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Growth phenomena in the surface layer and step generation from the edges of faceted crystals

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Abstract

The mechanism of growth step generation from the edges of faceted crystals obtained from experimental results with KDP crystals is described. It shows that growth from the crystal edges is initiated by the deviation of the edges from their crystallographic orientation and formation of incomplete shapes of singular facets. The conditions for formation of the incomplete faceted shapes during dislocation growth are considered. It is shown that the process of step generation from the edges is determined by the mutual positions of the vicinal slopes on the adjacent faces.

Keywords: rapid growth; surface layer; dislocation; crystal edges; faceted shape; KDP.

1. Introduction

KDP (KH_2PO_4) is a crystal widely used as a model for studies of different layer growth mechanisms. Rapid growth techniques developed during recent years [1, 2] stimulated the shift of these studies into the region of high supersaturation and revealed new phenomena that were difficult to see in slowly grown crystals. The observations made in the process of the development

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of rapid growth show that dislocation growth remains a dominant mechanism even at very high supersaturation. Crystal growth under extreme conditions (temperature range from 80° to 5°C, supersaturation up to 30%, growth rates exceeding 50 mm/day, crystal sizes up to 40 – 80 cm) offers a unique chance to extend our knowledge about the growth phenomena and defect formation processes determined by the dislocation growth. On the other hand, the ability to rapidly grow large bulk crystals reproducibly under controllable conditions allows us to consider the presence and the nature of other mechanisms, observed previously or predicted for high supersaturation, such as growth from the edges and two-dimensional nucleation. This paper is devoted to one of such mechanisms: growth originating from the crystal edges.

The idea of growth from the edges of faceted crystals is not new in principle. Growth steps produced on the edges of growing crystals were observed and described in many papers [3 - 7]. Surface patterns of KDP crystals very similar to those shown in the present paper were published more than 50 years ago [3]. In fact, the formation of growth layers on the crystal corners and edges seemed to be more natural than growth originated from the central parts of growing faces before the discovery of dislocation growth [3, 8]. And while the theory of dislocation growth has been advanced tremendously since that time, growth step generation from the crystal edges was typically explained only by the gradient of supersaturation along the crystal face and its higher value on the edges without description of possible mechanisms.

The results of our previous work [9] showed that the phenomenon of growth from the edges could result from the deviation of the crystal faces from their crystallographic orientation. KDP belongs to the symmetry group $\bar{4}2m$ and at equilibrium is faceted by the sets of {101} (pyramidal) and {100} (prismatic) faces. Each of the flat faces should be limited by the edges of the singular direction: <101> and <100> for the pyramidal, and <100> and <001> for the prismatic faces (Fig. 1). During the non-equilibrium growth process, the presence of dislocation hillocks leads to the distortion of the equilibrium shapes and their deviation from the crystallographic orientation. As it was shown in [5] this distortion should be taken into account during considerations of growth phenomena on the surface of faceted crystals.

The goal of this work was to consider more precisely growth step generation on the edges in connection with the deviation from the crystallographic shape. Experiments on surface regeneration were especially performed to understand a possible effect of this phenomenon in bulk crystals growing by the dislocation mechanism.

2. Apparatus and techniques

Crystals were grown by the rapid growth technique on a point seed in a temperature range of 70-20° C as described previously [1, 10]. The initial seeds and crystals for regeneration experiments were introduced into the overheated solutions at a temperature above the saturation point, t_o. Supersaturation was created by temperature reduction and expressed in the relative units, $\sigma = (C-C_0)/C_0$, where C and C_0 are the real and the equilibrium concentrations in g KDP/g solution. Typical supersaturation for the experiments was 0.06 – 0.1. Solution concentration was calculated from measurements of the crystal dimensions [10] or by taking concentration samples during the experiments. All experiments were performed at a reversible rotation of 50 rpm and a period of 30 sec in each direction.

Surface morphology was observed during growth on large crystals grown in 1000 l crystallizers and on a smaller scale on crystals grown in standard Holden-type crystallizers with volumes of 10 – 20 l. At high supersaturation the growth hillocks and intervicinal boundaries [11] were clearly seen in reflective light on the growing surfaces during the pause of the reversible rotation. Additional examination of the surface morphology was made after the crystals were extracted from the solutions by using an optical microscope provided with a Nomarsky prism.

Normal growth rate, R , was measured by using a cathetometer to an accuracy of ±0.1 mm. The growth rate of the thin surface layers was obtained by measuring the advancement of their front edges in the tangential direction of a face.

3. Experimental results

3.1. Regeneration of singular faces with incomplete crystallographic shape

Fig. 2 presents a set of pictures taken *in-situ* during the first experiment when the deviation from the crystallographic shape was made by simply cutting out a part of the crystal before it was introduced into the growth solution (Fig. 2, a). The cut surfaces were made close to (100) and (010) orientation. At this geometry each facet of the new crystal had an orientation close to the crystallographic planes of a KDP crystal. The only deviation produced by the cut was the destruction of the crystallographic shape of the (101) face which got a segmented edge LCBADN instead of the initial straight edge LN.

After the crystal was introduced into the overheated solution, it was slightly melted before regeneration and growth started when the supersaturation was reached. During the first stage all surfaces regenerated in the regular way, observed and described previously [12 - 15], by formation of plane terraces and steps, which spread from the higher to the lower parts of the surface roughness produced by polishing and melting. The (100) and (010) surfaces inside the cut also regenerated in the usual way, as if they were regular prismatic faces of the crystal (Fig. 2, b). The regeneration steps met in the vertical corners of the cut where no preferential growth was noticed. The peculiarity of this case was that the regeneration of these “negative” prismatic faces led to the formation of not the characteristic convex, but instead concave angles between them (A and B in Fig. 2). As soon as one of these angles (in this particular case it was angle A) was formed on the adjacent (101) face, which had the incomplete shape, the growth layers started generating from this angle. A specific feature of these layers was that they spread only in the surface plane of the (101) face without having preexisting layers of the same orientation under them (Fig. 2, c). These layers moved very fast in the tangential direction until the crystallographic shape of the (101) face and the corresponding straight edge LN were restored. When the first steps came to this edge, the same process of thin layer formation started in the surface plane of the adjacent prismatic face (100) until

the surface of the whole crystal was restored by the formation of a box-like structure filled with growth solution (Fig. 2, d).

A similar phenomenon when an incomplete crystal face turns into the full crystallographic shape by formation of thin surface layers can be seen in Fig. 3. The pictures present a process of joining two faceted crystals into a single one. In our experiment two separately grown, equally oriented crystals, with close shape and size, were glued to each other in such a way that the two parallel (101) faces were shifted a small distance. In the beginning, after the crystals were introduced into the growth solution, they grew completely independently, meeting on their interface without the creation of any visible defects (Fig. 3, a). As was expected, the crystal faces grew at slightly different normal growth rates, due to differences in dislocation activity and hydrodynamic flow. As a result, at some moment the parallel faces came to the same plane, and two previously independent crystals got a (101) common face. The newly formed face did not have the right crystallographic shape: it had a missing part BAC and a segmented edge MBACN with a concave angle A (Fig. 3, b). This condition immediately gave rise to the generation of steps from this angle. The steps moved in the plane of the common face (Fig. 3, c) parallel to the edges of the previous crystals, forming thin surface layers which completed the face with its correct crystallographic shape, similar to the case presented in Fig. 2. Their movement was limited by the length of the edges BA and AC. When the formation of the common face was finished, the generation of thin layers continued on the opposite pyramidal face (Fig. 3, d). The thin surface layers covered all of the concave spaces between the crystals leaving them filled with solution and turned two previously independent crystals into a single one. The formation of a new single crystal surface was finished in a few hours.

This mechanism of single crystal formation is obviously related to the process of joining the many small crystals formed on the roughness of z-cut plates during the regeneration of KDP seeds. It also can work when extraneous particles or subindividual crystals grow into the main crystal, as well as during the process of solution inclusion “healing”. Here it should be noted that since adjacent faces of KDP crystals have mirror symmetry, faces with different simple indexes,

for example, (101) and (011) never joined, while a small misorientation was not very important for the process.

3.2. Regeneration of singular surfaces with incomplete shape obtained as a result of deviation of adjacent faces

In the previous two experiments one could see a definite tendency demonstrated by the crystals to reconstruct the incomplete shape of their faces by the generation of growth steps in the singular surface planes from the concave angles on the edges. The next experiments were made to understand how this tendency could be pronounced during growth by the dislocation mechanism. The deviation from the singularity was specially made to simulate the conditions when the distortion of the crystallographic shape can take place as a result of the presence of vicinal slopes on crystal faces.

In the experiment presented by Fig. 4 the lower part of a pyramidal face (011) was artificially deviated by 7-8 degrees from its initial crystallographic orientation by polishing. As a result of this deviation the crystal apexes C and D were moved into new positions K and L, and parts of the edges AF, FK, BE and EL were deviated from their crystallographic orientation. This process led to the distortion of the crystallographic shape of faces (101), (100), ($\bar{1}$01), and ($\bar{1}$00), adjacent to the deviated one, through loosing their parts: AFC and BED (pyramidal) and FCK and EDL (prismatic faces) (Fig. 4, a). The first stage of the regeneration process in supersaturated solution began by the creation of steps and terraces on the deviated surface (011) (Fig. 4, b). The adjacent faces (101), (100), ($\bar{1}$01), and ($\bar{1}$00) started the restoration of their surface planes by the formation of growth layers generated from the deviated edges in their surface planes (Fig. 4, c). The area of spreading of these layers was limited by the crystallographic orientation of the initial edges. When these edges and the crystallographic shape of the adjacent faces (101), (100), ($\bar{1}$01), and ($\bar{1}$00) were restored, the formation of thin surface layers continued from these edges in the singular planes of the deviated (011) face (Fig. 4, d). The surface layers quickly formed these

faces burring under them the deviated surfaces and solution, similar to the cases shown in Figs. 2 and 3 (Fig. 4, d, e)**.** As a result of the surface regeneration process, the deviated apexes and edges were returned to their initial crystallographic orientation. The singular orientation of the deviated faces was restored by growth steps generated from the edges.

