

THE MARTENSITE CHARACTER OF THE POLYMORPHIC TRANSITION IN KCl

AT HIGH PRESSURES

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The characteristics of the polymorphic transition in KCl are investigated at pressures up to 30 kbar and temperatures up to 300°C. It is shown that between -77° and +30°C the polymorphic transformation possesses the following characteristics: self-inhibition of the process at constant pressure; co-existence of two phases in a broad pressure range: a significant hysteresis; sound phenomena ("clicks") appearing during the transformation; appearance of a lamellar microrelief on the surface of the single crystals. These traits are typical for martensite transformations. The effect of temperature on the characteristics is described and it is shown in particular that with increasing temperature the transition in KCl begins to resemble phase transformations with "normal" (nonmartensite) kinetics.

It is known that KCl, RbCl, and certain other alkali halides which have under normal conditions an NaCl-type lattice (phase I) undergo at high pressures a reversible polymorphic transformation with the appearance of a CsCl-type structure (phase II).^[1, 2] The phase diagrams of pure alkali-halide crystals under pressure have been rather well investigated, however the kinetics of the polymorphic transformations in this very simple class of solids have so far been little investigated. Therefore, along with an investigation of the parameters of the transition in KCl and its alloys with RbCl,^[3] it would be interesting to explain certain features of the kinetics of this polymorphic transformation.

At the time two of the authors of the present article investigating the operation of a "polymorphic buffer" in a two-stage piezometer^[4] observed that the production of the dense modification in a polycrystalline sample of KCl is accompanied by clearly audible clicks. Subsequently we observed the same effects in the transition of KBr, RbCl, and RbI. In this connection special measures were also taken in this investigation to record these sound phenomena.

METHOD OF MEASUREMENT AND SAMPLES

The measurements were carried out by displacement of a piston in the apparatus described previously in^[5, 6]. Lead was employed as the pressure transmitting medium. The experiments consisted in determining the dependence of the volume change of the sample ΔV (which is proportional to magnitude of the displacement of the pistons Δl) on the pressure p at constant temperature. The absolute accuracy of determining the pressure by this method is ± 0.15 kbar and of the volume change—of the order of 10^{-4} cm³. The sensitivity of the relative measurements of the monotonic variation of the pressure is by a factor of five and that of the volume by a factor of about 10-12 higher. In the region of the phase transformation which is accompanied by an appreciable volume change the $\Delta l(p)$ curves were recorded both "point by point" (with the pressure being increased in

steps and held at each step) and with the pressure varying continuously. To record the rapidly changing parameters the scales of the instruments (of the manometer, the displacement indicators, and of the timer) were brought into the same plane and filmed, or integer values of p and Δl were marked manually on the ribbon of a loop oscillograph with ribbon speeds of 4, 10, or 25 mm/sec. In both cases the accuracy of an individual time reading was 0.1-0.3 sec.

The clicks were also recorded on the oscillograph ribbon. For this purpose piezoelectric transducers (x-cut quartz platelets or UTS-19 piezoelectric ceramic) were glued to the frame of the piezometer. The signal from the piezoelectric transducers was recorded on an N-102 loop oscillograph using type-1 and type-4 loops. In recording use was made of an UMSH-1 loop amplifier. A PU-5M preamplifier with an input resistance of 10^9 ohm was used to match the piezoelectric transducers with the relatively low input resistance of the loop amplifier.

A small section of such an oscillogram is shown in Fig. 1. Trace 2 shows clearly the pulses from the piezoelectric transducer which exceed appreciably the noise level, trace 1 serves for recording the pressure, trace 3 is for the piston displacements, and on the very top is the time scale (10 Hz).

From the results of the experiments we plotted the dependences $\Delta l(p)$, $p(t)$, $\alpha(p)$, and $\alpha(t)$ where t is the time and α is the degree of transformation equal to $\delta V_t / \delta V_\infty$ (δV_t is the volume change in the process of the polymorphic transformation per time t , δV_∞ is the total volume change in the transition). The values of δV_t and δV_∞ were corrected for the compressibilities of both phases. By varying the rate of change of the pressure, one can change the time of the complete transformation. Usually the time of the complete transition in the experiments was between 1 minute and several dozen seconds. We did not use shorter or longer exposures because of the peculiarities in the construction of the press.

