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Review
Morphology of hollow crystals of II-VI compounds

S. SIMOV
Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

Published data on hollow crystals of II-VI compounds are reviewed. The experimental conditions for obtaining hollow crystals are discussed and presented systematically in tables. Some inferences concerning the effect of impurities, supersaturation, type of substrate and other factors on the growth of hollow crystals are made. Particular attention is paid to the structure, form and defects of hollow crystals and it is established that they can be classified in the following groups: hollow hexagonal columns and prisms, hollow pyramids, hollow crystals with spiral-like hexagonal form and hollow crystals with a more complex structure consisting of whisker-pyramid-prism. The mechanism and kinetics of the growth of hollow crystals as presented by different authors are discussed.

1. Introduction

The relatively low level of interest in hollow crystals is probably determined mainly by the fact that they are crystallographic objects less frequently studied. Their existence, however, attracts researchers by a number of specific questions related mostly to the growth mechanism.

The research interest in hollow crystals has already stimulated experiments in their practical application. Mash and Firth [1] and Paorici [2], for instance, report on the use of cadmium sulphide hollow crystals as detectors of high energy radiation since the placing of electrodes on the outer and inner faces constitutes a very suitable geometry for this purpose.

Buckley [3] in his well-known monograph has given information on some hollow crystals. In it, by making use of earlier results [4] and some new experimental ones, he describes the growth of $KClO_3$ crystals from a solution (grown in the presence of K_2MnO_4), as well as of NH_4ClO_4 and $KClO_4$. Certain questions related to the manner and the conditions of crystal growth are discussed.

Some data on hollow crystals are found also in a series of studies on ice crystals [5–13]. These studies are typical, showing a certain dependence of the nature of ice crystals on the conditions under which they are formed, namely the temperature and the supersaturation. Under certain conditions (slightly differing with the different authors), crystals are also observed with the form of hollow hexagonal prisms.

Hollow crystals of CsCl [14], NaCl [15, 16] and of KCl [16–18] and KBr [16] are observed, grown from a solution and forming long whiskers–hollow cylinders or prisms. With metal oxides $PbO–PbF_2$ and $PbO_2–B_2O_3$ [19], crystals are obtained in the form of hoppers from a solution and a melt; with TiO_2 hollow prisms with a quadratic hollow cross section [20] and with $\alpha–Al_2O_3$ whiskers with axial pores (axial channels) [21–23]. Jayatilaka *et al.* [24] have observed similar channels in silicon nitride with the aid of a scanning electron microscope.

The growth of silver–mercury whiskers, from water solutions of salts, having the form of hollow hexagonal prisms (capillary tubes) is described by Nanev and Milchev [25], and by Nanev *et al.* [26].

Hollow prismatic crystals of $\beta–SiC$ have been observed and studied by X-ray methods by Tomita and co-workers [27–29].

Among the F_2SiO_4 skeletal crystals described

TABLE I

Source	Gas medium	Flow speed	Source temperature (° C)	Growth temperature (° C)	Time of growth	Initial material	Impurities	Peculiarities of equipment and method	Form and size of hollow crystals
[1]	N_2	25 litre min^{-1}			20 h		Na, K	Two-element furnace $l \simeq 60$ cm. Substrate, Si; diameter 35 mm	Hollow cones with $l \simeq 2$ cm and thickness of the walls $d \simeq 0.5$ to 1 mm
[2]	H_2 without O_2 and $H + H_2S$	H_2, 12 to 20 cm^3 min^{-1} H_2S, 5 to 10 cm^3 min^{-1}	1140		20 h	CdS–powder	NaO.3%	Furnace with 1 heater and silica tube, diameter 6 cm. After Frerix	Hollow hexagonal pyramids $h = 4$–8 mm, diameter ≈ 2–3 mm and hexagonal prisms
[35]	Ar		650 of Cd	900–950			Ga 0.1% or In 0.1%		Hollow hexagonal columns
[36]	Ar	Dynamic and static methods $P \simeq 1$ atm	980–1000		30–40 h	99.99% 99.999% CdS	O_2 and oil vapour	Silica tube with dynamic and static regimes. Horizontal kanthal wound furnace	Hollow prisms with diameter = 2–3 mm and $l \simeq 8$ mm with light yellow to dark brown colour. Wurtzite structure c-axis parallel to l
[37]	$H_2 + H_2S$ /2:1/		1150	940	13 h	99.999% CdS powder		Silica tube with $l = 90$ cm and diameter 5 cm	Hollow prisms with $l = 3$–10 mm and diameter 0 = 0.5–2.5 mm with dark-red and orange colour
[38]	H_2S			860–890	4–7 days		Cu 33 000 ppm		Hollow cones with hexagonal structure determined by X-ray diffraction
[39]	H_2S N_2			1050	10 h	10 g CdS 0.5 g CdI_2		After Frerix and in vacuum	Hollow cones with $l = 0.2$–12 mm and angle of cone 12–20°. Structure 2H determined by X-ray diffraction $a = 4.14$, $c = 6.72$ Å
[40]	H_2S $P = 500$–530 Torr	Static method	950	900	140 h	CdS–powder	Na and K, 3 ppm; Ag, Cu, Mg, Si, 1 ppm	Hollow crystals grow on quartz wool	Hollow prisms
[41]				830					Hollow prisms with diameter $\simeq 0.5$ mm and $l \simeq 1$–6 mm
[42]	Ar at atm pressure	1 cm sec^{-1}	1100	900				Quartz tube with diameter 7 cm; two zone furnace	Hollow needles with diameter 1.2 mm, growing parallel to ⟨0 0 0 1⟩
[43]	Ar	Static method $P = 35$ kg cm^{-2}	1580					Growth from melt in Ar atmosphere at pressure 35 kg cm^{-2} speed of cooling, 200° C h^{-1}	Hollow spial-like crystals with $l \simeq 5$ mm and diameter 2 mm, walls with $d = 200\mu$m

by Kirov and Ivanov [30] a tubular form is also observed. In pure metals only Nanev and Ivanov [31] have observed hollow pyramidal forms of zinc skeletal crystals.

