New optical interference methods for studying the kinetics of crystallization in solution

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Modern methods for studying *in situ* the kinetics of crystals growth in solution are briefly reviewed. A Michelson laser interferometer makes it possible to measure simultaneously the normal and tangential growth rates of crystal faces as well as the slope angle of dislocation growth humps.

CONTENTS

Crystals usually grow in solutions by the layer-spiral mechanism. A screw dislocation emerging onto a face forms an open step. Attachment of crystallizing matter to the step causes the step to become twisted into a spiral, as a result of which a dislocation hump appears on the face. The constituent layers of the hump spread out along the face, and new layers, whose thickness equals the height of the starting step, form at the top of the hump. The formation of a dislocation hump is illustrated in Fig. 1. Figure 1a shows a screw dislocation with an elementary step formed by a displacement of the half-plane by one crystal lattice parameter, emerging onto the face. Attachment of particles to the step causes the step to become twisted into a spiral (Fig. 1b).

The study of crystallization is predicted on the study of the form of dislocation humps, their interaction with one another, the determination of the rate of formation of new layers, their velocity, and coalescence into the larger layers or decomposition into thinner layers. Aside from purely scientific interest in the study of the mechanism of crystallization, the growth of solid-state electronics, laser optics, and other fields of science and technology requires better crystal quality, larger crystals, and lower production costs achieved by accelerating and perfecting technological cycle of crystal growth.

The structure of the surface of a face can be comparatively easily studied after the crystal is removed from the solution. The problem of studying the phenomena listed above during the crystallization process is much more complicated and has not yet been completely solved. Until recently even the simpler problem of automating the measurement of crystal growth rates, which is especially important for the technology of growing single crystals, could not be solved. The measurements of linear dimensions with the help of devices with an eyepiece and a micrometer or motion pictures and photography, used for these purpose during the last decade, are of low accuracy, with such methods a long time is required to obtain results, and data acquisition cannot be automated.

A brief review of the methods used to study surfaces and crystallization processes is given in Ref. 1 together with an extensive bibliography. The same questions are examined in greater detail in Ref. 2.

The phenomenon of the interference of light makes it possible to measure with high accuracy the change in the linear dimensions of an object. The use of interference methods for studying crystallizaiton processes has been held up for a long time by misgivings about the instability and low contrast of the interference pattern owing to concentration and temperature fluctuations of the refractive index of the crystallization medium. This pshchological barrier has been largely overcome only in recent years, and today interference methods are successfully used to determine both the normal growth rate of crystals and the relief of the surface of crystallization.

The growth of strongly birefringent β-methyl naphthalene crystals was studied in Refs. 3 and 4. A parallel light beam passed through a cell with the growing crystal, placed between crossed polaroids on the object stand of a microscope. A photodetector, which recorded the change in the illumination of the interference pattern accompanying the increase in the thickness of the crystal, was attached to the eyepiece of the microscope. The crystal was several tens of microns thick, and the layer of solution in the cell was ~ 2 mm thick. An equally strongly anisotropic crystal ($C_{36}H_{74}$) was studied in Ref. 5 employing a scheme similar to the pre-

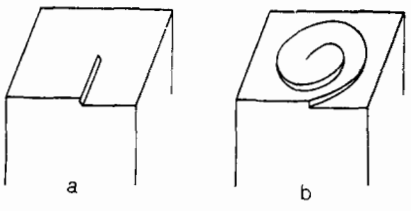

FIG. 1. Diagram of the formation of a growth hump on a screw dislocation.

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ceding one, but complicated by the fact that one of the polaroids rotated with a constant velocity and the signal measured at the rotational frequency of the polaroid was amplified. In Ref. 6 fringes of constant inclination were observed which were formed in converging light when light waves reflected from the growing face of the crystal interfered with those reflected from a mirror oriented parallel to this face, which had previously been grown into the crystal. In this manner both interfering beams were made to coalesce, so that the fluctuations of the refractive index of the medium surrounding the crystal made identical contributions to their noise. In Ref. 7 the growth rate was measured with the help of a Michelson interferometer arrangement. The object beam passed through the crystal (glued to the edges of the opening in the cell with the solution) and was reflected from its growing face. The reference mirror was attached to a piezoelectric element. The optical path difference arising during the process of crystal growth was compensated with the help of an electronic circuit by translating the crystal.