Experiments with KCl were carried out at -77° and

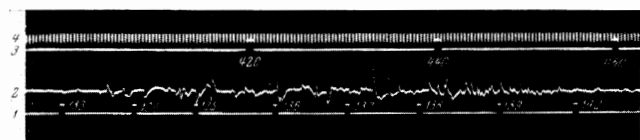


FIG. 1. Example of recording of clicks occurring in a transition with increasing pressure in a polycrystalline sample. 1—pressure marks (in relative units), 2—recorded clicks, 3—piston displacement marks (in microns), 4—time scale (10 Hz).

in the 22–300°C range, the experiments with the alloys— at 22–28 and 100–110°C. A basic number of experiments with KCl was carried out with pressed samples of chemically pure powder. In a number of experiments we used reprecipitated material as well as remelted and annealed samples, single crystals of KCl, and natural sylvite mineral (Solikamsk deposit).¹⁾

The polycrystalline samples of KCl and KCl–RbCl alloys were pressed in the form of pellets 4.8 mm in diameter and 5 mm high under a pressure of ~18 kbar.²⁾ Pellets of the remelted material and alloys and individual pellets of the starting material were annealed at 560° for three hours.³⁾ The sylvite and the KCl single crystals were cut in the form of small cubes. Some batches of the single crystal samples underwent annealing at 700°C for 6–7 hours and cooling to 20° for 10 hours. The experiments with single crystals were carried out only at room temperature under hydrostatic pressure in organosilicon fluid No. 5, a portion of the crystals being protected from contact with the pressure transmitting fluid by a rubber film.

It should be noted that we observed no effect due to contact with the fluid. Nor did we observe any effect of the method of preparation and thermal treatment of the samples on the parameters and the kinetics of the transformation in KCl. For this reason we shall not discuss these cases specially.

The quantitative results presented in the following section were obtained with samples of pressed KCl powder, alloys, and mixtures of KCl and AgCl powders. Silver chloride is a very plastic material and the experiments with the mixtures were carried out in order to exclude any possible influence of direct contacts between the KCl particles on the kinetics of the transition and on the sound effects by which it is accompanied, and also in order to decrease shear stresses in the sample.

EXPERIMENTAL RESULTS

The experiments which we carried out have shown that at room temperature the formation of the modification of KCl begins at a pressure $p_b = 20.9 \pm 0.3$ kbar and ceases at $p_c = 28.2 \pm 1.0$ kbar. The reverse transformation extends over a somewhat smaller range of pressures ($p'_b - p'_c$). The pressure at the beginning of the transformation (p_b, p'_b) was noted from

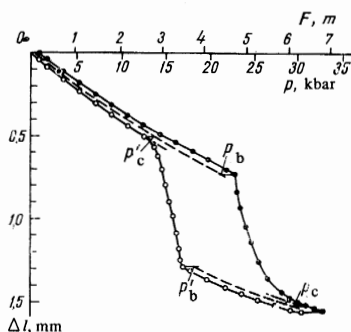


FIG. 2

FIG. 2. Example of an experimental $\Delta l = f(p)$ curve for KCl. \circ —increasing pressure, \circ —decreasing pressure. Dashed line— $\Delta l(p)$ dependence corrected for friction, dash-dot line—extrapolation of the hysteresis loop branches to the transition region. F —force of the press in tons.

FIG. 3. The dependence of the beginning and end of the transformation in the polymorphic transition in the KCl–RbCl system on the composition at room temperature: p_b (\bullet) and p_c (\blacktriangle) for the I→II transition, p'_b (\circ) and p'_c (∇) for the II→I transition.

the deviation of the $\Delta l(p)$ curves from a smooth course; the pressure at which the transformation ceased (p_c, p'_c) was arbitrarily taken to be the point at which the curve $\Delta l(p)$ joined the compressibility line of the given phase (Fig. 2).

