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ON THE RHYTHMIC CHARACTER OF THE GROWTH OF A NEW PHASE IN POTASSIUM NITRATE

(Presented by Academician A. V. Shubnikov, 15 IX 1969)

A number of alkali-metal nitrates have the same type of structure, and all of them have several polymorphic modifications. The mechanism of transformation, nucleation, growth morphology, and also the crystallographic relations between crystals of the two phases have been insufficiently investigated.

Previously we studied the transformation in silver nitrate ([1]). In the present work the morphology of the polymorphic transformation in potassium nitrate is considered.

It is known that potassium nitrate at room temperature has the aragonite structure (α-phase) with symmetry D_{2h}^{16}—P_{nma} ([2]), and at a temperature of 130° transforms into a structure very close to calcite, with symmetry D_{2d}^{6}—R_{3c} ([3]). On cooling, this structure first transforms near 124° into the γ-phase with symmetry C_{3v}^{5}—R_{3m} ([4]), and at a temperature of about 110° a transition to the α-phase occurs.

In ([5]), at a temperature of −60°, a new low-temperature transformation in KNO_3 was found. In ([6]) a microscopic investigation was carried out and it was shown that a single crystal of the low-temperature α-phase passes into a polycrystal of the high-temperature β-phase. In work ([7]) the effect of irradiation with γ-rays on transformations in KNO_3 was studied. Polymorphism in potassium nitrate at high pressures was investigated in work ([8]), and new modifications were found.

From an aqueous solution at room temperature we obtained well-faceted, perfect single crystals of the α-phase of potassium nitrate, with average dimensions $1 \times 0.5 \times 5$ mm^3, convenient for microscopic studies. In the work, great attention was paid to the perfection and purity of the crystals studied. Chemically pure potassium nitrate was additionally purified by repeated recrystallization. The crystals had a needle-like form in the direction [001].

First of all, the equilibrium temperatures of the α- and β-, β- and γ-, and γ- and α-phases were carefully measured. The temperature of the crystal was measured with thermocouples whose ends directly touched the surface of the specimens. The accuracy of temperature measurement at 300° reached $\pm 1°$. On a heating stage ensuring complete thermostating of the crystals studied, we established the equilibrium temperatures of the α- and β-phases, $T_{\alpha \rightleftarrows \beta} = 127°$, and of the γ- and α-phases, $T_{\gamma \to \alpha} = 111°$. The transformation $\beta \to \gamma$ usually begins at the temperature $T_{\beta \to \gamma} \simeq 125°$ and propagates very rapidly through the matrix β-crystal. In this case it is not possible to obtain a linear phase boundary and an equilibrium temperature. Stresses and deformations moving ahead of the phase boundary promote the formation at these sites of new crystallization centers, as a result of which the transformation front acquires a wave character.

The transformation $\alpha \to \beta$ always occurs at a temperature $T \geq T_0$. Here the temperature difference, as was established in our previous studies, depends on the perfection of the crystal, and the maximum deviation

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a *b*

Fig. 1. Successive stages of the rhythmic growth of β-crystals during the $\alpha \to \beta$ transformation in potassium nitrate having a needle-like form. Temperature $T_{\text{tr}} = 128°$, 90×. *a* —optical microphotographs I, II, and III illustrate the formation of a nucleus of the new phase and rhythmic growth. *b* —microphotographs I, II, III, and IV illustrate the rhythmic growth of the new phase and the change in the external shape of the matrix crystal.

is $\Delta T \approx 5°$. In most cases the morphology of the α-crystal growing during the $\beta \to \alpha$ transformation differs from the morphology of the α-crystal growing during the $\gamma \to \alpha$ transformation. Apparently this is connected with the difference in densities and with different degrees of strain of the α-crystal in the β- and γ-matrices. The $\alpha \to \beta$ transformation was studied in detail.

Crystals of the high-temperature β-phase of potassium nitrate grow rhythmically from the low-temperature α-phase. Rhythmic growth consists in the transformation of the α-phase into the β-phase by discrete, completely identical lamellae.

In Fig. 1a three microphotographs are presented of successive stages of rhythmic growth of a high-temperature β-crystal inside a low-temperature single-crystalline α-matrix at constant temperature. As can be seen, the lamellae of the growing β-crystal are identical; their thickness is approximately $d = 0.06$ mm. The thicknesses of the lamellae of the growing β-crystal are not the same in different α-crystals (see Fig. 1b). In Fig. 1b a case with $d = 0.01$ mm is shown. Rhythmic growth of crystals growing from a melt with impurities is a known phenomenon. The mechanism of periodic growth of crystals from a melt was explained by A. V. Shubnikov [9] (for Fig. 1 see the insert to p. 1271).

How does rhythmic growth occur in a single-crystalline medium during a polymorphic transformation? In our case the role of impurities is excluded. Evidently, here the principal role is played by the difference in densities of the two phases.

In the process of the transformation crystal → crystal, if the densities of the growing crystals and of the matrix crystal differ appreciably, irreversible changes in the shape of the transformed crystal naturally arise. The densities of the α- and β-crystals of potassium nitrate differ appreciably, $\rho_\alpha - \rho_\beta = 0.117$ g/cm^3. The nucleus of the β-crystal forms inside the α-crystal and grows at high speed along the width of the plate (i.e., in the direction [100]) of the α-crystal. After this, the phase boundary slowly moves along [001], the length of the plate. As the phase boundary moves along the length of the plate, under the influence of internal stress between the growing β-crystal and the α-crystal matrix, contact is broken for a certain period. Since the transformations always occur at $T_{\text{tr}} = T_0 + \Delta T$, and the crack that has formed is readily healed, contact between the lamellae is not broken; new nuclei are formed, and growth of the β-crystal does not stop. Since the density of the matrix crystal is the same everywhere, periodic traces remain from such weakening of the contact after the transformation.

A theoretical estimate of the stresses arising in such a transformation will be considered in the next paper.

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Note: Figure translations are in progress. See original paper for figures.