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'Tadpoles' On Cultured Quartz

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Very strange tadpole-like features are observed on rhombohedral faces of cultured quartz crystals. With the help of fringes of equal chromatic order these features have been shown to be elevations and their orientations have been established. Three different suggestions are made for the interpretation of the origin of these features and there is support for the view that they are a result of oriented inclusions which at some stage of growth were blown off and subsequent growth gave rise to such features.

Introduction

A microtopographical study of about four hundred rhombohedral faces of cultured quartz crystals was made, by the use of precision optical techniques. Some of these faces showed the presence of (*a*) tadpole-like, (*b*) bean-shaped and (*c*) elliptical oriented features. The crystals were grown from a solution of sodium carbonate at a low supersaturation, at a temperature of about 350 °C. and pressure between 1000 and 2000 atmospheres.

Experimental

The crystals were thoroughly cleaned and silvered in a vacuum coating unit and then examined with the help of a phase-contrast microscope and also interferometrically. We shall describe our observations in two parts, (*a*) observations on cultured quartz from the General Electric Co., London, England, and (*b*) observations on cultured quartz from Clevite Corp., Ohio, U.S.A.

Cultured quartz from G.E.C., London

Fig. 1 is a phase contrast photomicrograph which illustrates quite strange tadpole-like and elliptical features; all of them have strictly the same orientation. These features and also some bean-shaped features (not shown here) have been observed on an odd piece of a minor rhombohedral face of a synthetic quartz grown on a *C*-cut seed. Fig. 2 is a multiple-beam interferogram in transmission using three wavelengths (one green and two yellow) which reveals the nature of these features. The fringe definition is particularly noteworthy. That the tadpoles are elevations above the general crystal surface is clearly proved by fringes of equal chromatic order, shown in Fig. 3. It was also confirmed that beans and elliptical features are also elevations.

Cultured quartz from Clevite Corp., Ohio

Fig. 4 is a positive phase-contrast photomicrograph which illustrates a couple of isolated tadpoles on a rhombohedral face of a cultured quartz. Their tails are short and all of them are orientated the same way. Fig. 5, a positive phase-contrast photomicrograph, illustrates a bean-shaped feature and tadpoles. The tails of the tadpoles and the tip of the bean-shaped feature have the same crystallographic orientation, which is found to be about 8° with the $R-m$ edge of the crystal under investigation. This was found to be so for all the rhombohedral faces on which these features were found to occur. In some cases beans and tadpoles overlapped on themselves and also on each other, with clear evidence of growth layers on them. Fig. 6 illustrates fringes of equal chromatic order scanned on a portion of a bean-shaped feature. These fringes show its profile and confirm that these features are elevations.

Tadpoles on a basal plane

A couple of tadpoles were also observed on a basal plane of a cultured quartz, which also exhibited a number of spirals and associated features. A full account of these spirals has been given by Joshi & Tolansky (1961).

Fig. 7 is an ordinary photomicrograph, which shows two tadpoles on a basal plane of a cultured quartz. It is clear that unlike those observed on rhombohedral faces (Figs. 1, 4, and 5) these tadpoles have no strict crystallographic orientation. It should be mentioned that the crystal face (basal plane) is covered with a large number of growth patterns connected with the spiral mechanism.

Discussion

The tadpoles, beans and elliptical features appear to have the same origin, and although their interpretation is somewhat difficult, the following three possible explanations of these features will be discussed: (1) Inclusions. (2) Further growth on the cavities which presumably were formed owing to oriented inclusions being blown off at some stage of growth. (3) Result of interaction of growth forms due to dislocations.

Since the crystal faces under consideration were natural (uncut) habit faces of synthetic quartz crystals, the question of polishing marks does not arise.

