

Investigation of a Shock-Induced Transition in Bismuth*

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The structure of the shock-wave system to be expected in a material which can undergo a polymorphic transition is discussed. It is shown that the slope of the coexistence line in the p - T plane for the transition can be determined from shock-wave measurements at a given initial temperature. Shock waves produced by high explosives were used to investigate the equation of state of bismuth. An electrical contact technique was used to measure shock and free-surface velocities. The transition near 25 kilobars reported by Bridgman was observed but the transition pressure was about 3.5 kilobars higher than in static experiments. Other results indicated that recrystallization is a faster process than melting under shock conditions. Evidence suggests that the relaxation time for recrystallization in bismuth at 42°C and 27 kilobars is less than 1 μ sec.

INTRODUCTION

IN recent years shock-wave measurements have been used by several investigators¹⁻⁶ to determine very-high-pressure equation-of-state data for many liquid and solid materials. In the course of one of these investigations a phenomenon believed to be a polymorphic transition was observed in iron at a pressure of 0.13 megabar.⁷ Bridgman⁸ tried unsuccessfully to observe this transition statically by measuring the electrical resistivity of similar material. In addition, further shock-wave measurements were not in agreement with theoretical predictions based on the assumptions that the transition observed was a first-order transition in the thermodynamic sense and that the pressure behind the shock wave was uniform in all directions.

In view of these results, shock-wave techniques have been used to make a careful investigation of the transition observed by Bridgman at 25 kilobars in bismuth. This investigation will help establish the validity of dynamic equation-of-state work and shed light on the applicability of the assumptions made in reducing shock-wave measurements to equation-of-state data. Also a lower limit to the rate of transformation of bismuth from one crystal form to another can be gained from these measurements.

THEORY

Walsh¹ has recently prepared an extensive review of the theory, experimental methods, and results of equation-of-state determinations by shock-wave tech-

niques. It is unnecessary to repeat the basic ideas here. It is appropriate, however, to discuss briefly the structure of the shock-wave system which results from a polymorphic transition in a metal and the thermodynamic information about the transition that can be gained from shock measurements.

It has been pointed out earlier⁷ that the Hugoniot curve in the vicinity of the transition will have the qualitative features shown in Fig. 1 and that under certain conditions two shock waves moving at different velocities may be expected. It will be shown that knowledge of the slope of the Hugoniot segment above point A and the isothermal compressibility below A provide considerable information about the thermodynamics of the transformation.

In the following discussion of a first-order transition it will be assumed that the pressure behind a shock in a metal is essentially hydrostatic; that is, that the strength of the material is negligible. In addition, it will be assumed that the shock is moving into a semi-infinite medium. This imposes as a boundary condition the absence of lateral strain. H_1 and H_2 and v_1 and v_2 refer to the specific enthalpies and volumes of phases 1 and 2 at the same temperature and pressure; and λ_B is the mass fraction of phase 2 present at point B . It is then clear that the expressions for the total specific enthalpy and volume in the region of mixed phases can

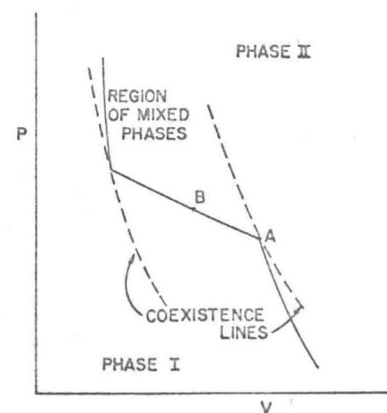


FIG. 1. Hugoniot curve and coexistence lines in the vicinity of a polymorphic transition.

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¹ Rice, McQueen, and Walsh, in *Solid State Physics, Advances in Research and Applications* (Academic Press, Inc., New York, to be published), Vol. 6.

² J. M. Walsh and R. H. Christian, *Phys. Rev.* **97**, 1544 (1955).

³ F. S. Minshall, *J. Appl. Phys.* **26**, 463 (1955).

⁴ H. Lawton and I. C. Skidmore, *Discussions Faraday Soc.*, No. 22, 188 (1956).

