white tin structure. Since the shock compression transition is at an elevated temperature ($\sim 160^\circ$C)[13] 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[17] 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[18] 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%.[16] 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, β 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[13] we find $dP/dT = -3{\cdot}1\times10^{-2}$ kb $^\circ C^{-1}$. 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[17,19,20] 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[17] 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,[16] ΔV, accompanying the transition we can compute the enthalpy change, ΔH, accompanying the transition from the Clausius–Clapeyron relation:

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

This change is found to be 12·5 cal/g which when compared to the estimated latent heat of fusion of $\sim$110 cal/g for Ge[17] 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[21,22] 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%)