Livermore Laboratory has recovered "black fluffy material" from shocked samples of CS_2 and suggests that the 6.2 GPa transformation may be the transformation to a black amorphous solid which occurs statically at about 4 GPa and 390 to 475 K.

The case for freezing in shock is not a strong one, and it is hard to invent any dramatic experiment which will resolve the question, even in principle. It seems more likely that confirmation will come through careful and thorough work with the phase diagrams, as has been done for melting in bismuth. In fact, Asay (1977) has recently reported evidence for refreezing in shock-loaded bismuth based on time-resolved measurements of unloading waves.

VIII. DISCUSSION AND CONCLUSIONS

The experimental observations summarized in previous sections of this review and in Table AI of the Appendix provide quantitative data with which the assumptions underlying theoretical treatments and interpretation of the data can be tested. Although it would be a mistake to generalize, it is possible to come to reasonably specific conclusions regarding interpretation of the shock loading data and directions for future work. Comments concerning specific materials also seem in order.

Perhaps the most important question regarding data obtained describing shock-induced phase transitions is whether they are credible. Do measurements under shock loading lead to determinations of thermodynamic properties of transitions which are as valid as measurements taken under static high-pressure loading? Do the transformations run to completion in the 10^{-6} s or less characteristic of the shock loading experiment? Do experiments under shock loading provide results which are representative of thermodynamic equilibrium?

It is certainly easy to understand how a scientist who has investigated phase transitions under static loading and watched the many minutes sometimes required to complete a transition would be incredulous concerning reports of the same transition running to completion in the eight or nine orders of magnitude shorter time characteristic of shock loading experiments. Nevertheless, the shock loading data speak for themselves and, when the fundamental differences between static and shock loading are considered, radically different reaction rates seem quite credible.

The data indicate that excellent agreement is achieved between the transition pressures established under shock and static loadings for the Bi I→ Bi II transition, the Bi I→ Bi II→ liquid triple point, the KCl transition, the martensite to austenite transition in 28.4 at.% Ni–Fe, and the $\alpha \rightarrow \epsilon$ transitions in Fe–Mn alloys. The comparison is clouded in iron by the different transition pressures obtained by resistance and x-ray diffraction measurements under static loading; the transition pressure determined from shock loading lies between the two. There is good agreement on the germanium transition and excellent agreement on the $\epsilon \rightarrow \alpha$ transition in iron on unloading. Other measurements under shock loading appear credible, but there are insufficient data on which to make a hard comparison between static and shock loading experiments. Notable exceptions to the generally good agreement are the CdS, InSb, and Si transitions under shock loading which do not appear to have counterparts in static experiments. Nevertheless, these differences can in part be anticipated from static observations of sensitivity to shear. Taken as a whole the data indicate that in spite of complications of shear strength, plastic flow, and limited experimental durations, shock loading experiments can provide accurate measurements of transition pressures and transition volumes. This is not to say that all shock loading measurements are equally credible, but the record demonstrates that comprehensive, careful investigations with carefully studied instrumentation and carefully controlled loading will provide credible determinations of thermodynamic characteristics of transitions.

Transformation rates for shock transitions are a matter of prime concern. The various measurements of initial transformation rates under shock loading show that the rates are fast enough to allow the transitions to go to completion in the normal shock experiment, except possibly for antimony. Measurements of the Plastic II wave show that the transformation is indeed completed when driving pressure is great enough. Unfortunately, there are inconsistencies and there is at present no physical basis on which to quantitatively predict reaction rates. Why is it, for example, that the transformation rate for antimony is relatively slow, while the transformation rate for bismuth is fast? In order to develop quantitative physical models for transformation rates, research on nucleation and growth of new phases in shock-loaded solids is of prime importance. If the theory is coordinated with experiments with time-resolved wave profile measurements, it is likely that good progress can be made.

Because of fundamental differences there is little reason to expect similar transformation rates under static and shock loading. Under static loading, rates are dominated by the statistical probability of forming nuclei in a low-defect solid under uniform compression. Under shock loading, the plastic deformation required to achieve the high pressure is a consequence of the creation and motion of copious quantities of defects, which are uniformly swept through the sample by the stress wave. Chief among such defects are dislocations, which are created in large numbers in the Plastic I shock. They are known to be effective nucleation sites for transformation (Christian, 1965), and Johnson (1972) has shown, using conventional numbers for transformation energies and shock-induced dislocation density, that significant numbers of nucleation sites may be created in a fraction of a microsecond. In some materials, twins, formed by plastic deformation, are effective nucleation sites, and German *et al.* (1970b) have suggested that nucleation around twins is responsible for the $\alpha \rightarrow \epsilon$ transition in iron. Forbes (1976) has suggested an alternative mechanism for production of nuclei which is peculiar to shock conditions. He has pointed out that there is an equilibrium distribution of new phase embryos under ambient conditions of temperature and pressure, but that such embryos cannot grow because the parent phase is stable. But when a step in pressure is applied, the driving energy for transformation becomes positive, and some of those embryos which existed ini-

tally have suddenly become growing nuclei under stable conditions for the new phase. Contrast of this suggestion with the conventional view of nucleation illustrates an important need for experiments that distinguish between the roles of shock-produced defects and ambient material state in determining transformation rates under shock conditions. If shock-produced defects control transition rate, then rates which depend upon crystallographic orientation may be manifestations of restrictions imposed by the crystal structure on plastic flow and subsequent growth of crystallites. Then it is important to develop a more detailed fundamental understanding of plastic flow under shock loading. If initial material conditions control transition rate, then a tool may exist for measuring the relative effectiveness of various kinds of nucleation sites. Such a tool would be a valuable aid in furthering our understanding of general processes of transformation.