The same phenomenon of the reconstruction of the complete crystallographic shape by the formation of thin surface layers generated from the edges takes place during deviation of any crystal face. Fig. 5 presents pictures taken in an experiment with the intentional deviation of two neighboring prismatic faces (schematic a and photo b). As a result the crystallographic shape of the faces adjacent to the deviated ones was destroyed through the loss of their parts ADK and CFM. Similarly to the previous case shown in Fig. 4, the formation of thin layers started from the deviated edges AK and CM (Fig. 5, c) in the planes of these faces in order to restore the initial edges AD, DK, CF and FM (Fig. 5, d and e). As soon as these edges were formed the generation of thin layers continued in the singular surfaces of the initially deviated faces (Fig. 5, f). When they met on the edges BE and EL the restoration of the full crystallographic shape of the crystal was finished with the formation of a large solution inclusion between the thin layers and deviated surfaces.

The results of these experiments show that the presence of the vicinal slopes on one crystal face always results in the distortion of the crystallographic shape of the adjacent faces and edges. In a similar way, the regeneration of the deviated surfaces always leads to the involvement of these adjacent faces and edges in the restoration process.

4. Discussion

4.1. The connection between incomplete shapes and step generation on the crystal edges

The experiments on surface regeneration present clear evidence that any time a crystal face has an incomplete shape, the restoration of its correct crystallographic shape occurs by the

generation of growth steps in the singular surface layer of this face. In general, the incomplete shape of any singular crystal face can result only from the deviation of its edges from their singular orientation. In the case when an edge consists of segments of the singular orientation, as it was in the macroscopic cases shown in Fig. 2, Fig. 3 and Fig. 6, the incomplete crystallographic shape of a face results from the existence of concave angles formed by these segments in the surface plane of this face. The regeneration of the cut surfaces led to the formation of the segmented edge LCBADN (Fig. 2 and Fig. 6, a). The singular segments of this edge (CB, BA, and AD) produced concave angles A and B in the surface plane of the incomplete face LMN. In the case of the joining of two crystals such a segmented edge BAC (Fig. 3, b, and Fig. 6, b) was combined from the singular parts BA and AC, which met in a concave angle in the plane of the common face. As it was demonstrated in these experiments, such concave angles on the edges were the points for the generation of the growth steps which moved in the surface planes.

The formation of incomplete shapes and segmented edges with concave angles also explains the transition of the thin surface layers from one face to another. Here we have to keep in mind that, based on all classical models, any growth step on the surface of a crystal face consists of sections with the singular orientation. When such a step comes to a crystal edge its front side has the orientation of the adjacent face. Then it will be clear that the growth layer which completes the face LMN on Fig. 6, a, has its edge C_1CDD_1 which coincides with the singular orientation of the adjacent (100) face. When the restoration of the crystal edge LN is completed, this faceted edge of the thin layer which originated on the (101) face forms the incomplete shape of the (100) face and the segmented edge FC_1D_1E. Step generation continues in the surface plane of this face (100) from the concave angles C_1 and D_1.

The thin surface layer which completed the common face BCED of the joining crystals had an edge of the same singular orientation as the adjacent opposite pyramidal faces of the crystals. When this layer came to the top, the existence of the step edge B_1BCC_1 resulted in the formation of the incomplete shape of the opposite pyramidal face $(\bar{1}01)$ with the following growth of a new thin layer B_1C_1F (Fig. 6, b).

The edges of the faceted layers originating on the faces adjacent to the deviated ones (Fig. 4 and Fig. 5) formed the incomplete shapes and segmented edges in the planes corresponding to the singular orientation of the deviated faces (edges $C_1A_1B_1D_1$ and $C_1K_1L_1D_1$ in Fig. 4, a, and D_1A_1B, F_1C_1B, D_1K_1L and F_1M_1L in Fig. 5, a). It follows from our results, that any of the concave angles on these edges could become a source of step generation in the surface layer.

The conditions of step generation resulting from the incomplete shape of the faces can be illustrated by the traditional model of the Kossel crystal. In this model, position 1 shown on the schematic of Fig. 7, a, corresponds to the moment of concave angles formation in our experiments presented in Figs. 3 - 6. As we could see from our results, independent of the presence or absence of the previous layers, each of such positions was a source of growth steps which moved only in the surface layers.

From a crystallographic point of view any deviated edge of a crystal consists of segments of the crystallographic orientation. This allows us to make an extrapolation to the elementary level, where we can define a concave angle as a kink. The initial incorporation of a building unit into any position 1 on a face creates two more surface kinks without a preexisting layer. The growth process continues by moving these kinks in the tangential direction (shown by arrows) until the correct crystallographic shape of the faces and straight edges are restored.

Here we should emphasize that this phenomenon takes place only in the surface layers. Even if a building unit attaches to position 3 inside the cut with the same probability as to position 1 on the surface, it does not produce layers of (001) orientation (see Fig. 2). If it did, the surface layers would not grow separately, and the entire cut would be gradually filled by layers originating from the inside corners.

Position 1 artificially created in our experiments can seem unrealistic in growing crystals, however more careful consideration shows its similarity with possible situations on the large macrosteps during the inclusion formation process. The much more obvious and frequent case when a kink without an underlayer forms on a crystal edge is shown on the same schematic as position 2. This position is produced by the existence of a half-crystal plane on face (001), which

results in the formation of stepped edges and incomplete shapes of the adjacent faces (010) and ($0\bar{1}0$). In traditional models position 2, is related only to face (001), and usually is not considered as a unique location for preferable incorporation. Meantime, the fact that position 2 also belongs to the surface layer of the adjacent (010) face, according to our experimental results, should lead to the preferential attachment of a building unit in this position. This attachment will simultaneously produce two more kinks. One of them, a kink without an underlayer of the same orientation, will move in the surface layer of the (010) face along the edge. The other one, a regular 1/2 kink on the (001) face, will move in the usual way along the step of the half-plane. If another 1/2 kink exists in the same step, they will move towards each other until the whole row is completed.

Now we can consider the situation on a deviated face (Fig. 7, b). The deviated part ABCD presents a set of singularly faceted steps. To simplify the example, we will assume that all other faces of the crystal remain singular and each step of the deviated face is limited by straight edges. The existence of steps on the deviated face leads to the formation of the stepped crystal edges (AB and CD) and the distorted shape of the adjacent singular faces (010) and ($0\bar{1}0$). The presence of concave angles on the edges is the condition necessary for the preferable nucleation on the edges, which tends to reconstruct straight edges and return the faces to their complete shape. Depending on the ratio between the growth rate on the deviated face and in the surface layers of (010) and ($0\bar{1}0$) faces, this process can result only in step generation on the terraces of the deviated face or in the formation of thin overhanging layers, as it is shown in Fig. 7, b.

A deviated stepped edge should not necessarily produce growth steps. In an ideal case when the elementary or macrosteps formed on the adjacent deviated faces completely coincide on the edge where they meet, the steps on this edge (edge CD in Fig. 7, c) will not be more preferable for nucleation than any other place on the steps (for example position 3), because there are no kinks in the singular surfaces which form this edge. The kinks will be produced on the edges AB and EF under the condition of the singularity of the adjacent faces. They will move on each step only in one direction simply meeting on the edge CD as it is usually presented in the traditional models of crystal growth.

A more complicated case, which is closer to the situation in real crystals growing like KDP by large macrosteps, is presented in Fig. 7, d. The elementary steps and macrosteps formed on the deviated faces do not match in their height and width on the edge CD. In this case the generation of the growth steps can go from the edge in both directions depending on the conditions which are produced by the macrosteps at the local points on the edges.

The presence of several vicinal slopes on each of the adjacent faces should obviously result in more complicated configurations which must differ in crystals of different symmetry. Depending on many possible factors, such as size and mutual orientation of the steps, anisotropy of kinetic coefficients, relative tangential and normal growth rates, etc., these configurations can result in straight or deviated edges, as well as in formation of stable bends on the edges.

Growth of thin surface layers during regeneration of incomplete shapes can be used to explain different phenomena connected with solution inclusions, such as the formation of box-like structures, an example of which can be presented by the KDP seed regeneration process. This phenomenon is usually explained by two-dimensional nucleation which happens as a result of higher supersaturation and flow velocity on the crystal edges [5, 15]. Our experiments show that the existence of the incomplete crystallographic shape of a singular face is a sufficient condition for the formation of a thin surface layer. Independent on the flow distribution, thin surface layers can form at any location on a crystal face (see Fig. 2 - 5). The observations made in many experiments also show that the process of KDP seed regeneration is nothing but a sequence of incomplete face formations resulting from the initial incomplete shape of the seeds [16].

It should be emphasized here, that the thin surface layers form in the singular planes only along the segments of the edges which have singular orientation. For example, the entire absent part CBAD of the (101) face in Fig. 6, a, can be completed by a thin surface layer only under the condition of formation of the segments of singular orientation CB, BA, and AD. If these segments are not singular and, in their turn, consist of smaller segments of singular orientation meeting under concave angles, the formation of the surface layers will go locally from these concave angles being limited by the length of these singular parts. It can explain the observation that in real

crystals box-like structures could exist for extended periods of time, especially under the influence of impurities or non-uniform flow which make the formation of straight growth steps and edges difficult.

