Hysteresis in polymorphic transitions of potassium chloride in shock waves

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The pressures of polymorphic transitions of potassium chloride in shock waves have been detected with Manganin resistance gauges. There is a high degree of asymmetry in the formation and decay of the high-pressure phase. This asymmetry stems from the particular mechanisms for martensitic transitions in shocks. The kinetics of the inverse transitions from metastable states of phase mixtures during the unloading has been observed experimentally. Dynamic data on the hysteresis of phase transitions in KCl are compared with static results found on the polymorphism of potassium chloride and also with the hysteresis of polymorphic transitions of several metals in shock waves. © *1994 American Institute of Physics.*

1. INTRODUCTION

The propagation of shock waves through many chemical elements and compounds induces the formation of denser crystal structures. Features of the phase transitions which occur in shock waves indicate that these transitions are martensitic.[1,2] They go at extremely high rates—many orders of magnitude higher than the rates of diffusion transitions. They are also characterized by wide ranges of the shock pressures which form metastable incomplete-transition segments on the Hugoniot adiabats and by a pronounced hysteresis in the pressures of the direct (inverse[3]) phase transitions in compressional (rarefaction) shock waves.

An understanding of the hysteresis during shock loading is necessary for reaching an understanding of the mechanisms for the ultrafast conversion of crystal structure. "Hysteresis" is used in this paper to mean either the total amplitude of the hysteresis loop or, as in Ref. 4, the differences $\Delta P_m^+ = P_m^+ - P_0$ and $\Delta P_m^- = P_0 - P^-$. In these expressions, P_0 is the thermodynamic-equilibrium pressure of the transition, P_m^+ is the upper martensitic point, corresponding to the onset of the direct phase transition from the low-pressure phase to the high-pressure phase, and P_m^- is the lower martensitic point, corresponding to the onset of the inverse transition from the high-pressure phase to the low-pressure one.

For small deviations from equilibrium we can write

$$P_0 \simeq \tfrac{1}{2}(P_m^+ + P_m^-). \tag{1}$$

Relation (1) is not rigorous, but it is supported by an elementary theory which has been derived for martensitic transitions.[4] Martensitic or athermal mechanisms are based on coherent small displacements of many atoms. Such mechanisms can operate if the initial, "mother" structure is converted into a new modification as the result of simple displacements and dilatation. An important characteristic of the transition is the angle γ_0, which specifies the crystallographic rotation of the final structure with respect to the original structure. At equilibrium pressures, martensitic mechanisms are blocked by the potential barriers of intermediate "saddle-point" states. Denoting by μ the elastic modulus of the corresponding deformation, we can write the energy height of the barrier as[4]

$$E_d \simeq \mu \frac{\gamma_0^2}{2\pi^2}. \tag{2}$$

The athermal "above-barrier" crystallization of the high-pressure phase begins under nonequilibrium conditions, when the thermodynamic stimulus satisfies

$$\Delta G = \Delta P_m^+ \Delta V = E_d.$$

According to Ref. 4, the same relation is satisfied by the hysteresis of the inverse phase transition (in these expressions we have $\Delta V = V_1 - V_2$, where V_1 and V_2 are the specific volumes of the low- and high-pressure phases, respectively). The pressure deviations are thus

$$\Delta P_m^+ = \Delta P_m^- = \mu \frac{\gamma_0^2}{2\pi^2 \Delta V}. \tag{3}$$

The high-pressure phase may persist after the load is completely removed if the condition $\Delta P_m^- > P_0$ holds, i.e., if $P_m^- < 0$.

Values of the parameters in Eqs. (2) and (3) were given for three elements and two halides in Ref. 4. Also given there were values of E_d and ΔP_m^+ calculated from these parameters and values of the hysteresis measured under static conditions. On the whole, the agreement of the theory with static experiments was satisfactory.

Some of the data of Ref. 4 on potassium chloride, zirconium, titanium, and iron—materials which have been studied under dynamic conditions on many occasions—are reproduced in Table I of the present paper, supplemented with values of P_0. The equilibrium transition pressures for potassium chloride were found in Ref. 5 from relation (1). High accuracy has been achieved by means of numerous static dilatometric measurements at elevated temperatures, in which case the total hysteresis is less than 0.1 GPa, with a reliable extrapolation to lower temperatures. The following relation was found in this manner for a wide range of parameter values:

$$P_0(t\ {}^\circ\mathrm{C}) = 1.955 \pm 1.310^{-2}\ \mathrm{GPa} - 0.015 \cdot 10^{-4}\ \mathrm{GPa/deg}. \tag{4}$$

TABLE I. Theoretical and experimental static polymorphism hysteresis of Ti, Zr, Fe, and KCl (Ref. 4) along with the equilibrium pressures P_0.