The methods described above are not widely used either because they are complicated or because they were intended to be employed with crystals which are too small, and moreover growing in an unmixed solution.

In recent years improvements of the methods employed to study crystal growth have been explored in order to ensure that the practice of interferometry meet today's requirements for laboratory and production measurements.

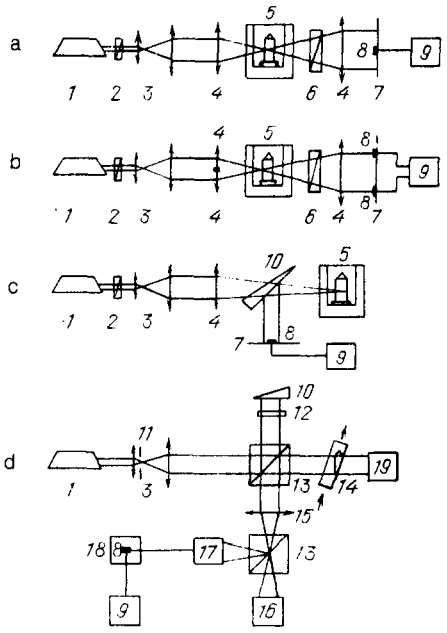

FIG. 2. Optical layout of interference methods for studying crystal growth in solution. a) Conoscopic method. b) Bilense method. c) Method of constant inclination fringes, d) Michelson interferometer. 1) laser; 2) half-wave plate; 3) telescope; 4) lenses; 5) thermostat with crystallizer and growing crystal; 6) polaroid; 7) screen; 8) photodetector; 9) automatic plotter; 10) glass wedge; 11) filtering diaphragm; 12) filter; 13) beam-splitting cube; 14) flow-through cell with growing crystal; 15) objective; 16) camera; 17) television camera; 18) television set; 19) microscope with a micrometer-eyepiece.

1. MEASUREMENT OF THE NORMAL GROWTH RATE OF FACES

1.1. Conoscopic method

Unlike previously used methods, interference in converging light based on a standard scheme for observing conoscopic figures was employed.[8] The optical layout of the experimental arrangement is shown in Fig. 2a. This substantially simplifies the alignment and makes it possible to increase the accuracy of the measurements. The photodetector (8) can be placed at any point in the interference pattern, where the period T of the change in its illumination intensity in time, associated with the growth of the crystal and displacement of the interference fringes, is also recorded. It is important to note that this scheme can be used to perform measurements on crystals of any size, growing in crystallizers of most of the well-known designs. The phase difference between the interfering beams arises only in the crystal itself, and since rays propagating along the same path strike the photodetector, the noise introduced by the temperature stabilizing liquid and the vigorously agitated solution, does not affect the determination of T.

The conoscopic method has been successfully used to study time-dependent changes in the growth rate of the (001) face of a TGS crystal. It was shown that the scheme was highly reliable and noise resistant. The birefringence of these crystals at the wavelength of the helium-neon laser equals 0.093. The indicated faces are oriented at an angle $\gamma = 18°40'$ to the plane of the optic axes. This plane is oriented normally to the incident light by rotating the crystallizer with the thermostat until the characteristic conoscopic figure appears on the screen. The photodetector is placed at its center. Under these conditions over the time T the thickness of the crystal increases by an amount $\lambda \cos\gamma\,(n_g - n_p) = 6.45\,\mu m$ (λ is the wavelength of the light, and n_g and n_p are the refractive indices of the crystal for two orthogonally polarized light waves propagating in the crystal). This accuracy is not high and is achievable with an eyepiece-micrometer, but it is very difficult to automate the microscopic measurements.

1.2. Bilense method

The conoscopic method can be easily modified for performing simultaneous measurements of the growth rate of different sections of a face. To this end the focusing lens is cut into two equal halves, which are moved apart by several millimeters (Fig. 2b). Both parts of the bilense focus light on sections of the face which are separated by the same distance are the lens halves. Each light beam forms on the screen one-half of a conoscopic figure. By placing photodetectors at their center it is possible to record two graphs of the change in the illumination intensity as a function of time (preferably on the same automatic plotter). The mutual displacement of the graphs plotted changes with time, which corresponds to the different growth rate of the different sections of the crystal face (different growth humps).

