Crystal morphology of sucrose influenced by rotation axes parallel to growth planes*

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Abstract Three different types of growth forms of sucrose ($P2_1$) were found by calculating with the Fourier transform method of crystal morphology. The observed central distances of the (100) and (001) faces are smaller than those calculated. It will be shown that the two-fold screw axis, which runs parallel to these faces, influences the rate of growth. The effectiveness of these symmetry elements is relative to the rotation angle around the face normal.

Keywords: sucrose, crystal growth mechanism, symmetry dependent growth, Fourier transform method of morphology.

The growth of a crystal is mainly determined by the symmetry of the structure. According to Bravais[1] and Friedel[2], Donnay et al.[3] and Hartman et al.[4], the thickness of the growth layers corresponds to the net plane distance. Symmetry elements with glide components, such as screw axes and glide planes, bring about a division of certain net plane layers and thus lead to accelerated growth parallel to these planes. A net plane layer, for example, is thus halved by a two-fold screw axis perpendicular to the layer. As recently shown with potassium dichromate, pseudotwo-fold rotation axes that run parallel to the growth planes also influence the crystal growth rates of these planes[5].

1 Crystal morphology of sucrose

(i) Fourier transform method. To calculate the growth form with the Fourier transform method of crystal morphology, the following is used as a basis[6, 7]. The plane indices and their multiples can be viewed as points in a reciprocal lattice. Similar to determining crystal structure, one can carry out a sign determination with the help of the Goldschmidt complication rule or with the triple product method. A Fourier transform produces the morphological or energetical lattice which corresponds to the lattice of the centers of gravity of the molecules or of the building units. With a division of space by Dirichlet domains to the morphological lattice, one consistently finds a convex polyhedron (reciprocal crystal), whose planes are indexed in reciprocal space. The plane contents of the reciprocal crystal are proportional to the bond strength between neighboring building units (or morphological units). According to Lacmann[8], the specific free surface energy σ(hkl) of the planes of a simple point lattice is

$$\sigma=\frac{1}{2}\cdot\frac{N}{V}\sum_{i}\frac{|W_i\cdot W_{\mathrm{hkl}}|}{|W_{\mathrm{hkl}}|}\cdot\varphi_i, \tag{1}$$

where N is the number of lattice points, V the volume of the unit cell, W_i the bond vector, W_{hkl} the face normal vector, φ_i the bond energy and i the number of bonds broken by the (hkl) plane. If one starts with the morphological lattice and replaces φ_i with the plane contents of the reciprocal crystal, the result σ(hkl) is as the surface of the reciprocal crystals parallel to (hkl) divided by S (hkl) (net plane mesh).

Considering the projection of the faces of the reciprocal crystals on the net plane mesh, one obtains the growth rates of the planes of the real crystal:

$$\sigma'=\frac{1}{2}\cdot\frac{N}{V}\cdot\frac{n}{N}\cdot\sum_{i}\frac{|W_i\cdot W_{\mathrm{hkl}}|}{|W_i|\cdot|W_{\mathrm{hkl}}|}\cdot\varphi_i=\frac{n}{2V}\cdot S(\mathrm{hkl})=\frac{1}{2}\cdot d^*(nh,nk,nl), \tag{2}$$

where d^* is the reciprocal net plane distance, and n indicates a division of the net plane distance.

(ii) Results and discussion. Sucrose crystallizes in the monoclinic space group $P2_1$ with the

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lattice constants[9] $a = 1.08633$, $b = 0.87050$, $c = 0.77585$ nm, $\beta = 102.945°$ and $Z = 2$. The following planes occur on the crystals[10]: $101\ominus$, $110\ominus$, $(1\bar{1}0+)$, $111\oplus$, $(1\bar{1}1-)$, 200−, 001−, 011−, $(0\bar{1}1+)$, $10\bar{1}+$, $\bar{1}11-$, $(\bar{1}\bar{1}1+)$. The last two faces are rarely observed. Using the Goldschmidt complication rule, it reveals that (100) is to be modified as (200). The sign determination occurs in $P2_1/m$ (origin fixing with encircled signs; triples in brackets are crystallographically dependent in $P2_1/m$). The Fourier synthesis leads to the morphological lattice with the coordinates $\frac{1}{4}$ $\frac{1}{4}$ $\frac{3}{8}$ (center of gravity of the sucrose molecule: 0.232; 0.25; 0.344). As mentioned above, (100) is to be changed into (200). This morphological extinction law is not determined by the space group symmetry. Rather, it results from the special arrangement of the molecules. Fig. 1(b) shows the Wulff construction obtained with the d^*-values from eq. (2). In fig. 1(a), the central distance of (100) is equal to $d^*(100)$ instead of $d^*(200)$, as shown in fig. 1(b). On this form, {101} is missing. Crystal growth experiments (fig. 2) demonstrate that the occurrence of both forms is dependent on the temperature and the supersaturation of the solution. Both forms are also found in industrial products[11]. The central distances of the planes of 8 Type A and 49 of Type B crystals were measured and scaled to the theoretical d^*-values, using the least squares method. The following values were obtained for the (100) planes: 0.092 for Type A: and 0.118 for Type B: (calculated $d^*(200)$ value 0.189).

