



FIG. 4. Phase diagram for bismuth.

velocity by the pin technique were unsuccessful because of the very low pressure of the wave. For this reason the existence of the elastic wave was ignored in the analysis of the experimental data.

The measured shock parameters and the calculated equation of state information are presented in Table I. All of the experimental results are compared in Fig. 4 with the phase diagram for bismuth determined statically by Bridgman⁹ and by Butuzov, Gonikberg, and Smirnov.¹⁰ In Fig. 5 the results of the four experiments at room temperature are presented. The transition pressure plotted is the average value from the four experiments. An estimate of the Hugoniot curve in the region of mixed phases above the transition is also included.

DISCUSSION

The temperature at which the transition began to occur, that is the temperature behind the first shock, was estimated by assuming the shock compression to be adiabatic. Under these conditions it is easy to show that

$$T_1 = T_0 \exp\left(\frac{\alpha}{C_p \kappa} (v_0 - v_1)\right),$$

where the ratio $\alpha/C_p \kappa$ is assumed independent of pressure. For present purposes all quantities were evaluated at zero pressure, the ratio was assumed independent of initial temperature, and the difference between C_p and C_v was ignored. The calculated shock temperatures are included in Table I with the experimental results, and

⁹ P. W. Bridgman, Phys. Rev. 48, 896 (1935).

¹⁰ Butuzov, Gonikberg, and Smirnov, Doklady Akad. Nauk S.S.S.R. 89, 651 (1953).

they are used in comparing the results of this investigation with those of Bridgman in Fig. 4. Clearly this estimate of shock heating is crude; but none of the conclusions to be stated would be altered by a more nearly exact treatment.

Several points deserve comment. The transformation observed in this investigation is undoubtedly the I-II transformation of Bridgman. A least-squares fit to the experimental data indicates a slope of $-50.8 \text{ bar}/^\circ\text{C}$ which agrees very well with the Bridgman number of $-50.0 \text{ bar}/^\circ\text{C}$. Therefore, the ratio of $\Delta H/\Delta v$ is the same in both cases. The transition is observed at about 3.5 kilobars higher pressure in the dynamic than in the static experiments. One experiment performed in an attempt to understand this pressure difference will be discussed later. Finally the high-temperature experiment indicates clearly that the transformation from one crystal lattice to another is a faster process in bismuth than melting because the crystallographic transformation apparently occurred where melting was expected. The observation of a shock-induced transition to an unstable crystal lattice instead of to a stable liquid phase in bismuth is one of the most surprising results of this investigation.

The four experiments at ambient temperature provide the information needed to determine the dependence of transition pressure on temperature through the use of Eq. (1). Several attempts have been made to fit a curve between the transition point and these data as plotted in Fig. 5 in order to determine a value of compressibility in the mixed-phase region at the transition point. Unfortunately, the limitations of the experimental data introduce an uncertainty of about 60% in the result. The value of mixed-phase compressibility tabulated in Table II along with other physical constants used in a test of the theory is the average of the several determinations. The predicted slope of the coexistence line in the p - T plane determined from measurements at a single temperature was $-67 \text{ bar}/^\circ\text{C}$. This result differs from that determined directly by 30% but it is within experimental uncertainty of the latter value. It would be necessary to do experiments closer to the transition point in order to determine the mixed-phase compressi-

TABLE II. Data used to calculate the dependence of transition pressure on temperature from measured mixed-phase compressibility and mixed-phase compressibility from measured dependence of transition pressure on temperature.

T_0 , Initial temperature	19°C
α , Thermal expansion coefficient	$40.2 \times 10^{-6}/^\circ\text{C}$
C_p , Specific heat	$1.21 \times 10^6 \text{ ergs/g}^\circ\text{C}$
κ , Isothermal compressibility	$2.46 \times 10^{-6} \text{ bar}^{-1}$
v_1 , Specific volume at transition	0.0953 cc/g
T_1 , Temperature of transition	42°C
κ_{AB} , Mixed phase compressibility	$13 \times 10^{-6} \text{ bar}^{-1}$
dp/dT , Slope of coexistence line deduced from the above numbers by using Eq. (1).	$-67 \text{ bar}/^\circ\text{C}$
dp/dT , Measured slope of coexistence line	$-50.8 \text{ bar}/^\circ\text{C}$
κ_{AB} , Mixed-phase compressibility consistent with measured slope of coexistence line	$16.5 \times 10^{-6} \text{ bar}^{-1}$