Because the features are bubble-shaped let us assume that they were due to oriented inclusions. According to Brown & Thomas (1956) in nearly all synthetic quartz the most common defects are minute bubbles distributed throughout the growth. The bubbles are two-phase liquid-vapour inclusions of various sizes. The concentration of these bubbles varies from crystal to crystal. It is known that they occur more readily when reclaimed seeds, *i.e.* seed crystals which have been used previously, are used again. The bubble type inclusions occur either just below the final growth surface or near the edges of the crystal face. If they were included long before the end of the growth they should have been overgrown and would not have appeared as elevations, but they may be visible in the body of the crystal. It is possible that these features may be inclusions which were partly overgrown, and thus formed elevations on the surface. In the case of inclusions the material inside the bubbles could be, for example, water or carbon dioxide. When the crystals (some of which were cut in the form of plates) were examined in transmitted polarized light, no difference was found in the refractive index inside and outside these features. It is possible that water or liquid carbon dioxide trapped in the bubble might have been converted into the gaseous state and then escaped leaving hollow bubbles, in which case the refractive index inside and outside these bubbles would be the same. To investigate this possibility a number of these beans were indented with a pyramidal diamond indentor, and it was found that they were solid.

The fact that all these features are solid means that they are not bubbles now; at the same time this does not preclude the possibility that they once were. They do in fact have the shapes of bubbles and when the unsilvered crystal (in the form of a plate) was gradually racked down towards the objective of a microscope the inner side of each of them was found to be very similar to the top, and of almost the same curvature.

This leads us to the second explanation, that these feature were oriented inclusions, and that at some stage of growth they were blown off forming oriented cavities. The formation of the tails of the tadpoles and the tips of the beams is still a problem. Further growth takes place and because these cavities are quite large kinks the rate of adsorption of atoms will be much greater than on the general crystal surface. Not only will the cavities be filled up rapidly but also a bump will be produced having almost the same curvature as the surface of the original cavity inside the crystal. A further question then arises, *viz.* How is a bump formed after the cavity is filled up to the general level of the crystal surface? In this case, since there is a discontinuity at the points where the boundary of the cavity meets the crystal surface, atoms which are adsorbed between such points cannot migrate to the general surface outside, and the rate of adsorption being greater for the cavity continues to be so even after filling up the cavity, and an elevation is thus formed. From careful observations it was found that the undersides of these features were appreciably further below the general crystal surface than their top-sides were above it; *e.g.* for one bean-shaped feature lateral extension (on the crystal face) was about 0·25 mm and its elevation above the crystal surface was about 0·008 mm, while the depth of its lower surface was about 0·7 mm. This means that the greater portion of the bubbles was covered over, and if they were not blown off they soon would have been completely overgrown and incorporated inside the crystal leaving no sign of elevations.

Let us now consider the third explanation. In the case of basal planes there are many 'mole-hills' which are spiral growth pyramids; in addition one or two spiral growth-fronts are visible, starting at the tips of tadpoles which may be the centres of initiation. The formation of the tadpoles as a result of interaction between several spiral growth pyramids is illustrated schematically in Fig. 8. Interactions between the growth pyramids due to dislocations 2, 3 and 4 form the tail of the tadpole, while those between 1 and others (not shown in the Figure) form its body. This interpretation appears to be quite convincing for the two tadpoles (Fig. 7) on the basal plane for which there is ample evidence

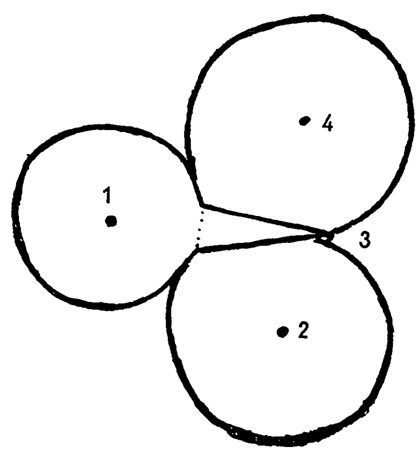

Fig. 8. Schematic illustration of 'tadpole' formation by interaction between spiral growth pyramids.

of spirals, screw dislocations and a large number of spiral growth hillocks. On the other hand, tadpoles (Figs. 1, 4 and 5) observed on the rhombohedral faces cannot be explained in this way, unless there is some evidence of dislocations on these faces.

