

MELTING AT ULTRA HIGH PRESSURES IN A SHOCK WAVE

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Melting curves for pressures up to several million atmospheres are calculated for Al, Cu, Ni, and Pb on the basis of experimental data on compression of matter by shock waves, and a semi-empirical equation of state of liquid metals is presented. The effect of melting of shock-compressed matter on the kinematic and thermodynamic parameters of the shock-wave front is considered.

INTRODUCTION

THE shock adiabats of substances, especially porous matter, pass at high pressures in the region of the liquid phase. For a correct interpretation of the obtained data, and also for an experimental determination of the melting curve of the substance at high pressures by the method of dynamic compression, it is therefore of interest to estimate the influence of melting on these adiabats. This question was never investigated, either experimentally or theoretically, until recently ([1], p. 540).

In this paper we determine the melting curve, and consider the difference between the shock adiabats in the regions of both phases, on the basis of the equations of state obtained for the liquid and solid phases with account of the experimental data on shock compression. Notice is taken of the growth of the entropy of the solid phase along the melting curve, which leads to a possibility of melting in the relaxation wave. It is shown that melting under shock compression produces appreciable breaks in the temperature-pressure variation along the shock adiabat, and has relatively little effect on the shape of the adiabat plotted in pressure-volume coordinates. The shock adiabats of the solid and liquid phases are approximated in the D-U plane (D — wave velocity, U — mass velocity) by straight lines with different slopes, making it possible to estimate the position of the melting curve from the experimentally measured plot of D(U). The melting leads to jumps in the velocity of sound behind the front of the shock wave on the boundaries of the coexistence region.

The deductions of this paper agree with the results of an earlier one [2], in which the melting of shock-compressed ionic crystals was first deduced from the experimental dependence of the tempera-

ture on the pressure behind the front of the shock wave. We have succeeded in describing the melting curves obtained there, in the pressure range 0.3—0.7 Mbar, and also the temperatures and pressures of the shock wave in the region of the liquid phase, by the method proposed here. The success with the description of ionic crystals makes it possible to apply this method also to metals, where the measurement of the temperature on the front of the shock wave, for the purpose of determining the melting curve, encounters very serious difficulties [2]. The calculated pressure at the point of intersection of the melting curve and the shock adiabat of the solid phase of aluminum agrees with the deduction obtained from the experiments on measurements of the viscosity behind the front of the shock wave by Sakharov et al. [3], that aluminum under shock compression remains solid up to a pressure of 1 Mbar.

EQUATION OF STATE OF THE LIQUID PHASE

We represent the difference between the free energies of the solid and liquid phases $F_s(\rho, T)$ and $F_l(\rho, T)$ in the form

$$F_l(\rho, T) - F_s(\rho, T) = -3RT \ln \alpha(\rho, T), \quad (1)$$

where ρ is the density, T the temperature, and R the gas constant. The function α is determined from the condition that: (a) F_l should go over smoothly at high temperatures to the free energy of an ideal gas (with a separate account of the electrons), (b) correct values should be obtained for the entropy discontinuity $\Delta S = S_l - S_s$ and for the specific volume $\Delta V = V_l - V_s$ at the melting point T_0 at atmospheric pressure.

The free energy F_s of the solid phase is given by the well known theory of metals [4,5] (quasi-harmonic vibrations of the nuclei, thermal ener-

Table I. Parameters of elastic curve

	n	$\rho_{CR},$ g/cm ³	$a_1,$ Mbar	$a_2,$ Mbar	$a_3,$ Mbar	$a_4,$ Mbar	$a_5,$ Mbar	$a_6,$ Mbar
Al	0	2.744	-8.725	39.127	-69.341	56.589	-20.346	2.696
Cu	0	9.049	-34.216	118.13	-152.202	82.453	-14.165	0
Ni	1	8.969	-9.872	41.837	-63.242	32.989	0	-1.712
Pb	-1	11.6	-16.51	64.856	-98.131	68.989	-21.899	2.695

gies, and electron pressure $\sim T^2$), and is of the form

$$F_s = E_c(\rho) + 3RT \ln \frac{\Theta(\rho)}{T} - 0.5\beta(\rho)T^2, \quad (2)$$

where $\rho = 1/V$ is the density and

$$\Theta(\rho) = \text{const } \rho^{1/3} \left(\frac{dP_c}{d\rho} - \frac{2}{3}n \frac{P_c}{\rho} \right)^{1/2} \quad (3)$$

The curve of elastic interaction of the atoms will be represented in the form^[6]

$$P_c = \rho^2 \frac{dE_c}{d\rho} = \sum_i a_i \delta^{i/3+1}, \quad (4)$$

where $\delta = \rho/\rho_{CR}$, ρ_{CR} is the density at absolute zero and $P = 0$. The numerical values of the parameters of this curve, for the metals in question, are listed in Table I.