Material	Initial and final phases	ΔV, cm^3/mole	E_α, cal/mole	ΔP_m^+, GPa theor	ΔP_m^+, GPa expt	P_0, GPa (~300 K)
KCl	B_1(NaCl) B_2(CsCl)	4.36	710	0.68	0.57 (4.2) K	1.95 (Ref. 5)
Ti	α(hcp) ω(dist. bcc)	0.18	165	3.60	2.7 (20 °C)	2.20 (Ref. 6)
Zr	α(hcp) ω(dist. bcc)	0.18	195	2.70	1.8 (20 °C)	2.20 (Ref. 6)
Fe	α(bcc) ε(hcp)	0.38	195	2.20	2.5 (20 °C)	10.7 (Ref. 1) ±0.8

The value of P_0 for titanium and zirconium was determined in Ref. 6 through cyclic experiments involving the application and removal of pressure, accompanied by a shear deformation, which stimulates phase transitions. No such measurements have been carried out for iron. The P_0 (Fe) values in Table I were estimated within a relatively large uncertainty from the greatly varying values of P_m^+ and P_m^- given in Ref. 1.

The dynamic information available on potassium chloride is very comprehensive, but it is not entirely unambiguous. The Hugoniot adiabat and the phase transition in compressional shock waves were studied[7] in 1963 by an electrical-contact method. Profiles of the mass velocities were measured with the help of magnetoelectric gauges in 1965 (Ref. 8), and the value of P_m^+ for the direct phase transition was redetermined. An overall profile of the shock pulse, including the rarefaction shock wave, was first obtained in 1967, by the same method.[3] Two successive stages in the phase transition of an initial structure of the NaCl type (structure B_1) into a structure of the CsCl type (B_2) were discovered[9] in 1974 by a piezometric method involving quartz gauges during the shock compression of crystals along a cube diagonal. The fast stage occurs at the wavefront; the second, slower stage, which completes the transition, occurs behind the front. Thin Manganin foils embedded in the test crystal were used as pressure gauges in 1980 (Ref. 10).

The results of all earlier experiments are generalized in Table II. The deviations of recent data[10] from other results are far from trivial. Accordingly, we have carried out some new Manganin measurements on KCl single crystals. It was also necessary to clarify the extent to which the kinetics of the inverse transitions depends on the maximum pressures of the unloading isentropes. If the initial unloading pressure is high enough, the inverse phase transition begins in the uniform crystal structure of the high-pressure phase. In the case of unloading from segments of phase mixtures, the abundance of "relic" nucleating regions of the low-pressure phase would seemingly reduce the hysteresis and accelerate the transition. According to another concept, developed in Ref. 11, however, an elastic interaction between the crystallites of the high- and low-pressure phases should increase the deviation from equilibrium and should retard the inverse transition.

TABLE II. Experimental pressures of phase transitions in shock waves in potassium chloride.

Authors	Year	Method	P_m^+, GPa	P_m^-, GPa
(Ref. 7)	1963	Electric-contact	2.00	—
(Ref. 8)	1965	Magnetoelectric	1.89	—
(Ref. 3)	1967	Magnetoelectric	2.01	1.10
(Ref. 9)	1974	Piezometric	2.10	—
(Ref. 10)	1980	Manganin	2.34?	1.6?

2. EXPERIMENTAL PROCEDURE

Figure 1 shows the layout of the new experiments carried out to find profiles of the loading and unloading waves. The test samples were pure KCl single crystals with an initial density $\rho_0 = 1.99$ g/cm^3. The shock compression of these samples was carried out along the ⟨001⟩ direction, i.e., along a cube edge. The loading pressure was varied by using explosive charges of various strengths. The pressure gauges, which were bifilar spirals of Manganin foil with four leads, were cemented into the KCl sample with epoxy resin. The thickness of the gauges was 0.03 mm and their resistance ~1.5 Ω. The pressure of the shock loading of the KCl was determined from the measured electrical resistance R of the Manganin gauge in its compressed state. To convert from R/R_0 to the pressure P, we used the dependence of the resistance of Manganin on the shock-compression pressure, $P = f(R/R_0)$, from Ref. 12.

