CRYSTALLOGRAPHY

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Abstract

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POLYMORPHIC SINGLE-CRYSTAL–SINGLE-CRYSTAL TRANSITION IN *p*-DICHLOROBENZENE

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The present work is the first in a series of investigations devoted to the mechanism of polymorphic transformations in organic molecular crystals. The authors made their initial choice of *p*-dichlorobenzene. This substance has already been studied repeatedly by various authors (see, for example, ([1], [2])), and it was established that at a temperature of 30.8° a polymorphic transformation occurs from the low-temperature monoclinic phase (α) to the high-temperature triclinic phase (β). The structures of the aforementioned crystalline phases were determined ([3], [4]), and in each case the crystals were grown from solution at the temperature of equilibrium for the modification being studied. Visual observations ([5], [6]) made it possible to suppose that the polymorphic transition proceeds according to the unstudied "single-crystal–single-crystal" scheme. Measurements of the rate of the $\alpha \quad \beta$ transformation were also carried out ([2], [6], [7]), and optical microphotographs were obtained ([8]), one of which is reproduced by us in Fig. 1.

The first part of the investigation presented here consisted in observing the processes of $\alpha \quad \beta$ transformations under an optical microscope equipped with a heating stage, a polarizing attachment, and a camera for microphotography. Since solid *p*-dichlorobenzene has high volatility, special attention was given to selecting a liquid inert medium in which crystals of this substance could be preserved for a long time. It turned out that glycerin fully satisfies these requirements. For microscopic study, the crystals were placed in an open cuvette with low walls filled with glycerin, the bottom of which was the microscope slide. *p*-Dichlorobenzene of "pure" grade was subjected to additional purification by distillation in vacuum. In contrast to many previous works, in the present work great attention was paid to the perfection of the crystals under study.

Observations using the above-mentioned simple apparatus showed that the $\alpha \rightarrow \beta$ transformation always occurs at a temperature higher than the phase-equilibrium temperature of 30.8°. In general, the following rule holds: the purer the substance and the more perfect the crystal, the higher the temperature of the $\alpha \rightarrow \beta$ transition. Perfect crystals, especially those obtained by sublimation, in most cases do not transform into the β phase at all and melt in the α form

Fig. 1

Figure 1: Fig. 1

at a temperature of 52.7°* (the β form melts at 53.2°).

The $\alpha \quad \beta$ phase transition always manifests itself as the advance of a clearly visible (especially in polarized light) phase-boundary surface. All cases of transition can be divided into two groups– "single-center" and "multicenter." It is not possible to predict in advance which type of transition will be found in a given crystal (if the crystal is sufficiently perfect). If not a single growth center of the new phase is formed, then, as already stated, the transition will not occur. If only one growth center is formed, a transition of the "single-crystal–single-

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* The melting temperature of the α phase is reported for the first time.

To the article by A. I. Kitaygorodskii, Yu. V. Mnyukh, Yu. G. Asadov, p. 1065

Fig. 2. $\alpha \rightarrow \beta$ transition in a needle-shaped single crystal. 80×

Fig. 3. Successive stages of growth of a faceted single crystal of the β phase inside a single crystal of the nonequilibrium α phase. 40×

crystal." When several growth centers arise, a phase transition occurs that leads to the formation of a system of crystallites, the orientation of which will be discussed below.

Single-crystal–single-crystal transitions, which can be obtained only on sufficiently perfect crystals, are shown in two series of microphotographs (Figs. 2 and 3). The photographs presented indicate that the polymorphic single-crystal –single-crystal transition is nothing other than the **growth of a single crystal from a solid single-crystalline medium** of a nonequilibrium phase. In outward appearance, the growth of single crystals from a solid phase very strongly resembles the growth of single crystals from liquid and gaseous media. In Fig. 2, two from a series of successive microphotographs of the $\alpha \leftrightarrow \beta$ transition in a needle-shaped single crystal obtained by sublimation are presented. The arrows indicate the direction of growth. This direction could be changed at will by raising or lowering the temperature. One can see the perfect faceting of the boundary separating the phases, which in a growing single crystal always has a convex form, indicating the latter' s tendency toward a minimum of surface free energy. Figure 3 shows successive stages of growth of a well-faceted β single crystal inside an α single crystal, from nucleation to the completion of the phase transition. The nucleus appeared at a temperature of 48° and grew very rapidly: the intervals between photographs range from several seconds to several tens of seconds.

Fig. 1. Microphotograph of the $\alpha \rightarrow \beta$ transition, given in (8). Bright stripe of the new polymorphic form against the background of an extinguished single

crystal of n-dichlorobenzene. Temperature 49.5°. 120×

The next experimental task was to determine the mutual orientation of the α and β lattices. It was necessary to answer the following questions: 1) is there a unique ("rigid") relation between the orientations of the crystal lattices α and β; 2) if there is, what is this mutual orientation; 3) if there is not, does there exist a discrete set of possible mutual orientations, or are the latter random in character?

