PECULIARITIES OF PHASE TRANSITIONS IN COMPRESSION AND RAREFACTION SHOCK WAVES

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Submitted to JETP editor September 1, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 400–408 (February, 1967)

The structure of compression and rarefaction shock waves causing the formation and decay of high-pressure phases in potassium halides is determined experimentally. The rate of the phase transitions is determined and the existence of metastable states is established. For boron nitride, under shock-compression conditions, the parameters for the formation of dense phases are determined and the course of their adiabats is traced up to pressures of 3.5 $\times 10^6$ bar. In the pressure range from 180 to 900 kbar, the results reveal the existence of relaxation phenomena due to the finite time of the phase transitions.

THE passage of shock waves through crystalline matter is a complex and unique process of compression and change in form of the crystal lattice.[1,2] As follows from symmetry considerations, the deformation of the medium behind the shock-wave fronts is one-dimensional. Inasmuch as the minimum elastic energy is possessed by the crystal lattice under hydrostatic compression, its one-dimensional deformation is unstable. The transition to symmetrical compression and to quasihydrostatic stressed states is realized on the front of the wave as a result of plastic microshears occurring there.

Of particular interest is the formation under these conditions, within very short time intervals, of new crystalline modifications, which sometimes remain in a metastable state even after the pressures are removed. The occurrence of dense phases violates the monotonic course of the shock-compression curves. In the presence of phase transformations, the shock-transition processes are described in P-V coordinates (P—pressure, V—specific volume) by broken lines of the type 011'34 (Fig. 1).[2,3]

The pressure P_1 at the point 1 corresponds to the start of the transformation. In the interval $P_1 < P < P_3$ the decay of the shock front takes place (the point 3 lies at the intersection of the adiabat of the second phase and the wave line 0–1). Moving in front is in this case a wave of critical amplitude P_1, followed, at lower velocity, by propagation of the phase-transition wave with amplitude $P_2 > P_1$. In the section 1–1', the final states behind the second wave are mixtures of low- and high-pressure phases. Owing to the adiabaticity of the process, the section 1–1' is not horizontal at

transformation heats $q \neq 0$.[4] $P_1' > P_1$ for both exothermal and endothermal transformations.

The total-transformation states are described by the adiabat of the second phase 1'—4. The kink at the point 3 is due[2] to a weak entropy discontinuity occurring when the two-wave configurations vanish and a unified discontinuity surface is restored.

The reverse recrystallization of matter upon removal of the pressure leads to a kink in the expansion isentropes and to the appearance of rarefaction shock waves.[5,8] In the first stage, expansion from a certain state m on the adiabat of the second phase occurs in the relaxation wave along the isentrope mn. Below the phase-transition pressures, a jumplike reduction in pressure in the rarefaction shock wave can occur and trans-
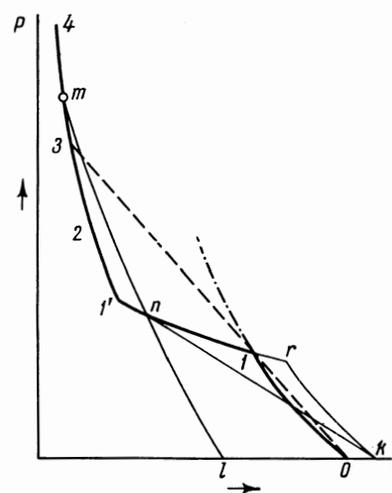
FIG. 1. Schematic P-V diagram of shock compression and expansion.
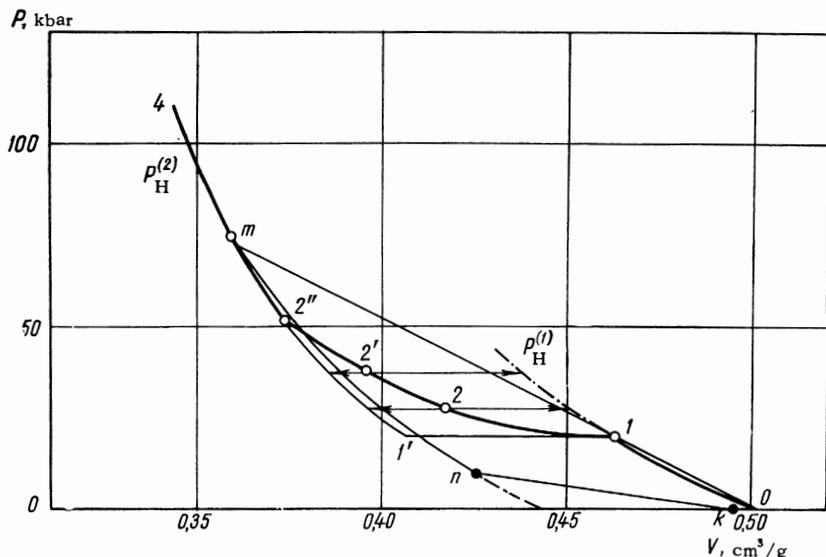
FIG. 2. Diagram of shock compression of KCl in the two-phase region: 1—start of transformation, 01—shock adiabat of initial phase—$P_H^{(1)}$, 1'4—equilibrium shock adiabat of high-pressure phase $P_H^{(2)}$, 122'2''—experimental curve of shock compression in two-phase region, mnk—curve showing expansion of KCl samples from the state m, including the shock transition n—k; O—experimental points on compression curves, ●—experimental points on expansion curves.