Figure 2 shows an oscilloscope trace of a pulse generated by a pressure of 7.3 GPa, which is above the phase-transition pressure. This experiment detects the sharp leading front of the direct ($B_1 \rightarrow B_2$) phase transition, the elastoplastic unloading wave, and the amplitude ($P_3 = P_m^-$) of the rar-

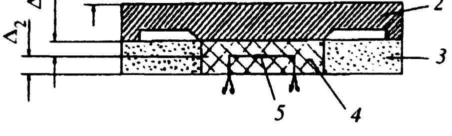

FIG. 1. Layout of the experiment to determine the profile of the loading and unloading waves with the help of a Manganin pressure gauge. *1*—Explosive charge; *2*—copper shield 10 mm thick; *3*—epoxy resin; *4*—KCl test crystal; *5*—Manganin pressure gauge. $\Delta_2 = 2.0 \pm 0.1$ mm.

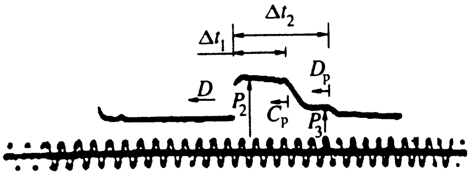

FIG. 2. Profiles of a shock unloading pulse in KCl: P_2=7.3 GPa. C_p—Elastoplastic unloading wave; D_p—unloading shock wave. The frequency of the reference sine wave is 5 MHz.

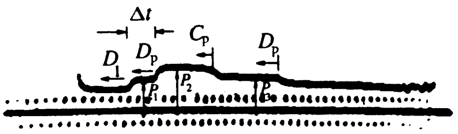

FIG. 3. Profiles of a shock pulse in KCl: P_2=4.1 GPa, Δ_1=2.78 mm, Δt =0.28 μs. The frequency of the reference sine wave is 10 MHz.

efaction shock D_p, with a finite time for the B_2-B_1 transition. In subsequent experiments, the applied pressure P_2 was reduced. This approach made it possible (Fig. 3) to detect the critical pressures for the transitions, $P_m^+=P_1$, in the compressional wave. To detect polymorphic transitions at elastic-loading pressures below 3.0 GPa, we used a method involving a partial cancellation of the initial stress at the gauge. This method made it possible to substantially improve the accuracy of the measurements. The accuracy was a major concern because of difficulties in measuring the small amplitudes of the pulses taken from the Manganin gauges. As detectors we used S9-8 storage oscilloscopes, with subsequent analysis of the data on a personal computer. Figures 4–6 show characteristic profiles of the shock pulses.

3. RESULTS AND DISCUSSION

In a medium with a strength Y, the amplitudes of the shock waves give us normal components σ_x which exceed the pressures P by $\sigma_x-P=2/3Y$. For KCl with Y=0.04–0.09 GPa (Ref. 9) we have $\sigma_x \simeq P$. The primary result of this study is a direct determination of the pressures of the martensitic points, $P_m^+=P_1$ and $P_m^-=P_3$, at various applied pressures P_2, under shock-compression conditions. The results found are shown at the left in Table III. The essentially complete agreement between the pressures P^+, at which the B_1-B_2 phase transition begins, and the boundary of the thermodynamic equilibrium of the phases is not a trivial result. According to Eq. (4), at 300 K the pressure is P_0=1.95±0.013 GPa. According to the new measurements (Table III) we have an average $P_m^+=1.92\pm0.03$ GPa. Taking an average over all sources except Ref. 10, we find $P_m^+=1.97\pm0.03$ GPa.

The pressure of the inverse transition, $P_m^-=1.15\pm0.15$ GPa, is much lower than the equilibrium pressure. In Ref. 3 and the present experiments, P_m^- was found from the amplitudes of the rarefaction shock waves. At pressures $P_2<4$ GPa, they are formed in a metastable phase mixture. With decreasing pressure, the relative concentration of crystallites of the low-pressure phase increases, and the inverse transitions slow down. Evidence for this behavior comes from the shock-pulse profiles in Figs. 4–6. In agreement with the concept developed in Ref. 11, this effect is apparently associated with an elastic interaction in a phase mixture of nonequilibrium crystallites of the high-pressure phase with a stable matrix of "relic" crystallites of the low-pressure phase. It turns out that the latter, which reach their stability field again during the unloading, do not convert into active growth centers.

