

STRUCTURAL IMPERFECTIONS IN QUARTZ CRYSTALS

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ABSTRACT

A method for examining the topography of atomic planes is developed and applied to quartz crystals. It is thought to have higher resolution than the method of Wooster and Wooster (*Nature*, 155, 786 (1945)), or that of Ramachandran (*Proc. Ind. Acad. Sci.*, 19A, 280 (1944)). Because of the higher resolution it gives more detailed information. A fair percentage of ostensibly perfect quartz is shown to have slight irregularities.

Quartz crystals that seem to be perfect by the ordinary tests such as etching and single crystal x -ray double reflection, can be shown to be imperfect by x -ray double reflection. The apparatus for examining crystals in this way is shown in Fig. 1. X -rays from the target T are reflected at the Bragg angle from the reference crystal R onto the work crystal W .

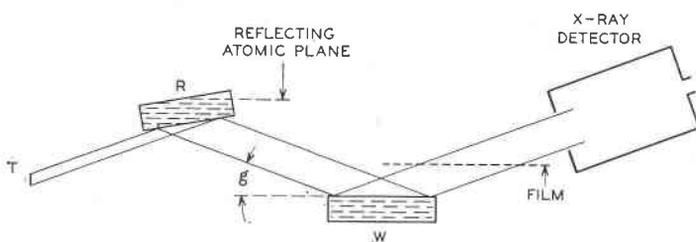


FIG. 1

If the reflecting planes of W are parallel to those of R and the Bragg angles are the same, the rays can also reflect from W into the x -ray detector or can be intercepted by a photographic film to give a picture of the reflecting area of W . If the reflecting planes of the two crystals are not parallel, no ray can be reflected from both crystals. With nearly perfect crystals, if the planes are a few seconds out of parallel the energy received by the x -ray detector (ionization chamber or Geiger counter) is noticeably below maximum as shown by the rocking curve, Fig. 2 where the intensity of reflection is plotted against the grazing angle g .

As shown in Fig. 1 the reflecting surface of crystal R is cut several degrees from the atomic plane in order to expand the beam width. This enables larger W crystals to be examined. The reflecting face of R is optically polished, otherwise shadows of grinding pits show on the film. A number of quartz crystals were cut and polished $6\frac{1}{2}$ degrees from an $(01 \cdot 1)$ plane and slightly etched. The one showing the cleanest reflection

was chosen as R . A slight etch after polishing narrows the width of the rocking curve. Rough ground crystals may have a peak width at half max. of 3 minutes. Polished and etched crystals may have a width of less than 10 seconds.

The film is placed as close to W as possible because the copper radiation used has two wave lengths $K\alpha_1$ and $K\alpha_2$ both of which reflect but at slightly different angles. Hence two overlapping pictures are given, but if the film is close to W the offset can be kept to a few thousandths of an inch. The (d) spacing of quartz for the (01·1) plane is 3.3432 Å at 26° C.

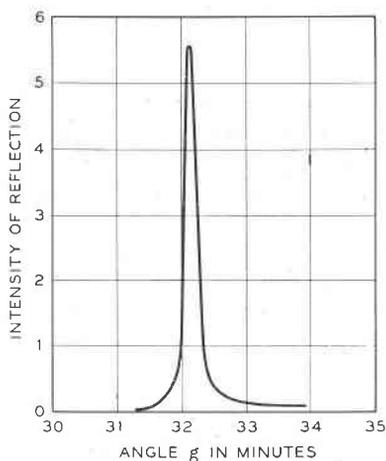


FIG. 2

$K\alpha_1$ (which is twice as strong as $K\alpha_2$) has a wave length 1.54050 Å. Hence, from Bragg's law: $\lambda = 2d \sin \theta$ we see that the θ 's for α_1 and α_2 differ by 2.03 minutes.

If a minor part of crystal W is slightly misoriented, this part will not reflect most strongly at the same angle setting as does the major part of the crystal. If W is rotated to make the minor part reflect most strongly, then the major part reflects less strongly. The photographic film will show in each case from where the strong reflection came. Figure 3 illustrates such a case. The two pictures are of a natural (01·1) face of a small quartz crystal found in Herkimer County, New York—a so called Herkimer County Diamond. The crystal was turned through 50 seconds between pictures a and b . The rocking curve indicates where interesting features may be found. Picture a was made with the crystal set at the peak as indicated by the letter (a) over the taller peak of the rocking curve. Picture b was made at the crystal setting indicated by the letter

b on the lower peak of the rocking curve. The bright area of picture *a* shows that about a third of the face was reflecting at this setting. Picture *b* shows that the larger part of this face is about 50 seconds in orientation away from the smaller part, but is curved so that only a small part reflects at any one setting. The sketch above the rocking curve shows the direction in which the *x*-rays approach and leave the crystal. This is important because the resolving power is highest if the plane containing the incident beam direction and the reflected beam direction is perpendicular to the line in which the atomic planes of the two crystal parts intersect. For this reason in investigating a surface, rocking curves are made for

