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CRYSTAL GROWTH DURING POLYMORPHIC TRANSFORMATION IN GLUTARIC ACID AND HEXACHLOROETHANE

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In works on the polymorphic transformations of organic crystals ($^{1-8}$), results were presented mainly for n-dichlorobenzene. It was found that, at its basis, the process of polymorphic transformation is the growth of faceted single crystals from a single-crystal matrix, as from a more or less isotropic medium. The processes of polymorphic transformation and of crystal growth from "ordinary" (liquid, gaseous) media are not only extremely similar to one another, but are closely related, in mechanism, varieties of one and the same phenomenon (^{5,8}).

The occurrence, during polymorphic transformation, of very considerable internal stresses owing to differences in the densities of the two solid phases (least of all manifested in n-dichlorobenzene, for which the density jump $\rho_\alpha - \rho_\beta$ is close to zero (^{7})) greatly complicates the obtaining of sufficiently perfect growth faces in crystals arising within a solid matrix, and explains why the phenomenon of unoriented growth of faceted single crystals during polymorphic transformation was discovered only quite recently (^{1}).

For the reasons indicated above, an experimental study of polymorphic transformation in one substance or another, undertaken with the aim of confirming the generality of the phenomenon and detecting its individual features, requires prolonged and painstaking work. On the other hand, the random orientation of the daughter crystal relative to the matrix crystal, and the impossibility of mechanically isolating from it an all-sidedly faceted crystal for optical goniometry, make the indexing of its faces and a fully rigorous proof of the fact that these faces are crystallographically determined by the lattice of the growing crystal and are not associated with the lattice of the matrix an extremely difficult problem.

The present work is devoted to a study of the growth of single crystals during polymorphic transformation in glutaric acid and hexachloroethane. Glutaric acid occupied a special position among our other objects in that the transformation in this substance systematically proceeded in an extremely disordered manner, and for a long time it proved impossible to establish the fact of the growth of faceted crystals in the solid phase. However, after improving the method, it has now been possible to show that the polymorphic transformation in glutaric acid does not fall outside the general scheme. The method employed was as follows. First of all, the equilibrium temperature of the α and β phases was carefully measured and found to be $T_0 = 64 \pm 0.5^\circ$. Using suitable organic solvents (ethyl alcohol, acetone) and a starting substance purified by repeated recrystallization, matrix crystals as perfect as possible, less than 1 mm in size, were grown. The crystals had the form of plates with the plane (001). For the study, the thinnest plates were selected; in these, as was found, the conditions for the growth of crystals of the new phase are more favorable, presumably because the internal stresses arising in this process have the opportunity to emerge at the surface. The selected crystal was placed in a transparent cell with vaseline oil, which was mounted on the heating stage of a polarizing microscope. Transformation on heating always occurs at a temperature $T_{\mathrm{tr}} > T_0$, and $\Delta T = T_{\mathrm{tr}} - T_0$ depends—

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Fig. 1. Successive stages of growth of faceted crystals during the polymorphic transformation $\beta \to \alpha$ in a single-crystal matrix of glutaric acid having the form of a plate. Temperature 65°, 150×. *a* —2 hours after the start of the transformation, *b* —after 4 hours, *v* —after 8 hours.

Fig. 3. *a* —growth of faceted crystals during the polymorphic transformation $\gamma \to \beta$ in a single-crystal matrix of hexachloroethane having the form of a thin plate; *b*, *v* —subsequent stages of growth of the crystal located in the right part of photomicrograph *a*. Temperature 44°, 75×

depends on the quality of the crystal, since the crystallization centers of the new phase arise in defects ($\widehat{}$3). Up to 60° the heating was carried out at a rate of $\sim 4^\circ$ per minute, and from 60° to the temperature at which the transformation began (usually $\sim 69^\circ$)—at a rate of $\sim 2^\circ$ per minute. After the first signs of transformation appeared at separate points of the matrix, the temperature was quickly lowered, by means of a cooling device, to $\sim 67^\circ$, and was kept at this level for several minutes, allowing the crystals to grow slightly. During this time some of them showed the first signs of regular external faceting. Finally, the temperature was lowered to 65° and its constancy was monitored for many hours, using manual adjustment by means of a rheostat. Under these conditions, extremely slow growth of α-crystals occurred inside the matrix β-crystal, simultaneously from several centers. The external faceting of some crystals gradually improved. During observations over many hours it was possible to notice how some crystals acquired more regular faceting, while others lost it. Some crystals acquired their best faceting after 5–8 hours.

