

Pressure self-multiplication effect in a phase transition under quasihydrostatic conditions

V. D. Blank, Yu. Ya. Boguslavskii, M. I. Eremets, E. S. Itskevich, Yu. S. Konyaev, A. M. Shirokov, and É. I. Éstrin

Institute of High-Pressure Physics, Academy of Sciences of the USSR, Akadengorodok, Moscow Province
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An investigation was made of the influence of shear on pressure distributions in potassium and sodium chlorides subjected to pressures up to 16 GPa in a diamond chamber. The shear strain in KCl, which was in a two-phase state, resulted in a considerable redistribution of the pressure in a sample when the external load and the chamber geometry were kept constant. This redistribution altered the pressure at the center of the chamber by up to 50–70%. The effect was attributed to changes in the elastic moduli as a result of a phase transition.

The knowledge of the pressure distribution in the working zone under quasihydrostatic conditions is essential for the understanding of the processes that occur in the substance being investigated and also for identifying the optimal conditions for attaining the maximum pressures. Information on local values of the pressure and its changes are particularly important in studies of the influence of shear strains on polymorphism at high pressures, since there may be considerable changes in the phase transition pressure.¹ Construction of a chamber for producing shear under pressure applied by single-crystal diamond anvils² made it possible to carry out experiments for the first time.

Our investigation was aimed to determine the distribution of pressure before and after shear in samples of sodium and potassium chlorides subjected to pressures up to 16.0 GPa and to find the characteristics of this distribution in the case of a polymorphic transition, particularly the distribution near phase boundaries. We also considered the possibility of using this method in determining the ranges of stability of the phases and in plotting the equilibrium PT diagram of the investigated substance.

METHOD

We used a shear pressure chamber² in which the support of one of the anvils was attached to the chamber wall via a thrust bearing that made it possible to rotate the support by up to 30°. The pressure distribution was determined at intervals of 2–5 μ in the working zone for the luminescence of ruby using a method described in Ref. 3.

The investigated substances, which were chemically pure KCl and NaCl, were employed in the form of powders mixed in the proportion of 100:1 by volume with a ruby powder. The average particle size of the ruby powder was $\approx 2 \mu$, which was considerably less than the thickness of the layer of the substance (15–20 μ) between the anvils when the pressure was at its maximum. It was estimated that the average distance between the ruby particles was $\approx 10 \mu$.

This powder mixture was placed between the anvils in the absence of a gasket, a certain load was applied, and then the mixture was viewed under a microscope and the pressure distribution was determined in the radial direction of the sample. This was followed by smooth rotation (in ≈ 10 sec) of the mobile support with the anvil through an angle of

$\varphi \approx 5^\circ$ and then the mobile assembly was rotated back to the initial position and the pressure distribution was recorded once again. This procedure was repeated after each load. Before and after the rotation through an angle 2φ the point with the maximum pressure was identified and a section passing through it was selected. As a rule, the coordinates of the maximum were maintained throughout an experiment. The precision of the motion of the chamber in the determination of the pressure distribution over the cross section of a sample was at least ± 0.002 mm.

EXPERIMENTAL RESULTS

1. Sodium chloride

We can see from Fig. 1 that in the investigated range of pressures (up to 16 GPa) a shear strain had practically no effect on the pressure distribution under load rising and falling conditions. During the first loading the maximum pressure could decrease somewhat after shear, but on further

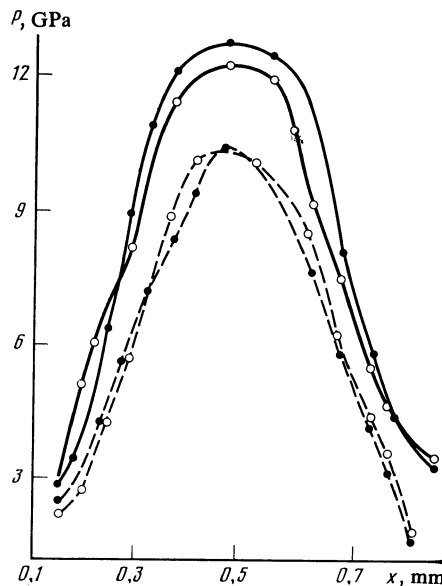


FIG. 1. distribution of the pressure in a sample of NaCl before (O) and after (●) shear deformation ($\varphi = 15^\circ$): the continuous curves were obtained by increasing the load and the dashed curves by reducing it. The edge of an anvil was taken as the zero point along the axis in Figs. 1, 3, and 4.