As an auxiliary criterion of the beginning and end of the transformation we also used an analysis of the $\Delta l(t)$ dependences under constant pressure on various sections of the $\Delta l(p)$ curves. On the whole the accuracy of determining the pressure at the beginning and end of the transformation is determined by the sensitivity of the method, the rate of change of the pressure in a given experiment (the detailed reading of p and of Δl) and by peculiarities in the kinetics of the transition. According to our estimates the average accuracy in the determination of p_b and p'_b (in groups of independent experiments with samples of the same composition) amounts to ± 0.3 kbar, and the average accuracy in determining p_c and p'_c amounts to ± 0.8 kbar.³⁾

As is accepted in the method of piston displacement, the difference between the values of p_c and p'_c expresses the hysteresis of the transformation and their arithmetic mean (\bar{p}) is arbitrarily taken to be the thermodynamic equilibrium pressure of the two crystal modifications.⁶⁾

In Fig. 3 the ranges within which the two phases coexist ($p_b - p_c$ and $p'_b - p'_c$) in KCl and the alloys are marked by arrows pointing in the direction of the pressure change. In the two-phase regions, when the change of the pressure ceases, the rate of the transition decreases sharply and the process stops rapidly.

This phenomenon is illustrated by the graph (Fig. 4)

³⁾ All experimentally determined pressures were corrected for the friction in the sample which was as usual taken to be equal to the half-width of the hysteresis loop obtained on raising and lowering the pressure.

¹⁾ The authors express their gratitude to S. S. Gorbach for providing the KCl single crystals.

²⁾ The alloy samples were prepared by casting of a superheated (by about 100°C) melt of pure reactants into a cold trough. The composition of the samples was determined by previous weighing of the components.

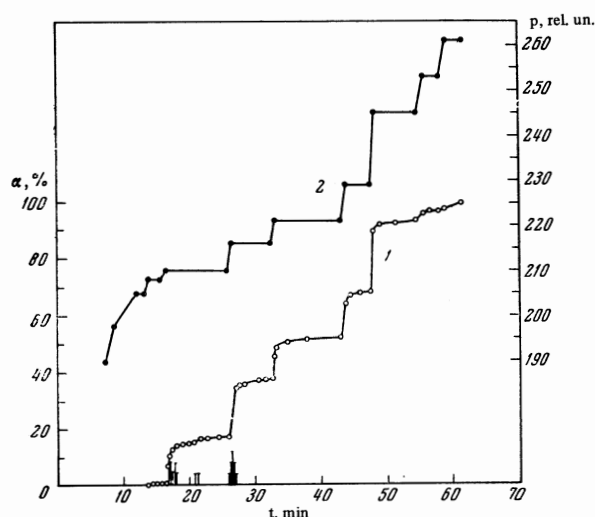


FIG. 4. The $\alpha(t)$ and $p(t)$ dependences in the transformation in KCl at room temperature and a pressure increase in steps with the pressure held at intermediate points. 1— $\alpha(t)$, 2— $p(t)$. Pulses are marked by vertical lines.

which shows the time dependences of the degree of transformation (α) and the pressure (p) at room temperature. In this experiment the pressure was increased in steps and was then held for several minutes (curve 2). Each increase in the pressure was accompanied by rapid formation of a certain amount of the dense modification of KCl, and upon being subsequently held at constant pressure the rate of transformation decreased sharply regardless of the presence of the initial phase (curve 1).⁴⁾

In Fig. 5 we present graphs of the dependence of the degree of transformation on increasing pressure obtained in five experiments for different modes of pressure change at room temperature. As the argument on the graph (Fig. 5) we have taken the value of the "excess of pressure" $\Delta p = p - \bar{p}$ where the value of \bar{p} was averaged in accordance with the data of these experiments.

In experiments 1 and 3 the pressure was continuously varied during the transformation in the course of four and three minutes respectively, whereas in experiment 5 the pressure was varied in steps in the course of fifty minutes as shown in Fig. 4. The spread of the values of α for a given Δp does not exceed 15–17 percent. Curves 2 and 4 obtained with samples which consisted of a mechanical mixture of KCl and AgCl powders taken in a ratio of 1:9 of their molecular weights also fall on the general dependence. The linear dimensions of the powder particles of the KCl did not exceed 50–100 μ . The agreement in the course of the $\alpha(\Delta p)$ curves permits one to assume that the phase transition takes place within the confines of a single crystallite and is not transferred from particle to particle by way of motion of the phase boundary.