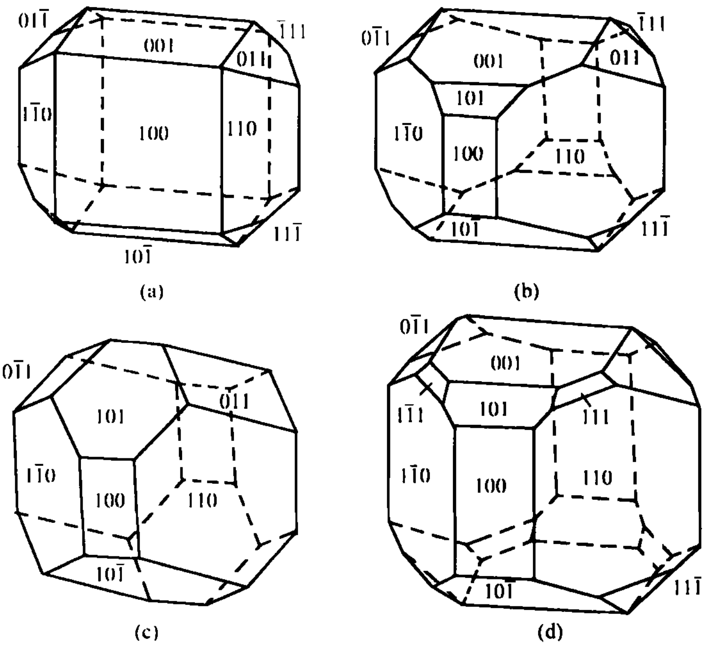

Fig. 1. Theoretical growth forms of sucrose (central distances according to eq. (2)). (a) and (b) are based on the morphological lattice $\frac{1}{4}$ $\frac{1}{4}$ $\frac{3}{8}$ ((a) $d^*(100)$, (b) $d^*(200)$); (c) on the morphological lattice $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$ ((c) $d^*(200)$, $d^*(002)$) and (d) equilibrium form (morphological lattice as in (a) and (b), central distances according to eq. (1)[10]).

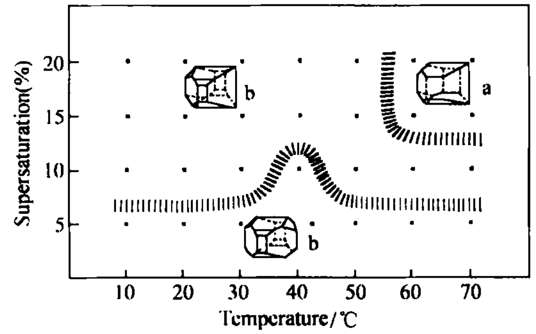

Fig. 2. Growth forms of sucrose dependent on temperature and supersaturation of the solution. Spherical polished crystals were used as nucleus crystals. At low concentrations, nearly centrosymmetric crystals were obtained. The classification of the types agrees with that in fig. 1 (see ref. [11]). Type A is obtained only at high temperatures and high levels of supersaturation.