With hydrothermal crystallization small hollow needles are obtained [32] from selenium; from NiF_2, hollow crystals having the form of hollow rods [33], and from SbS_3, hollow prisms [34].

It is evident from the articles mentioned so far that hollow crystals are obtained by various methods, from different substances and vary greatly in their properties. The number of studies concerning hollow crystals from a given substance is rather limited and no articles are found dealing with the general features of hollow crystals.

Passing to hollow crystals from II–VI compounds which are the subject of the present review, the state of research is little different. The greatest number of studies published is on hollow crystals from CdS [2, 35–43] and ZnO [44–48]. There are reports for ZnSe [48, 49], CdTe [50, 51] ZnS [53–55] and single reports for CdSe [52], and HgSe and HgTe [56].

2. Experimental conditions for obtaining hollow crystals

As an illustrative example, the results on CdS hollow crystals published in the above-mentioned articles are given in Table I, which shows data characteristic of the experimental methods and the form of crystals obtained. As the table shows, CdS hollow crystals obtained from a vapour phase grow over a quite wide temperature range with source temperatures of 950–1150° C and temperatures of 830 to 1050° C in the zone of growth. Great differences are found between the various authors as regards the type of gas used and the flow speed, as well as the time taken to obtain the crystals. The equipment used for obtaining hollow crystals also differs substantially with the various authors.

The data on hollow crystals obtained from other II-VI compounds are presented in Table II.

The tables point to the fact that, apart from the crystals obtained from a melt by Fujisaki *et al.* [43] and by flux techniques by Kumar [47], hollow forms are obtained from a vapour phase in all other cases. Other methods, e.g. condensation in vacuum, are not used. This might be due to the fact that methods employing a vapour phase create conditions favourable for the growth of hollow crystals (or alternatively that experiments using other methods have so far not been carried out).

3. Effect of impurities on the growth of hollow crystals

A number of authors [2–4, 35–40, 52, 53, 55] have obtained hollow crystals in the presence of impurities of Ga, In, I, Na, Cu, O_2, Mn, etc. Some of them even consider that the presence of impurities favours the production of hollow crystals. For instance, Mash and Firth [1] consider that Na and K impurities assist their growth, establishing that they are not obtained with ultra-pure material. The same authors believe that oxygen is not necessary for the achievement of CdS hollow crystals. On the other hand, Soxman [53] (based on Buckley [3] considers that impurities account for this type of structure in ZnS, assuming that atmospheric oxygen acts as an impurity. Kumar [47] links the growth of ZnS hoppered hollow crystals with the presence of a supersaturation gradient and impurities. Dreeben [40] observed CdS hollow crystal growth at concentrations of Na < 3 ppm and Ag, Cu, Mg, Si < 1 ppm. By neutron activation analysis Paorici [37] shows that among the CdS crystals with various crystal forms, obtained under the same conditions in an iodine atmosphere, hollow crystals have an iodine content smaller by one order of magnitude.

Contrary to the results obtained on the effect of impurities on CdS hollow crystal growth, Paorici again [52] establishes that hollow crystals are obtained from CdSe without the addition of impurities. Sharma and Malhotra [36], Park and Reynolds [44], Sharma [45], Sharma and Kashyap [46], Iwanga and Shibata [48], Simov *et al.* [51], Soxman [53], Kume *et al.* [54] and Cruceanu, Niculesku and Vancu [56] have also obtained hollow crystals, apparently without impurities.

In the studies discussed, the effect of impurities is assessed primarily from the point of view of the empirical result and is not linked with the growth mechanism. As Buckley [3] notes in his discussion, it is not yet known whether the periodicity of the crystal emerging with the introduction of impurities is determined only by changes in its physical properties or whether it is dependent on some more complex mechanism.

The contradictory experimental results show that probably impurities have some effect on the

TABLE II

Material and source	Gas medium	Flow speed	Source temperature (° C)	Growth temperature (° C)	Time of growth	Initial material	Impurities	Peculiarities of equipment and method	Form and size of hollow crystals
CdTe [51]	Ar	0.2 litre h^{-1}	760–780	530–545	3h	99.999%			Hollow prisms with l = 20–100 μm and diameter 5–20 μm
CdSe [52]	Ar	8–10 litre h^{-1}	1048 ± 1	700–750	8h	99.999%	Na, Ga, In	Quartz tube with diameter 2 cm and l = 12 cm	Hollow prisms with l = 8–12 mm and diameter 0.4–2.5 mm
ZnS [53]			1150–900–400			10g luminescent powder		Double crucible method	Hollow pyramids and prisms with l = 1 mm and hexagonal structure a = 3.84 Å, diameter ⩽ 0.4 mm
ZnS [54]	Ar:H_2 = 95:5 (volume)	Closed system P = 160–260 Torr at 80° C	1280–1190	1190	20h	99.999% ZnS powder 7–10g		Method of pulling sealed tube. Quartz tube sealed, l = 200 mm diameter 20 mm. Pulling rates 2.8–3 mm h^{-1}	Hollow needles-hexagonal prisms with l = 7 mm and diameter 0.5 mm, thickness of the walls d = 0.1 mm. Structure 2H
ZnS [55]	N_2: H_2S: HCl = 1:9:6 well dried	2–20 cm^3 sec^{-1}	1300–1400		30h		$CuCl_2$ and $MnCl_2$ with conc. 10^{-5}–10^{-2} gMe/gZnS	Open tube-transport system with 5 zone furnace (II zone with Pt wire). Speed of cooling 0.5° C min^{-1}	Hollow prisms with l = 10–15 mm and diameter 4–5 mm
HgSe HgTe [56]	H_2 or Ar	5 litre h^{-1} and static method P = 10^{-1}–10^{-2} Torr	400 (HgSe) 580 (HgTe)	370				Horizontal quartz tube, furnace with diameter 20–25 mm. Substrates: quartz, ring-like screen	Dynamic method: crystals with l = 1–1.5 mm. Static method: hollow hexagonal prisms with thin walls; cubic structure-sphalerit, determined by X-ray diffraction
ZnSe [49]	Ar		1150	1000–800				Si substrates	Whiskers-hollow hexagonal prisms with $l \simeq$ 10 mm and thickness of the walls 0.1 mm