Growth fronts visible on tadpoles and allied features could only be edges of circular growth layers, filling

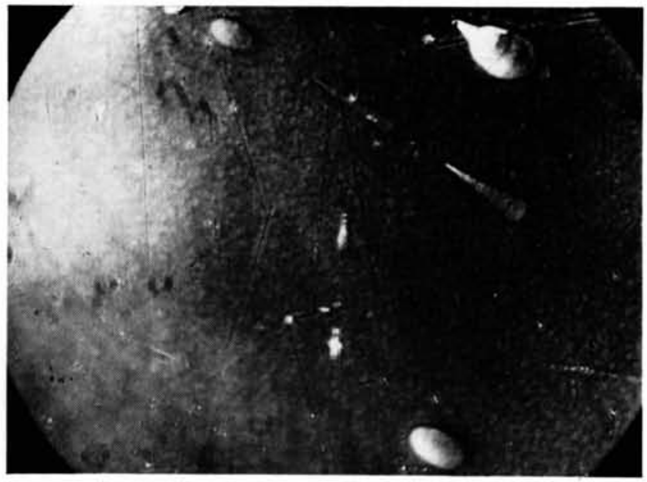

Fig. 1. 'Tadpoles' and elliptical features on cultured quartz (× 56).

Fig. 2. Multiple-beam interferogram revealing the nature of the features (× 93).

Fig. 3. Fringes of equal chromatic order proving the 'tadpoles' to be elevations.

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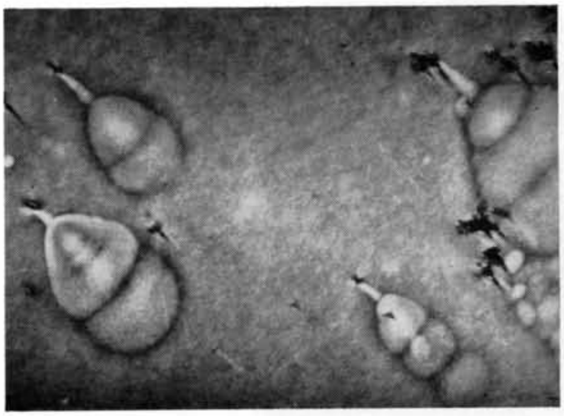

Fig. 4. 'Tadpoles' on a rhombohedral face (×81).

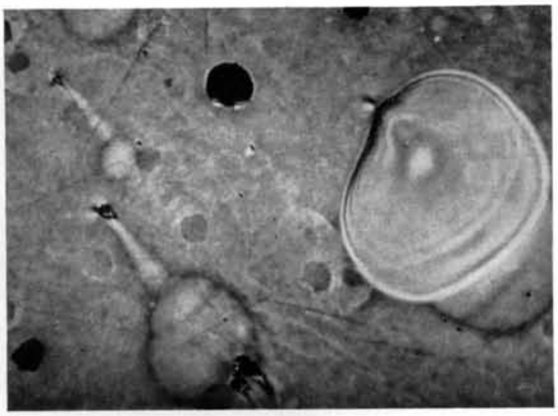

Fig. 5. A bean-shaped feature and 'tadpoles' (×81).

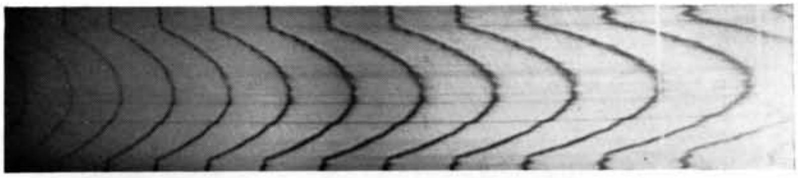

Fig. 6. Fringes of equal chromatic order scanned on part of a 'bean'.

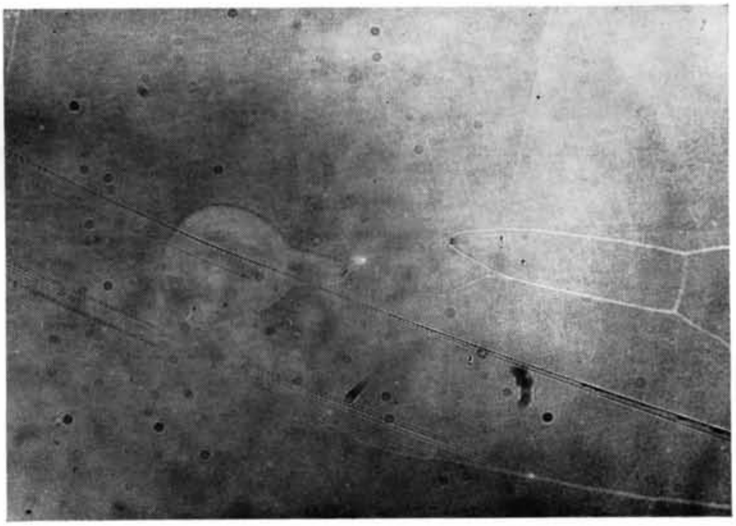

Fig. 7. 'Tadpoles' on a basal plane (×79).