The third term in (2) describes the free energy of thermal excitation of the metal electrons. The numerical values of the electronic component, which is of the form $\beta = \beta_{CR} \delta^{-g}$, are given in Table II. For aluminum, copper, and nickel the values of the parameters were taken from^[7].

Table II. Parameters of electronic component

		Cu	Ni
$\beta_1 \cdot 10^7, \text{ J/g-deg}^2$	518	109	1240
g	0.5	0.5	1

To reconcile the results with the experimental data on shock compression of Pb, it is necessary to introduce a variable parameter $g = -d \ln \beta / d \ln \delta$, where

$$\beta = 144\delta^{-0.2} \exp \{-1.15(1 - \delta^{-2}) + 0.4(1 - \delta^{-3})\} 10^{-7} \frac{\text{J}}{\text{g-deg}^2}.$$

To satisfy the conditions listed above we assume for the function $\alpha(\rho, T)$ the form

$$\alpha = (1+z)^{-1/2} \exp \{b - f(\delta)T_0/T\},$$

$$z = lRT \left(\frac{dP_c}{d\rho} - \frac{2}{3}n \frac{P_c}{\rho} \right)^{-1}, \quad (5)$$

where b and l are empirical constants. The applicability of such a method of interpolation was demonstrated earlier (see^[7]), where Eq. (5) was written in the form $\alpha = (1+z)^{-1/2}$. The exponential factor was introduced to describe the jumps in the entropy and the volume and the conditions of phase equilibrium. Its role decreases with increasing temperature. Therefore at high temperatures the experimental shock adiabats of porous metals are described as in^[7].

The limiting conditions impose no limitations on the form of the function $f(\delta)$ in (5). We assume a power-law dependence

$$f(\delta) = c + \frac{a}{r} \left[\left(\frac{\delta}{\delta_0} \right)^r - 1 \right], \quad (6)$$

where δ_0 is the liquid density of the liquid phase at atmospheric pressure and at the melting temperature; a , c , and r are constants. The parameters b in (5) and a and c in (6) are determined from the experimentally known jumps of the entropy and of the volume at $P = 0$ and from the phase equilibrium condition

$$F_l - F_s + P(V_l - V_s) = 0.$$

The parameter r for the metals in question will be assumed equal to unity, which, as will be shown below, agrees with the experimental shock adiabats. The constant l in Eq. (5), for aluminum, copper, and nickel, was taken from^[7]. In view of the definite spread in the experimental values of ΔS and ΔV , we assumed in the calculation values which were reconciled with the experimental values of the slope of the melting curve at $P = 0$. The calculated parameters are listed in Table III.

The equation of state in the liquid phase can be checked against the experimental isobars of the liquid metals at atmospheric pressure. The agreement between the isobars $\rho(T)$ calculated from the equation of state of the liquid phase (1) and the experimental values^[8-10] is fully satisfactory. The

Table III. Parameters of equation of state of the liquid phase

	<i>l</i>	<i>a</i>	<i>b</i>	<i>c</i>
Al	6	1.280	0.386	0.308
Cu	9	1.328	0.378	0.280
Ni	10	1.111	0.412	0.299
Pb	21	1.672	0.386	0.281

calculated coefficient of thermal expansion of the liquid differs from the experimental value by up to 30%.

MELTING CURVES

We used the parameters obtained above to calculate for the metals the melting curves defined as the boundaries between the phases with corresponding equations of state. The results of the calculations are shown in Table IV and in Figs. 1 and 2.