The pronounced asymmetry of the direct and inverse transitions is of particular interest. To reach an understanding of the physical nature of this asymmetry, we should compare the results found with dilatometric measurements[13] of phase transitions of KCl under static conditions, over the temperature range from 4.2 to 300 K. The $P-T$ diagram found in Ref. 13 (Fig. 7) demonstrates a symmetry of the hysteresis effects and a sharp decrease in these effects with the temperature during static compression. At 4.2 K the hysteresis corresponds approximately to the calculated value in Table I. An increase in temperature triggers[14] an Arrhenius rate in the transition process, reducing the effective thermodynamic stimulus required to overcome the activation barrier. According to Ref. 14, what is required for the onset of the transitions in this case is, instead of Eq. (3), a deviation

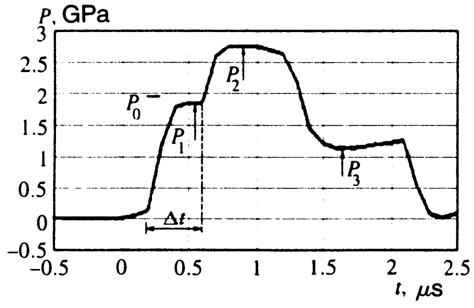

FIG. 4. Profiles of a shock pulse in KCl: P_2=2.76 GPa, Δ_1=2.53 mm, Δt=0.41 μs.

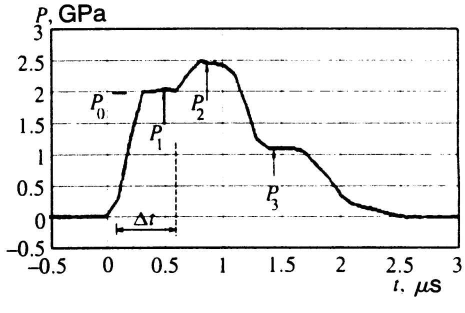

FIG. 5. Profiles of a shock pulse in KCl: P_2=2.48 GPa, Δ_1=1.90 mm, Δt=0.45 μs.

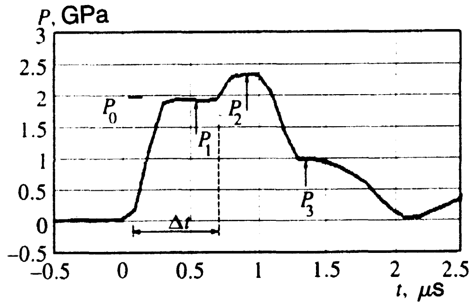

FIG. 6. Profiles of a shock pulse in KCl: $P_2=2.30$ GPa, $\Delta_1=2.30$ mm, $\Delta t=0.63$ μs.

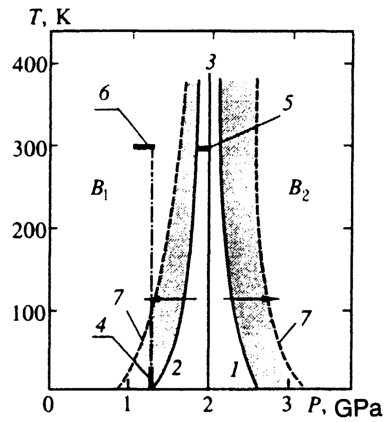

FIG. 7. $P-T$ diagram of the $B_1 \rightleftarrows B_2$ transition in KCl: *1,2*—Curve of onset of transitions in the static case according to Ref. 13; *3*—phase-equilibrium line;[5] *4*—calculated hysteresis ΔP_m at 4.2 K (Table I); *5*—pressure of the $B_1 \to B_2$ transition, P_m^+, under dynamic conditions (present study); *6*—pressure of the $B_2 \to B_1$ transition, P_m^-, under dynamic conditions (present study); *7*—Curve of the end of the phase transitions.[13]