Thus it follows from the data of Figs. 4 and 5 that under the conditions of our experiments at room tem-

⁴⁾The slope of type-1 curves on the flat sections depends on the strict maintenance of constant loading on the piston: even with pressure variations of 10 bar it is possible to observe a very slow ($\sim 10^{-5}$ cm³/min) volume change.

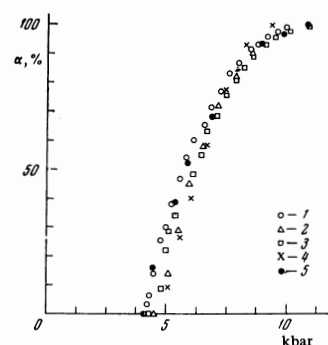


FIG. 5. The dependence of the degree of transformation (α) in the I→II transition in KCl on the magnitude of the excess pressure (Δp) in experiments with various durations of the change of p from p_b to p_c at room temperature. Δp is measured from the average pressure of the transformation. 1—4 min, 2, 4—1 min (KCl mixed with AgCl in a 1:9 ratio of the molecular weights), 3—3 min, 5—50 min (experiment of Fig. 4).

perature when p varies in the range p_b – p_c the degree of transformation is determined principally by the magnitude of the "excess pressure" and not by the experimental regime: by the rate dp/dt , by the magnitude of the steps in which the pressure is changed, by the duration of each step or total time during which the pressure changes from p_b to p_c .

As is seen from Fig. 3, in alloys of KCl and RbCl the pressure of the transition and the reverse transition depends monotonically on the chemical composition, the hysteresis of the transition remains in general the same as in the pure components, and the two-phase intervals are broader than in KCl (in pure RbCl the transition at room temperature takes place under very small constant excess pressure).

The character of the transition of the $\Delta l(p)$ curves from the single-phase region to the beginning of the transition also changes in the alloys: in pure components the beginning of the transformation is always recorded as a sharp break (Fig. 2), whereas in the majority of experiments with alloys the beginning has a more or less smoothly rounded off shape. Bridgman,^[7] investigating by the method of sliding contact the polymorphism of RbCl and RbI under purely hydrostatic pressure, noted the appearance of rounding of the hysteresis loops in these salts. He related the rounding of the $\Delta V(p)$ curves with possible solution of impurities in both phases or with the presence of moisture in the initial samples.

The following observation is also noteworthy: if in the process of formation of the dense modification, after holding the pressure constant one decreases somewhat the pressure acting on the piston, then the transition is damped more rapidly than for $p = \text{const}$; at the same time, of course, the decreased pressure does not extend beyond the preceding step and remains larger than p_b . In individual instances one can even observe on decreasing the pressure by 0.6–0.15 kbar a volume increase which is reversible. These volume changes (up to 5×10^{-5} cm³) are close to the sensitivity limit of the method and are therefore most noticeable either after holding p constant or at the beginning or end of the transformation, i.e., in the absence of a spontaneous process masking them. It should be noted that in the

single-phase sections of the hysteresis loop when the sign of the change in the force of the press (F on Fig. 2) changes a noticeable volume change (a movement of the displacement indicators by $0.5-1$ which corresponds to $\Delta V \approx 2 \times 10^{-5} \text{ cm}^3$) begins only after a pressure change of the order of $0.7-1.3$ kbar.

In all the KCl and alloy samples investigated the formation of the dense modification at room temperature is accompanied by clicks, an example of whose recording was shown on the oscillogram (Fig. 1). In the processing we determined the total number of pulses, their distribution in the course of the transformation, and the relative intensity. Some typical examples are presented in Fig. 4 and below in Fig. 7 in which the pulses are denoted by vertical lines. The height of the lines reflects the pulse amplitude (large, medium, and small) on a relative scale.

Combined processing of the oscillograms and of $\Delta l(p)$ curves of the type depicted in Fig. 2 showed the following.

1. At the beginning of the transition ($\alpha \leq 20-35\%$) the clicks are more frequent and their amplitude is larger. Rather often a single pulse or group of pulses precedes the acceleration of the transition. At times an appreciable deviation of the $\Delta l(p)$ curve from a smooth dependence begins with a click, although with very careful detection one can usually observe that the click was preceded by some acceleration of the piston displacement at constant pressure or constant rate of change of the pressure.