The experiments described above show the conditions of the thin surface layer formation and their connection with the generation of growth steps on crystal edges. At the same time the most important part of the process remains unexplained: this is the mechanism of thin layer formation itself. Our experimental results clearly show that the surface layers can freely move without the existence of previous layers of the same orientation under them. The most unexpected finding is that the growth velocity of these layers has the same order of magnitude as the tangential growth rate, V, of a dislocation step. The direction of the measurements made on the (101) face of a KDP crystal during the process of thin layer formation is shown in Fig. 6, a. The comparison was done with the tangential growth rate, V, measured in [17] on the steepest slope of a dislocation hillock of a pyramidal face because of the same step orientation parallel to the [100] edge. Our estimations give us measurements for the velocity of the thin film advancement from $1 \bullet 10^{-4}$ to $4 \bullet 10^{4}$ cm/s for a temperature of 30°C and σ about 0.09, while the value of V from [17] is $7 \bullet 10^{-4}$ cm/s, for about the same growth conditions. The measurements done in another experiment at 60° C gave higher values of about $1 \bullet 10^{-3}$ cm/s at approximately the same supersaturation. A direct comparison is difficult to do because of the low precision of our macroscopic measurements. We also have to take into account a possible effect of hydrodynamic conditions (kinetic flow in the small cells and diffusional-kinetic regime in the big crystallizers). A surprising result of this comparison shows that the normal bonds with the underlying half-crystal do not have any large influence on the growth kinetics in the surface layer.

All these facts can not be explained within this experimental work. The mechanism of growth of thin surface layers requires more detailed consideration and we hope, will be the subject of future work. Simple models presented in Fig. 7 are far from a full description of the growth phenomena in the surface layer. Nevertheless, they already can be used to understand some

peculiarities in the surface structure of real crystals, which have been observed and could not be explained previously.

4.2. Step generation from the edges during growth of bulk faceted crystals

In an ideal case, when a KDP crystal grows on a point seed, vicinal hillocks form in the middle of each face on screw dislocation bunches originating from the seed (Fig. 1). In this situation, despite the presence of vicinal slopes on each face, approximately parallel growth steps coming from adjacent faces would meet at any crystal edge without causing a deviation of the crystal edges from their singular orientation or conditions for step formation on the edges. In real crystals, due to such factors as asymmetry of the seeds, differences in the growth rates and the possibility of formation of new dislocations during growth, vicinal hillocks usually are located on faces in asymmetric positions. In this case the orientation of the elementary and macrosteps coming under an angle to a crystal edge should lead to the formation of places of preferable incorporation of the building units on the edges (Fig. 7, b).

One of such situations is presented schematically in Fig. 8 where a dislocation hillock is located in an asymmetric position close to a crystal apex. If we assume that all other crystal faces have singular orientations or symmetrically located growth hillocks, it will not be hard to see that the difference between the cases presented in Fig. 4 and Fig. 8 are determined only by the quantitative level of the deviation. Vicinal slopes 1 and 2 generated by the dislocation hillock O (Fig. 8, a) preserve the singular orientation of the edges on their parts KA and KB. At the same time vicinal slope 3 produces a deviation of the edges below the points A and B and a shift of crystal apexes C and D to the positions C_1 and D_1. The steps of the dislocation slope 3 at their intersection with the neighbor faces will form kinks and growth layers generated from the edges AC_1 and BD_1 to the deviated face in the way shown in Fig. 7, b. Simultaneous movement of the steps generated by the crystal edges and by the dislocation results in the formation of intervicinal boundaries along the lines where they meet (AE and BF in Fig. 8, a).

The same situation will happen at any other asymmetric position of the hillock on a face, when the steps of a vicinal slope cross a crystal edge under some angle. These boundaries usually originate at the points where the edge of a dislocation hillock crosses the crystal edge (Fig. 8, b). Their configuration can be different depending on the deviation of the edges produced as a result of the mutual position of the hillocks on the adjacent faces (Fig. 9). When crystals are grown from pure solutions at moderate growth rates the intervicinal boundaries are hardly distinguished under the microscope. In the case of large macrosteps formed under the influence of impurities and non-uniform flow, and big deviations caused by very steep hillocks, the intervicinal boundaries become more visible. In rapidly grown crystals it is especially clearly pronounced on the prismatic faces which usually have steep vicinal hillocks and grow with the formation of large macrosteps.

Fig. 10 presents schematics and photos of some surface configurations at dislocation hillock positions typical for prismatic faces of KDP crystals rapidly grown on a point seed. The natural deviation caused by the vicinal slopes corresponds to the case of artificial deviation presented in Fig. 5. The destruction of the crystallographic shape of the adjacent faces stimulates the initial nucleation on the stepped edges ADK and BFM (Fig. 10, a) in the same way as described in Fig. 5 and Fig. 7. This process produces typical intervicinal boundaries (Fig. 10, b and photo 1) originated in the place of the intersection between the hillock and crystal edges. At high growth rates on very steep hillocks the layers generated on the horizontal [100] edge can be also clearly seen (schematic and photo 2). Large macrosteps which do not coincide in height and width result in layers generated on the edge between the deviated faces NL, similar to the case shown in Fig. 7, d.

A consideration of the mechanisms of step generation on crystal edges leads us to a very interesting conclusion about the function of growth from the edges. We can say that during bulk crystal growth it works as a response to the dislocation mechanism. The more the dislocation growth deviates the crystal from its crystallographic shape, the more active become the edges in their tendency to correct it.

In the real dynamic process of bulk crystal growth there can be many variations in the number, steepness and mutual position of the growth hillocks on all faces. This leads to the formation of various, sometimes very complicated, intervicinal boundaries produced by the growth generated from the crystal edges to the deviated faces. Such complicated structures often can be accompanied by formation of solution inclusions (Fig. 11).

The fact that large inclusions, formed by growth layers visibly moving from the edges very often appear only on one face, while other crystal faces remain perfect is difficult to explain by the supersaturation gradient along the face. In the symmetric flow used in the present work, this gradient should be about the same for all crystal faces. Our observations show that the inclusion process is always connected with the surface structure: rough and sudden inclusions usually form on the largest, the most deviated face with an asymmetric position of a growth hillock. Such inclusions often “heal” and never appear again under the same hydrodynamic conditions. Formation of thin layers on the deviated edges and their ability to spread above the dislocation vicinal slopes can be an explanation of this phenomenon.

This mechanism most likely worked during the formation of solution inclusions in the first crystals grown in the 1000 l crystallizers. Extraneous particles produced by large-scale equipment led to a high dislocation density in the crystals. Under these conditions the leading dislocation hillocks were typically located in an asymmetric position on the faces close to the crystal apexes and edges. This fact resulted in a large deviation of the edges from their crystallographic orientation and in highly pronounced growth from the edges. The use of continuous filtration allowed us to perform the growth on the dislocation hillocks formed during the regeneration of the point seed. The location of these hillocks in the center of the faces during the entire growth process [18], together with the purification of the initial salts and improvement in hydrodynamic conditions, became one of the most important conditions for obtaining large inclusion-free crystals.

The mechanism of thin layer formation can also be important in the consideration of the structure of the overhanging layers during the morphological instability on the macrosteps of the

same dislocation vicinal slope. Based on our results, formation of the thin overhanging layers can more likely be initiated by the presence of concave angles on the singular facets of these macrosteps, rather than by two-dimensional nucleation on their upper edges [19]. This mechanism can be related to the nature of "channel" or "hair" inclusion [20] and play the main role in the phenomena of tapering. All these problems require further investigation as well as the need to test these mechanisms on crystals of different structure and symmetry. The well known fact that the regeneration of seeds with incomplete shape occurs by formation of box-like structures for many crystals, together with the observations made on the surface of a crystal with different symmetry (monoclinic DKDP), allows us to believe that these phenomena might be common for all faceted crystals.

5. Conclusions

The experiments described in the present work show that growth phenomena on one separate face can not be fully understood without consideration of the processes happening on the other faces. The crystal surface should be considered as an entire system where the structure of one separate face is connected with the phenomena which take place on the other faces. This connection is provided through the crystal edges which are not passive geometrical places of meeting steps generated on separate faces, but play an important role during the crystal growth process.

Experimental results show that the mechanism of step generation from the edges of faceted crystals is connected with the formation of incomplete crystallographic shapes:

- An incomplete crystallographic shape of a singular face is determined by the existence of concave angles formed by the edges in the plane of this face;
- These concave angles are sources of growth steps in the surface layer;

- The surface layer generated from a concave angle on a singular crystal face completes the crystallographic shape of the face;
- Growth of this surface layer does not require the existence of a preceding layer of the same orientation; the velocity of its growth in the surface plane has the same order of magnitude as the tangential growth rate of a dislocation step.

During the growth of faceted crystals this mechanism works in combination and in addition to the dislocation mechanism of growth:

- Dislocation sources of steps form vicinal slopes which lead to a deviation of the crystal faces and edges from their crystallographic orientation (singularity);
- This deviation leads to the formation of incomplete shapes of the adjacent faces;
- The reconstruction of the complete crystallographic shape of these faces occurs by the incorporation of building units into the crystal edges;
- This process results in the generation of growth steps to the deviated faces;
- The deviation from singularity caused by the presence of vicinal slopes of a crystal face is compensated for and corrected by growth steps generated from the edges;
- Growth from the edges should be common for all faceted crystals grown by the dislocation mechanism.