In Fig. 1 (see insert facing p. 341) microphotographs are given of three successive stages of growth of α-crystals inside a single-crystalline β-matrix. Only a small region of it is presented here, in which separate crystals of the α-phase, chaotically arranged and oriented, are quite clearly visible; these crystals possess the regular external faceting characteristic of single crystals. Together with the fact that opposite faces in each α-crystal are parallel, and with the tendency, clearly manifested in some crystals, to assume a definite equilibrium external shape, this logically constitutes sufficient proof that the faces observed are nothing other than ordinary growth faces, rationally indexed in the α-lattice and having no rational indices in the β-lattice of the matrix.

A detailed examination of the microphotographs showed that the faceted α-crystals can be divided into two types: 1) three-dimensional crystals, randomly rotated with respect to the matrix about all three spatial axes, and 2) flat hexagons lying in the plane of the matrix crystal but rotated within it relative to one another quite randomly. In the matrix, part of which is shown in Fig. 1, we were able to measure the angles in about 12 completely or partially faceted plate-like α-crystals and to confirm the fulfillment of the law of constancy of angles. These angles were $\sim$ 116–117° and $\sim$ 126°. The directions of the bisectors of the 126° angles in different α-crystals were completely uncorrelated with one another, and also with the a and b axes of the matrix.

Since there are no reliable data on the structure of the high-temperature form of glutaric acid, at present we cannot assign indices to the faces of crystals of the second type. However, it was decided to test the supposition that these are the same faces as those possessed by crystals of the high-temperature form grown from the melt. For this purpose, single crystals of the α-form were grown from a drop of melt on the heating stage of a microscope. A small crystal was melted, and, by periodically raising and lowering the temperature, preservation in the drop of only one crystallization center was achieved; from this center a well-faceted crystal was then readily grown. The crystals obtained had the form of thin plates. One of such crystals is shown in Fig. 2a, while in Fig. 2b and c its outlines and angles are compared with those for one of the crystals visible in Fig. 1c. The agreement of the angles may be considered complete.

Thus it was possible to confirm that the faceting of crystals of the high-temperature modification growing in a solid matrix during a polymorphic transformation does not differ from the faceting of crystals of the same modification obtained directly from the melt. The fundamental aspect of the question is not changed by the fact that, during the polymorphic transformation of glutaro-

acid, individual crystals arise far from always, are very small in size ($\sim$ 0.1 mm), and, because of the presence of a density discontinuity at the phase boundary, can hardly be much larger. It is interesting to note that in the solid phase the crystals tend to assume a somewhat different equilibrium shape than in the melt, since the faces which in the first case are more developed tend, in the second case, to grow over (Fig. 2b). This can be explained by the fact that in both cases the crystals are in contact with the surrounding medium, while the solid matrix and the melt affect differently the relative magnitude of the specific surface energy of the faces.

Fig. 2

Figure 1: Fig. 2

Fig. 2. *a* —crystal of the high-temperature phase of glutaric acid, grown from a drop of melt on the heating stage of a microscope; *b* —another crystal of glutaric acid, also obtained from the melt, on which it is visible which faces tend to grow over; *c*, *d* —outlines and angles, respectively, of crystal *a* and of one of the crystals visible in Fig. 1b

The visual detection of two different types of crystals, discussed above, required clarification of the orienting role of the matrix. For this purpose an X-ray study was undertaken. Crystalline plates of the β form were oriented in the beam in the same way, so that the axes a and b, lying in the plane of the plate, were perpendicular to the beam and the b axis was vertical. From each crystal, in an RKV-86 camera placed inside an air thermostat, the following 4 Laue photographs were obtained: 1) β, room temperature, a and b perpendicular to the beam, b axis vertical; 2) β, room temperature, a axis along the beam, b axis vertical; 3) α, $T = 72^\circ$, position 2; 4) α, $T = 72^\circ$, position 1. In addition, for several crystals rotation X-ray photographs about the b axis of the β phase were obtained before and after its transformation into α.