form the matter from the state n into the state k, bypassing the section nrk.

An alternate variant in which the dense state is retained in a metastable state, is characterized by isentropic expansion to zero pressures along the curve mnl. In this case there is no rarefaction shock wave. Intermediate variants are also possible. In the case of delayed transformations, the kink shifts along the isentrope to pressures $P < P(n)$, and in the case of incomplete transformations the final state is located to the left of the state k.

Polymorphism phenomena in shock waves are observed in iron[3], bismuth,[4] quartz,[9] potassium chloride and bromide,[10] carbon,[11] silicon,[2] and many mineral rocks.[12] We report in this communication results obtained by us in the study of the kinetics of the formation and decay of high-pressure phases of potassium halides and boron nitride.

In KCl and KBr the formation of dense phases is connected with the realignment, under the influence of the pressure, of a NaCl type lattice into a CsCl type lattice. Under static compression, these transitions were first observed by Bridgman[13] at pressure of ~20 kbar, and were later observed

FIG. 3. Variant of experiment on determining the profile of the waves by a magnetoelectric method: 1—TNT charge, 2—copper screen 10–13 mm thick, 3—investigated crystal, 4—aluminum U-shaped pickup.

many times by x-ray structure analysis methods.[14,15] The heats of formation of the new phases of the potassium halides are quite small. For KCl, this is evidenced by the independence of the transformation pressure of the temperature.[16] Taking this circumstance into account, the equilibrium curve 011'24 of the shock transitions of KCl is shown in Fig. 2. The adiabats $P_H^{(1)}$ and $P_H^{(2)}$ of the first and second phases are constructed in accordance with the equation of state given in [10], reconciled with the data of static[13,14] and dynamic[10,17] experiments.

To obtain experimental information on the kinetics of the phase transitions, the wave configurations were registered, just as in [2] and [18], by the Zavoĭskiĭ method,[2] with the aid of U-shaped pickups (Fig. 3) built into the samples and moving together with the matter in a constant and homogeneous magnetic field. The emf induced by their motion is proportional to the intensity of the magnetic field, the length of the frame cross bar, and the speed of its displacement. In the compression phase, the pickup registers the jumps of the velocities following successive passage of the shock fronts through the sample. In the rarefaction phase, full increase of the pickup speed is registered under the influence of the expansion waves going from the free surface of the sample.

The pressures were produced by explosive devices[10] consisting of TNT charges with plane detonation fronts and copper screen separated from the charges by air gaps. The KCl and KBr single crystals were always compressed in the [001] direction of the edge of the cube.

Typical magnetoelectric records of two-wave configurations produced in the pressure range
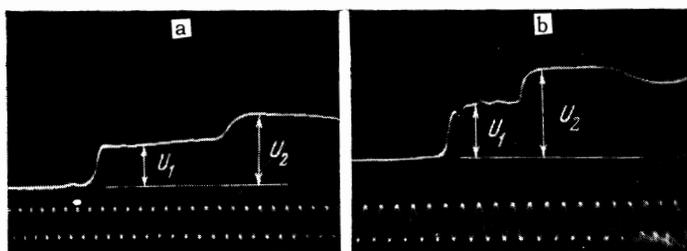
FIG. 4. Configuration of compression shock waves in KCl at pressures of 28 (a) and 38 (b) kbar. One cycle of the timing sinusoid is equal to 0.20 (a) and 0.25 (b) μsec (the sweep direction is from left to right).