Table II continued

TABLE II continued

Material and source	Gas medium	Flow speed	Source temperature (° C)	Growth temperature (° C)	Time of growth	Initial material	Impurities	Peculiarities of equipment and method	Form and size of hollow crystals
ZnSe ZnO [48]	Ar O_2		1150	1100–1150		ZnSe		Oxidation of ZnSe vapour in open system of two quartz tubes and horizontal furnace	Hollow prismatic needles with $l = 5–10$ mm and diameter 0.2–0.5 mm with walls $\{1\,0\,1\,0\}$ established by etching. Hollow pyramids with walls $\{1\,0\,1\,0\}$ and/or $\{1\,2\,1\,0\}$
ZnO [44]	Ar O_2	Ar–0.5 $ft^3\ h^{-1}$ O_2 –0.1 $ft^3\ h^{-1}$	1275		16 h	ZnSe powder		Interaction of ZnSe vapour with oxygen. Quartz and ceramic tubes with diameters 2 and 2.5 in. Globar furnace	Hollow prisms with sizes 30 × 5 × 5 mm. Hollow pyramids
ZnO [45]			800–850			Zn 99.99%		From vapour phase Furnace with suitable temperature gradient	Hollow whiskers
ZnO [46]								From vapour phase. Spontaneous oxydation of Zn vapour	Hollow whiskers prisms with $l = 10$ mm and diameter 1 mm
ZnO [47]			500–600		50–80 h	ZnO 99.9%		Flux methods. In silver crucible – 11.6 g ZnO dissolved in 60 g KOH at 200° C. Heating in furnace. KOH flux is dissolved in CH_3OH or H_2O	Hollow needles with $l = 6–7$ mm and diameter 0.4 mm yellow colour

growth of hollow crystals, although the lack of systematic studies does not yet allow any definite inference in this respect. The fact that the purposeful experiments of Paorici [52] have shown that hollow crystals emerge also without impurities is an indication that they are probably an important though not necessarily an essential factor.

4. Effect of supersaturation and type of substrate

In most cases hollow crystals are obtained on the walls of the silica tube and there appear to be no studies aimed at investigating the effect of the substrate. Dreeben [40] has obtained CdS hollow crystals on a substrate of quartz wool, considering that the particularly suitable nucleation centres formed by it are important for a formation of this type. Mash and Firth [1] have used Si substrates on which CdS hollow crystals have been grown. Cutter and Woods [49] have also obtained ZnSe hollow crystals on Si substrates.

Supersaturation as a basic factor in hollow crystal growth has been left without much attention in the literature. Woods [35], and Chandrasekharaiah and Krishna [39], note that CdS hollow columns grow at higher supersaturation which is also observed with ice hollow crystals [13]. A similar conclusion is reached by Lendvay and Kovacs [55] where the observed two-dimensional nucleation on the $(0\,0\,0\,\bar{1})$ plane is assumed as evidence for high supersaturation.

5. Structure, type and defects in hollow crystals

Hollow crystals have also been discussed by various authors according to their particular form.

5.1. Hollow hexagonal columns and prisms

Dimensions: length 1 to 30 mm, diameter 0.5 to 5 mm, Figs. 1a and 2 [2, 35–37, 40–42, 44–49, 52–54]. The outer faces are usually smooth, while the inner ones are uneven with microsteps. Woods [35] assumes that hollow hexagonal columns are probably formed from regular plates wrapping themselves around their axis. The crystals of Sharma and Malhotra [36], Paorici [37] and Dreeben [40] are hollow prismatic rods, as are those of Maeda *et al.* [41] but with the difference that inside, at the bottom of the hollow crystal, either a spinal growth structure is observed (Fig. 3a) or a consistent column grows, at the top of which a spiral appears (Fig. 3b). In some crystals

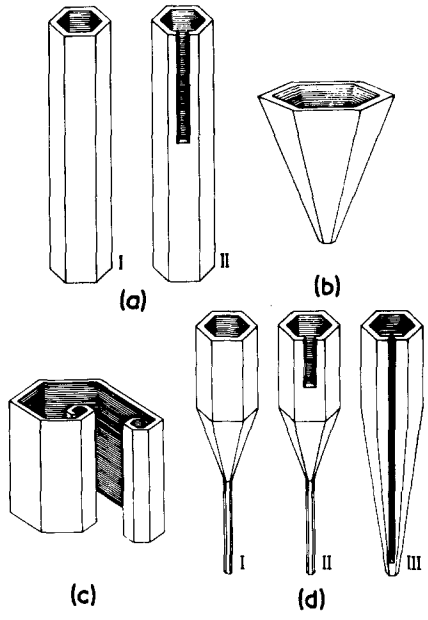

Figure 1 Hollow crystal types: (a) hollow columns and prisms, (b) hollow pyramids (cones), (c) hollow crystals with a spiral-like hexagonal form, (d) hollow crystals consisting of whisker, hollow pyramid and hollow prism.

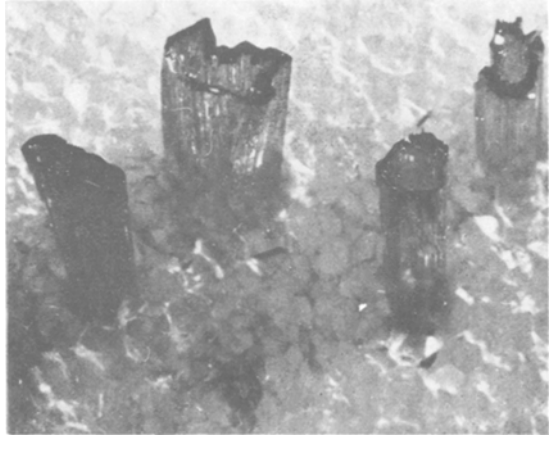

Figure 2 Hollow prismatic crystals. Dreeben [40].

clusters are observed at the bottom of the hollow.