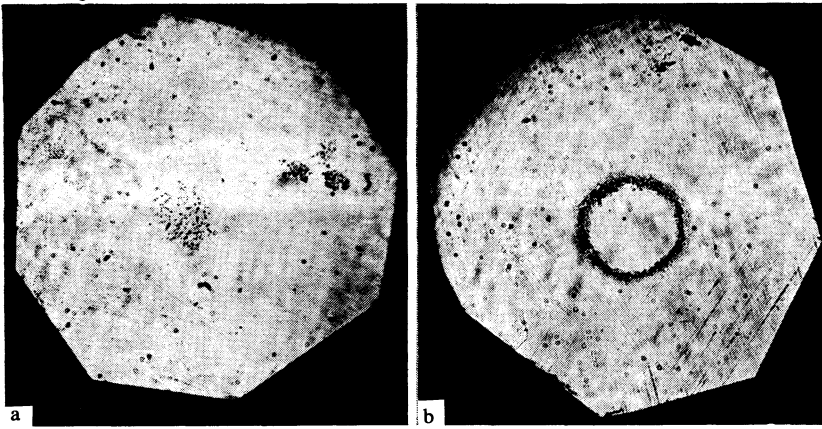


FIG. 2. Boundary between the B_1 and B_2 phases in KCl before (a) and after (b) shear deformation ($\varphi = 15^\circ$).

loading and unloading (up to the moment of formation of cracks in a sample) a shear strain either did not alter the pressure distribution or it increased the pressure in the central region by 5–7%. It should be pointed out that in the investigated range of pressures we did not observe any phase transition in NaCl under shear conditions.

2. Potassium chloride

The relatively low pressure of the $B_1 \rightarrow B_2$ polymorphic transition in potassium chloride ($P^{I \rightarrow II} = 2.0\text{--}2.5$ GPa at 300 K) and the possibility of visual observation of this transition in the diamond-anvil chamber made potassium chloride a convenient model sample.

An initial increase in the load gave rise to a two-phase region in the central part of the sample and this corresponded to the onset of the transition under quasistatic conditions (Fig. 2a). A shear strain gave rise to a fairly clear boundary between the phases and increased the region containing the B_2 phase (Fig. 2b).

The shear strain resulted in a considerable redistribution of the pressure in the KCl sample when the polymorphic transition pressure was exceeded. If the load was increased first ($B_1 \rightarrow B_2$ transition) and then a shear stress was applied, it was found that the pressure in the central part of the sample increased and it decreased at the periphery (Fig. 3). The effect was reversible: during the reverse run ($B_2 \rightarrow B_1$ transi-

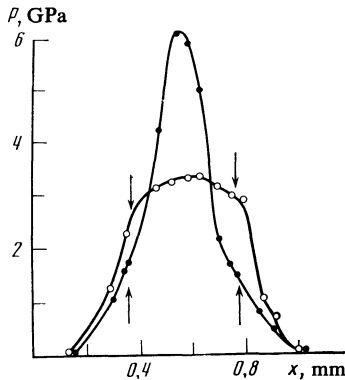


FIG. 3. Distribution of the pressure in a sample of KCl before (O) and after (●) shear deformation ($\varphi = 15^\circ$) recorded by increasing the load. The arrows identify the position of a visible phase boundary.

tion) the pressure decreased at the center and increased at the periphery after shear. The changes in the pressure at the center could reach 50–70% of the initial value before the shear and this was true for the rising and falling loads.

It was interesting to note that the displacement of the phase boundary after shear deformation was considerably less than one could deduce from the positions of the points with $P_0 \approx 1.9$ GPa in the initial distribution of the pressure (Fig. 2).

Detail measurements in the region of a phase boundary revealed a background of a monotonic variation of the pressure with the distance with a superimposed characteristic anomaly in the form of a step (Fig. 4) which was located at the visible phase boundary or slightly closer to the center. The pressure at the step before shear deformation was $P^{I \rightarrow II} = 2.4\text{--}3.0$ GPa (symbols O in Fig. 4) and $P^{II \rightarrow I} = 1.2\text{--}1.4$ GPa for rising and falling loads, respectively. After shear deformation the pressure in both cases was $P^{I \rightarrow II} = 1.8 \pm 0.1$ GPa (symbols ● in Fig. 4). The good agreement between these values and the published data⁴ indicated that the method could be used to plot the PT diagrams of the investigated substance. One should point out that lowering of the load created cracks which were accompanied by plastic flow of the material and this reduced the hysteresis and increased the pressure of the $B_2 \rightarrow B_1$ transition.

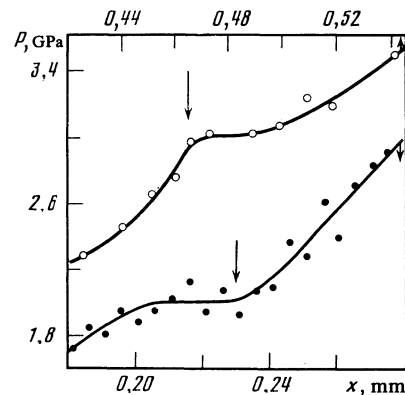


FIG. 4. Distribution of the pressure in the region of a phase boundary in KCl obtained in two different experiments: (O) on increase in the load without shear; (●) after shear deformation ($\varphi = 15^\circ$). The arrows show the position of a visible phase boundary.