$$\Delta P(T) = \Delta P_m + C\,\frac{RT}{\Delta V} \tag{5}$$

from equilibrium pressures. The constant C in Eq. (5) contains as a factor the minimum measured transition rate. The sign of the second term is always opposite the sign of ΔP_m. Accordingly, the hysteresis of the transition decreases linearly with the temperature. This conclusion is supported approximately by the experimental data. Figure 7 shows the calculated athermal hysteresis of KCl (Table I for 4.2 K) and the results of a study of phase transitions in shock waves, in which the role of the KCl temperature is negligible. The agreement of P_0 and P_m^+, i.e., the vanishing of ΔP_m^+, is evidence of some particular mechanisms for martensitic phase transitions in shocks, which produce high-energy "embryos"[15] of new phases by virtue of the tangential stress. On the phase-equilibrium line they instantaneously convert into active crystallization centers. The term "tensogenic" kinetics, introduced by Voropinov and Podurets,[16] applies here. According to the figurative expression of Alder,[17] the shock front can be compared with a mill which crushes unconsolidated material in its bow region and then flings the atoms into a high-density region, into states which are stable under these conditions.

The tangential stress in isentropic rarefaction waves is minimal; the conditions required for the formation of active "protonuclei" do not hold; and the large hysteresis of the inverse transitions is approximately the same as the athermal hysteresis at 4.2 K.

The experimental information found can be used to calculate the specific volumes and the approximate content of the low-pressure phase in the states which were detected, as shown at the right in Table III. Here we used the measured pressures P_2 and P_1, the time intervals Δt (taken from the oscilloscope traces), the known velocity of the first shock wave ($D_1=3.6$ km/s), and the conservation laws:

$$U_1=\frac{P_1}{\rho_0\cdot D_1},\quad \rho_1=\frac{\rho_0\cdot D_1}{D_1-U_1},\quad D_{12}=\frac{\Delta_1+U_1\cdot\Delta t}{\Delta_1 D_1^{-1}+\Delta t}-U_1,$$

$$U_{12}=\frac{P_2-P_1}{\rho_1\cdot D_{12}},\quad V_2=\frac{D_{12}-U_{12}}{\rho_1\cdot D_{12}}.$$

Here $D_{12}=D_2-U_1$ is the velocity of the second compressional wave with respect to the moving matter, $U_{12}=U_2-U_1$ is the change in the mass velocity behind the front of the second compressional wave, and V_2 is the specific volume of the KCl behind the front of the second compressional wave.

Figure 8 shows a pressure-specific-volume diagram of KCl according to the combined experimental data from the present study and Refs. 3 and 9. Shown for comparison in Fig. 9 is a corresponding diagram for ion, according to Ref.

TABLE III. Parameters of the polymorphic transitions and the Hugoniot adiabat of KCl.

P_2, GPa	$P_1=P_m^+$, GPa	$P_3=P_m^-$, GPa	D_{12}, km/s	U_{12}, km/s	V_2, cm^3/g	% LPP (vol.)
7.30	—	1.28	3.63	1.01	0.362	0
4.10	1.97	1.33	2.44	0.405	0.387	~5
3.17	1.97	1.35	2.196	0.253	0.410	~30
2.76	1.84	1.10	2.117	0.203	0.422	~40
2.56	1.83	0.93	1.858	0.183	0.421	
2.48	2.01	1.09	1.797	0.125	0.431	~55
2.30	1.91	0.96	1.684	0.108	0.436	~60

*In an experiment with $P_2=7.30$ GPa the loading shock front had a single-wave configuration. Here LPP means the low-pressure phase.