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Figures

Fig. 1. Crystallographic shape of a KDP crystal. Point symmetry group $\bar{4}2m$.

Fig. 2. Regeneration of KDP crystal surfaces of incomplete crystallographic shape:

a) - initial crystal with a cut part;
b) - first stage of the regeneration process;
c) - formation of a thin surface layer from a concave angle on the edge of the (101) face;
d) - formation of the (100) surface by thin layers;

t_o = 65 °C; σ = 0.08; crystal cross section about 10x10 cm^2.

Fig. 3. Formation of a single crystal surface during the joining of two crystals:

a) – initial crystals;
b) – schematic of the incomplete crystallographic shape of a common face obtained as a result of joining; dashed line corresponds to the complete shape;
c) - formation of the complete shape of the (101) face by step generation from concave angle A;
d) – surface regeneration of the opposite ($\bar{1}01$) face;

t_o = 63 °C; σ = 0.09; each crystal cross section about 5x5 cm^2.

Fig. 4. The restoration of the crystallographic shape of a crystal with a deviation of a pyramidal face from singularity:

a) – schematic of the deviation;
b) – formation of steps and terraces on the deviated face; the initial formation of the thin layers can be seen on the right deviated edge;
c) – reconstruction of the adjacent faces by growth steps generated from the deviated edges;
d, e) – successive stages of the reconstruction of singular orientation of the deviated face (011) by formation of thin surface layers;

t_o = 65 °C; σ = 0.08; crystal cross section about 10x10 cm^2.

Fig. 5. The restoration of the crystallographic shape of a crystal with a deviation of the prismatic faces from singularity:

a) – schematic of the deviation;
b) –initial crystal with deviated faces;
c-e) – formation of the adjacent faces by growth steps generated from the deviated edges;
f) - reconstruction of the singular orientation of the deviated prismatic face by formation of thin surface layers generated from the edges;

t_o = 64 °C; σ = 0.08; crystal cross section about 6x6 cm^2.

Fig. 6. Schematics of transition of the surface layers to the adjacent faces. The faceted edges of the layers generated on the incomplete faces produce the incomplete shape and segmented edges on the adjacent faces:

a) – segmented edge FC_1D_1E in the plane of (100) face produced by the faceted edge CC_1D_1D of the surface layer which belongs to (101) face (corresponds to Fig. 2);

b) - segmented edge and a missing part C_1B_1F in the plane of the opposite pyramidal face $(\bar{1}01)$ produced by the faceted edge CC_1B_1B of the surface layer of the common (101) face (corresponds to Fig. 3). Formation of box-like structure in the front right corner (shaded) will complete the full crystallographic shape of the new single crystal.

Fig. 7. Schematic illustration of the process of step generation from crystal edges:

a) – different location (positions 1 and 2) of the preferential incorporation of building units;
b) – step generation from the deviated edges;
c) - edge (CD) configuration which does not produce growth steps;
d) – edge configuration which produces step generation to both adjacent faces.

Fig. 8. Formation of intervicinal boundaries resulted from step generation on crystal edges at asymmetric position of a dislocation hillock on (101) KDP face:

a) – schematic of the deviation of edges caused by the vicinal slope 3 of a dislocation hillock O; AE and BF - intervicinal boundaries originated from the points of intersection of crystal edges by the edges of the vicinal hillock;
b) – same in the different position of a dislocation hillock;
1 and 2 - microscopic photos of the vicinal boundaries AE shown on the schematics; steps are generated from the edges KC;

As grown surface corresponds to t = 26 °C at σ=0.07; $R \approx$12 mm/day .

Fig. 9. Microscopic photos of typical surface configurations formed as a result of step generation from the edges with the schematics of the deviation produced by the vicinal slopes of dislocation hillocks on pyramidal faces of KDP:

a) - t = 25 °C at σ=0.06; $R \approx$10 mm/day

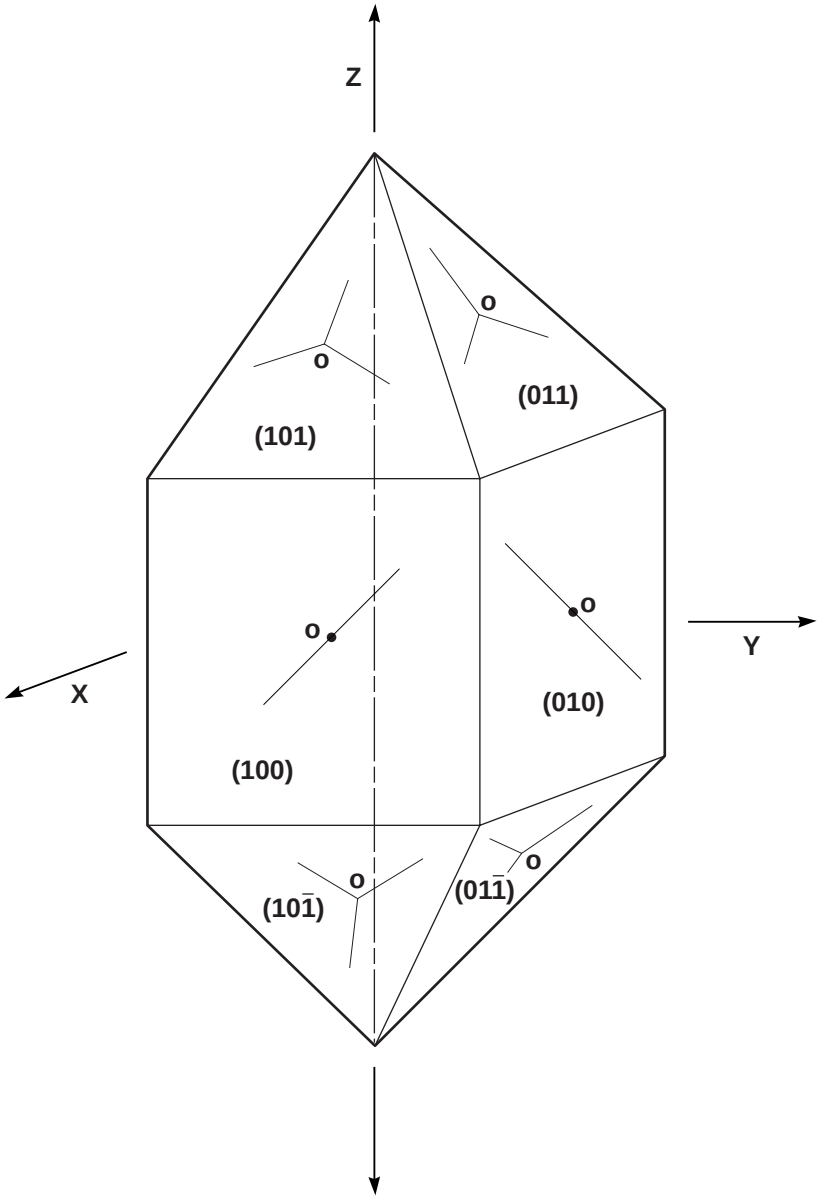
b) - t = 23 °C at σ=0.03; $R \approx$3 mm/day.

Fig. 10. Intervicinal boundaries and growth steps generated from the edges on prismatic faces of KDP:

a) - schematic of the deviation caused by the vicinal slopes of dislocation hillocks O;
b) - typical intervicinal boundaries between the steps generated on dislocations and crystal edges;
c) - microscopic pictures of the locations shown on schematic b):
1 - typical boundary (AE) originated from the point of intersection of the crystal edge by the edge of the vicinal hillock; steps are generated from the edge AD;t = 26 °C at σ=0.06; $R \approx$ 7 mm/day;

2 - growth steps generated from the edge NF; t = 24 °C at σ=0.09; $R \approx$10 mm/day;
3- growth steps generated from the edge NL to both prismatic faces (see Fig. 7, d);
t = 23 °C at σ=0.06; $R \approx$ 6 mm/day.

Fig. 11. Surface structures of pyramidal (a) and prismatic (b) faces of KDP crystals with rough solution inclusions resulted from the interference of the growth layers generated on dislocation hillocks in asymmetric position and crystal edges. On schematic (a) one can see a connection between the vicinal structure of the adjacent faces. Crystal length about 25 cm.