⁵ R. Schall, *Z. angew. Phys.* **2**, 252 (1950).

⁶ Dapoigny, Kieffer, and Vodar, *J. phys. radium* **8-9**, 733 (1955).

⁷ Bancroft, Peterson, and Minshall, *J. Appl. Phys.* **27**, 291 (1956).

⁸ P. W. Bridgman, *J. Appl. Phys.* **27**, 659 (1956).

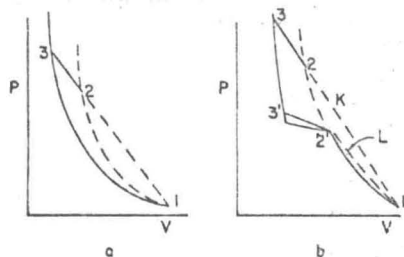


FIG. 2. Hugoniot curves for a gas which can dissociate and for a metal which can undergo a polymorphic transition.

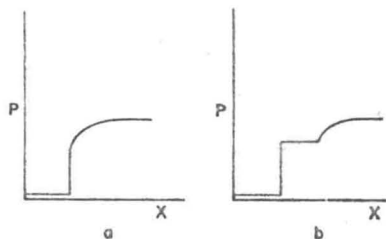


FIG. 3. Pressure profiles of a shock wave in a dissociating gas and of a wave system in a metal undergoing a transformation.

be written as

$$H_B = (1 - \lambda_B)H_1(T_B, p_B) + \lambda_B H_2(T_B, p_B) = H_1 + \lambda_B \Delta H_B,$$

$$v_B = (1 - \lambda_B)v_1(T_B, p_B) + \lambda_B v_2(T_B, p_B) = v_1 + \lambda_B \Delta v_B,$$

where ΔH_B and Δv_B are the changes in specific enthalpy and volume in the transformation at the temperature and pressure corresponding to an arbitrary point B in the region of mixed phases. From the Hugoniot equation, we have a relation between the specific enthalpy and volume at point B and on the coexistence line at point A .

$$H_B = H_A + \frac{1}{2}(p_B - p_A)(v_A + v_B).$$

$H_1(T_B, p_B)$ and $v_1(T_B, p_B)$, quantities associated with phase 1 at a pressure and temperature corresponding to point B , can be represented by the first two terms of a Taylor series in T and p about H_A and v_A . Finally, the Clapeyron equation gives for a first-order transition

$$\Delta H / \Delta v = T dp / dT,$$

where dp/dT is the slope of the coexistence line. From the above equations, one obtains

$$\left(\frac{\Delta H}{\Delta v} \right)_B = \frac{(p_B - p_A) \left[\frac{1}{2}(v_B + v_A) - (\partial H / \partial p)_T \right] - C_p (T_B - T_A)}{v_B - v_A - (\partial v / \partial p)_T (p_B - p_A) - (\partial v / \partial T)_p (T_B - T_A)}$$

In the limit as point B approaches point A , that is, in the limit of a very weak second wave, it can be shown that the above equation reduces to

$$\left(\frac{dp}{dT} \right)^2 + \left(\frac{2\alpha}{\kappa_{AB} - \kappa} \right) \frac{dp}{dT} - \frac{C_p}{Tv(\kappa_{AB} - \kappa)} = 0, \quad (1)$$

where $\alpha = (1/v)(\partial v / \partial T)_p$, the thermal expansion coefficient; $\kappa_{AB} = -(1/v) \lim_{B \rightarrow A} [(v_B - v_A) / (p_B - p_A)]$, a shock compressibility directly related to the velocity of the second wave; and $\kappa = -(1/v)(\partial v / \partial T)_p$, the isothermal compressibility of the original phase. All unspecified quantities are evaluated at point A in the original phase. Thus the slope of the coexistence line and the ratio of enthalpy to volume change in the reaction can be determined from careful equation of state experiments and knowledge of the thermal expansion coefficient, specific heat, and compressibility

of the original phase in the vicinity of the transition point. An additional conclusion which can be drawn from this development is that the slope of the Hugoniot curve above the coexistence line in the p - v plane will be nonzero so long as ΔH for the reaction is finite.

