LAYERED GROWTH OF CRYSTALS

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LAYERED GROWTH OF CRYSTALS

DURING A POLYMORPHIC TRANSFORMATION

(Presented by Academician A. V. Shubnikov, 27 IV 1965)

In a series of works devoted to the study of the mechanism of polymorphic transformations in *n*-dichlorobenzene and other organic crystals ([1–6]), it was shown that, on the basis of a combination of external features (the presence of a proper, perfect faceting in the growing single crystal of the new phase, the absence of a crystallographic dependence between the orientations of the lattices of the growing crystal and of the matrix crystal, the tendency of the growing crystal toward a minimum of surface free energy, etc.), a polymorphic transformation may be regarded as the growth of a crystal from a solid medium, obeying the basic laws of crystal growth from liquid and gaseous media. In order to confirm this conclusion and to take the next step in the study of the mechanism of polymorphic transformations, it was necessary to determine whether the analogy between the growth of crystals from a solid single-crystal medium and the growth of crystals from ordinary media (i.e., liquid and gaseous) extends to the phenomena indicated below.

It is known that studies of crystal growth from liquid and gaseous media led in due course to the discovery of layered (stepwise) growth (see, for example, ([7,8]) and the literature cited there). Although initially it was possible to observe only relatively thick layers of several hundred angstroms and more, subsequent studies showed that the existence of these layers is regularly connected with the existence, on the surface of the growing crystal, of steps of elementary (for organic crystals—molecular) thickness. An explanation of the energetic advantage of such a crystallization mechanism was given by Kossel ([9]). We assumed that a stepwise growth mechanism should be energetically favorable regardless of whether the medium from which the molecules are supplied to the growing faces of the crystal is gaseous, liquid, or solid; we therefore undertook a study of the interface between two solid phases by optical microscopy.

n-Dichlorobenzene was again chosen as the object of investigation, since the $\alpha \to \beta$ transformation in this substance is accompanied by an insignificantly small density jump (^{10}), which is very important, since it permits exclusion from consideration of the complicating factor of internal stresses. However, n-dichlorobenzene sublimes readily in air, especially at the elevated temperatures necessary to induce the $\alpha \rightarrow \beta$ transformation. Therefore observation of such transformations (occurring at various temperatures T_{tr} in the interval between the phase-equilibrium temperature $T_0 = 30.8^\circ$ and the melting temperature 53.2°) was carried out on crystals immersed in glycerin. Having raised the temperature of an α-crystal, located in a glycerin bath on the heating stage of a microscope, to the temperature at which transformation began, we centered the region of the object of interest in the microscope field of view and replaced the 9× objective with a 95× oil-immersion objective. Focusing was carried out either on the horizontal flat surface of the original crystal at the place where it intersected the inclined interface between phases α and β, or into the depth of this crystal onto the surface of the new-phase crystal growing from below. In observation in reflected light, the limiting resolution of the optical microscope was achieved (0.2 μ in the horizontal plane).

To the article by Yu. V. Minin, P. P. Petropavlov, and A. I. Kitaigorodskii, p. 80

Fig. 3. 730×

Fig. 1. 460×

Fig. 4. 750×

Fig. 2. 1200×

It has been established that during the growth of a crystal of the new phase inside the initial crystal (usually β inside α, although the entire discussion also applies to the reverse process), its faces do not move in the directions of their normals, but grow by separate thin layers, as is demonstrated by the motion-picture frames in Fig. 1 and the microphotographs in Figs. 2 and 3.

In three successive motion-picture frames in Fig. 1, taken at intervals of 1.3 sec, a portion of the surface of an n-dichlorobenzene crystal is shown during the growth of a β-crystal at the expense of α. The phase boundary line is formed by the intersection of the plane of observation with an inclined phase-boundary surface. The successive growth of layers of the β-crystal is clearly visible. The height of the macrosteps* is $\sim 2.5\ \mu$. The motion of the macrosteps is accompanied by the appearance of lines on the surface of the new-phase crystal, better distinguishable in the case of higher steps. The nature of these lines has not yet been clarified.

Another example is given in Fig. 2. The growth steps recorded in this microphotograph are apparently formed from steps of smaller magnitude than the smallest distinguishable steps, about 0.3 μ high. The blurred bands above the phase boundary, on the side of the α-phase, are interference bands of equal thickness, since the α-phase forms a wedge. The sharp straight lines below this boundary appeared as a result of layered growth.

The preceding explanations are sufficient for understanding the picture of growth of a β-crystal presented in Fig. 3.