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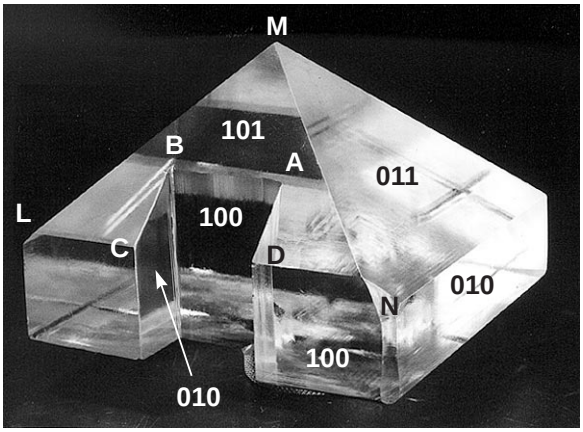

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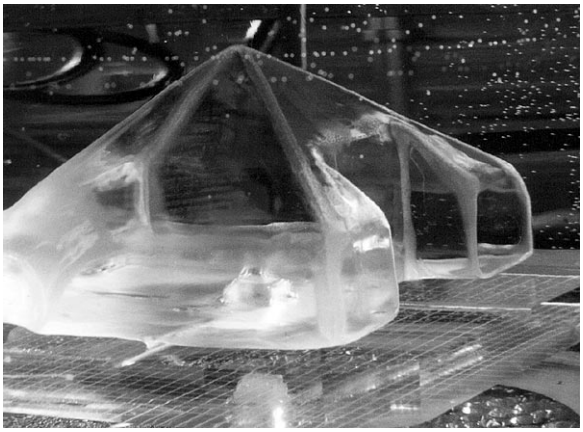

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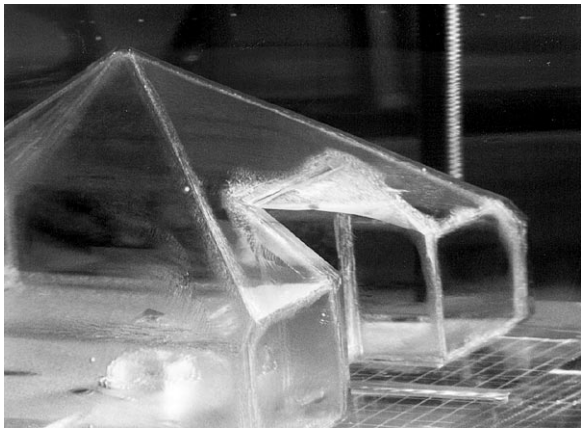

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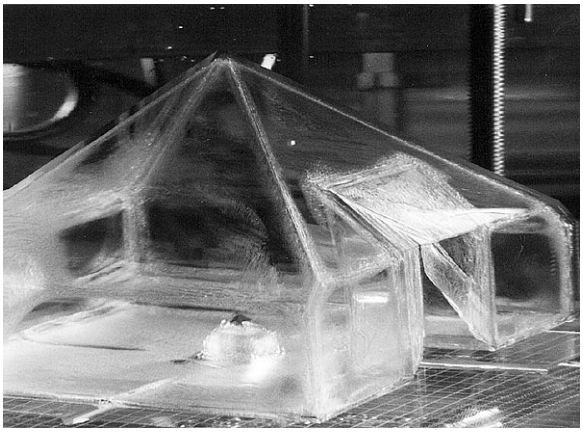

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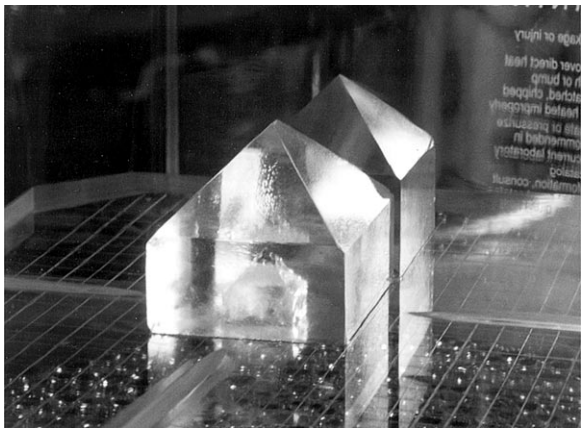

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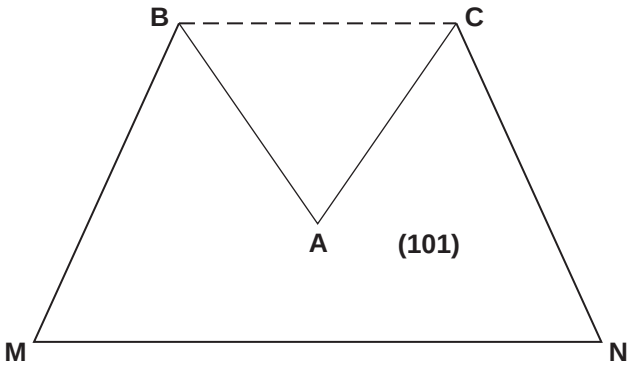

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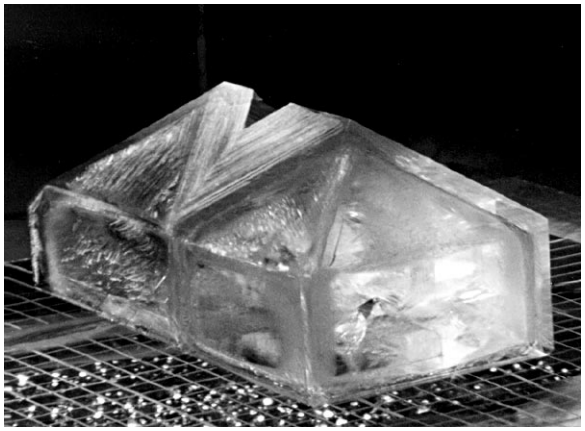

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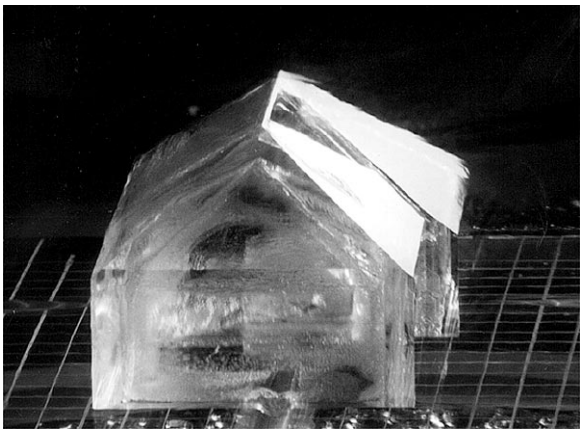

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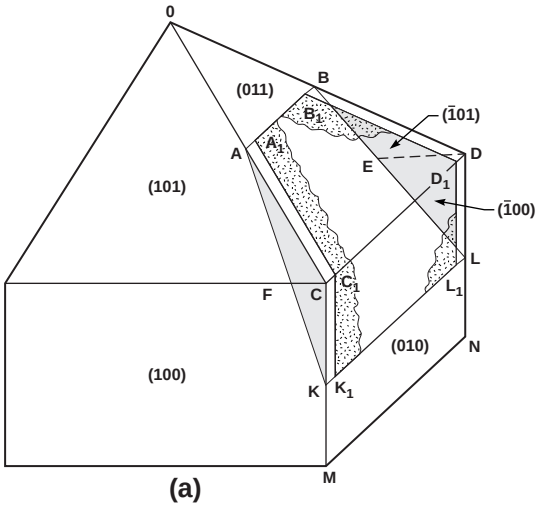

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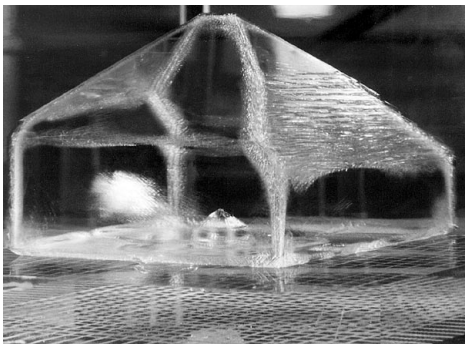

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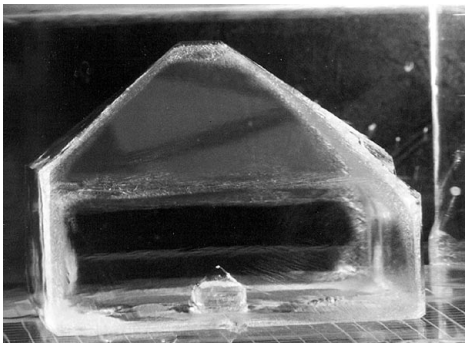

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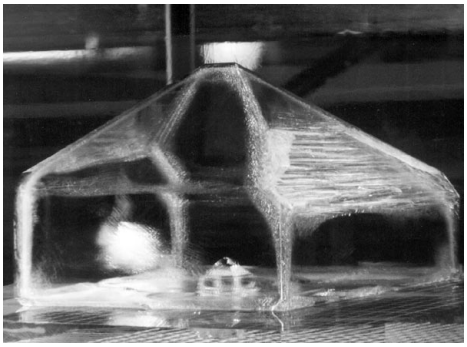

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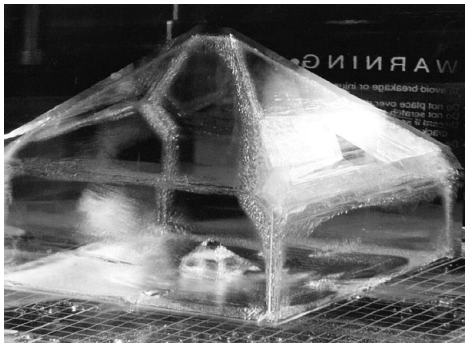

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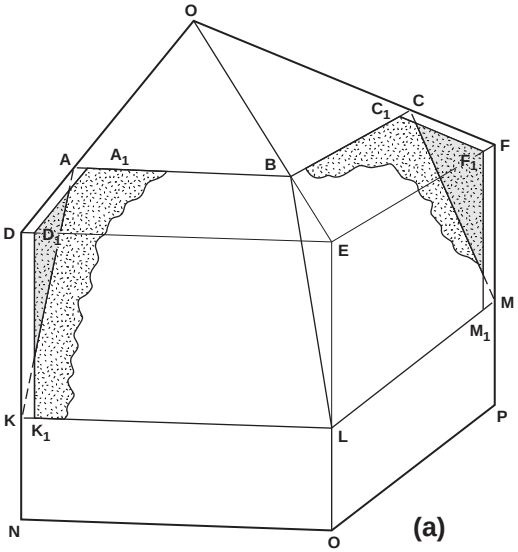