This type of CdS hollow crystal is referred to by some authors [36, 39] as the hexagonal–wurtzite structure. Maeda *et al.* [41] have also established that the growing crystals have a $\langle 0\,0\,0\,1\rangle$ orientation. By etching procedures they have shown that the upper face of the hollow crystal is $(0\,0\,0\,1)$ and the lateral ones $\{1\,0\,\bar{1}\,0\}$ and $\{1\,\bar{2}\,1\,0\}$. Again by etching procedures, Iwanaga and Shibata [48] have found that with ZnO and ZnSe hollow crystals the prismatic faces are $\{1\,0\,\bar{1}\,0\}$ and/or

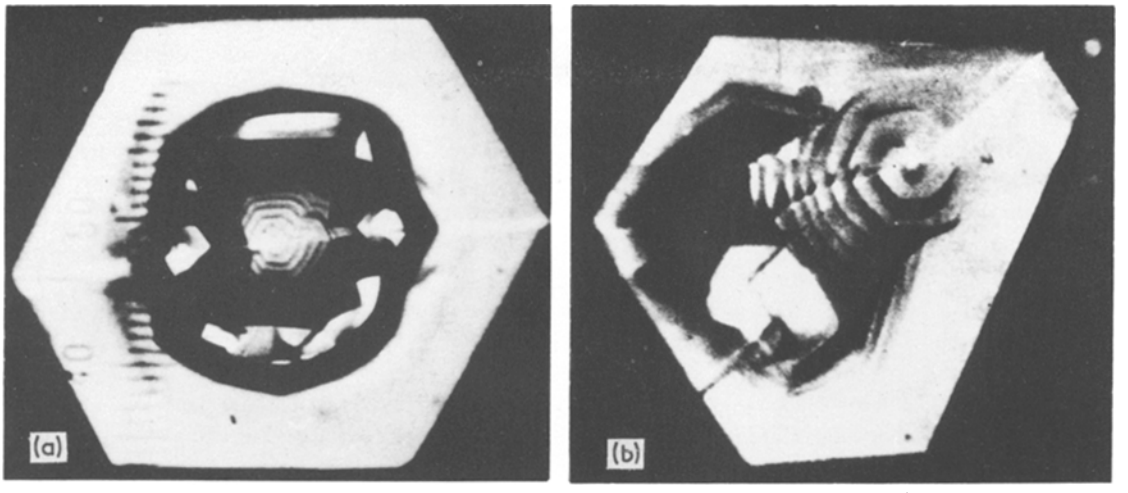

Figure 3 Growth structure with a growth spiral at the bottom of a hollow prismatic crystal (a) and a whisker grown inside the hollow crystal (b) as presented by Maeda *et al.* [41].

Figure 4 Hollow prismatic crystal with an opening in a prismatic face, after Iwanaga and Shibata [48].

$\{1\bar{2}10\}$. Wurtzite structures for ZnSe hollow prisms have also been established by Soxman [53] and Kume *et al.* [54]. Cutter and Woods [49] consider that in ZnSe hollow crystals transitions exist which alternate from one polytype to another which, according to them, accounts for the anomalous photovoltaic effect in these crystals. The presence of polytype structures also in ZnS hollow crystals has been established by Kume *et al.* [54] using X-ray methods.

The hollow crystals obtained by Cruceanu *et al.* [54] from HgSe and HgTe are columns with a hexagonal cross-section; the studies conducted by X-ray methods showing the presence of a cubic structure, of a sphalerite type only.

The hollow prismatic crystals of Iwanaga and Shibata [48] have yet another peculiarity, namely that some of them have an opening in one of the prismatic faces (Fig. 1aII and 4).

5.2. Hollow pyramids (cones)

Figs. 1b and 5 [1, 2, 38, 39, 44, 48, 53]. Their length as given by Mash and Firth [1] is 2 cm; by Paorici [2] it is 4 to 8 mm, with a diameter of 2 to 3 mm, and by Chandrasekharaiah and Krishna [39], 0.2 to 12 mm. The last two authors also

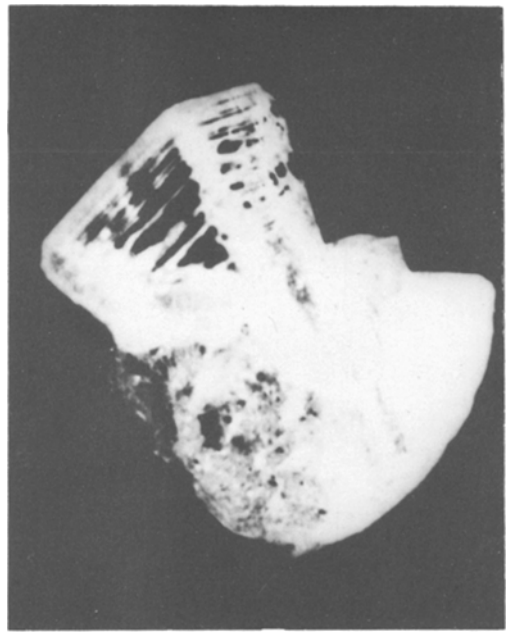

Figure 5 Hollow hexagonal pyramid after Paorici [2].

establish the angle of the cone as 12 to 20°, as well as the structure of the crystals as 2H (by X-ray diffraction). The axis of the cone here coincides with the *c*-axis. The inner and the outer

faces of these crystals carry step-like irregularities. Paorici [2] has obtained simultaneously two types of crystal – prisms and hollow pyramids – in different parts of the quartz tube, the hexagonal prisms being found nearer to the source.

5.3. Hollow crystals with spiral-like hexagonal form

Figs. 1c and 6a. Such crystals have been obtained by Fujisaki *et al.* [43] from CdS at high pressure from a melt. The Debye–Scherrer pattern shows that the structure of the crystals is hexagonal–wurtzite ($a = 4.14$ Å $c = 6.72$ Å). The planes parallel to the prismatic faces are $(1\,0\,\bar{1}\,0)$, which is established from Laue-patterns using a beam perpendicular to these faces. The thickness of the prismatic walls is up to 200 μm, and they grow parallel to the *c*-axis. On the prismatic faces striations occur parallel to the basal plane.