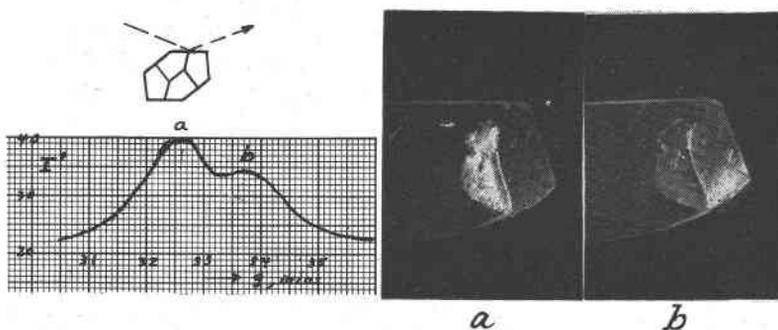


FIG. 3

two directions at 90° to each other. The poorer reflection is then investigated photographically.

The intensity axis of the rocking curve, Fig. 3, is marked I' . In this figure and subsequent ones meter readings are plotted and $I=0$ corresponds to a reading of 20. The meter is non-linear so that if Fig. 3 were corrected for this, as was done in Fig. 2, the peaks would appear somewhat sharper.

Figure 4 shows a crystal from Hot Springs, Arkansas. The crystal was cut in two in a plane parallel to $(01 \cdot \bar{1})$. It is seen that the crystal is quite imperfect. The fine parallel lines along two nearly perpendicular edges are probably "growth lines." Picture *b* shows that below the major part is a smaller region turned about 50 seconds from the major part about a vertical axis. The small peak at the left of the rocking curve was photographed but not included here. It is due to a very small area of the face below *b* and also reflection from the prism face which does not lie in the plane of the cut face. Since the largest part of this reflection is from an area not parallel to the photographic plate it appears as a long streak going to the right of the film. The pictures are without distortion only when the film is parallel to the reflecting face.

Figure 5 shows six pictures from a plate made by the W. E. Co. at Kearny to be used as a reference crystal *R*. Although it is unsuitable for a reference crystal it should make a perfectly good oscillator plate. The diagonal stripes are parallel to a rhombohedral edge, the vertical stripes are parallel to an *a* axis. The six pictures were made to determine