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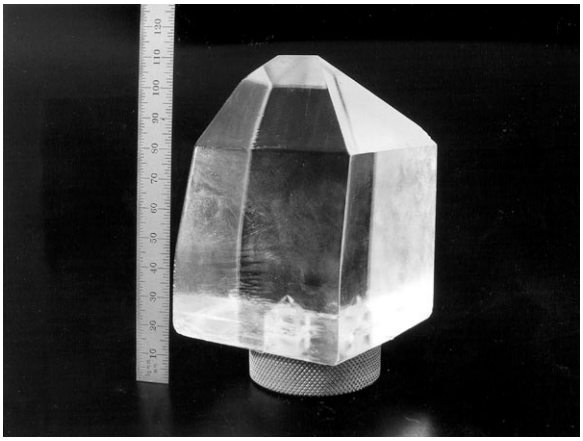

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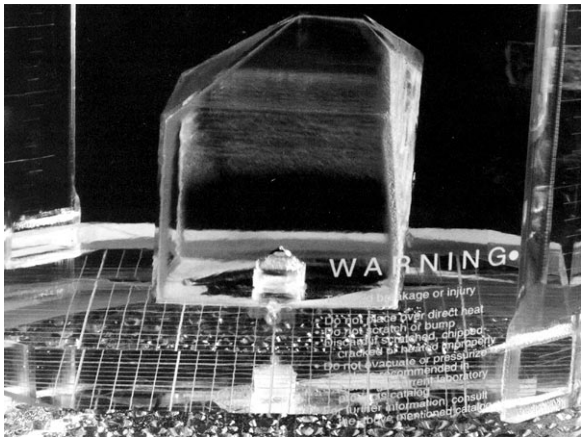

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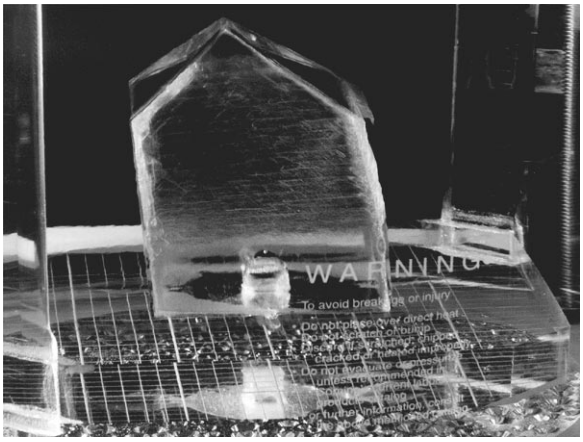

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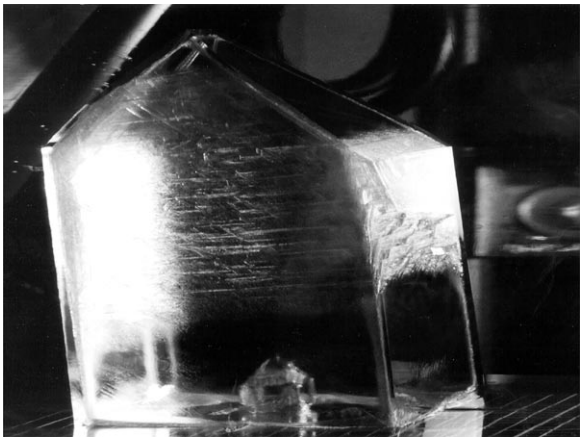

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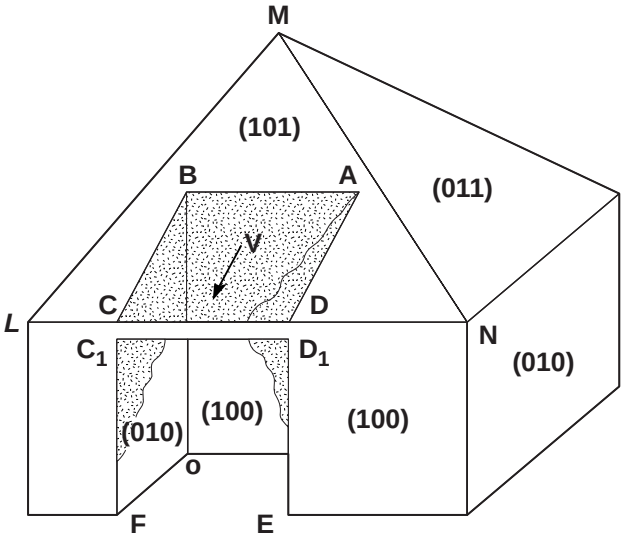

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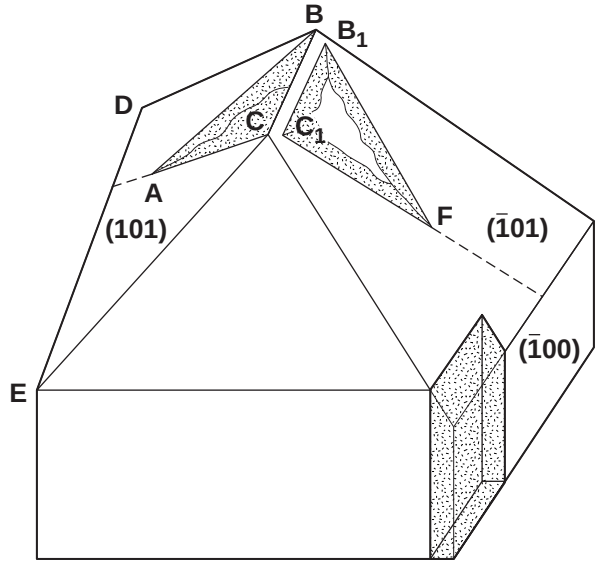

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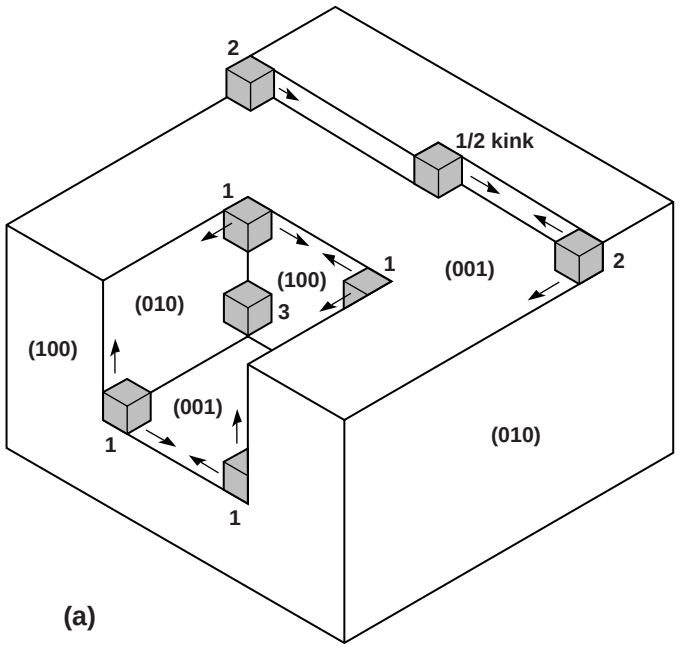

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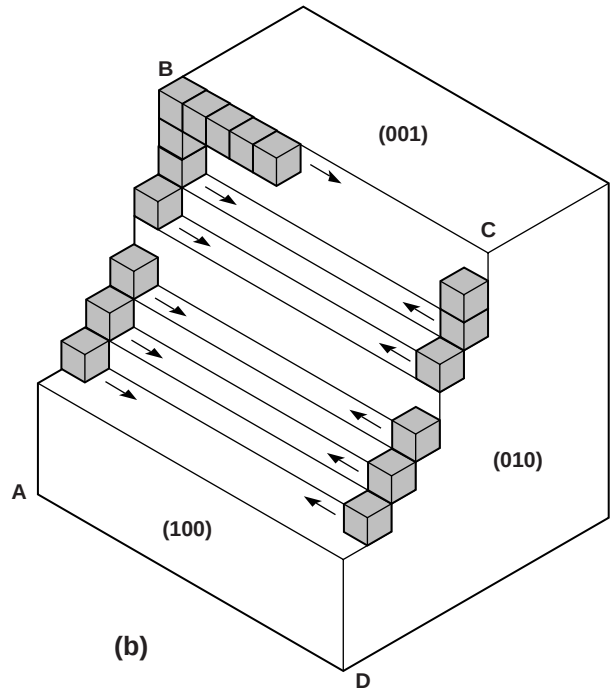

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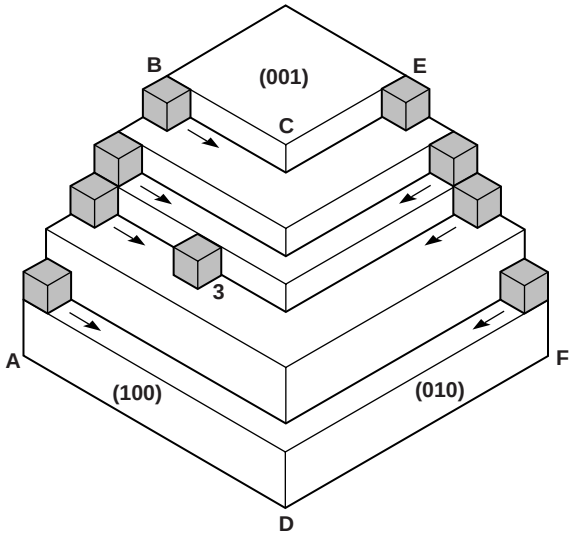