The following considerations show that we are dealing with a new growth mechanism. In the case of a two-fold screw axis perpendicular to a growth layer, the effectiveness of this symmetry element is independent of a rotation around the face normal. In fig. 3 this is shown with a diagram of a rectangle. The screw axis causes a halving of the interplanar distance, and the growth rate is proportional to the doubled d^*-value (Mechanism 1). In the case of a two-fold rotation or screw axis that runs parallel to the growth layer, the axis is effective when it runs in the projection plane normal to the growth layer (rotation angle around the face normal: 0°) or is perpendicular to it (90°). This is shown in the sawtooth-like function in fig. 3. If one normalizes the plane contents of the rectangle to 1, then the plane content under the sawtooth-like function is 0.5. This means that the plane actually grows with only one half of the growth layer ($d(2h, 2k, 2l)$). The growth rate behaves as if the plane grew with the original growth layer (d(hkl); Mechanism 2). This definitely applies to the Type A (fig. 1(a)). For Type B (fig. 1(b)), a central distance is obtained for (100) that lies between $d^*(100)$ and $d^*(200)$. This indicates the presence of a rather different growth mecha nism. If one postulates that, under certain external conditions, the tilting of the two-fold axis from the ideal positions (0°, 90°) is not as strongly effective as expected, then this fact can be presented in a simple sine function. The nor-malized plane content under the sine function in fig. 3 is 0.637 (Mechanism 3). Multiplying this value by $d^*(200) = 0.189$, one obtains nearly the measured d^*-value 0.120 for (100) of Type B (measured 0.118). This mechanism is apparently dependent on temperature and the super-saturation of the solution .

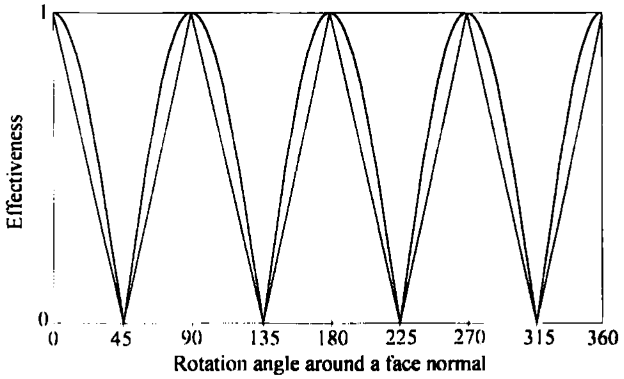

Fig. 3. The effectiveness of two-fold rotation and screw axes with respect to their position to a growth layer and their dependence on the rotation angle around the face normal. (a) A two-fold screw axis perpendicular to the growth layer leads to a halving of the growth layer. The growth rate corresponds to the doubled d^*-value of the plane. The effectiveness is independent of the rotation angles: rectangle function (Mechanism 1). (b) A two-fold rotation or screw axis parallel to a growth layer has the highest degree of effectiveness in the projection normal to the growth layer (0°) or perpendicular to it (90°). The plane grows with halved growth layers; the rate of growth is only half as fast as in (a): sawtooth-like function (Mechanism 2). (c) In the case of sucrose ($P2_1$), the rates of growth for (100) and (001) lie between the values of (a) and (b). Slight tilting of the symmetry element from the ideal position (0°, 90°) reduces the effectiveness to a lesser degree: sine function (Mechanism 3).

Type C (fig. 1(c)) has only been found in industrial products. This means that additions to solutions also play an apparent role. If one modifies the (111) planes, which are seldom observed on these crystals, into (222) (this implies (001) as (002)), the morphology can be interpreted as follows: 101⊖, 110⊖, ($1\bar{1}0$+), 222−, ($2\bar{2}2$ −), 200−, 002−, 011−, ($0\bar{1}1$+), $10\bar{1}$+, $\bar{2}22$− ($\bar{2}\bar{2}2$ −). Since only four linearly dependent index parity groups are present ((EEE), (OEO), (OOE), (EOO), E = even, O = odd), two signs are sufficient for fixing the zero point. The Fourier synthesis provides a morphological lattice with the coordinates $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$ (I lattice). Measurements of 10 crystals of Type C provide the following mean central distances: (100): 0.114, (001): 0.164 (theoretical values: $d^*(200) = 0.189$, $d^*(002) = 0.265$). If one multiplies the calculated d^*-values by 0.637, the values obtained are 0.120 for (100) and 0.169 for (001) respectively. In a few cases, (001) was observed only on one side as very narrow stripes. The distances between the edges formed by the corresponding (101) planes were used as approximate values for the growth rate of (001).

2 Conclusion

Two-fold rotation or screw axes that run parallel to growth layers influence crystal growth only when a division of the net plane distance occurs due to a symmetrical arrangement of the molecules or building units, which results in the formation of sublayers with equal amounts of energy. If the morphological lattice is known, it is easy to determine if a division of the interplanar distance is present. As shown in the case of sucrose, the effectiveness of these symmetries is determined by internal and external factors.

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