Table IV. Melting curves

Metal	<i>T</i> ₀ , deg		<i>T/T</i> ₀			
			1	2	3	4
Al	933	<i>P</i> , Mbar	0	0.25	0.69	1.37
		δ_s	0.934	1.158	1.395	1.645
		δ_l	0.873	1.121	1.363	1.615
		<i>z</i>	0.106	0.085	0.074	0.067
		$\Delta S/R$	1.372	1.401	1.058	1.047
Cu	1356	<i>P</i> , Mbar	0	0.45	1.28	2.62
		δ_s	0.930	1.132	1.357	1.590
		δ_l	0.881	1.099	1.329	1.566
		<i>z</i>	0.156	0.141	0.117	0.098
		$\Delta S/R$	1.075	0.929	0.928	0.942
Ni	1728	<i>P</i> , Mbar	0	0.79	2.50	5.35
		δ_s	0.907	1.172	1.460	1.752
		δ_l	0.855	1.145	1.438	1.732
		<i>z</i>	0.210	0.148	0.118	0.100
		$\Delta S/R$	1.217	1.015	1.014	1.026
Pb	600	<i>P</i> , Mbar	0	0.12	0.34	0.68
		δ_s	0.947	1.123	1.319	1.518
		δ_l	0.917	1.104	1.303	1.504
		<i>z</i>	0.191	0.159	0.130	0.111
		$\Delta S/R$	0.959	0.860	0.865	0.907

We calculated also the values of $\Delta V/V_s$, ΔS , and *z* along the melting curve. It is seen from Table IV that the first quantity changes quite appreciably with increasing pressure. This is in agreement with the experimental data obtained by Bridgman^[1] for metals, and with the data of Kormer et al.^[2] for ionic crystals. The jump of the entropy changes very little. The value of *z*, which is a measure of the deviation of the thermodynamic properties of

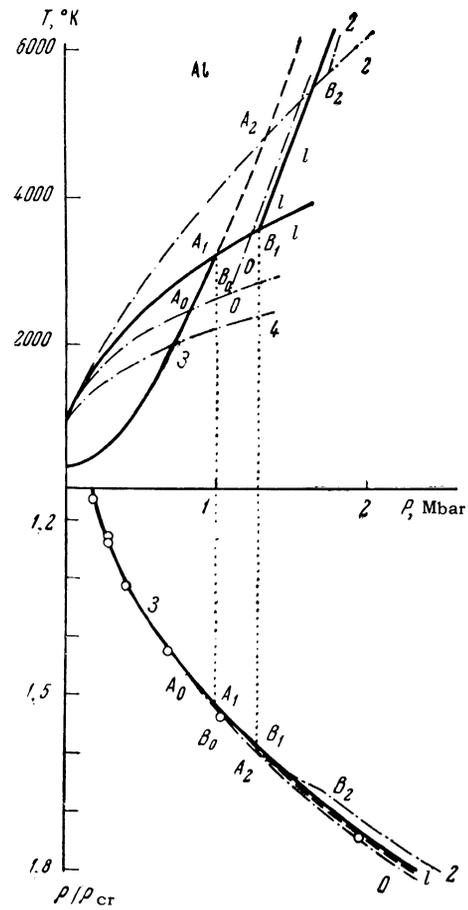


FIG. 1. Melting curves and shock adiabat of aluminum in the liquid and solid phase regions: O – experimental data; 0, 1, 2 – melting curve and shock adiabat in the region of the liquid phase with *r* = 0, *r* = 1, and *r* = 2 in Eq. (6), respectively; 3 – shock adiabat in the region of the solid phase; 4 – isentropes; dashed – “superheated solid phase”; A₀, A₁, A₂, B₀, B₁, B₂ – start and end of the melting.

the liquid from the properties of the solid, also changes little. From the data of Table IV we can calculate the dependence of TdP/dT on *P* by means of the Clapeyron-Clausius equation $dP/dT = \Delta S/\Delta V$. For the metals considered here it is close to linear, being slightly convex towards the pressure axis. This coincides at low pressures with the known experimental fact for the melting of the majority of substances—that TdP/dT is linear in *P* (Simon’s equation).

We calculated the isentropes from the points with *T* = *T*₀ and *P* = 0, using the equation of state of the solid phase. In Figs. 1 and 2 they are shown by the dash-dot curves. For all the metals considered, the temperature on the melting curve at equal pressure is higher than on the isentrope. This indicates that the entropy of the solid phase increases along the melting curve. It is clear therefore that if the substance has not gone into the liquid phase