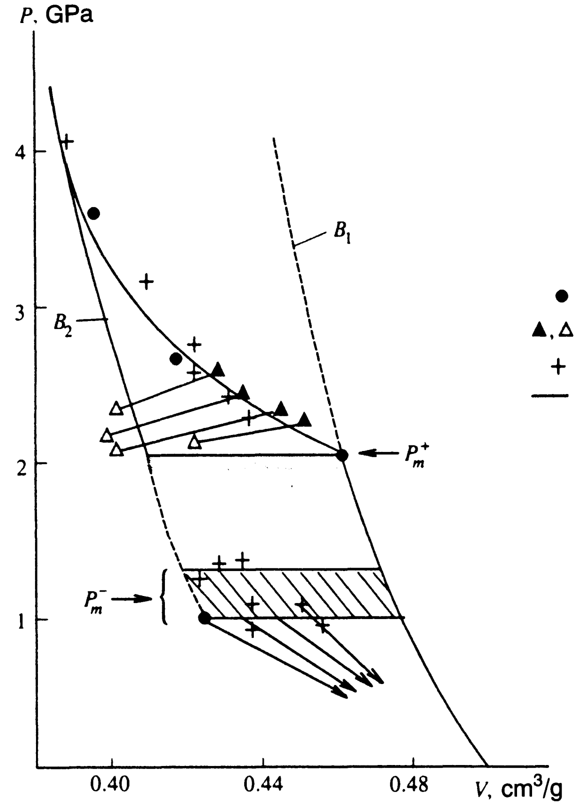

FIG. 8. $P-V$ diagram of phase transitions in KCl according to the data of Refs. 3 and 9 and the present study. *1*—⟨001⟩ direction, Ref. 3; *2*—⟨111⟩ direction, Ref. 9; *3*—⟨001⟩ direction, present study; *4*—phase-equilibrium line.

18. On the basis of numerous experiments,[18–20] which are in good agreement with each other, we have $P_m^+=13\pm0.3$ GPa and $P_m^-=9.8\pm0.4$ GPa for iron.

The large hysteresis range in the case of Fe has been interpreted in different ways. According to the Andrews equation,[21] we have $P_0=13.3$ GPa; i.e., this pressure is the same as P_m^+, as in the case of KCl. An equation of state proposed subsequently by Zhukov[22] uses relations (1); the result is a value $P_0=10.7$ GPa. At this point, the two interpretations look equally good. For tin,[23] the situation is close to that of KCl. Zirconium and tin have identical crystal structures in their low-pressure phase. Under pressure, they undergo an isomorphic structural evolution. The hysteresis of the direct transitions in these materials is large in shock waves, but different for the two materials: For zirconium[24] with $P_0=2.2$ GPa we have $P_m^+=6.75$ GPa; while for titanium with $P_0=2.0$ GPa we have $P_m^+=10.4-12.0$ GPa (Refs. 25 and 26).

There are ambiguities in the determination of the crystal structure of the high-pressure phase of potassium chloride in the metastable range. According to classical ideas,[15] the material here is a two-phase mechanical mixture. As the pressure is raised, the concentration of the dense phase increases, because new crystallization centers continually come into play as a result of the increasing thermodynamic stimulus. New information[27,28] has been obtained in recent years through direct measurement of the structure of KCl crystals behind the fronts of shock waves by means of pulsed x-ray structural recordings. The simultaneous presence of two intermediate crystalline modifications was detected by this method[28] in the metastable range for KCl. One modification has an approximately CsCl structure, while the other is a highly distorted structure of the low-pressure phase (of the NaCl type). These studies, which are very promising, are being pursued.

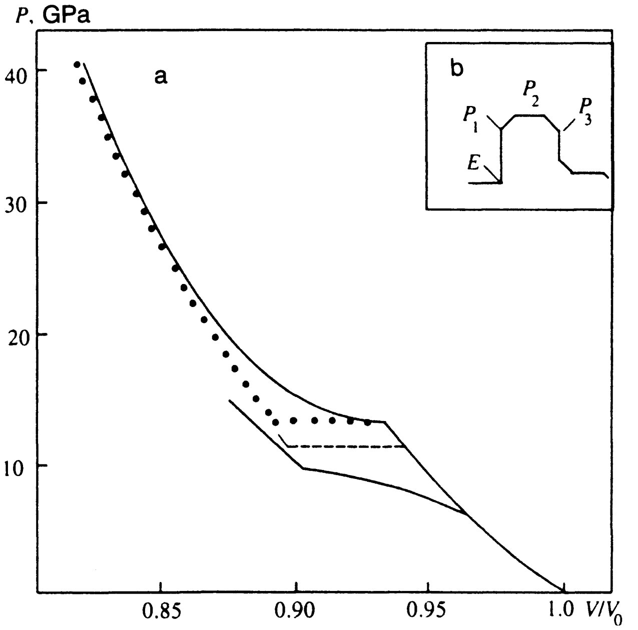

FIG. 9. a: $P-V$ diagram of phase transitions in iron[18] (solid line). Also shown are two alternative phase-equilibrium lines, according to Refs. 21 (dots) and 22 (broken line). b: Profile of the shock-pulse pressures in iron according to Ref. 19. P_1—Pressure P_m^+ of the $\alpha\rightarrow\varepsilon$ phase transition; P_2—applied pressure; P_3—pressure P_m^- of the $\alpha\rightarrow\varepsilon$ phase transition, which is equal to the amplitude of the rarefaction shock wave.

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