2. A sharp rise in the pressure at the beginning of the transition and an increase in the rate of transformation ($d\alpha/dt$) facilitate the manifestation of sound effects (they are louder and more frequent). For $\alpha \geq 50\%$ clicks do not as a rule occur even when the pressure is raised sharply and when the volume is changed appreciably and rapidly (Fig. 4).

3. After several cycles of transitions in both directions the sound effects become weak, but after the sample "rests" for 10-20 hours at normal pressure they are to some extent re-established.

4. In samples which are mechanical mixtures of AgCl with KCl powder taken in various molecular ratios (up to 9:1) the general picture of the phenomenon does not differ from that observed in samples consisting entirely of KCl.

In the alloys the intensity of the clicks and their number is generally lower than in samples of pure KCl.

No sound effects were observed in the reverse (II \rightarrow I) transition in polycrystalline samples, although this process does not differ from the forward (I \rightarrow II) transformation in its other kinetic characteristics (represented by the graphs of Figs. 3-5).

The above features of the kinetics of the transformation in KCl are retained in the temperature range from -77° up to $30-35^\circ \text{C}$. An appreciable change in the kinetics of the forward and reverse transitions in KCl takes place on further increasing the temperature; the transition can occur at constant pressure with the rate of the process ($d\alpha/dt$) increasing with rising values of the excess pressure (Δp). These changes become particularly noticeable at 60° .

In Fig. 6 we present $\alpha(t)$ curves of four experiments in which the pressure was kept approximately constant.

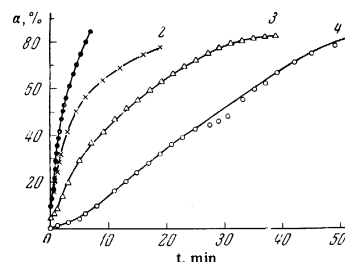


FIG. 6. The $\alpha(t)$ dependences in the I \rightarrow II transitions at $t = 63^\circ \text{C}$ and for various constant excess pressures Δp ($\Delta p = p - p_0$): 1— $\Delta p = 0.9$, 2— $\Delta p = 0.7$, 3— $\Delta p = 0.5$, 4— $\Delta p = 0.3$ kbar.

From the curves of Fig. 6 it is seen that under these conditions $d\alpha/dt$ also depends on the amount of unreacted material, whereas at 25° and below (within the limits of experimental accuracy) $d\alpha/dt$ for a given Δp practically does not depend on α .⁵⁾

The possibility of an isobaric process proceeding at a high rate at higher temperatures even for relatively small excess pressure [$\Delta p \approx (0.01-0.02)\bar{p}$] leads to the fact that α is determined both by the value of Δp as well as by dp/dt and the time during which p is held constant. In mixtures of KCl and AgCl one observes the same phenomenon although the isobaric process is rendered more difficult.

The spontaneous isobaric process at $t = 60^\circ \text{C}$ and above is not accompanied by clicks and in order to bring them back one must change the pressure sufficiently rapidly. Apparently the rate of change of the pressure should be such that the rate of transformation at a given instant exceed the rate of the spontaneous isobaric process at the corresponding value of the varying pressure. Figure 7 shows for comparison $\alpha(t)$ and $p(t)$ —the curves of two experiments carried out at 63°C . In the first experiment (curves 1 and 2) the pressure was varied at an approximately constant rate. The transformation to within 94% took place during a time shorter than 100 sec; it was accompanied by intense clicks which commenced at $\alpha \approx 25\%$ and ceased at $\alpha \approx 75\%$. Curves 3 and 4 depict the course of the second experiment in which the pressure was kept constant (curve 1 of Fig. 6 corresponds to this experiment). On increasing the pressure after such treatment we recorded on the oscillogram a small number of relatively weak pulses which occurred during the last 10% of the transformation.

A further increase in the temperature of the experiment also changes somewhat the kinetics of the direct transition. On the whole, a comparison of the pulse distribution over α at various temperatures with the other experimental conditions approximately the same shows that heating in the $25-170^\circ \text{C}$ range shifts the beginning of the appearance of sound effects from $\alpha \approx 0$ to $\alpha \approx 45\%$. In the upper half of the temperature range investigated by us we also noted a tendency towards a decrease of the effect of the excess pressure Δp and of the temperature on the rate of the isobaric I \rightarrow II transition: for $p = p_0 + 0.3$ kbar and 177°C an almost 100%

⁵⁾In the experiments of Kennedy and La Mory [8] the beginning of the transformation in KCl at 25° was only noted after holding a certain excess pressure for four hours.