If it is assumed that the rate of the crystallographic transformation from one lattice to another is slow compared to the rate at which kinetic energy can be distributed in the lattice, it is possible to gain some insight into the structure of the shock-wave system produced near a transition by noting the similarity to the structure of a shock wave in a reacting gas. In Fig. 2 the Hugoniot curves are shown for a gas which can dissociate and for a metal which exhibits a transformation. In both cases the dashed curves represent the unstable states produced by the shock before reaction has had time to occur.

In the reacting-gas case it is well known that an essentially discontinuous shock process changes the initial state of the gas to one in which only the translational and perhaps the rotational degrees of freedom are fully excited. Then as other degrees of freedom are excited or as chemical reactions proceed, the pressure and volume point moves up the Rayleigh line from point 2 toward the equilibrium point 3 at a rate determined by the kinetics of the reactions involved. The structure of this shock is illustrated by the pressure profile shown in Fig. 3(a).

A similar structure would be expected for the strong shock in a metal represented by line K in Fig. 2(b). An essentially discontinuous shock will carry the metal to point 2 on the extension of the Hugoniot of the low-pressure modification of the material. Then as the transformation occurs, the state point will move from 2 to 3. The shock-wave structure illustrated in Fig. 3(a) persists as the shock in the metal becomes weaker until the velocity represented by Line L in Fig. 2(b) is reached. At still lower shock strengths the wave causing the compression from point 2' to 3' moves at a slower velocity, causing two waves to be produced with a pressure profile as sketched in Fig. 3(b).

The foregoing is concerned only with the steady-state wave system. The transient flow which leads to this steady-state shock configuration is not well understood at the present time; but it probably has the important features discussed below. When a shock first enters the metal, the state produced by the shock must lie on the unstable extension of the first-phase Hugoniot

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 $^{\circ}\text{C}$, 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 cm^3/g ; D_{10} and D_{21} are the velocities of the first and second waves measured relative to the material ahead of them in $\text{mm}/\mu\text{sec}$; $2u_1$ and $2u_2$ are the free-surface velocities after the first and second waves in $\text{mm}/\mu\text{sec}$; 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 previously⁷ 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 $2.15 \text{ mm}/\mu\text{sec}$ were measured by a standard pulsed-crystal technique. Attempts to observe the Hugoniot elastic wave moving with this

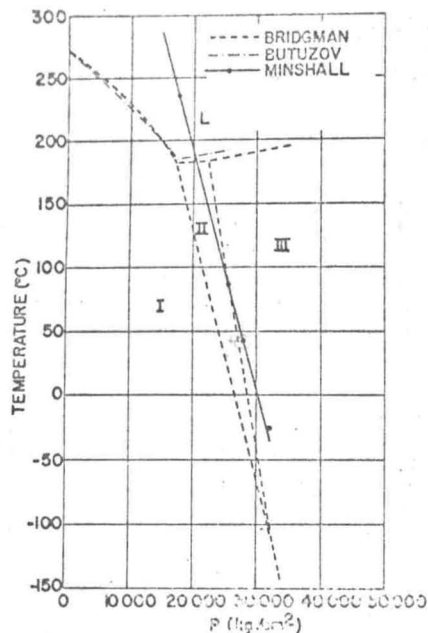


FIG. 4. Phase diagram for bismuth.

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 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

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

where the ratio α/C_{vK} 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	$16.5 \times 10^{-6} \text{ bar}^{-1}$

bility and the slope of the coexistence line with greater precision. The approximate agreement of theory and experiment suggests that the basic assumptions made in the derivation of the theory are tenable.

Equation (1) was used with the directly determined slope of the coexistence line to determine a value of mixed-phase compressibility consistent with the known variation of transition pressure with temperature. This value is included in Table II and is represented by the dashed line of Fig. 5.

Another interesting observation from the ambient temperature experiments concerns the rate of this recrystallization transition in bismuth. Note that there is no systematic dependence of observed transition pressure on metal thickness. Therefore, the transition must have occurred in a time considerably less than the shock transit time of the thinnest plate because all evidence of the transient shock configuration has disappeared. The shock transit time through the 6-mm plate is a little more than $3 \mu\text{sec}$. This suggests that the relaxation time for this recrystallization reaction at 42°C and 27 kilobars is less than $1 \mu\text{sec}$. Unfortunately it was not possible to use still thinner bismuth plates in an effort to refine this estimate of relaxation time. The estimate, however, shows the transition rate to be much faster than "widely held opinion"⁸ expected.