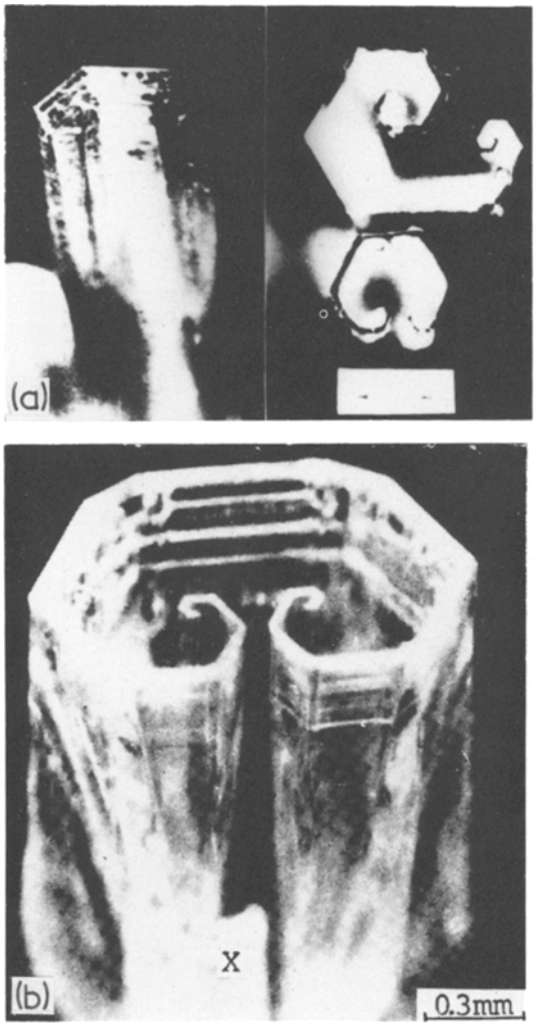

Figure 6 Hollow crystals with a spiral-like hexagonal form. (a) Fujisaki *et al.* [43], (b) Iwanaga and Shibita [48].

Similar crystals from ZnS have been observed by Kume *et al.* [54] and also by Landvay and Kovacs [55], some of them having closed forms consisting of two crystals.

The hoppered crystals of Iwanaga and Shibata [48] are quite similar to those of Fujisaki (Fig. 6b). They are from ZnO and ZnSe, having an open surrounding surface. The prismatic faces of this type of crystal are $\{1\,0\,\bar{1}\,0\}$ and $\{1\,\bar{2}\,1\,0\}$.

Hollow crystals of a more complex form have been observed in CdTe [51] using a scanning electron microscope. The crystal formation here consists of a whisker–needle connected with the CdTe layer, passing into a cone, or a hexagonal (dodecahedral) pyramid ending with a hexagonal prism (Figs. 1dI and 7a). The surrounding surface of the prismatic part can be either open (Figs. 1dII, 1dIII 7b, 7c) or closed (Figs. 1dI and 7a).

Data on the defects of hollow crystals are scarce in the literature. Fujisaki *et al.* [43], using a polarized optical microscope, have established that the spiral-like hexagonal crystals are single crystals without strains, since the Laue-patterns exhibit no streaks at all. Soxman [53] considers that the absence of asterism is an indication that ZnS hollow crystals are essentially free from strains. The absence of stacking faults, disorder and polytypism in the hoppered hollow crystals is attributed by Chandrasekharaiah and Krishna [39] to the wide temperature range in which the hexagonal phase is stable. According to these authors, polytype structures are expected at temperatures at which the free energies of the cubic and the hexagonal phases are very close.

By etching procedures, Maeda *et al.* [41] have discovered dislocation etch pits on the upper surface of the periphery of the hollow crystal. The great density of dislocations (shown through the etch pits) on the upper surface is caused, according to the authors, by thermal stresses induced by the differences between the speeds of cooling of the inner and the outer surface of the crystal. In this article etch pits, with a hexagonal form are shown on the upper face, and are assumed to be due to stacking faults on the $\{0\,0\,0\,1\}$ face. The growth spiral observed inside at the bottom of the hollow crystal, both in [41] and in [55], is related to a screw dislocation.