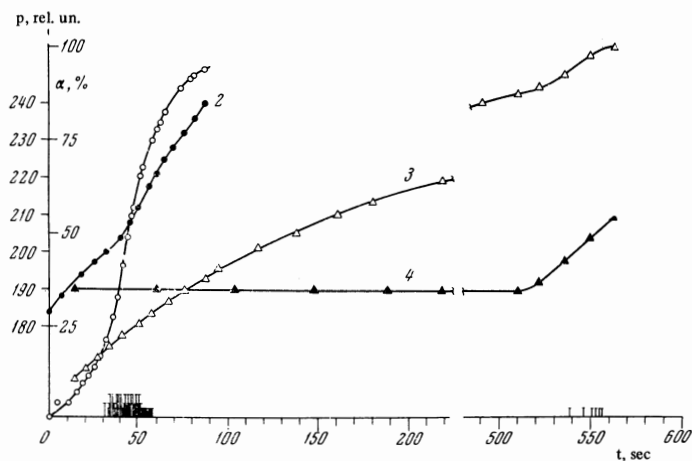


FIG. 7. The dependences $\alpha(t)$ (curves 1 and 3) and $p(t)$ (curves 2 and 4) in the I \rightarrow II transition in KCl for $t = 63^\circ\text{C}$. Pulses are marked by vertical lines.

transition occurred within 8.5 min, at 231° and the same excess pressure—90% in 9 min; at 287° and $p = p_b + 0.8$ kbar after holding the pressure for 7 minutes α was 70%. The time during which the transition to $\alpha = 50\%$ occurred was in these experiments 3, 5, and 4 min respectively.

The hysteresis of the transformation (the value $p_b - p'_b$) ceases abruptly at a temperature above 40° . In the majority of the experiments in the $40\text{--}300^\circ\text{C}$ range the pressure at which the reverse transition begins (p'_b) turns out to be equal or even greater than the pressure at the beginning of the transition p_b so that approximately in half the experiments the reverse transformation begins at a higher pressure than the forward transformation (see Fig. 8). No correlation has been observed between the magnitude of the hysteresis of the transition and the number of compressions or the maximum pressure in the experiment; the rate of decrease

of the pressure from p_{max} to p'_b was approximately the same in all the experiments.

In silvite and in single crystals of KCl the formation of the dense modification is also accompanied by clicks; in the latter the clicks were also noted in the reverse transition.

Single crystals which underwent transformation in both directions basically retain their transparency, their original form, and the details in their surface structure.⁶⁾

The most frequent damage consists of local cracks which do not come out to the surface and appear sometimes within the volume of the crystals. The cracks are oriented along cleavage planes of the low-pressure modification and their surface has a very complex relief. This relief can be observed in a microscope both through the crystal and when it is cracked along these cracks.

After a I \rightleftharpoons II transition there appears on the habit planes of the KCl crystals a regularly oriented platelike relief which sometimes forms a rather regular lattice (Fig. 9). Two different types of new formations are observed: plates with more relief (dark on Fig. 9a) and light "furrows" with less relief (Fig. 9b); the latter have sharp needle-like ends. The length of such individual needles attains several millimeters with a width of $10\text{--}20 \mu$.

DISCUSSION OF THE RESULTS

The material presented in this article shows that the process of polymorphic transformation in KCl has many common features with the martensite transformations in metals and alloys which occur when the temperature changes and which are usually studied at atmospheric pressure.^[10]

1) It is known that the crystal-geometry scheme of the transition under consideration reduces to the appearance of a regularly oriented shear deformation in the lattice. The shifts of the lattice points are small