from 20 to 60 kbar are shown in Fig. 4. The transformation times, obtained from these photographs by observing the smearing of the second shock front, are very low. At 28 kbar they do not exceed 0.4−0.6 μsec, and at 38 kbar they amount to ~0.2 μsec. The oscillograms of Fig. 4 fix the times of arrival of the first and second waves at the pickups and the pickup velocities, which are proportional to the vertical deflections of the beam. By the same token, they determine the mass velocities of the matter U_1 and U_2 behind the front of the shock waves, the front velocities D_1 and D_2 in the laboratory coordinate frame, and the flow velocities N_0, N_1, N_1', and N_2 in coordinate systems in which the discontinuity surface is at rest ($N_0 = D_1$, $N_1 = D_1 - U_1$, $N_1' = D_2 - U_1$, and $N_2 = D_2 - U_2$). The pressures P_1 and P_2 and the specific volumes of the compressed states are calculated from these data using the equations for the conservation of mass and angular momentum:[19]

$$V_0^{-1}N_0 = V_1^{-1}N_1, \qquad V_0^{-1}N_0^2 = V_1^{-1}N_1^2 + P_1,$$
$$V_1^{-1}N_1' = V_2^{-1}N_2, \qquad V_1^{-1}N_1'^2 + P_1 = V_2^{-1}N_2^2 + P_2. \tag{1}$$

The initial kinematic parameters and the characteristics of the compressed states of KCl, obtained at different shock-wave amplitudes are listed in the table. When plotted on Fig. 2, they trace a smooth curve which merges with the adiabat of the second phase at pressures ~50 kbar.

A similar result was recently obtained by Dremin, Pershin, and Pogorelov[20] with damped waves. The same character is possessed by the KBr curve, but it is less clearly pronounced. At pressures lower than 50 kbar, but still greatly higher than critical, the compressed matter con-

sists of a thermodynamically nonequilibrium mixture of two modifications. Their relative amounts at a specified pressure are determined by the "lever rule"[21] using a relation in which the experimental curve divides the distance between the adiabats of the first and second phases.

The large transformation velocities and the fact that the transformations are not completed at pressures greatly exceeding critical values, are nontrivial peculiarities of the crystallization of new phases under shock-compression conditions. They can be explained naturally by assuming, in accordance with the views of Smith[1] and Alder,[22] that the kinetics of the transformations induced by shock waves is determined primarily by the intensity of the plastic microshears on the shock-wave fronts, stimulating the formation of nuclei of new phases along the slip planes.

To obtain the profile of the relaxation wave and to study the kinetics of the inverse recrystallization, we increased the times of observation of the motion of the pickups in the experiments carried out in accordance with the scheme of Fig. 3. The experiments were made on both single-crystal and powdered samples of KCl and KBr. Some of the obtained oscillograms are shown in Fig. 5. As seen from the photographs, on which the profile of the combined relaxation wave with rarefaction discontinuities were recorded for the first time, the variants actually realized are those with recrystallization occurring in rarefaction shock waves.

The trajectories of the waves and of the pickups, located at two different distances from the surface of the samples of single-crystal KCl, are shown in the x-t diagram of Fig. 6. The dispersion of the centered expansion wave varies with the distance from the pickup to the free surface in self-similar fashion. At the same time, as shown by the photographs, the width of the rarefaction shock wave, which characterizes the time of decay of the dense phase, is constant and is equal to ~0.2 μsec.

To find the coordinates of the kink point n and of the final state k (Figs. 1 and 2) we use conservation equations of the type of (1):

$$N_n V_n^{-1} = N_k V_k^{-1}, \qquad N_n^2 V_n^{-1} + P_n = N_k^2 V_k^{-1} \tag{2}$$

Number of point	U_2, km/sec	D_2, km/sec	P_2, kbar	V_2, cm^3/g
2	0,46	2,15	27,0	0,417
2'	0,62	2,45	36,0	0,395
2''	0,79	2,95	51,0	0,373