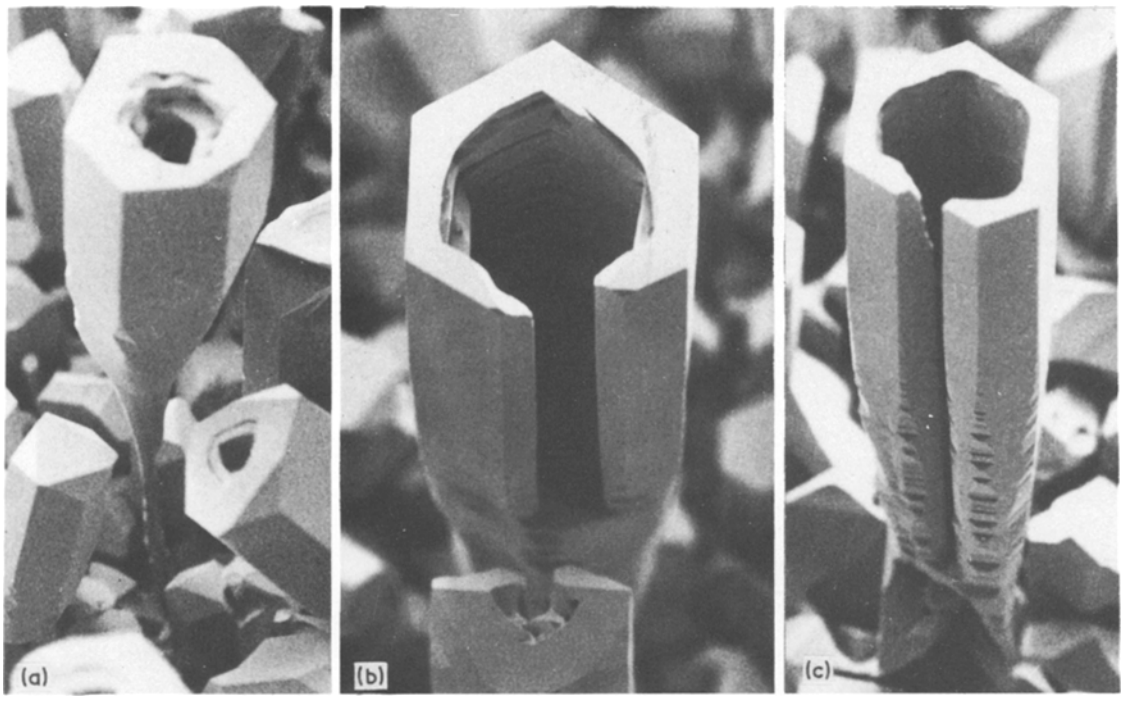

Figure 7 Hollow crystals, consisting of (a) whisker-pyramid-prism with closed and (b), (c) open surrounding surface.

It is rather difficult to make any definite inference regarding the defects of hollow crystals owing to the contradictory results obtained by different authors and to the lack of systematic studies in this field.

6. Mechanism and kinetics of hollow crystal growth

While the problems related to the methods of obtaining hollow crystals are discussed by most authors in detail, the mechanism of crystal growth has drawn rather less attention while some authors have neglected it completely.

In accordance with the views and basic principles on which they are founded the hypotheses for the mechanisms of hollow crystal growth can be classified in three groups. These are discussed below.

6.1. Growth mechanism based on the form of the nuclei

In considering the mechanism of hollow crystal growth from HgSe and HgTe, Cruceanu *et al.* [56] state only that they accept the view of Frank [57] who assumes that the dislocation theory of growth cannot explain the growth of hollow crystals and that the cross-section observed is related to the form of the nuclei. Frank [57] in discussing the growth of hollow metal whiskers from a solid phase, indeed expresses the opinion that dislocation theories are unable to explain why whiskers often have irregular cross-sections and are sometimes hollow. At the same time, however, he considers the possibility of the existence of nuclei with ring-like form to be improbable.

The mechanism suggested by Frank [57] has certain limitations as regards its application to the problems discussed here since it involves growth from a solid phase and concerns only crystals with a specific morphology, namely hollow ones closed at the top. In view of this we shall not discuss this further.

It could be assumed that Sharma and Malhotra [36] have in mind growth from nuclei with a specific form, when they note that the CdS hollow prismatic crystals grow through polygermination on platelets. A certain similarity to this model could be found in the mechanism of growth of hollow prisms from ZnO and ZnSe developed by Iwanaga and Shibata [48]. These authors consider that the striations parallel to the *c*-axis, on the outer surface of the walls, show that the prismatic faces are obtained by the growth of whisker clusters growing parallel to the *c*-axis and a process of space filling between the whiskers Such an array of whiskers is also observed in

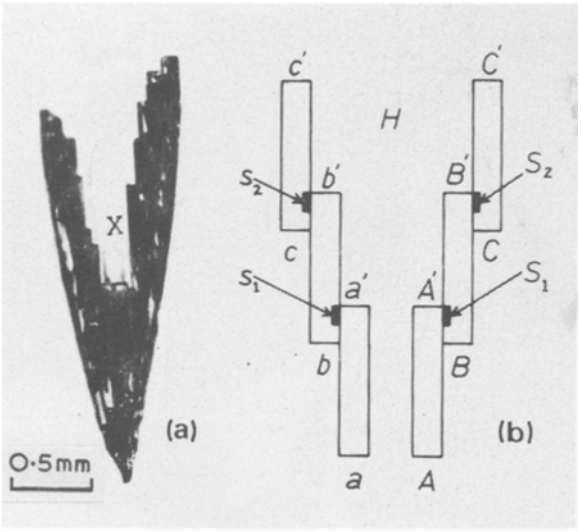

Figure 8 Mechanism of growth of hollow pyramidal crystals. Iwanaga and Shibata [48].

CaS [42] and ZnS [58]. The openings in the prismatic faces are explained through a possible difference in the velocity of growth of the whiskers. However, there is no reasonable explanation for the fact that even in the nucleation stage the array of whiskers is of regular hexagonal form so that hollow hexagonal prisms are obtained, the cross-section of some of them being close to that of a regular hexagon.

The growth of hoppered crystals is explained by the same authors in terms of a mechanism similar to that for prisms by assuming that on the upper outer surface of the grown whisker faces, the growth of new whiskers is initiated by two-dimensional nucleation (Fig. 8).

Tomita [29] also considers the importance of processes taking place in the nucleation stage which determine the growth of β-SiC hollow crystals. He assumes that during the initial stage perfect ideal lamellas grow, but they are bent or twisted by motion of the medium or by the interrupted growth of other crystals. In discussing the hollow crystals obtained he mentions a twinning of the nuclei.

6.2. Dislocation mechanism

Maeda *et al.* [41], and Lendvay and Kovacs [55] confine themselves to indicating only that the mechanism of hollow crystal growth is of a spiral form originating from a point with a screw dislocation associated with a layer-like process.

An interesting attempt at examining the mechanism of CdS hollow crystal growth is made by Chandrasekharaiah and Krishna [39] who have used the approach developed by Amelinckx [59] involving a dislocation growth mechanism of hoppered crystal faces (crystal growth from salol either from a solution or a melt). Chandrasekharaiah and Krishna assume that growth begins with a narrow step expanding from large dislocation groups in the middle of the crystal to its end, and (owing to nature in the diffusion process [60]), only the outer part of the step is able to advance forward by a diffusion mechanism (Fig. 9a to c). In this way the growth of a hollow cone or a pyramid begins, since the step can enlarge only outwards. According to the authors, the large steps observed on the outer surfaces indicate such a possibility.