1.3. Method of constant inclination fringes

In this case the interference pattern is formed not in transmitted light, but rather as a result of the reflection of a converging light beam from two parallel faces of the crystal, which substantially increases the sensitivity of the measurements.[9] The layout of the experimental arrangement is shown in Fig. 2c. The polarization of the light beam incident on the crystal relative to its optic axes is chosen so that only one light wave propagates in the crystal (i.e., there is no

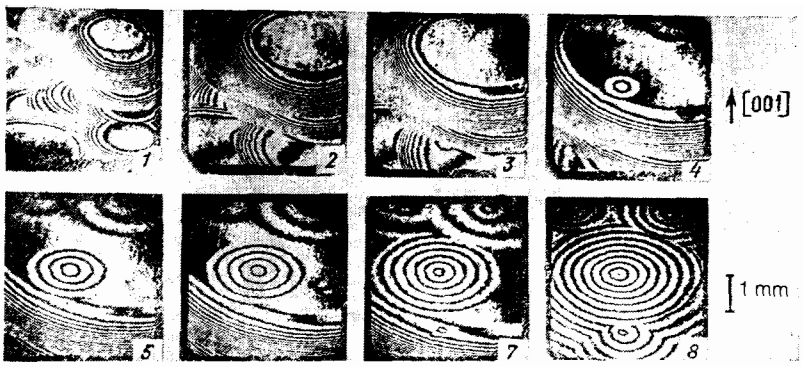

FIG. 3. Initial stages of the growth of the (100) face of a KH_2PO_4 crystal.

birefringence). An interference pattern in the form of concentric light and dark rings—fringes of constant inclination—is observed on the screen. The period of the change in illumination intensity at any location in the interference pattern corresponds to the change in the thickness of the crystal by an amount $\Delta d = \lambda/2n$, where n is the refractive index of the crystal for light with the given polarization.

This scheme is resistant to noise for the same reasons as the conoscopic method. It can also be employed for large crystals and does not require special crystallizers.

For a typical value $n = 1.5$ and with a helium-neon laser $\Delta d \approx 0.2$ μm. If the growth rate equals 0.3 mm/day, $T = 1$ min. There are no difficulties in measuring lower growth rates.

Comparing the method constant inclination fringes with the conoscopic method we note that the former is more sensitive by a factor of $2n/(n_g - n_p)$ (approximately by a factor of 30–60) and it can be used for crystals belonging to the cubic system as well as for measuring along directions close to the optic axes in the case of crystals of the lowest symmetry (which cannot be done in the conoscopic method). Its drawbacks are that the growth rate can be measured only parallel to the growing faces and it is more difficult to align the system.

The relative accuracy with which T is measured from the graph recorded on the automatic plotter is identical in both cases and equals 2–3%.

The conoscopic method is best used when the growth rate of the faces exceeds 0.5 mm/day and the faces are oriented at a small angle to the plane of the optic axes (or to the optic axis for uniaxial crytals). In other cases the method of constant inclination fringes is used.

2. OBSERVATION OF THE RELIEF OF A GROWING FACE, MEASUREMENT OF THE TANGENTIAL AND NORMAL GROWTH RATES OF DIFFERENT SECTIONS OF THE SURFACE

The methods studied above do not give any information about the location on the surface where the growth is determined. The arrangement described below makes it possible to obtain such information.[10]

The optical layout of the Michelson interferometer (Fig. 2d), in which the object light beam was reflected from the crystal face under study (14) while the reference beam was reflected from a flat mirror (10), was employed. The intensities of the object and reference beams were balanced with the help of a neutral light filter (12). An image of the face, on which the interference fringes characterizing the relief of the face were superposed, was formed in the plane of the photographic film (16) and the input window of the television camera (17) with the help of an objective lens ($F = 15$ cm). The itnerference pattern can be observed on a television screen (18). The photoresistance (8) could be fixed at any location on the screen. The experiments showed that although in this scheme the reference and object beams propagate along different paths the observed interference pattern is completely stable for a fixed supersaturation of the solution. This is attributable to the low compressibility of the solution and the insignificant concentration fluctuations. As is well known, in the gas phase, in which the compressibility is high and the refractive index depends strongly on the pressure, turbulence smears the interference pattern.