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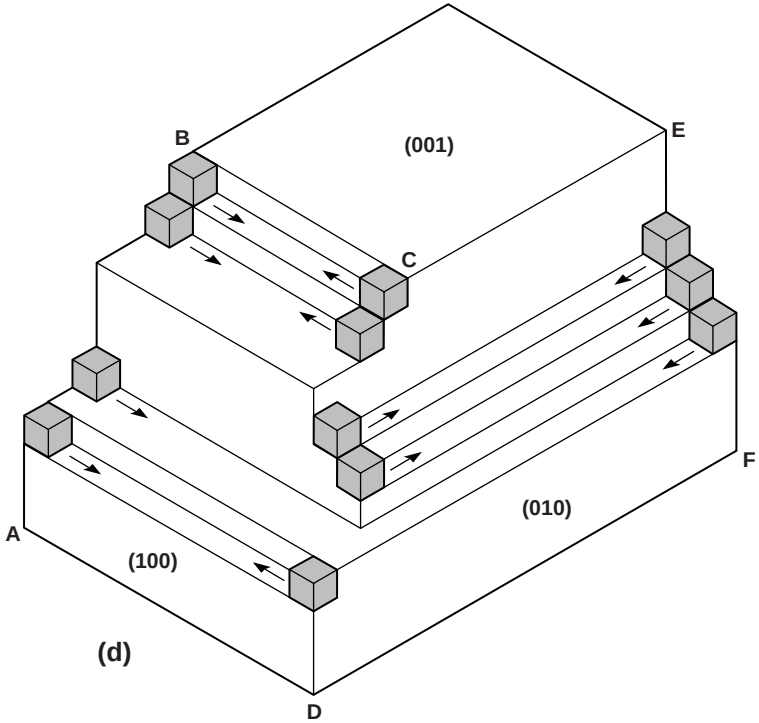

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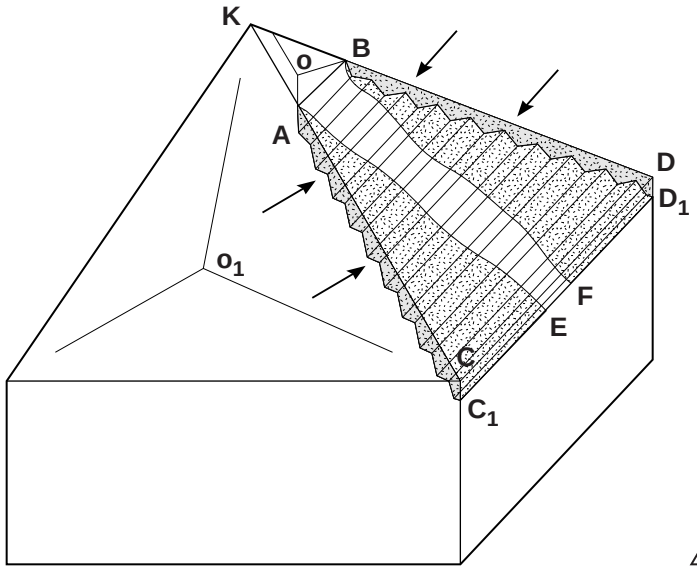

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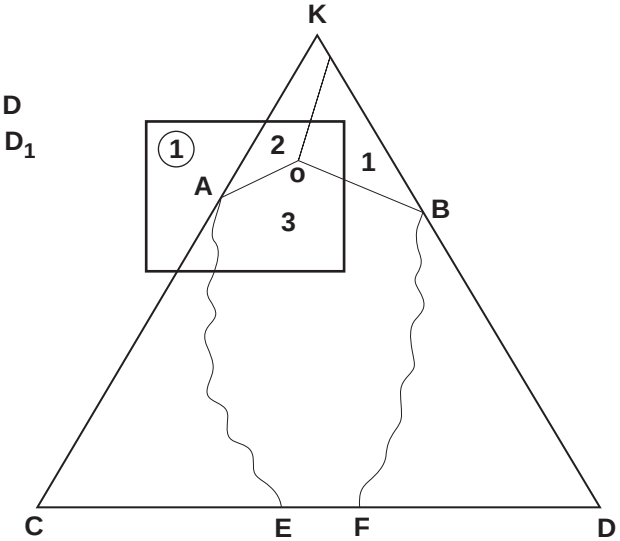

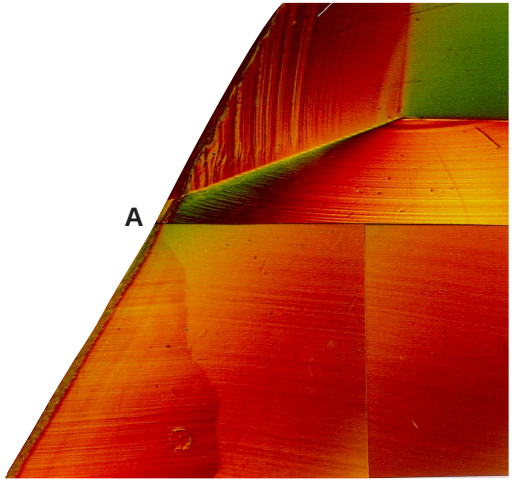

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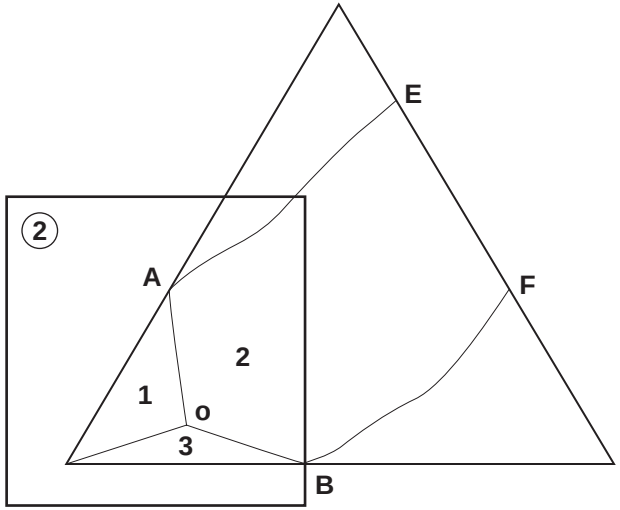

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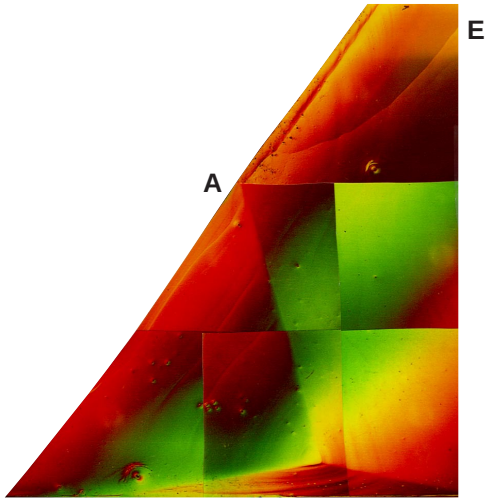

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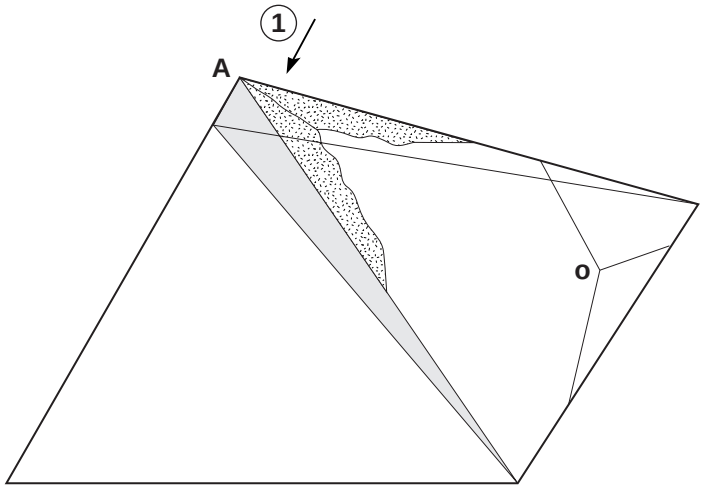

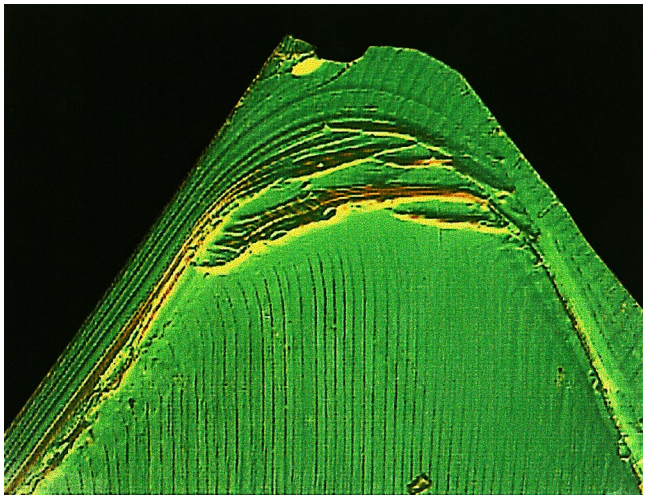

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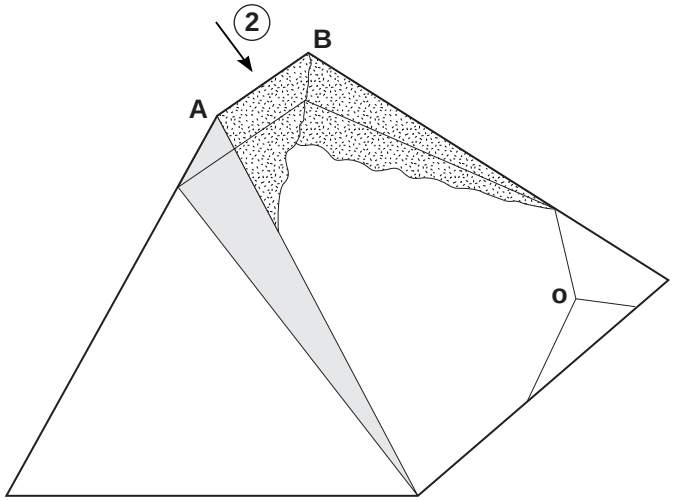