To clarify these questions, X-ray Laue photography was applied to one and the same crystal before and after the phase transition, with preservation of the external orientation of the crystal. The procedure was as follows. A well-formed single crystal of the α phase (usually grown from solution in ethyl alcohol) was placed in a small thin-walled flat cuvette filled with glycerin and, in this form, mounted on a goniometer head. By means of Lauegrams, careful adjustment was carried out, since it was important to achieve exact coincidence of the initial orientation for all crystals studied. The X-ray chamber was placed in a specially constructed air thermostat, in which the elevated temperature necessary for the $\alpha \rightarrow \beta$ transformation was maintained, and then Laue photography of the β phase was performed. This X-ray study involved overcoming a number of experimental difficulties (a description of which will be given in a more detailed article); nevertheless, it was possible to establish reliably that **there exist many orientations of the lattice of the new phase with respect to the initial one**. And at present there are sufficient grounds to assert that β crystals grow in a completely arbitrary orientation with respect to the lattice of α crystals, since the number of different orientations obtained is very large.

A very convincing experiment proved to be one with one of the single crystals of rather large size ($1 \times 3 \times 8$ mm), in which it was possible to induce successively 10 transformations:

$$\alpha_1 \text{ (initial)} \rightarrow \beta_1 \rightarrow \alpha_2 \rightarrow \beta_2 \rightarrow \alpha_3 \rightarrow \beta_3 \rightarrow \alpha_4 \rightarrow \beta_4 \rightarrow \alpha_5 \rightarrow \beta_5 \rightarrow \alpha_6.$$

$$\downarrow$$

$$\beta_5'$$

In view of the impossibility, for lack of space, of directly illustrating all these phase transitions by Lauegrams, we shall confine ourselves to giving only the first two (Fig. 4) and Table 1.

Table 1

Crystallographic modification	Character of the transition	Lattice orientation	Form of the spots on the Lauegrams
α_1	(Initial)	Symmetrical Lauegram. The c axis is vertical	Characteristic of a perfect crystal
β_1	Single-center	Not determined	Characteristic of a perfect crystal
α_2	Single-center	Coincides with α_1	Spots are split. Mutual misorientation of the two lattices $0.7 \pm 0.2^\circ$
β_2	Multicenter	–	Some spots are of regular form; the others are split or smeared
α_3	Single-center	Coincides with α_1	Spots are split, as on α_2
β_3	Single-center	Strongly differs from β_1	Characteristic of a perfect crystal
α_4	Single-center	Coincides with α_1	Irregular spot form
β_4	Single-center	Similar to β_3, but differs by $\sim 5^\circ$	Spots are slightly split
α_5	Single-center	Coincides with α_1	Characteristic of a perfect crystal
β_5	Multicenter	Differs from β_2 and even partially does not coincide with other β lattices	The Lauegram consists of a large number of small spots
β_5'*	Mainly single-center	Differs from β_1-β_4. It is contained as a part in β_5	Some spots are split; there are also weak smeared spots
α_6	Single-center	Differs from all the preceding ones	Characteristic of a very perfect crystal

* This Lauegram was obtained as a result of photographing another region of the crystal without changing its orientation.

As we see, among the β phases presented in the table there are none that coincide in the orientation of the crystal lattice. This conclusion is also confirmed by X-

Fig. 4

Figure 2: Fig. 4

ray photographs of many other crystals.

From Table 1 it is seen that, in successive ... $\alpha \rightarrow \beta \rightarrow \alpha \rightarrow \beta$ ... transformations, one and the same crystal can give both single-center and multicenter transitions; moreover, in the second case the single crystal is transformed into a system of differently oriented crystals of another phase. It is interesting to note that from such a disorganized crystal a perfect single crystal can again subsequently grow. Indeed, return to a perfect crystal of the α phase occurs not only after a single-center but also after a multicenter transformation (see α_5 in Table 1). We also find it very interesting that the orientation of the α crystals is sometimes restored in its original form with an accuracy of up to 1°.

The X-ray part of the present investigation has led us to two results that are in apparent contradiction with one another. On the one hand, in the large number of $\alpha \rightarrow \beta$ transformations studied, no two recurring cases of mutual orientation of the α and β crystals were found. This, it would seem, indicates a diffusional, disordered transformation. On the other hand, transformations according to the scheme ... $\alpha \rightarrow \beta \rightarrow \alpha \rightarrow \beta$ ... in a number of cases gave α crystals in one and the same orientation. Thus, the path of the $\alpha \rightarrow \beta$ transformation is somehow "remembered" by the β crystal and

is reproduced in the reverse transition to the β-form, and this indicates a regular rearrangement of the lattice. The investigations now in progress should, we hope, clarify the cause of this apparent contradiction.

Before carrying out this study, the authors considered the most probable of the hypothetical possibilities listed above to be a "rigid" connection

Fig. 4. Lauegrams a_1 (left) and β_1 (see Table 1), illustrating the polymorphic single-crystal–single-crystal transition

between the orientations of the α- and β-lattices. However, it is now possible to see a direct logical connection between the results obtained and the well-known case of the polymorphic transformation "single crystal $\rightarrow$ polycrystal," when a single crystal is transformed into a system consisting of a large number of differently oriented crystallites. It is very probable that the difference between the phase transitions "single crystal $\rightarrow$ single crystal" and "single crystal $\rightarrow$ polycrystal" may reduce merely to the conditions determining the number of nucleating crystallization centers.

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