The principles of this proposed dislocation mechanism for the growth of hollow hoppered (pyramidal) crystals, from a solution based on Amelinckx's work could be used in studying hoppered hollow crystals obtained from a vapour phase. However, no sufficiently convincing solutions could be found to such questions as: why growth begins, not near to the axis of dislocation (which has long since been substantiated) but somewhere near to the end, and for what reason does each step drive further outwards, thus forming a cone? Probably the answer should be sought by considering the action of impurities and the nature of the diffusion process (as Nabarro notes [60]).

In support of Amelinckx's dislocation mechanism are the observations of Maeda *et al.* [41] concerning the presence of a dislocation spiral at the bottom of a hollow crystal.

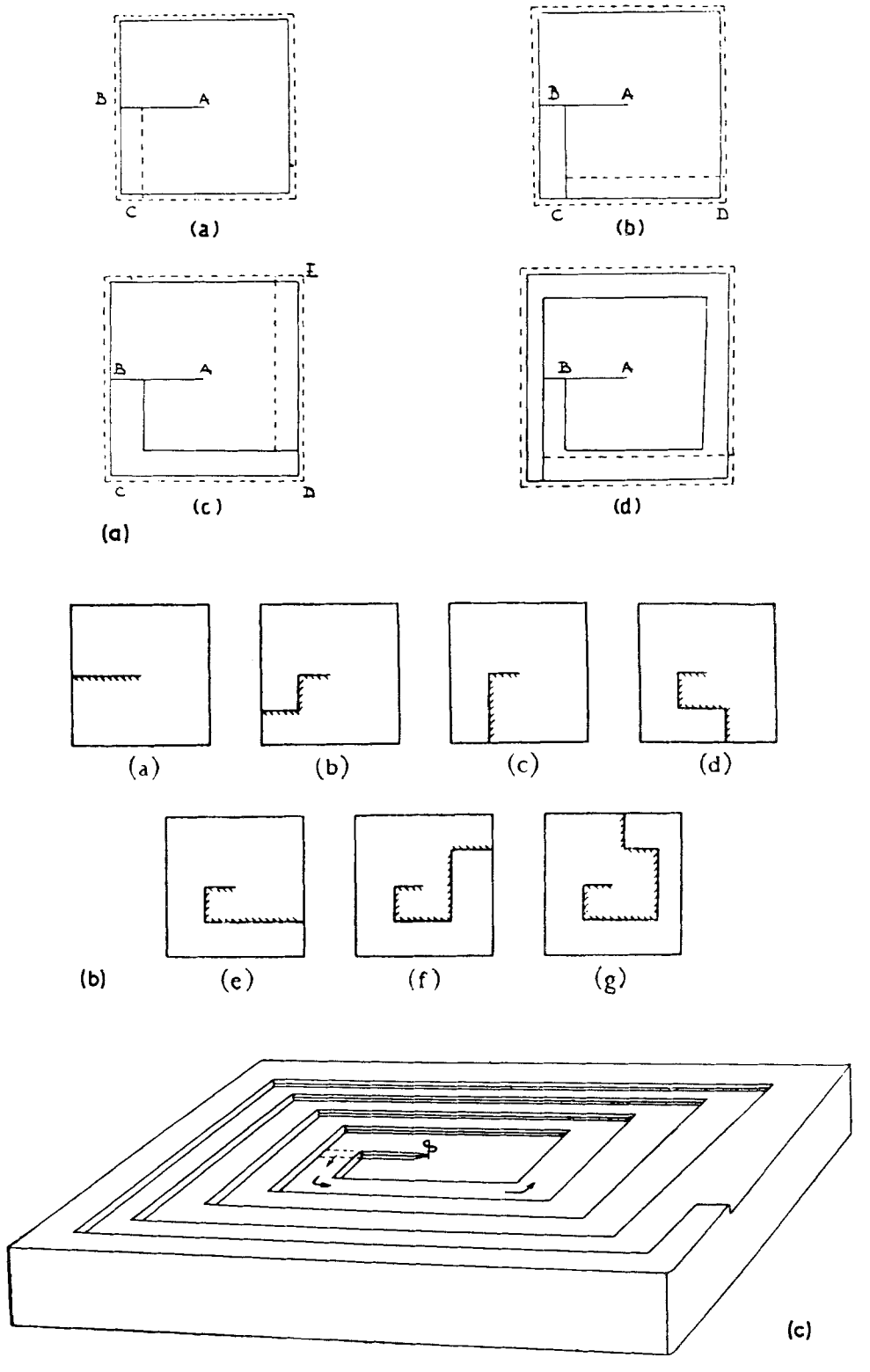

Figure 9 Growth of hollow pyramidal crystals after the dislocation mechanism of Amelinckx given by the author in [59] (a) and (c), and illustrated by Nabarro in [60] (b).

The same dislocation mechanism could be used in explaining both the growth of hollow pyramids (cones) and of hollow prisms. If it is assumed that under certain conditions the growing step ceases to expand outwards and the pyramidal faces pass into prismatic ones, then further growth should produce a hollow prism. This mechanism, however, cannot provide a sufficiently good explanation of the growth of hollow prisms and pyramids with an open surrounding surface or of hollow crystals with a spiral-like hexagonal form.

The growth of CsCl hollow whiskers [14] from a solution cannot be directly linked to the growth of whiskers from a vapour phase (which is usually the case with II-VI compounds) since this requires a capillary ascent of the nutrient liquid phase through the axial channel to the top of the whisker. Attention should, however, be drawn to a finding of Webb and Bertolone [14] that the size of the hollow of CsCl whiskers is close to that calculated from the theory of Frank [61] for a hollow dislocation with a large Burgers vector. Frank has shown that dislocation with a Burgers vector exceeding some critical value is in equilibrium only with a hollow channel in its core. The Webb and Bertolone conclusion could explain hollow whisker growth around a channel with a dislocation of large Burgers vector. Yoshida [18] has developed this idea for tube-like KCl whiskers in discussing the presence of twistings and hollow dislocations in them. Sharma [45] calculates the Burgers vector using the expression given by Yoshida and linking the values of the Burgers vector with the observed equilibrium radius of the cylindrical hollow in ZnO whiskers. Sharma considers that the results he has obtained support the inferences of Yoshida, for hollow whisker growth on a cluster of dislocations with the same sign. The interaction of these dislocations makes them equivalent to a multiple dislocation with a large Burgers vector and, owing to their presence, the field of strain is enlarged causing the hollow to have a radius greater than that calculated from Yoshida's formula. Cutter and Woods [49] also think that hollow crystals – ZnSe hexagonal prisms – grow from screw dislocations with a large Burgers vector, with a hollow core. However, it should be noted that the authors mentioned here only sought correspondence between theory and experiment for hollow whiskers of small dimensions.