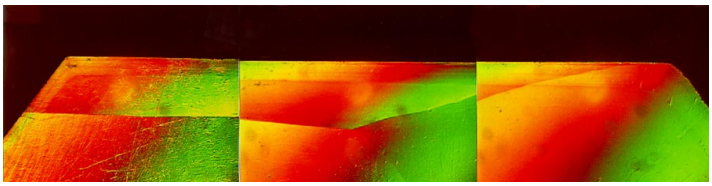

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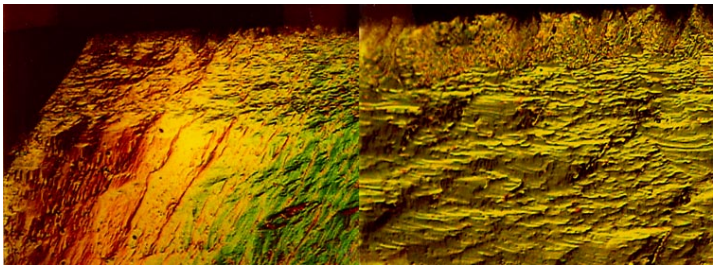

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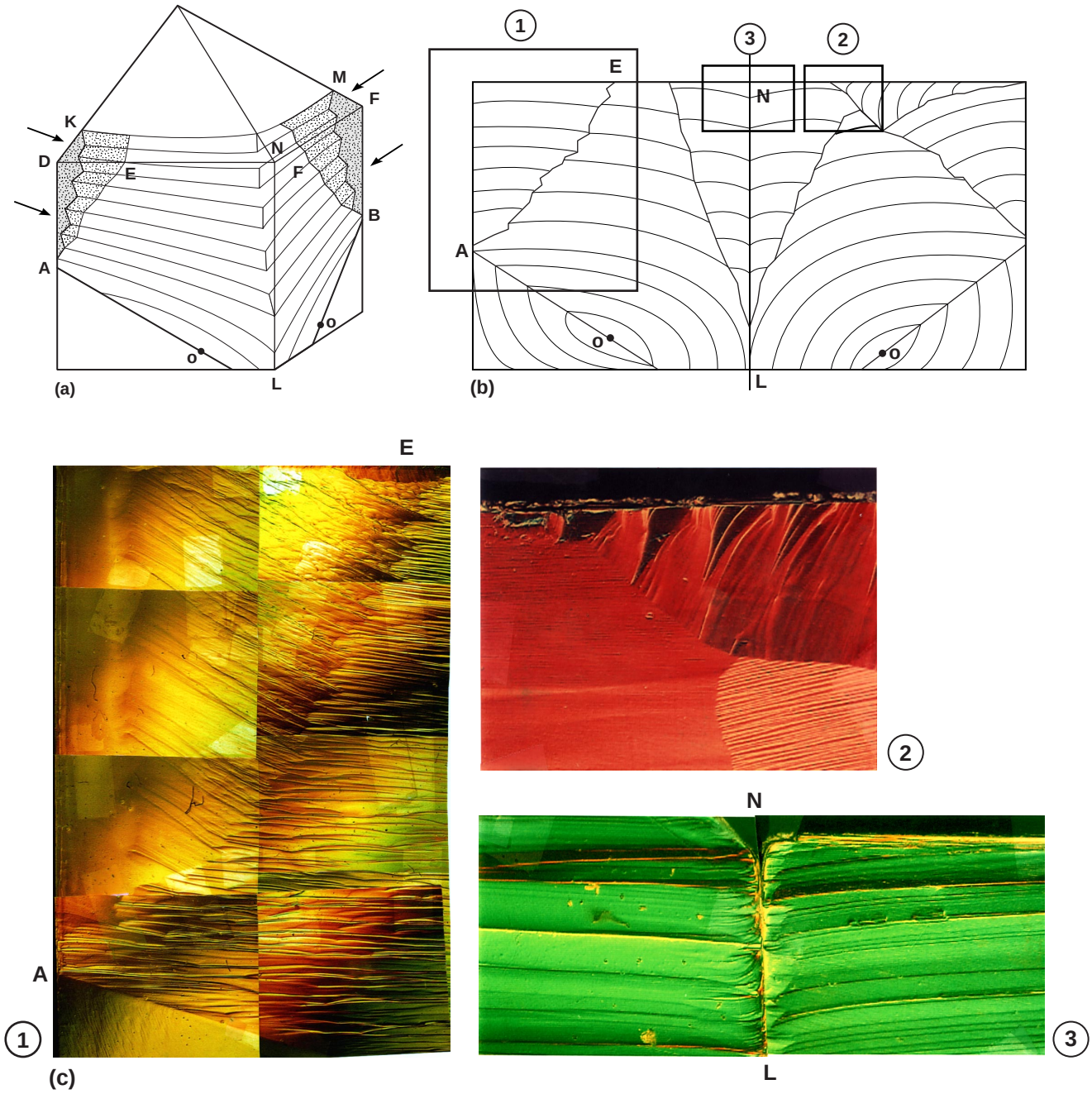

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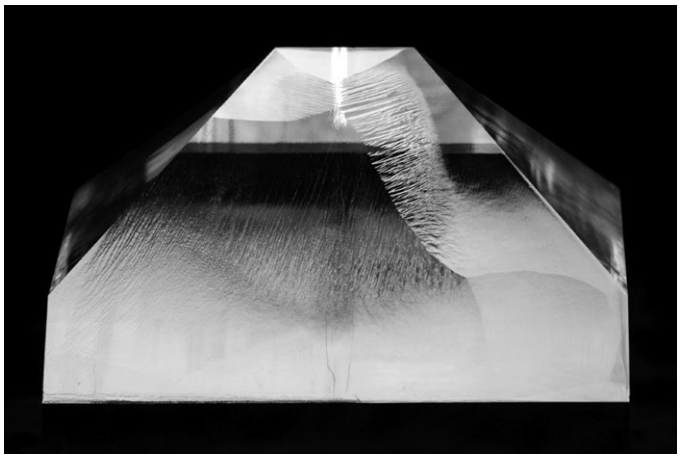

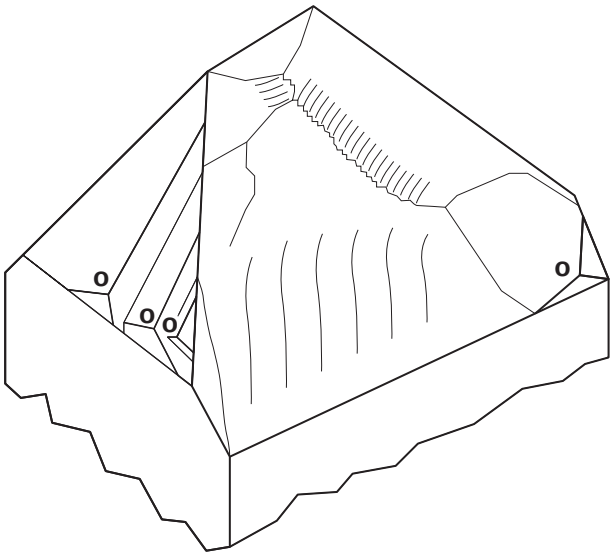

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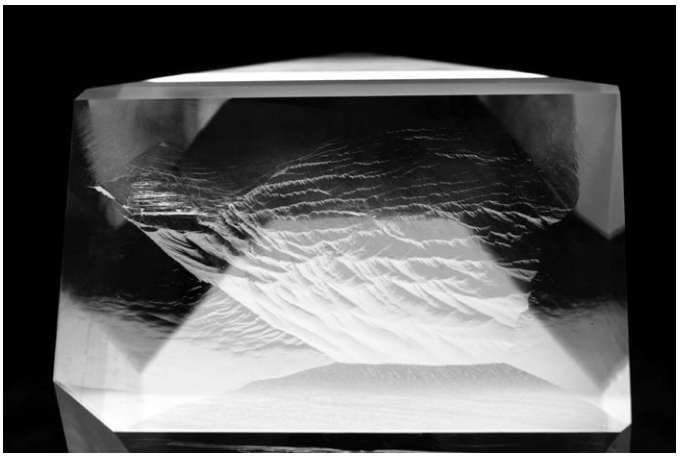

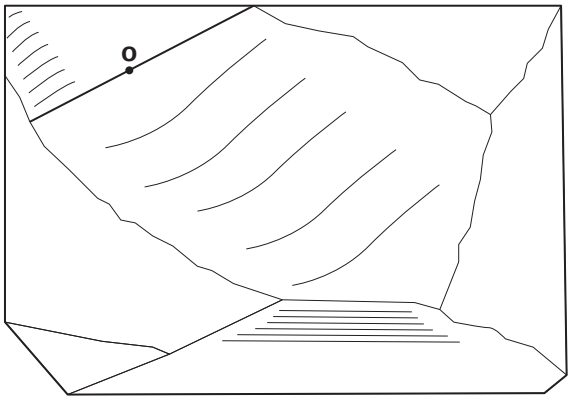

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