

the various investigators and within data obtained by the same investigator. The pronounced stress relaxation observed behind the elastic wave by all the previous investigators suggests that the yield process is quite complex and, as is evident from the data, sensitive to experimental conditions. With our technique of obtaining the Hugoniot elastic limit all measurements are made in direct compression without unloading from free surfaces, and the region around the Hugoniot elastic limit may be investigated for small increments of stress over the critical value rather than for the large input stresses characteristic of an explosive experiment.

#### *Intermediate pressure region*

Our data in the stress region intermediate between the two cusps show the usual linear relation between  $U_s$  and  $u_p$ . In comparing our data to that of other investigators, it should be observed that interpretation of the data from a free surface velocity experiment for a material with a multiple wave structure and time dependent mechanical properties is sensitive to assumptions concerning the various wave interactions and relaxations. Our experiment characterizes the material for the total particle velocity imparted to the material and gives the wave velocity of all waves without complications resulting from the interaction of the waves. Thus the data relating the total particle velocity to wave velocities is obtained with minimum qualification. However, as was previously stated, to compute the stress in the multiple wave region, it must be assumed that the particle velocity of the leading wave is independent of the total particle velocity. This assumption is open to criticism since WACKERLE<sup>(14)</sup> has observed that the particle velocity and wave velocity of the Hugoniot elastic wave in crystalline quartz increase with increasing driving pressure. However, our wave velocity measurements provide some indication of the amplitude of the leading wave since a change in wave velocity is expected to result from a change in particle velocity. As can be seen in Table 1 the wave velocity of the leading wave was found to be constant with driving pressure. Thus large changes in the amplitude of the elastic wave are not likely. The stress-volume values which result when a constant amplitude elastic wave is assumed are shown in Table 1. Our previous brief report on

Ge compares our stress-volume data to that obtained from a free surface velocity technique.<sup>(15)</sup>

#### *Characteristics of the transition*

The large shear component of the elastic wave in the shock experiment results in a transition characterized by a stress rather than by the pressure of the transition. Therefore, we must consider the effect of the elastic compression on the transition. MINOMURA and DRICKAMER<sup>(10)</sup> have reported that the static transition is insensitive to shear; thus, if this observation is quantitatively correct, we would expect the transition to occur at the same volume regardless of the stress tensor producing the volume change. Our data show that the specific volume at the transition is between  $0.870 V_0$  and  $0.880 V_0$  when the very small correction to room temperature is made. Thus the transition does occur at the same volume in the static and shock wave experiment since Jamieson's static value<sup>(16)</sup> for the volume at the transition is  $0.875 V_0$ .

In order to compute an equivalent pressure from the observed transition stress, several assumptions must be made. Assuming that all stress increments in excess of the Hugoniot elastic limit are hydrostatic (the elastic-plastic assumption) and that the transition pressure is not changed by the shear component, an equivalent hydrostatic pressure may be computed from the observed transition stress. Since it is the volume which is independent of the stress configuration, the equivalent pressure for the elastic range is computed from the volume at the elastic limit and the compressibility. This yields a value from 114 to 122 kb\* for the equivalent pressure compared to MINOMURA and DRICKAMER's<sup>(10)</sup> value of from 120 to 125 kb. Thus, good agreement is achieved between the static and shock wave compression values for the pressure of the transition.

There has been some question,<sup>(1,13)</sup> whether the shock induced transition is an anomalous melting and perhaps not the solid-solid transition identified by JAMIESON<sup>(16)</sup> as a transition to a metallic

\* Cusps in the stress-volume curve are located between particle velocity points below and above the cusp. The values shown indicate the range of values possible within the observed points. Consideration of the  $U_s - u_p$  values indicates that the cusp is most likely toward the upper end of the range quoted.

white tin structure. Since the shock compression transition is at an elevated temperature ( $\sim 160^\circ\text{C}$ )<sup>(13)</sup> the small difference in values between the shock transition pressure and quasi-hydrostatic transition pressure indicates that the slope of the pressure-temperature phase diagram is close to zero. This is in agreement with the phase diagram determination for the solid-solid transition reported by BUNDY<sup>(17)</sup> and indicates that the shock wave transition is polymorphic. This observation is also confirmed by the independent measurement described below.