the cavities and thus forming elevations. There is no evidence whatsoever of spiral patterns on the crystal faces on which these features occur.

Conclusion

Having examined the merits and demerits of the three possible explanations, we feel that the tadpoles and similar features on the rhombohedral faces are best explained by the second of these, while those on the basal planes fit in best with the third.

One of us (M. S. J.) would like to express his sincere gratitude to Prof. S. Tolansky, F.R.S. for his continued guidance and helpful discussions. Crystals from the General Electric Co., London, were studied in his laboratory. We also wish to thank Dr I. Sunagawa, Geological Survey of Japan, and Dr A. F. Seager, Birkbeck College, London for their helpful suggestions. We are thankful to Dr L. A. Thomas and Dr C. S. Brown of G.E.C., London and Dr D. R. Hale of Clevite Corp., Ohio, for an adequate supply of cultured quartz for carrying out the work. Our thanks are also due to Dr A. R. Patel for his interest in our work.

References

Brown, C. S. & Thomas, L. A. (1956). Monograph No. 205R., Inst. Elec. Engrs., 675, 1–11.

Joshi, M. S. & Tolansky, S. (1961). *Proc. Roy. Soc.* A, **260**, 475.

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The Crystal Structure of a Hydrogen Bonded Complex of Adenosine and 5-Bromouridine

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The crystal structure of a 1 : 1 crystalline complex of adenosine and 5-bromouridine has been determined by heavy atom and trial and error methods, and has been refined by the full-matrix least-squares method to a final residual of 13·8% for 1986 measureable reflections. The space group is orthorhombic, $P22_12_1$, with $a=4{\cdot}82$, $b=15{\cdot}19$, and $c=31{\cdot}76$ Å. The bromouracil and adenine rings form a planar complex joined by a N–H...N hydrogen bond (2·80 Å) and a weak N–H...O hydrogen bond (3·10 Å). The overall structure is fully hydrogen bonded with O–H...O contacts of 2·72, 2·79, 2·80 and 2·91 Å and O–H...N contacts of 2·78 and 2·90 Å. Both ribose sugars are puckered with C(3′) lying out of the plane formed by C(1′), C(2′), C(4′), and O(1′), and are oriented *anti* to the bromouracil and adenine planes. The structure was found to contain one water of crystallization per nucleoside pair. Refinement indicated considerable disorder in the water molecule position.

Introduction

The first successful co-crystallization of purine and pyrimidine derivatives was reported by Hoogsteen (1959, 1963). He found that 9-methyladenine and 1-methylthymine form an interlocking structure in which the two bases are hydrogen bonded in a planar complex. Other purine–pyrimidine crystalline complexes which have been studied include 9-ethylguanine and 1-methylcytosine (O'Brien, 1963); 9-ethyladenine and 1-methyluracil (Mathews & Rich, 1964); 9-ethylguanine and 5-bromo-1-methylcytosine (Sobell, Tomita & Rich, 1963). In each case the purine and pyrimidine rings form a highly planar hydrogen bonded complex. These structures are of particular interest because of their relation to the naturally occurring biological polymers, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

This communication describes the structure of a crystalline nucleoside complex containing adenosine and bromouridine. The hydrogen bonding between bases is different from the adenine–thymine pairing found by Hoogsteen (1959, 1963) and from that proposed by Watson & Crick (1953) for DNA. A preliminary report has been published elsewhere (Haschemeyer & Sobell, 1963).

Experimental

Commercial preparations of adenosine and 5-bromouridine were obtained from California Corporation for Biochemical Research, Los Angeles, California. Upon

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