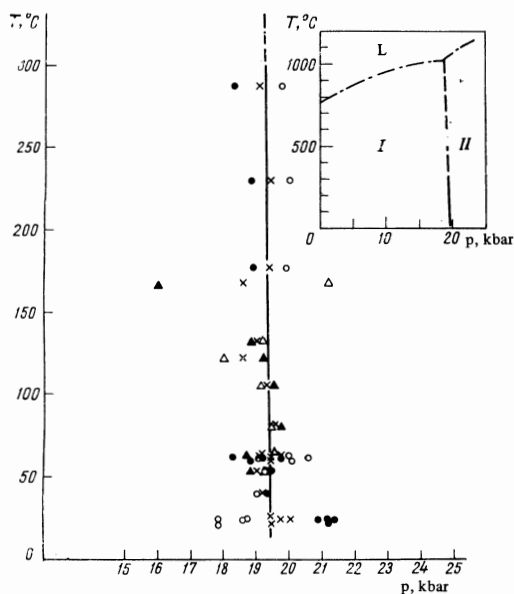


FIG. 8. Temperature dependence of the hysteresis of the transition in KCl. Circles—first compression, triangles—repeated compressions. Black symbols denote values of p_b , light ones— p'_b , and crosses mark \bar{p} . The nominal boundary between the phases has been drawn with account of the break in the fusion curve [9] shown by the dash-dot lines on the upper right.

⁶⁾In a phase transformation under compression, when the pressure transmitting medium is, for example, not a liquid but lead, the characteristic deformation of a cubic crystal is its approach to the rhombohedral form. Instances of appearance of residual macroscopic deformation under hydrostatic conditions were also observed for a sharp pressure drop from the region of existence of phase II.

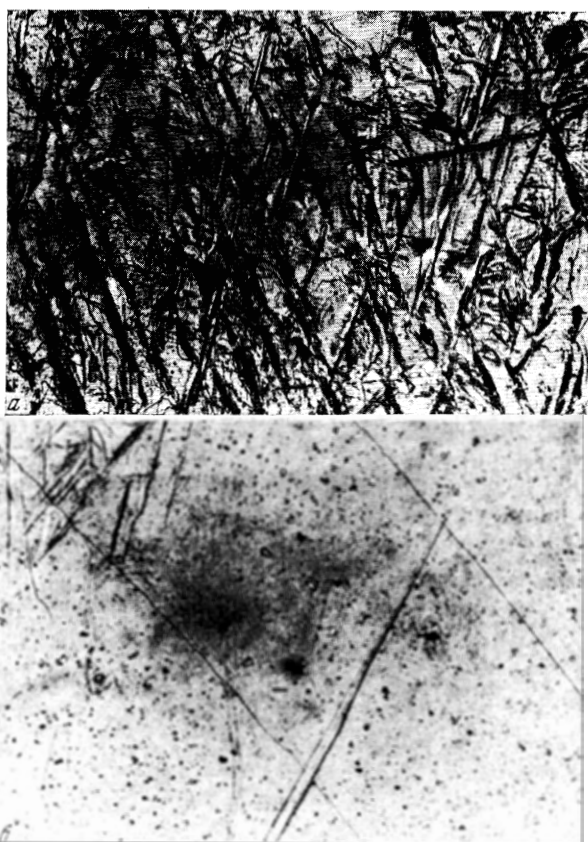


FIG. 9. Microphotographs of the relief on the habit planes of KCl single crystals which underwent transformation in both directions (X58).

and the atoms retain their neighbors.^{7)[11]} The possibility of such a transition mechanism from one crystal structure to another is according to Kurdyumov^[12] the principal requirement for martensite transformations.

2) As a result of the reversibility of the polymorphic transformation in KCl we could not directly investigate crystals of the high-pressure phase, as is done in investigations of martensite transformations at normal pressure. However, judging from the microstructure of the surface after transformation in both directions, crystals of modification II were in the form of needles or platelets typical of martensite phases (Fig. 9).

3) At room temperature the polymorphic transformation in KCl has a number of features: a) it extends over a broad range of pressures; b) the degree of transformation is determined principally by the pressure and not by the time it is held under pressure or by the rate of change of the pressure; c) the pressure at the beginning of the transformation does not depend on the rate of change of the pressure (in the range of rates from ~ 0 to ~ 100 bar/sec which we investigated) and changes continuously on changing the concentration of the solid solution; d) it is accompanied by sound phenomena which are probably due to transformations taking place at a high rate in individual regions of the grain.