The parameters of the first wave are: U_1 = 0.28 km/sec, D_1 = 3.60 km/sec, P_1 = 20.1 kbar, and V_1 = 0.463 cm^3/g.
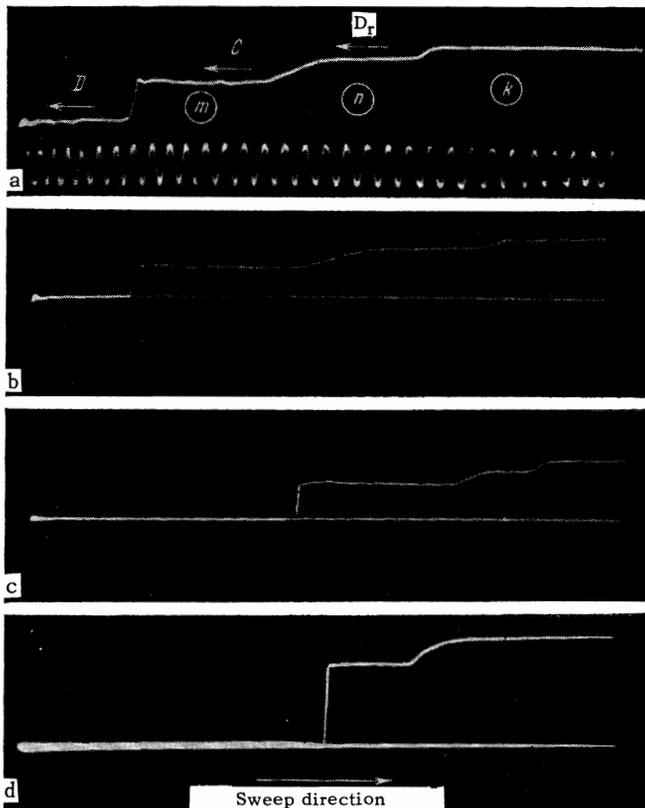
FIG. 5. Oscillograms of the expansion process: a—KCl single crystal, b—KBr single crystal, C—porous KCl, $\rho_0 = 1.41$ g/cm³; d—polycrystalline BN, $\rho_0 = 1.95$ g/cm³; D—compression shock wave, C—centered rarefaction wave, D_r—rarefaction shock wave (missing in the case of BN). Frequency of the timing wave—5 Mcs.

FIG. 6. x-t diagram for single-crystal KCl. ABCR and O 'A 'B 'C 'R '—pickup trajectories; AA 'Q—compression shock wave D; QBC—centered relaxation wave C, QR—relaxation shock wave D_r; m, n, k—status indicated in Fig. 2 (the velocities are in km/sec).

and the isentrope equation

$$U_m - U_n = \int_{P_n;\, V_n}^{P_m;\, V_m} \sqrt{-dP\, dV}. \qquad (3)$$

In (2) N_n and N_k are the flow velocities relative to the discontinuity surface to the left and to the right of it: $N_n = D_r - U_n$, and $N_k = D_r - U_k$. The states n and k calculated from the data of Fig. 6 are shown in Fig. 2.

An analysis reveals hysteresis in the inverse recrystallization process. Both for single-crystal KCl and KBr samples and for samples with reduced density made of powders (Fig. 5c) the transformations occurring under relaxation begin at pressures P_n that differ from the critical pressure P_1 by approximately 10 kbar. The position of the point k is evidence at the same time of a total or almost total completion of the process of transformation in the unloaded matter located behind the rarefaction shock wave.

Let us turn now to the results obtained with boron nitride. At atmospheric pressure, BN has a

structure which is isomorphic to graphite and has almost the same crystallographic density, 2.22 g/cm³ (graphite has 2.25 g/cm³). On compression with static pressures on the order of ~120 kbar, the BN forms diamond-like modifications of the sphalerite and wurtzite type, which have at atmospheric pressure densities 3.48 and 3.49 g/cm³.[23] The initial material used in the experiments on shock compression were pressed samples of the "graphite" modification of BN with density 1.95 g/cm³. The states of single compression for the adiabat sections 0−1 and 3−4 (Fig. 1) were obtained by the reflection method,[2] by electric-contact registration of the velocities of the shock waves produced in the samples with the aid of the explosive devices described in [10, 24].

The shock-transformation curve obtained by this method for a wide range of pressures is shown in Fig. 7. The transformations into diamond-like modification begin at a specific volume V = 0.365 cm³/g and a pressure P = 120 kbar. In the pressure interval from 120 to 190 kbar, the electric-contact measurements fix the constant velocity of the shock wave, equal to ~4.65 km/sec, thus evidencing a realization at these pressures of two-wave configuration of the shock front. This region was not investigated in detail.