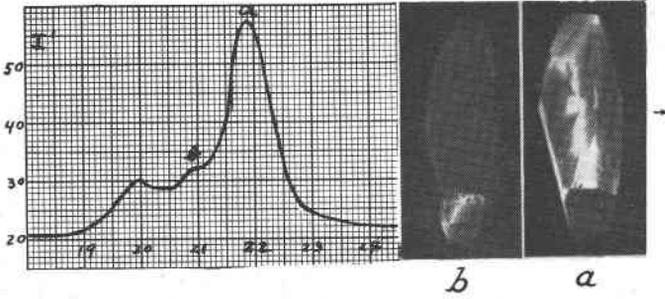


FIG. 4

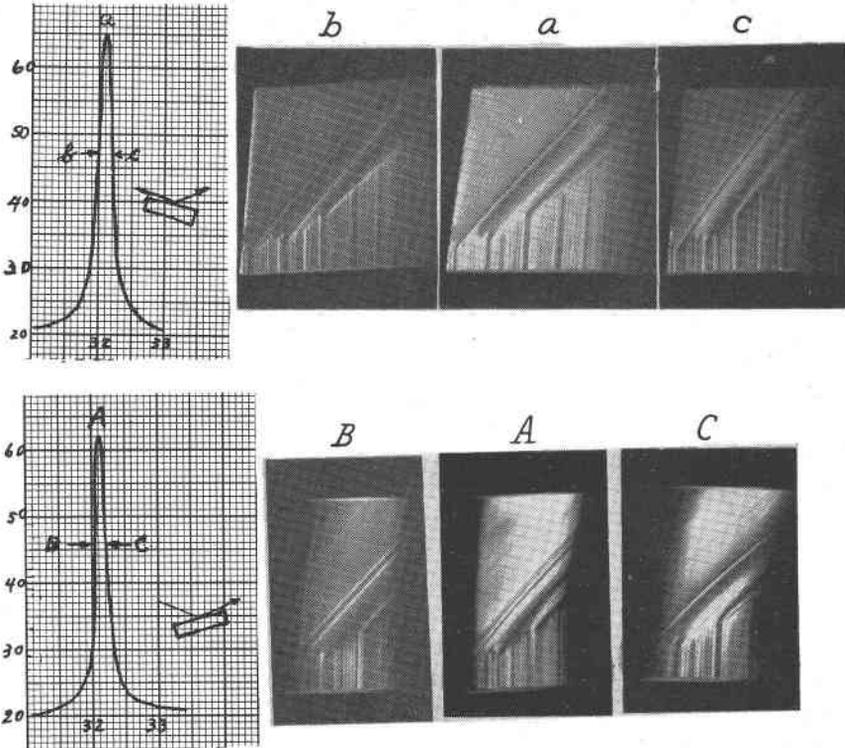


FIG. 5

whether the stripes were due to different orientations, or could possibly be interpreted as showing regions of different atomic spacing d (which would necessitate different θ 's). If a plate has a small part in which the d constant is slightly larger than that of the major part but whose atomic planes are parallel to those of the major part, the best reflection for the minor part occurs at a slightly smaller angle regardless of direction of x -ray beam. Hence turning the plate 180° in its plane does not reverse the positions of the reflection, that is, the minor part always appears at a lower angle than does the major. On the other hand, if the minor part has the same d constant but its atomic planes are not quite parallel to those of the major part, turning the plate 180° does reverse the order of occurrence of reflection. By choosing a point on the crystal that can be identified, for instance the tip of an inverted V that terminates a group of lines one can study the relative intensities of adjacent lines throughout the six pictures. Two lines thus checked showed that the line order does reverse on reversing the crystal. Hence it is concluded that it is primarily an orientation difference (of about 5 seconds), not a d spacing difference. If impurities can change the d spacing by, say, one part in 10^6 , then roughly every half millimeter the fit of the old material on the new is out by one cell. We may be able to find here a mechanism whereby a slight d spacing difference caused by changing impurity content can, by an accumulative effect, cause regions to be misoriented by amounts such as are observed even if the d spacing difference is too small to detect by this method.

The narrowness of the pictures of the second series, Fig. 5, is caused by the plate in this reversed position being more nearly perpendicular to the x -ray beam, hence the beam covers less of the crystal width. The curved edges of the pictures A , B , C show the conical nature of a reflection. The locus of all lines from a point (on the x -ray target) making a constant angle θ with a plane is a cone. The slight curvature of some of the diagonal lines is caused by the film not lying perfectly flat. With the x -ray beam coming onto the film at only $13^\circ 20'$ a slight curvature of the film gives an exaggerated curve to what would otherwise be a straight line.

The large quartz piece Fig. 6A was seen to be clear to the left of the line 1-1 but smoky to the right. This boundary proved to be (10·1) plane. The piece was sawed on the lines 1-1 and 2-2, the piece between these lines proved to be also part clear and part smoky with a (11·1) plane boundary as shown in Fig. 6B. The surface 2-2 of this piece was investigated. A pair of light scratches were made on the surface to mark the ends of the clear-smoky boundary (see arrows, Fig. 6b). At maximum reflection, picture a shows only the edges of the piece are reflecting. If we turn to smaller angles, picture b shows that we have poorer reflections

everywhere. Going to larger grazing angles, picture *c* shows two zones of reflection separated by a narrow dark band. Picture *d*, which is 24 seconds away from picture *a*, has only a narrow band of reflection. This indicates that the atomic layers at the surface are warped into an (*s*) curve, Fig. 6*E*. With the atomic planes warped in this way regions such as *m* and *n* have the same orientation and give a picture such as Fig. 6*c*. A maximum slope occurs at *p*, which gives Fig. 6*d*. If we turn the crystal further we get no picture.