This observation of a recrystallization rate fast compared to shock transit time shows the transition in bismuth to be unique among the three shock-induced transitions in metals investigated to date. Specifically, a small dependence of transition pressure on plate thickness was reported for Armco iron.⁷ In addition, preliminary experiments with antimony show a striking increase in apparent transition pressure as plate thickness is reduced. The experimental results for the shock-induced transition in antimony will be published at a later date.

An experiment was performed to verify that the bismuth samples used in the shock-wave experiments transformed as reported by Bridgman under static conditions. This precaution was taken because no attempt was made to insure that the bismuth used was of the highest purity; and the possible effects of impurity concentration on transition behavior are unknown. This is not to suggest that poor grade material was used. Spectrographic analysis showed that the bismuth contained only traces of impurities.

The static experiments were done by copying all essential details of the technique used by Bridgman¹¹ for determining the electrical properties of materials at high pressure. Bridgman had found that the resistance of a sample of bismuth decreased many fold in the transition of interest here. This rapid change in resistance with pressure made the identification of the transition quite simple.

At room temperature Bridgman reported the transi-

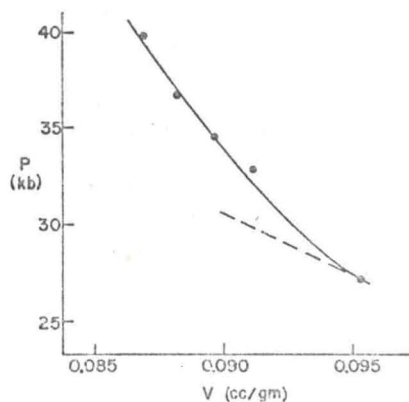


FIG. 5. Experimental Hugoniot in the vicinity of the transition point; and limiting slope of the Hugoniot above the transition point consistent with the directly determined slope of the coexistence line in the p - T plane.

tion pressure to be $25\,650 \text{ kg/cm}^2$. The value determined in this investigation was $26\,080 \text{ kg/cm}^2$ with an uncertainty of approximately $\frac{1}{2}\%$. The disagreement between the two numbers is larger than the uncertainty in the recent determination; but the difference is small compared with that between static and dynamic determinations of transition pressure. Therefore, some feature of the dynamic experiment must be basically different from that of the static case. At the present time the cause of the disagreement between the two types of experiments is unknown.

Though the reason for the disagreement is unknown, one may speculate on possible causes. From the point of view of the continuum theory it can be argued that the effective hydrostatic pressure behind the shock is less than that determined from shock-wave measurements because of residual strength of materials effects.

An alternative suggestion more satisfactory to the authors is based on speculations concerning possible differences in the detailed mechanisms of transformation in dynamic and static experiments. In the dynamic case the transformation region must move with shock velocity through the material; and the rate of transformation must be high or no transformation would be observed within the limited time available. On the other hand, in the static case the transformation can begin to occur anywhere within the sample and can proceed at a relatively slow rate. The constraints on the shock-induced transformation imposed by hydrodynamic considerations probably force the transformation mechanism to be quite different than in the static case where the recrystallization can be accomplished through the growth of nuclei of the new phase. Probably some array of climbing dislocations as suggested by Smith¹² could satisfy the dynamic constraints and produce the required recrystallization. The critical pressure or activation energy for the motion of such a dislocation array would be that characteristic of a perfect lattice

¹¹ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 165 (1952).

¹² C. S. Smith (private communication).

and would probably be somewhat higher than that needed to cause the growth of a nucleus in a static experiment.

If this speculation were correct, the transition pressure at a given temperature would be lower in the static than in the dynamic experiments as is observed. Another conclusion is that the shock-induced transformation might be easier to analyze theoretically because the microscopic transition mechanism is subject to

severe constraint and should be relatively easily determined.

ACKNOWLEDGMENTS

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