⁷⁾The transformation under consideration belongs (according to Burger^[11]) to dilation-type displacement transformations (with a change in the primary coordination) which he assigns to rapid transitions.

These features are characteristic for martensite type transitions.^[10] Sound phenomena have, for instance, been observed in martensite transformations at normal pressure in lithium and its alloys with manganese^[13] and in alloys of iron with 23, 25, and 29–30% nickel.^[14, 15]

The enumerated features of the kinetics do not depend on the existence of direct contact between the crystallites.

With increasing temperature features a) and b) are obliterated and the appearance of sound effects which are obviously connected with "instantaneous" formation of needles depends appreciably on the rate of change of the pressure. Under these conditions the $\alpha(t)$ curves at constant pressure take on an S-like shape characteristic of phase transformations with normal (nonmartensitic) kinetics.

A series of details of the process of polymorphic transition in KCl mentioned in the previous section is explained or at any rate finds analogies in the concept of martensite transformations. For instance, the broadening of the two-phase region ($p_b - p_c$ and $p'_b - p'_c$) in KCl–RbCl alloys can be related to the change of the real crystal structure in the formation of solid solutions. It is known that alloying of ionic compounds is accompanied by a series of changes of their real crystal structure: by an increase in the number of point defects, by deviation of the lattice from the correct geometry (in our case a face-centered cube), and by the retention of only a certain degree of short-range order. These changes manifest themselves, for example, in the appearance of a maximum in the hardness^[16] and entropy^[17] of solid solutions in the region of equimolar compositions. A martensite transition is apparently difficult in crystals with such lattice faults and requires additional energy, which leads to an increase in the width of the two-phase region in alloys compared with KCl. Such faults may also result in some weakening of the sound effects in alloys.

The weakening and cessation of sound phenomena after several cycles of I \rightleftharpoons II transitions in KCl and the alloys is obviously connected with deep deformation in the multiple compression of the substance undergoing phase transformation and with the resulting decrease in the number and dimensions of regions in which the coupling of the lattices of both phases in the transition is retained.

The decreasing hysteresis of the transition on heating and the formation of the I modification at pressures exceeding the I \rightarrow II transition pressure is similar to the inversion of the martensite point and the temperature at which there occurs the reverse transition in Cu–Al–Ni^[18] and Cu–Zu^[19] alloys which is related with the effect of the deformation energy appearing in the course of the transformation.^[18, 20]

The instances of a reversible volume increase on decreasing the pressure in the process of a I \rightarrow II transition recall the "thermoelastic" behavior of martensitic crystals.^[21] By analogy they could be called a manifestation of "piezoelectricity" if we understand this term to mean a decrease of the dimensions of newly formed crystals after some decrease in the excess pressure in the stability region of the new modification.

According to our estimate the nonrelaxed portion of

the elastic deformation energy appearing in the reversible volume change in the region of stability of phase II amounts to 3×10^7 erg/cm³. This value constitutes about 10% of the change of the internal energy in the transition in KCl ($\sim 5 \times 10^8$ erg/cm³) and is comparable with the energy of mechanical stresses in CaCO₃ according to the data of ^[22]: 1–2 cal/g which recalculated for KCl ($\rho_0 \approx 2$ g/cm³) gives $2-4 \times 10^7$ erg/cm³. Thus the estimate shows that the energy of the mechanical stresses appearing in the crystal as a result of the polymorphic transition can prove to have an appreciable countereffect on the very process of polymorphic transformation in ionic crystals.

CONCLUSIONS

1. It has been established that at room temperature the polymorphic transformation in KCl under pressure possesses the main attributes of martensite-type phase transformations.

2. The peculiarities of the manifestation of a sound effect in a I → II transition occurring on increasing the pressure are noted. This effect is a structure sensitive property and depends on the state of the sample and the experimental regime.

3. The effect of increasing the temperature on the peculiarities of the kinetics of the polymorphic transition in KCl is described, and it is shown in particular that at higher temperatures the process takes on the "features" of normal (nonmartensitic) transformations.

4. Using KCl as an example, it is shown that the possibility of a rapid rearrangement of the crystal lattice in microregions does not determine the high rate of the polymorphic transformation in the macroscopic volume and that the latter depends on external conditions and the state of the substance.

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