The left-hand curve, which moves steeply upward, is the shock adiabat of the dense phases of BN. It is obtained by joining the experimental points fixed in the pressure range from 3.5 to 1.0 Mbar, to the initial state of the "diamond" phases, lying on the abscissa axis. In the inter-
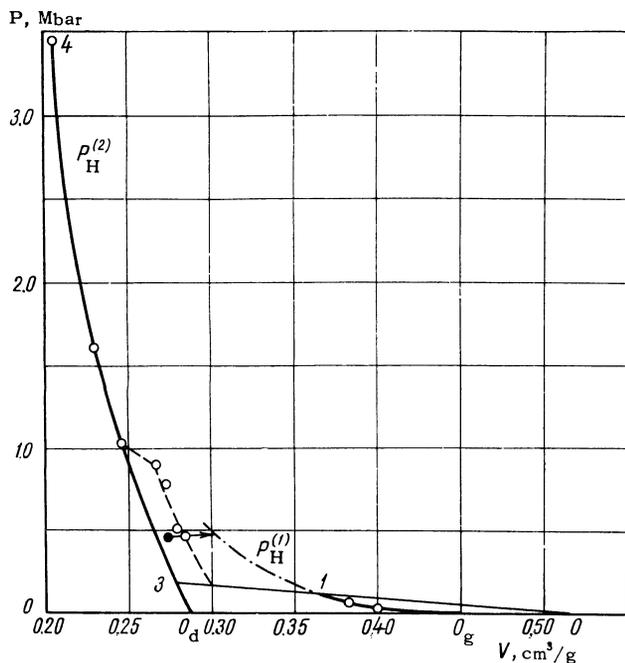
FIG. 7. P-V diagram of shock compression of BN: O—states
produced after traversal by the wave of a path S = 2 mm (sam-
ple thickness d = 4 mm), ●—the same but for S = 5 mm;
34—adiabat $P_H^{(2)}$ of the "diamond" phases. O_g1—adiabat $P_H^{(1)}$
of the "graphite" phase; dash dot line—extrapolated section
of the "graphite" adiabat; O_g and O_d—states, under normal
conditions, of the "graphite" and "diamond" phases (crystal-
lographic planes), O—initial state of porous samples, 013—
line of constant D ≈ 4.65 km/sec.

FIG. 8. Speed W of motion of the free surface at different
thicknesses L of the BN samples.

mediate range of pressures from 900 to 190 kbar,
the experimental points obtained with samples of
4 mm thickness go off to the right, forming on the
P-V diagram of Fig. 7 a unique ledge, giving the
impression of the existence of a second-phase
transition. Actually, however, in this pressure
region the results of the registration of the wave
velocities, and consequently also the position of
the experimental points, depend on the measure-
ment base—owing to the relaxation pressure re-
duction caused by the phase transformations.[4, 25, 2]
When the registration bases are increased, the
experimental points approach the adiabat of the
dense phases, and at small bases they approach
the metastable section of the "graphite" adia-
bat (Fig. 7).

The presence of relaxation damping of the shock
waves at pressures on the order of 450 kbar is
confirmed by the W(L) curve (Fig. 8). This figure
shows the speeds W of the surfaces of the samples
of different thicknesses L after emergence of the
shock waves to the surfaces. The shock waves in
the samples and in the aluminum screens covering
them were produced by impact of aluminum plates
accelerated by explosion products to a velocity

5400 m/sec. The sharp bending of the curve on the
right side of the diagram is connected with the
emergence of a relaxation wave, traveling from
the striker,[1] unto the trajectory of the shock
wave.[1]

At a pressure of 1 Mbar and higher, the dis-
placement of the experimental points to the left
(Fig. 7), toward larger densities, is attributed by
the authors to a decrease in the time of the phase
transformation. This is possibly connected with
the melting of the matter compressed and heated
by the shock wave. It is also possible that here, in
accordance with the views developed in [25], the
reduction and the time of transition of the equilib-
rium arrangement of the atoms—in this case, tet-
rahedral—occurs in the liquid phase, when the
values of the thermal energy of the atoms become
comparable with the activation energies of the
transition of the atom through the potential bar-
riers.

Special notice should be taken of the fact that at
densities characteristic of tetrahedral modifica-
tions, which as is well known have a very non-
dense atom packing, are retained in the liquid
phase up to very high pressures, several mega-
bars. This circumstance is evidence of the large
strength and stability of the tetrahedral valence
bonds. This is also evidenced by the absence of a
metallic phase of carbon,[27] the shock-compres-
sion adiabat of which practically coincides at high
pressures with the adiabat of BN. It is therefore
not surprising that when the pressures are re-
duced the isentropic expansion of the shock-
compressed BN (P ≈ 400 kbar) is not accom-
panied, over measurable time intervals, by re-

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[1]The point of inflection has enabled the authors to deter-
mine, by the procedure proposed in [26], the velocity of propa-
gation of the sound disturbances in BN at a pressure ~460 kbar.
The obtained value, 13.5 km/sec, corresponds to the "dia-
mond" modification of BN.

crystallization of BN in the "graphite" phase. This is evidenced by the absence of rarefaction shock waves, which were not observed in magneto-electric registration of the expansion process (Fig. 5d).

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