther away from the equilibrium conditions. Since there exists an interface between the embryo and its surroundings with an attendant surface energy proportional to the square of the embryo dimensions, the embryo must have minimal size at a specified pressure and temperature in order to grow rather than diminish. The free energy difference is the driving force for the reaction. The embryos are generated with a statistical distribution, and the smaller embryos are unstable. The required size is smaller further from the equilibrium condition since the critical size is a function of the change ΔG in the Gibbs energy per atom due to the transformation, and this difference increases as one moves further from the equilibrium condition. At pressures and temperatures very near the equilibrium conditions one would find it necessary to wait a very long time for a sufficiently large embryo to be statistically generated, but further from the equilibrium condition the much smaller embryos required are produced profusely, and the transformation proceeds. This effect gives rise to an observed sensitivity to pressurization rate or heating rate. If a *non*-statistical energy barrier were causing the hysteresis, no time-dependence should be observed.

Davidson and Lee (1964) working under hydrostatic conditions determined an average hysteresis interval of 0.79 kbar for the Bi(I-II) transformation and showed that it was dependent on the pressurization rate. Zeto, et al. (1968) concluded that the generally observed hysteresis in the Bi I-II transition is nucleation limited. Their work was carried out under hydrostatic conditions, and the observed hysteresis interval was shown to be highly time-dependent. This result suggests the statistical generation of nucleation sites. In the work of Jeffrey, et al. (1966) the measured hysteresis on the Bi I-II transformation under non-hydrostatic conditions was several times larger than the hysteresis measured by Zeto, et al. (1968) and by Davidson and Lee (1964). The work by Jeffrey, et al. suggests a greatly increased nucleation energy in the solid environment. This fact implies the existence of strain energy set up around the embryo due to its formation and indicates that hysteresis measurements in hydrostatic environments *cannot* be used to interpret results in non-hydrostatic environments.

Nucleation mechanisms have been suggested for various types of solid-state transformations but are not well-understood, especially as they apply to the ultra-high pressures. Reconstructive-type transformations are expected to have higher nucleation energies than