The results of the X-ray examination of approximately 20 crystals may be summarized as follows. Laue photographs of types 3 and 4 showed the transformation of a β single crystal into a coarse-grained α polycrystal. The spots were distributed over the diffraction rings nonuniformly, i.e. texture was observed. However, superposition of Laue photographs from different crystals showed that the character of the texture changes from case to case and, in the sum, gives a uniform distribution of spots over the diffraction rings. Thus, there was a predominance of some preferred orientation (or orientations) in each separate case of polymorphic transformation. As for the rotation X-ray photographs, they demonstrated an isotropic powder pattern, i.e. a complete loss of the crystallographic direction of the b axis after the transition $\beta \to \alpha$.

The reason for the formation of individual textures that are not reproduced in other specimens should be sought in the special features of the course of a reaction of the type M $\to$ P*. The transformation begins from a randomly oriented crystallization center and, as a rule, proceeds in the presence of a single phase boundary. In this process, the crystallization centers of newly appearing grains

* Here and below the following abbreviated designations of transformation types are used, in which the corresponding letters mean: M —single crystal, P —polycrystal, K —crystal, RCS —rotational-crystalline state (a state with rotating molecules and long-range order in the arrangement of their centers).

arise not independently of one another, not in different parts of the matrix, but at the boundary or in its immediate vicinity. Naturally, under these conditions the grains that have already appeared will influence the lattice orientation of the subsequent ones. It remains to be clarified what role is played here by stresses propagating through the crystal from the phase boundary.

There remains a certain discrepancy between the results of the X-ray study, which indicate the absence of a regular orienting influence of the matrix, and the visual observations, which reveal in the matrix a certain number of crystals of the second type. Apparently, the contradiction is removed if the following two circumstances are taken into account. First, Laue photography is not always capable of detecting certain types of textures, especially weak ones, and in reality there nevertheless exists a small orienting influence of the matrix, due, in all probability, not to its lattice but to its habit (a thin plate). Second, the crystals of both phases have a tendency to grow in the form of thin plates (which is generally characteristic of all substances with chain molecules), and the very fact of observing a plate-like α-crystal indicates a more or less exact coincidence of its plane with the plane of the matrix, regardless of the degree of randomness of such a coincidence. The important question of the orienting influence of the matrix has not yet been resolved completely and remains an object of investigation.

The experimental method for studying the $\gamma \rightarrow \beta$ transformation in hexachloroethane* was, in general outline, the same as for glutaric acid. The results obtained are also in many respects analogous. Measurements of the phase-equilibrium temperature gave the value $T_0 = 43.6 \pm 0.3°$. Figure 3 (see insert to p. 341) presents photomicrographs in which one can see the very perfect faceting of β-crystals growing from the γ-matrix. Symmetrically faceted individual crystals may be obtained (Fig. 3 shows three stages in the growth of one of them), but conglomerates arise more often (see the left-hand part of Fig. 3a), in which the individual grains have external faceting only in those places where they are in contact not with one another, but with the matrix. If the latter has the form of a thin plate, this facilitates the conditions for crystal growth, and they acquire more perfect faceting. Whereas in glutaric-acid crystals of size ~ 1 mm it is never possible to obtain a transformation of the M—M type, it proves possible to carry this out in thin plates of hexachloroethane of size 5–6 mm. However, the matrix in the form of a thin plate begins to exert some orienting influence, although both optical photomicrographs and X-ray photography indicate the absence of a strict crystallographic relation between the orientations of the β-crystals among themselves and with the γ-matrix.

The results of the study of polymorphic transformations in glutaric acid and hexachloroethane provide the missing experimental material needed for a more reliable confirmation of our thesis that all phase transitions of the K—K type in organic substances have the same mechanism, characterized by: a) the growth of faceted crystals of one solid phase within another, b) the absence of a crystallographic relation of orientations between the lattices, c) the possibility of considering the boundary between solid phases as a crystallographic face that is rationally indexed in the lattice of the growing crystal but is not indexed in the lattice of the matrix.

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* In this substance one more transformation is observed, namely α—β with $T_0 = 71.8°$. However, it belongs to the K—RKS type, and not to the K—K type considered in the present work.

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

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