#### *Slope of the phase diagram*

DUFF and MINSHALL<sup>(18)</sup> have shown that shock wave velocity measurements in the mixed phase region of a shock wave induced polymorphic transition are sufficient to compute the slope of the phase diagram at the particular pressure and temperature of the transition and that this computation is essentially independent of the measurement of the transition pressure. Qualitatively, this unique condition results from the pressure increase which must accompany the volume change associated with the transition if the enthalpy change at the transition is finite.

Our data indicate that the highest stress experiment is in the mixed phase region, since the volume change from the transition stress to the input stress above the transition is not more than 8% while the volume change to complete the transition is 20.7%.<sup>(16)</sup> Thus the third wave is in the mixed phase region and the slope of the phase diagram may be computed from our measurement of the velocity of this wave. Following Duff and Minshall's development:

$$\left(\frac{dP}{dT}\right)^2 + \frac{2\beta}{(K_c - K)} \frac{dP}{dT} - \frac{C_p}{TV(K_c - K)} = 0, \quad (3)$$

where  $dP/dT$  is the slope of the phase diagram,  $\beta$  is the volume coefficient of thermal expansion of the solid before transition,  $C_p$  is the specific heat of the solid before transition,  $T$  is the temperature,  $V$  is the specific volume,  $K_c$  is the compressibility of the mixed phase region indicated by the wave velocity measurement and  $K$  is the compressibility of the solid before the transition. Using atmospheric pressure values for the thermodynamic parameters and McQueen's temperature rise

calculation<sup>(13)</sup> we find  $dP/dT = -3.1 \times 10^{-2} \text{ kb } ^\circ\text{C}^{-1}$ . The uncertainty involved in using atmospheric pressure values and in the temperature calculation leads to an estimated accuracy of the  $dP/dT$  value of 10%. This value of  $dP/dT$  is consistent with the comparison of our transition pressure amplitude to the static data. Further, the slope of the phase line is at least an order of magnitude less than the slope of the phase line for the transition from solid to liquid observed statically<sup>(17,19,20)</sup> and clearly not the solid to liquid transition. The slope of the solid-solid transition phase line is too low for accurate measurements under static conditions; however the measurements indicate that it is negative and very small<sup>(17)</sup> in agreement with our determination. The present value of  $dP/dT$  for the polymorphic transition in Ge appears to be the best measurement made to the present time.

Since values are now available for  $dP/dT$  and for the volume change,<sup>(16)</sup>  $\Delta V$ , accompanying the transition we can compute the enthalpy change,  $\Delta H$ , accompanying the transition from the Clausius-Clapeyron relation:

$$\Delta H/\Delta V = T \frac{dP}{dT} \dots \quad (4)$$

This change is found to be 12.5 cal/g which when compared to the estimated latent heat of fusion of  $\sim 110 \text{ cal/g}$  for Ge<sup>(17)</sup> is much too small to be consistent with a melting hypothesis.

In summary, the properties of the shock compression observations when compared to static experiments as in Table 3 clearly illustrate that the shock transition is a solid-solid transition with critical values in agreement with those obtained statically for the transition to the white tin structure. Further, we are able to compute the slope of the phase diagram from wave velocity measurements in the mixed phase region. We find no evidence for intermediate phases<sup>(21,22)</sup> below the 120 kb transition. Since our experiment includes a large shear strain component the agreement between our values and the static values indicates that the transition is not influenced by shear.

### SECTION 3 RESISTIVITY RESULTS

The elastic limit of 44 kb observed in the shock compression experiments results in large (2.5%)