DISCUSSION

Our experiments thus established that the application of a shear stress to a substance undergoing a polymorphic transition under quasihydrostatic conditions and capable of existing in a two-phase state causes a redistribution of the pressure in a sample. The pressure in the central part of the sample may rise (self-multiplication) or decrease (self-demultiplication). The terms self-multiplication and self-demultiplication indicate that a change in the maximum pressure occurs at a fixed external load and for a constant chamber geometry: it is due to a change in the properties of the investigated sample, for example, those due to shear.

We shall first give a qualitative explanation of the observed effect. We shall assume that the pressure is applied by the anvils to two substances with identical Young moduli at atmospheric pressure, but the Young modulus of one of these substances rises more strongly with the pressure, whereas the Young modulus of the other does not change. Then, the pressure at the center of the chamber is higher in the first substance (for the same load) because the pressure distribution is then physically equivalent to the distribution in a system of loaded coaxial cylinders with the Young moduli that increase from the periphery to the center. An increase in the load increases the pressure and the Young modulus, and the increase in the modulus automatically ensures a faster rise of the pressure at the centers of the anvils, i.e., a positive feedback is established.

The self-multiplication effect should be manifested most effectively by substances that undergo a phase transition, because such substances have strongly nonlinear elastic properties. Their elastic moduli are nonanalytic functions of the pressure

$$E = E_2(P) + [E_1(P) - E_2(P)]\theta,$$

$$\mu = \mu_2(P) + [\mu_1(P) - \mu_2(P)]\theta,$$

where E_1 , E_2 , μ_1 , and μ_2 are the Young and shear moduli of the first and second phases, respectively. The Heaviside step function is $\theta = 1$ for $P \leq P^{I \leftrightarrow II}$ and $\theta = 0$ for $P > P^{I \leftrightarrow II}$. The self-multiplication effect appears if

$$E_2(P) > E_1(P), \quad dE_2/dP > 0, \quad dE_2/dP > dE_1/dP.$$

In our experiments a shear deformation eliminates a hysteresis of the transition and facilitates the spread of the transition to an additional part of a sample which is in a metastable state.

A sample experiences both elastic and plastic deformation during an experiment. Naturally, in a rigorous formulation the problem of self-multiplication should be considered in the framework of the theory of finite strains. Since such a problem is fairly complex to deal with, we shall estimate the magnitude of the effect simply because of an abrupt change in the modulus E at a phase transition and we shall do this using the approximation of a homogeneous elastic strain. We shall approximate the investigated system by coaxial cylinders consisting of two phases with the moduli E_2 (inner)

and E_1 (outer). When a compressive force F is applied, we obtain⁵

$$F = \frac{1}{4}\pi d^2 P_2 + \frac{1}{4}\pi (D-d)^2 P_1, \quad P_2/P_1 = E_2/E_1,$$

where P_1 and P_2 are the pressures in the first and second phases; d and D are the diameters of the inner and outer cylinders (rings). In the case of a substance consisting of just one phase ($d = D$, $d = 0$), but with the same values of D and F , we find that

$$\bar{P} = 4F/\pi D^2.$$

We thus have

$$\frac{P_2}{\bar{P}} = \left[\frac{E_1}{E_2} + \left(1 - \frac{E_1}{E_2}\right) \left(\frac{d}{D}\right)^2 \right]^{-1}.$$

We can see from the above formula that the maximum effect is observed for low values of d/D and it is of the order of

$$P_2/\bar{P} \sim E_2/E_1.$$

There was no information on the abrupt change in the Young modulus as a result of a transition in polycrystalline KCl, so that we had to use the data for polycrystalline RbCl characterized by $E_2/E_1 = 1.5$ (Ref. 6). Rubidium chloride is a structural analog of KCl and, moreover, the volume changes as a result of the $B1 \leftrightarrow B2$ transition under pressure are identical. Therefore, there are grounds for assuming that the relative values of the jumps in the moduli are of similar magnitude for these two compounds. It is then found that

$$\frac{P_2}{\bar{P}} = \frac{1.5}{1 + 0.5(d/D)^2}.$$

Since $0 \leq d/D \leq 1$, it follows that $1 \leq P_2/\bar{P} \leq 1.5$. An increase in E_2 on increase in the pressure enhances the effect. If these calculations are applied to the case illustrated in Fig. 3, where $D = 0.085$ cm, $d = 0.04$ cm, and $F = 1.7$ kN, we find that $P_1 = 2.65$ GPa and $P_2 = 4.0$ GPa, in qualitative agreement with the experimental results, and the multiplication effect is $P_2/\bar{P} \sim 1.3$.

We shall conclude by noting that the pressure self-multiplication (self-demultiplication) effect can be observed also in those cases when the phase transition is initiated not only by a shear strain, but also by other factors (for example temperature, radiation, etc.).

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