TABLE I. Summary of data from experiments with bismuth. The captions are defined as follows: T_0 and T_1 are the temperatures before and after the first wave in °C, t is the bismuth plate thickness in mm; v_0, v_1, and v_2 are the specific volumes initially, after the first wave, and after the second wave in cm³/g; D_{10} and D_{21} are the velocities of the first and second waves measured relative to the material ahead of them in mm/μsec; $2u_1$ and $2u_2$ are the free-surface velocities after the first and second waves in mm/μsec; and p_1 and p_2 are the pressures behind the first and second waves in kilobars.

T_0	T_1	t	v_0	D_{10}	$2u_1$	p_1	v_1	D_{21}	$2u_2$	p_2	v_2
Ambient (19)	42	6.61	0.1021	2.043	0.272	27.2	0.09524	1.172	0.478	39.9	0.08687
	42	15.13	0.1020	2.041	0.270	27.0	0.09533	1.127	0.434	36.7	0.08839
	42	20.13	0.1020	2.048	0.268	26.9	0.09536	1.098	0.398	34.5	0.08963
	42	25.22	0.1020	2.063	0.272	27.5	0.09531	1.067	0.366	42.8	0.09112
				Average		27.15	0.09531				
−28	−27	22.05	0.1019	2.088	0.305	31.3	0.09422				
62	87	20.37	0.1020	2.033	0.254	25.3	0.09576				
208	236	20.38	0.1019	1.990	0.183	17.6	0.09800				

[segment 2′–2 in Fig. 2(b)] because there has not been time for a significant amount of transformation to occur if the assumptions concerning the rate of recrystallization made above are satisfied. As the shock proceeds through the metal the transition occurs and the steady-state configuration is approached. During this transient phase the strength of the first shock will decrease.

The experimental technique used in this investigation employs measurements made at the free surface of a metal plate for the deduction of shock strength. Therefore, if the strength of the first shock is observed to decrease with thickness of the metal plate, this is equivalent to a decrease with time and is evidence that the transition transient persists. Since the transient persists, the time required for the transformation to occur under shock conditions is of the same or a slightly smaller order of magnitude than the time during which the shock strength is observed to change.

EXPERIMENTS

The foregoing ideas were tested in a series of experiments with bismuth using the pin technique. Experimental techniques and data analysis procedures were similar to those described previously[7] in connection with a study of iron. As in previous work, pains were taken to maintain the planarity of the shock waves used. This insured that the flow behind the wave was one-dimensional. In the present investigation it was necessary to modify the shock-wave attenuator because the transition pressure is much lower in bismuth than in iron. The desired pressures, of the order of 35 kilobars, were obtained by using thick plates of iron and Plexiglas between the explosive and the bismuth. The 130-kilobar wave in the iron was attenuated by impedance mismatch at the iron-Plexiglas and Plexiglas-bismuth interfaces. The dimensions of the various pieces were chosen so that no multiply-reflected wave could reach the free surface of the bismuth in the time interval of interest in this experiment.

The bismuth used for these experiments was first cast as a cylinder, allowed to cool, heated in an oil bath to slightly less than the melting point, and then pressed to approximately one-half of the original height of the cylinder. This process resulted in a plate composed of crystals of less than $\frac{1}{8}$ in. size, randomly oriented.

Three groups of experiments were made with the system described above. Four shots were fired at ambient temperature (about 19°C) in an effort to determine the shock Hugoniot in the vicinity of the transition point and to investigate the kinetics of the recrystallization reaction. Also single-shot tests were made at 72°C and −48°C to determine the temperature dependence of the transition pressure directly.

After studying the results of these six experiments, it was thought desirable to determine the transition pressure at a much higher temperature. This required several modifications of the technique. Melting and possibly more catastrophic changes in the explosive system were prevented by attaching the explosive just before firing and by providing a $\frac{1}{8}$-in. air gap between the explosive and the heated metal parts. It was found that slowly heated Textolite had sufficient dimensional stability to act as the shock-wave attenuator. Finally a careful investigation was made of the offsets of the pins from the free surface of the bismuth as a function of temperature so that these offsets would be accurately known. One experiment was made under these conditions; and the temperature of the bismuth plate was 208°C at the time of firing.

Pressure and compression behind the first shock wave were determined from measurements of shock and free-surface velocity by using the simple conservation equations for mass and momentum and the good approximation that the free-surface velocity is twice the shock-particle velocity. The determination of conditions behind the second wave for the four experiments at ambient temperature was carried out as described previously.[7] In the other three experiments only a single shot was fired at each temperature; and sufficient information is not available to allow a significant calculation of the state produced behind the second wave.

Sound velocities of about 2.15 mm/μsec were measured by a standard pulsed-crystal technique. Attempts to observe the Hugoniot elastic wave moving with this

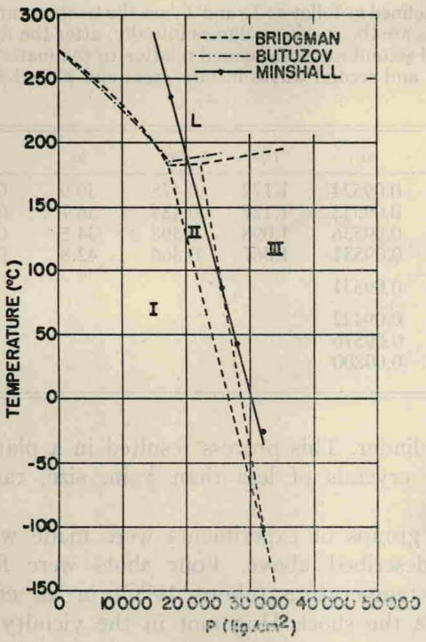

FIG. 4. Phase diagram for bismuth.

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 Bridgman[9] 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

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

where the ratio $\alpha/C_v\kappa$ 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 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 bar/°C which agrees very well with the Bridgman number of -50.0 bar/°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 bar/°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	40.2×10^{-6}/°C
C_p,	Specific heat	1.21×10^{6} ergs/g°C
κ,	Isothermal compressibility	2.46×10^{-6} bar^{-1}
v_1,	Specific volume at transition	0.0953 cc/g
T_1,	Temperature of transition	42°C
κ_{AB},	Mixed phase compressibility	13×10^{-6} bar^{-1}
dp/dT,	Slope of coexistence line deduced from the above numbers by using Eq. (1).	-67 bar/°C
dp/dT,	Measured slope of coexistence line	-50.8 bar/°C
κ_{AB},	Mixed-phase compressibility consistent with measured slope of coexistence line	16.5×10^{-6} bar^{-1}

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

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