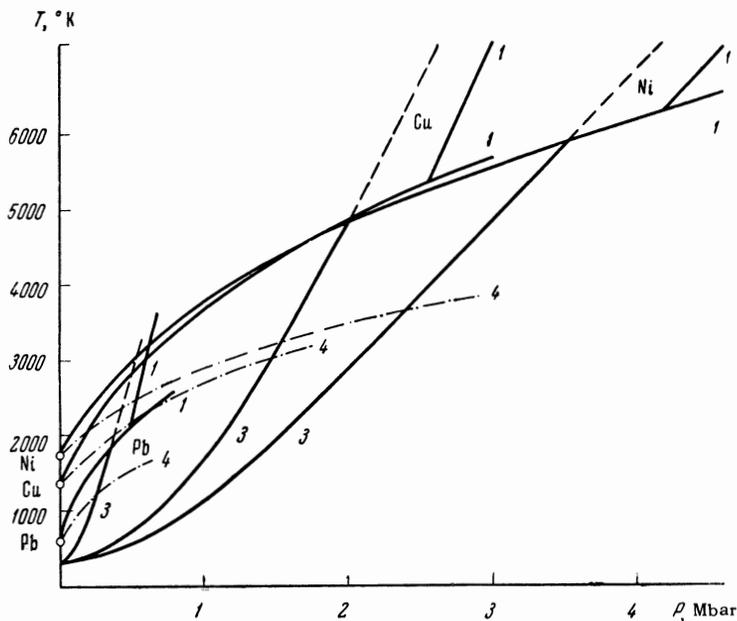


FIG. 2. Melting curves and shock adiabats for nickel, copper, and lead with $r = 1$. Notation same as in Fig. 1.

under shock compression, it can melt partially on relaxation from this state. Conversely, relaxation in the liquid state behind the front of the shock wave never will bring the substance to the solid phase.¹⁾

SHOCK-ADIABAT ANOMALIES DUE TO MELTING

The equations of state (2) and (1) of the solid and liquid phases were used to calculate the shock adiabats of solid metals, which are shown in Figs. 1 and 2, and in coordinates D (wave velocity) and U (mass velocity) also on Fig. 3. The shock adia-

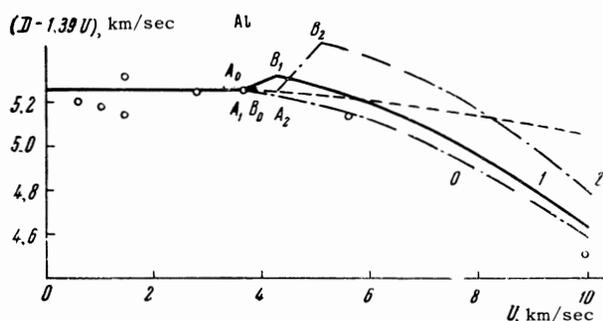


FIG. 3. Wave velocity D vs. mass velocity U for a shock wave in aluminum: \circ - experimental data; 0, 1, 2 - shock adiabats in the region of a liquid phase with $r = 0, 1$, and 2, respectively; $A_0, A_1, A_2, B_0, B_1, B_2$ - start and end of melting.

¹⁾Taylor^[12] measured the residual temperature after relaxation to atmospheric pressure from the state behind the front of the shock wave in copper. The isentrope of the solid phase, going out of the melting point at $P = 0$, coincides in this paper with that calculated by us (see Fig. 2).

bat of the "superheated" solid phase are shown by the dashed lines. As can be seen from Figs. 1 and 2, the shock adiabats experience strong kinks in the T - P plane on entering and leaving the region of coexistence. This is inherent in all the phase transitions that occur in the front of the shock wave, except those having the slope of the lines of phase equilibrium $dP/dt = 0$, since, on the one hand, the pressure can only rise along the shock adiabat and, on the other, the states on the shock adiabat which passes in the two-phase region should lie on the curve of phase equilibrium in T - P coordinates. The kinks in the T - P plane were found experimentally on the shock adiabats of ionic crystals. This has allowed the authors of [2] to find the melting curves at 0.3–0.7 Mbar. This method, however, entails measurement of the temperature behind the front of the shock wave, and is applicable only for substances which are transparent prior to compression^[2].

To determine the melting curves of metals it becomes necessary to search for other methods. Shock adiabats experience kinks on the boundaries of the region of coexistence also when plotted in P - ρ coordinates. Inside this region, the slope of the shock adiabat depends on the slope of the melting curve^[13]. The larger dT/dP , the greater the slope. This can be seen in Fig. 1 with aluminum as an example.

The second kink of the shock wave occurs on going out into the region of the liquid phase. Here the slope decreases, because the liquid is more compressible than the solid. For a given substance, the kinks in the dynamic adiabats increase strongly

with increasing degree of its porosity in front of the shock wave.