If the face is flat, straight parallel interference fringes, the distance between which depends on the angle between the object and the reference light beams, will be superposed on the image of the face. This angle can be regulated by turning both the cell containing the growing crystal and the reference mirror.

In the case when the face contains irregularities together with flat sections, the interference fringes will be curved. After uniform illumination of the flat sections has been achieved by turning the reference mirror or the cell the relief can be judged from the form of the fringes: the interference fringes are equivalent to horizontal contours on a topographic chart. The distances along the height of the relief between neighboring fringes equal $\Delta h = \lambda/2n'$, where n' is the refractive index of the solution. For a typical value $n' = 1.4$, $\Delta h = 0.23$ μm. By measuring the distance between the fringes Δd (taking into account the scale) the slope of the

FIG. 4. Impurity-induced competition between dislocation growth humps.

FIG. 5. Competition between dislocation humps accompanying a change in the supersaturation of the solution.

relief at a given location can be determined: $p = \Delta h / \Delta d$.

It could happen, however, that the face does not have a flat section correspoinding to a crystallographic plane with simple indices. Under these conditions the position of the singular face can be determined with the help of an additional experiment, which we shall not describe here.

As the crystal grows the thickness of the layer of solution between the face and the window of the cell decreases, which causes the interference fringes to move, i.e., it causes the illumination intensity of a given location of the interference pattern to change periodically (with period T). To measure T a photodetector can be attached anywhere on the television screen. The normal (R) and tangential (V) growth rate at any point of the surface were determined from the relations $R = \Delta h / T$ and $V = R / p$.

As an example we present photographs characteizing the initial stages of growth of a face of a KH_2PO_4 crystal prism (Fig. 3).

Terraces bounded by curvilinear slopes and flat sections parallel to the crystallographic (100) plane, arise on the initially rough surface. The latter increase in size, and the top terraces climb onto the lower terraces owing to the tangential motion of the slopes. The crystal does not grow upwards perpendicularly to the plane of the face (1–3). The dislocation initially emerging onto the slope transforms into a flat section and begins to generate a dislocation hump (4), which gradually occupies an increasingly larger part of the face. This gives rise to the onset of crystal growth (5–8). Almost simultaneously, owing to internal stresses from inclusions of the solution near the top edge, dislocations, also forming humps, emerge onto the face. For dislocation humps linear generatrices are characteristic; an elliptical form (in section) of the humps indicates that the tangential growth rate of elementary layers depends on the direction along the surface.

A change in the supersaturation of the solution or addition of impurity affects the slope of different dislocation humps differently. Because of this they "compete" with one another, and the steepest hump wins. Figure 4 demonstrates the decrease in the slope of the humps as chromium ions with constant supersaturation are added to the $NH_4H_2PO_4$ solution. The photographs 1–3 show the increase in the distance between the interference fringes, characterizing the slope of the left-hand hump, after 10^{-5} moles of Cr are added to 1 mole of $NH_4H_2PO_4$. A steeper hump appears at the same time (on the right). Further increase in the chromium content (by a factor of 1.5) reduces the slope of this hump also (photograph 6).

A change in the supersaturation of the crystallization solution has an analogous effect. Figure 5 shows the change in the relief of the surface accompanying a change in the supersaturation. Phototgraph 1 demonstrates the initial image of the face at a temperature of 34.7 °C. The face is a hump, whose top lies on the bottom edge of the phototgraph. Lowering the temperature of the solution reveals two other growth humps (photograph 2). Later the first hump vanishes, and of the two new ones one, which is stable with the new supersaturation (33.3 °C) remains (photographs 3 and 4). Increasing the temperature decreases the slope of this hump and leads to the appearance of the starting hump, which is steeper under these conditions (photograph 6). The "competition" between the humps is explained by the different effects of supersaturation on their slope, the steeper hump is always stable.

The above-described methods for studying the mechanism and kinetics of crystal growth in solution have made it possible to obtain previously inaccessible information and to determine based on it the effect of impurities, the temperature, and the supersaturation of the solution on the rate of crystallization and to obtain more accurate values of the parameters determining the appearance of different types of defects in the crystal. The methods for determining the growth rate of crystals make it much easier to monitor the technolgoical process of crystal growth and enable automation of this process under industrial conditions.

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