The problem of measuring equilibrium pressure–volume states is an old one and is not peculiar to shock measurements. Vanfleet and Zeto (1971) describe differences among initiation pressure on loading, initiation pressure on unloading, boundaries of the "region of indifference," and the inferred equilibrium pressure for the Bi I→ Bi II transition. In that case the initiation pressure on loading is about 300 MPa greater than the equilibrium pressure. This difference is reduced by encapsulating the bismuth sample in epoxy, but the pressure excursion in the mixed phase region is increased. It should not be surprising, then, that shock initiation pressure, p_x^{TL}, even when corrected for shear, differs from the equilibrium pressure of transition, nor that the slope $(-dp_x/dV)$ of the R–H curve in the mixed phase region exceeds that calculated for equilibrium, as shown in Fig. 18. Reasons for large values of $(-dp_x/dV)$ are of interest, however. Part of the effect may arise from the presence of shearing stresses not accounted for, as suggested by Vanfleet and Zeto; part may arise from sensitivity of nucleation sites to applied pressure. This latter suggestion is made by Forbes (1976), who shows that the fraction of iron transformed to the ϵ-phase in shock is exponentially related to the difference between Gibbs energies of new and old phases ("driving force"). An analogous relation exists between the amount of α-phase material produced and driving force for athermal martensite transformation in iron. These speculations are stimulating, but do not substitute for good experiments, carefully done. Unloading experiments, like those by Barker and Hollenbach in iron (1974), will aid in establishing equilibrium transition pressures.

Although the flash x-ray diffraction measurements under shock loading are not expected to give complete crystallographic descriptions, the work is of importance in establishing consistency with similar static loading measurements and for assessing general conditions in the shock-loaded state. The work to date has been successful in establishing that inelastic deformation under shock loading does not significantly alter the ordered crystalline nature of solids. In agreement with other transformation rate measurements, the flash x-ray diffraction measurements on boron nitride show that crystallites of significant size are grown in times of a few tens of nanoseconds.

In order for the shock loading experiment to provide full thermodynamic descriptions of transitions, it is necessary to take full advantage of the capability to determine stress and volume. (If there are unknown shear strength effects, the volume at the transition is perhaps a better measure for comparison with static data.) Complete studies include measurements of p_x^T, η_T on loading and unloading, compressibility in the mixed phase region, the HEL, compressibility of the high-pressure phase, and measurement of the dependence of the data on sample thickness and input pressure. These data, with Gruneisen parameter Γ and specific heat C_v, can then be used to determine isothermal compressions. Comprehensive investigations such as these will provide especially useful data characterizing pressure-induced phase transitions.

At this point special comments on specific materials are important to evaluate directions for further work. The calculated triple point in iron appears to be in significant disagreement with the measurements of Johnson *et al.* (1962) and in better agreement with the new equilibrium pressure near 300 K established from loading and unloading measurements. It was pointed out in Sec. IV.C that the measurements of Johnson *et al.* would not be expected to yield accurate values for pressure. In spite of that situation, the static high-pressure work of Bundy (1965) is tied directly to the data of Johnson *et al.*; hence, it appears that a new evaluation of the triple point of iron is urgently needed. If shock loading techniques are employed, plane-wave loading methods that include both loading and unloading should be employed.

Antimony appears to be an especially interesting material to investigate with time-resolved sample response measurements. If roles of the 7 and 8.8 GPa transitions can be separated, the relatively slow transformation rate would be important for more detailed study.

Further studies of the KCl and KBr transitions in the high-pressure phase would be expected to yield more detailed descriptions of the transitions. The low shear strength and simple crystal structures make them excellent candidates for both theoretical and experimental study.

The large apparent shear strength effects in CdS and InSb are significant exceptions to the usual behavior of solids under shock loading, yet the investigations on these materials are incomplete. Detailed studies seem to be in order for these materials. Work on them may provide key information for understanding the role of shear stress in phase transition.

The behavior of quartz under shock loading is the most complex of the materials whose response has been studied in detail. The strong possibility that upon yielding the material develops a heterogeneous structure of α-quartz and localized regions of very high temperature and low viscosity, perhaps melting, greatly complicates analysis of the high-pressure data and raises serious questions concerning interpretation of the data concerning dense phases of quartz and other similar materials. The possibility that local temperatures are thousands of degrees could explain the presence of stishovite under shock loading at average temperatures which were previously thought to be too low compared to the static data. The heterogeneous melting combined with transi-