The considered jumps in the slopes of the shock adiabats are manifest in the $D(U)$ curve. More significant here, however, is the difference in the variation of the function $D(U)$ in the solid and liquid phases. It is known^[14,15] that the experimental data on most metals in the region up to 1.5 Mbar are well described by a linear dependence. The calculated $D(U)$ variation in the region of the liquid phase can also be roughly represented in the form of a straight line, but with a smaller slope than for the solid phase (see Fig. 3). The slope of the function $D(u)$ is connected with the average Gruneisen coefficient

$$\bar{\gamma} = (P - P_c) / \rho(E - E_c).$$

It is smaller in the region of the liquid phase (as can be readily seen from Eq. (1)), and this leads to the indicated change of the slope. The experimental data on shock compression of solid metals up to 9 Mbar^[16] confirm this picture qualitatively. This is especially typical of the easy-melting metals Pb, Cd, Zn, Sn, which were investigated in the last-cited reference.

Some smooth decrease in the slope of $D(U)$ is connected with the increased role of the electronic component in the equation of state of the metal at higher temperatures. For the metals considered in this paper, this component is assumed in accord with^[7], where it was investigated on the basis of experiments on shock compression of metallic powders.

The experimental data plotted in $D-U$ coordinates, taken from^[15,6], exhibit no noticeable kinks connected with the region of coexistence, but can be approximated by two straight lines with different slopes. This already gives some information on the melting curve of the substance. The position of the melting curve is calculated more accurately from the equation of state of the liquid (1), with the parameter r in (6) obtained from the experimental shock adiabat in the region of the liquid phase.

In Fig. 1 we show for Al three shock adiabats with $r = 0, 1,$ and 2 . The best agreement with experiment is for $r = 0$ and $r = 1$. The adiabat with $r = 0$ differs little from the adiabat of $r = 1$ in the plane $P-\rho$, just as the melting temperatures differ at 1 Mbar by only 20%.

Sakharov et al.^[3] concluded on the basis of a measurement of the viscosity behind the front of the shock wave in aluminum that aluminum remains solid under shock compression up to 1 Mbar.

This agrees with the position of the melting curve calculated in the present paper with $r = 1$.

More clearly pronounced kinks in $D(U)$, connected with the melting, can be observed in dielectrics, where the role of the electronic component in the equation of state is small in the region of interest. This is indicated by the experimental data on the measurement of shock adiabats of ionic crystals^[17,18], and the measurement of the temperatures in them^[2]. Alder and Van Thiel^[19] also relate the experimental kink in the $D(U)$ plot for liquid argon to the crossing of the boundary of the region of coexistence with the liquid phase by the shock adiabat.

The effect of melting on the speed of sound behind the front of the shock wave was also considered. The difference between the squares of the speeds of sound in the two-phase region $C_f^2 = (\partial P / \partial \rho)_S^f$ and in the solid phase at the melting temperature C_s^2 it is described by the equation

$$\frac{C_s^2}{C_f^2} - 1 = \frac{\rho^2}{T} \left(\frac{\partial \rho}{\partial P} \right)_S \left(\frac{\partial E}{\partial T} \right)_\rho \left[C_s^2 \frac{dT}{dP} - \frac{T}{\rho^2} \left(\frac{\partial P}{\partial E} \right)_\rho \right]^2 + \frac{\rho}{\rho_s} (\rho_s - \rho) \left(\frac{dT}{dP} \right)^2 - \frac{d^2 P}{dT^2} C_s^2, \quad (7)$$

where E is the internal energy. The partial derivatives in (7) are taken with respect to the equation of state of the solid phase at a value of P on the melting curve, i.e., at the point (P, T, ρ_s) . We see that C_f is always smaller than C_s , and the jump depends essentially on the slope of the melting curve dT/dP . An analogous conclusion can be drawn also for the velocity of sound in the liquid phase. For the melting curves obtained in the present paper, the numerical value of the jump lies within 0.5%. However, for the melting curves with $r = 2$ in Eq. (6), it increases to 2–3%. The existing experimental data on the dependence of the velocity of sound $C(\rho)$ ^[20] did not allow us to draw any definite conclusions regarding the position of the melting curve, but a more detailed investigation of this dependence gives at least the limit of the position of the melting curve.

In the paper we do not touch upon the question of the characteristic time of the melting process in the shock wave. We present only the calculated curves for two cases: when the relaxation time is small compared with the time necessary for the shock wave to traverse the measurement base, and when it is large. In the latter case, shock adiabats of the "superheated" solid phase are realized.

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