6.3. Mechanism of development of skeletal forms

The mechanism of development of skeletal forms developed by Lemmlain *et al.* [62] for diamond crystals is directly relevant to the hollow crystals considered in this review and will thus be discussed in greater detail.

According to these authors "at low supersaturations, the steps of growth usually begin from the emerging point of dislocations with screw components. The dislocations come out to the surface most frequently in the centres of the faces where convexities (vicinal hillocks) are formed.

"If high supersaturation is present, the probability of two-dimensional nucleation is increased and a second source of steps arises. The transfer of crystallization heat at the apexes and the edges is better than in the central region. Owing to this, the supersaturation there, and consequently also the probability of nucleation around the apexes and the edges is greater than in the centres of the faces. The steps emerging on the periphery move to the centre and new ones arise in their place on the apexes and the edges. Such new layers could precede the covering the whole face by the previous layers. As a result concavities occur whose depth increases with the ratio between the normal and the tangential velocity of advancement of the layers." In advancing to the centre, the low layers are united and form high macrosteps. Since the nutrition of the convexities of the macrosteps is better than that of the concavities, projections overhanging the surface of the lower layer occur. Such steps on the inner surface of hollow crystals have been noted by Iwanaga and Shibata [48], Simov *et al.* [51] (Figs. 4 and 7). Chernov and Budurov [65, 66] have discussed in detail the kinetics and the mechanism of appearance and growth of macrosteps. The above condition concerning the relationship between the two speeds can be realized when the crystal reaches a certain size. Growth of skeletal forms is also studied in greater detail in [63] and [64] where the phenomenologic theory of the growth of skeletals is discussed.

As becomes evident from the above, the growth of hollow pyramidal (hoppered) crystals, described in the previous section, could be explained by the mechanism of growth of skeletal forms. It is clear that hollow prisms could also grow by the same mechanism provided that the following

limiting condition is introduced; namely, the new layers from two-dimensional nuclei near the edges and the tops must be formed only on the basal face and not on the prismatic faces. The crystal would not then expand outwards to form a hollow pyramid, but would grow as a hollow prism.

Hollow crystals of the third type with a spiral-like hexagonal form (Fig. 6) could be described in the terms of Lemmlain, Klija and Chernov as "wrappings", for the occurrence and growth of which these authors provide the following qualitative description: all the described conditions for the growth of skeletal forms being observed. It is also assumed that the growth through two-dimensional nuclei begins from one of the apexes where the supersaturation is greatest and continues near the edges in both directions (Fig. 10). With the drawing nearer of the two branches, their heat flows, induced by the developed heat, begin to overlap substantially, the supersaturation on them decreases and the bending of the two branches towards the centre becomes more favourable. In this way skeletal structure are obtained in the form of hollow prisms with an open surrounding surface and in the case discussed by us – with a spiral-like hexagonal form. By analogy, the existence could be explained, of openings in the prismatic faces of the hollow crystals described by Iwanaga and Shibata [48] (Figs. 1aII and 6b) and Simov *et al.* [51] (Figs. 1dII, III, 7b and c). Here it should be noted that only from a certain height upwards will the hollow crystal, growing by the usual mechanism for skeletal forms begin to develop as a "wrapping", because of a change in the conditions, growth does not begin uniformly from *all* the edges and apexes, but only from *one* of the apexes.

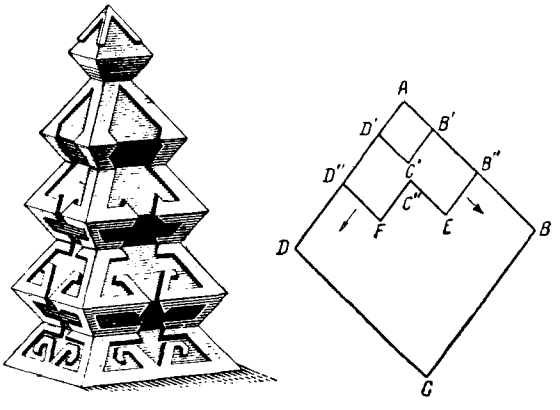

Figure 10 Growth of a diamond skeletal crystal. Lemmlain *et al.* [62].

Even the more complex forms of Simov *et al.* [51] could be interpreted as a consecutively alternating growth of whisker, hollow pyramid and finally hollow prism, the last two considered as skeletal crystals. Moreover, the surrounding surface, could be closed or open, or might grow as a "wrapping" even from the beginning (Fig. 7a, b and c respectively).

To elucidate the mechanism of growth of ZnO hollow crystals, Park and Reynolds [44] and Kumar [47] employ views which are very close to those of skeletal crystal growth and, in general terms, could be referred to this group. Kumar adds also that the action of impurities is quite consistent with the mechanism of skeletal crystal growth being only a necessary supplement, because the movement of the steps towards the centre can also be limited by the action of impurities which likewise favours the development of the skeletal crystal.

Also in support of the assumption that hollow crystals grow by the mechanism suggested by Lammlain *et al.*, are the inferences of Woods [35], Chandrasekharaiah and Krishna [39] and of Lendvay and Kovacs [55], revealing that hollow crystals grow at higher supersaturations.

In conclusion, it should be noted that in comparison with the dislocation mechanism, and that based on the form of the nuclei, the mechanism of skeletal development provides a more complete picture of the growth of hollow crystals in all of their diversities.

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