Figure 4 gives a photograph of a growing β-crystal obtained through a layer of the α-phase. The β crystal grows in the form of a stepped pyramid, which may be called a growth pyramid. The latter microphotograph is one of the frames of a motion-picture film in which a change in the mutual arrangement of the steps from frame to frame is observed, owing to nonuniform growth of the individual steps. Observation of the growth of such pyramids often makes it possible to see the breakup of individual macrosteps with the separation of macrosteps of smaller height. Calculation of the average height of macrosteps on growth pyramids, carried out by focusing at two different levels and counting the number of visible macrosteps between them, usually led to values from 1000 to 2000 Å, and in one case gave a value of 700 Å. It may be assumed that the thinnest of the observed growth layers had a thickness one order of magnitude smaller than the average values given above.**

Investigation using microcinematography has convinced us that the layered growth of crystals during polymorphic transformation may be considered a reliably established fact. The observed patterns of layered growth are very diverse and depend strongly on ΔT ($\Delta T = |T_{\mathrm{tr}} - T_0|$). At small ΔT, predominantly uniform motion of macrosteps in trains occurs, with each macrostep retaining an unchanged height, as in Fig. 1. With increasing ΔT, a tendency appears toward the breakup and merging of macrosteps, or else toward their blurring. With further increase of ΔT, the picture of layered growth becomes increasingly disordered, and then the phase-boundary front begins to move as a whole. In one case, the dependence of the velocity V of motion of a blurring macrostep on its height h was measured. It turned out that the dependence $V \sim 1/h$ is not obeyed: whereas the height of the macrostep smoothly decreased from 3 to 0.6 μ (i.e., by a factor of 5), while the rate of its motion increased by no more than 30%. It is intended in the future to carry out more detailed studies of the kinetics of motion of macrosteps.

To what has been said it is useful to add a few more observations. The rate of motion of thin macrosteps proves, in general, to be higher than that of thick ones. The contours of growing layers are sometimes faceted. The profile of macrosteps in some cases is rectilinear, but more often diffuse. The most characteristic profile has a strongly diffuse convex corner and a less diffuse reentrant corner.

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* This term is usually applied to steps whose height is many times greater than the height of elementary steps.

** In an ordinary microscope the vertical resolution may be many times better than the limiting horizontal resolution.

In the present study, the methods of phase-contrast microscopy and multiple-beam interferometry were not used. Attempts to use these methods in further investigations are planned; however, there are weighty reasons to believe that these methods, which have yielded so much with respect to elementary steps in the growth of crystals from liquid and gaseous media, may prove useless in studies of growth from a single-crystal solid medium. The main difficulty is that, in a polymorphic transformation, the growth steps are located not on the surface of the solid phase, but at the interface between two contacting solid phases, where the jump in refractive index is much smaller and the deposition of a reflecting silver layer is impossible.

Although the method used did not permit observation of elementary growth steps, their existence appears beyond doubt. It is interesting to note that in the literature there is one mention of the layer-by-layer character of the process of transformation of $\beta \rightarrow \alpha$ sulfur in thin specimens enclosed between a slide and a cover glass ([11]); however, this important observation subsequently attracted no attention, apparently because it was not regarded as a characteristic feature of the mechanism of polymorphic transformations.

It may be supposed that the next steps toward elucidating the mechanism of polymorphic transformations should be studies that would answer the questions: 1) what is the role of two-dimensional nuclei and screw dislocations in the process of layered growth of crystals of the new phase, and 2) whether there is any intermediate layer at the phase interface. As for the intermediate layer, whose presence has been assumed by various authors, its existence appears extremely doubtful. Indeed, growth of a crystal of the new phase by a step mechanism will occur only at individual kink sites on the steps. Leaving these sites out of consideration, one may assert that over the entire remaining phase interface no changes occur for a long time. This means that at the phase boundary there can be no interlayer of material in an excited transitional state. The possibility of the existence of an interlayer of a gas phase* must also be rejected, since the attractive forces at the phase boundary, for a gap thickness of only two molecular layers, would be much too weak to hold together the separate parts of the crystal. In practice, crystals of n-dichlorobenzene retain sufficient mechanical strength even when they have the form of a thin needle or plate and are intersected transversely by a flat phase boundary. There are a number of other weighty arguments against the existence of a gas interlayer. Thus, one may mention the inevitable rapid change in the width of the gap during the transformation as a consequence of differences in the densities of the phases, and also the incompatibility of the existence of a gap with the fact that internal stresses arise for the same reason.

It appears most probable that the lattices of both phases are in close contact with one another at the interface, held together by molecular–

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* If the authors who adhere to the theory of a gas interlayer give the latter not only a mathematical but also a real physical meaning.

···forces, like surfaces brought into optical contact. Such a representation is readily consistent with the previously established fact that, in a polymorphic transformation, there is no crystallographic correspondence between the orientations of the lattices.

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