

Investigation of a Shock-Induced Transition in Bismuth*

RUSSELL E. DUFF AND F. STANLEY MINSHALL

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

(Received August 1, 1957)

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

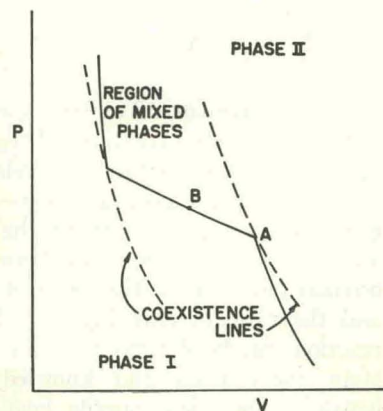


FIG. 1. Hugoniot curve and coexistence lines in the vicinity of a polymorphic transition.

* This work was done under the auspices of the U. S. Atomic Energy Commission.

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 Dapigny, 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).

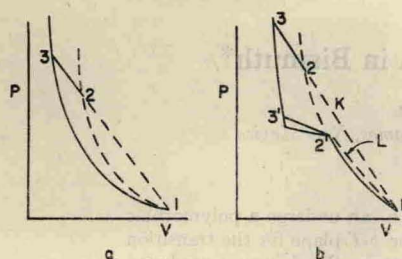


FIG. 2. Hugoniot curves for a gas which can dissociate and for a metal which can undergo a polymorphic transition.

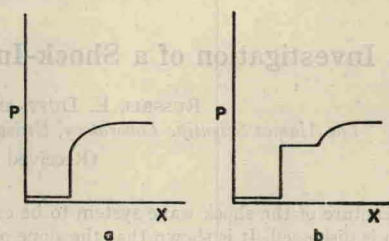


FIG. 3. Pressure profiles of a shock wave in a dissociating gas and of a wave system in a metal undergoing a transformation.

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