If the unit cell of smoky quartz is larger than the unit cell of clear

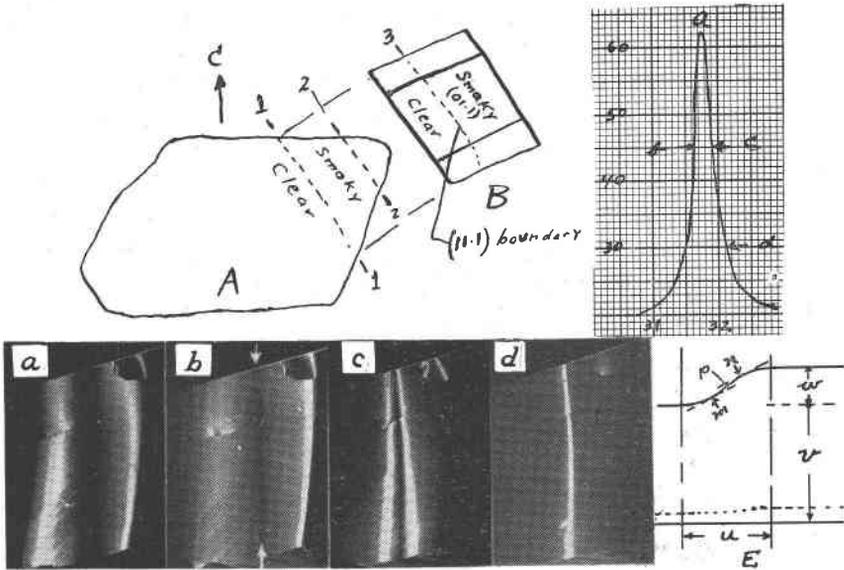


FIG. 6

quartz and the atomic layers are continuous (i.e. no dislocations), the layers would warp to such a continuous curve. In laying on a thickness *v* (Fig. 6*E*) the accumulated difference is *w*. If we assume the transition is a sine curve of length *u* height *w* and with a maximum slope of 24 seconds it is easily shown that $(\pi w \sqrt{2}/4u) \approx 116 \times 10^{-6}$. On picture *a*, *u* was found to be about 1.5 cms.

Whence $w \approx 70 \times 10^{-6}$

If the difference *w* is accumulated in a thickness 0.9 cm. (the thickness of the plate, since the lower face borders on clear material) then the cell dimensions of clear and smoky quartz would differ by one part in *v/w* or 1 part in 13,000 which seems not unreasonable. H. D. Keith (*Proc. Phys.*

Soc., B63, 208) says "Quartz parameters vary from sample to sample by amounts as large as .01% according to impurity content."

The "smoke" was cleared by heating the specimen to 300° C. Pictures taken after cooling were the same as before.

Figure 7 is a study of vicinal faces on a quartz crystal found at "Crystal Hill," Pennsylvania (near Stroudsburg). The obvious vertical line in the pictures divides the face into two nearly equal areas. These areas

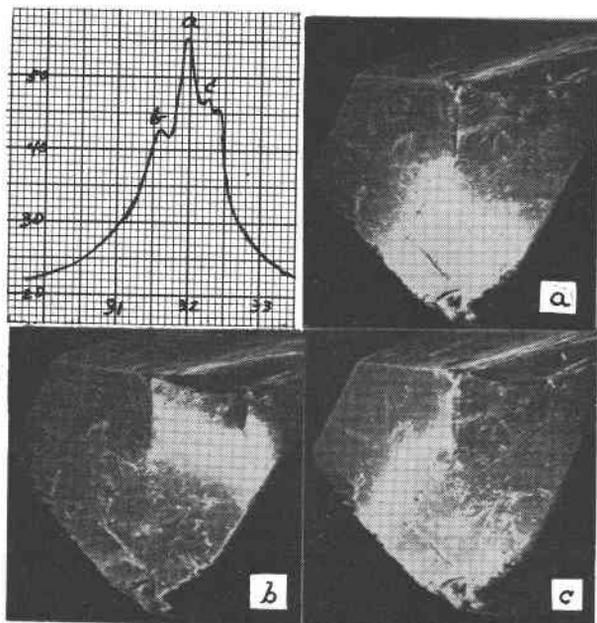


FIG. 7

form a low "roof" of angle eleven minutes as determined by optical reflection (two very sharp images are seen in the optical goniometer). The x -ray rocking curve shows a quadruple peak with a total spread of less than a minute—and no other reflections within 30 minutes to either side. The eleven minute roof angle does not appear in the x -ray data. Hence we conclude that the apparent faces are ones of very high indices, not two crystals joined at eleven minutes. A hint of the cause of vicinal faces is given by this crystal and a few others examined. A thin sheet of flawed material comes up from the base of the crystal and points directly at the ridge of the roof. This probably puts the material in a state of stress, the stress reversing sense at the end of the flawed sheet. If the speed of growth is altered by stress this might cause the growing face to have

indices $h+\Delta_1$, $k+\Delta_2$, $l+\Delta_3$ on one side of the flawed region and $h-\Delta_1$, $k-\Delta_2$, $l-\Delta_3$ on the other side—the Δ 's being very much smaller than unity.

The pictures, Fig. 7, show many scratches. The crystal (from the private collection of Mr. George Shoemaker of Summit, New Jersey) was in a box with many other quartz crystals. They probably scratched one another slightly but it is not apparent to the naked eye. Experiments with ammonium dihydrogen phosphate show that when a metal point is pressed against a polished face there is a misoriented region much larger than the obviously damaged region. Probably minute fissures are

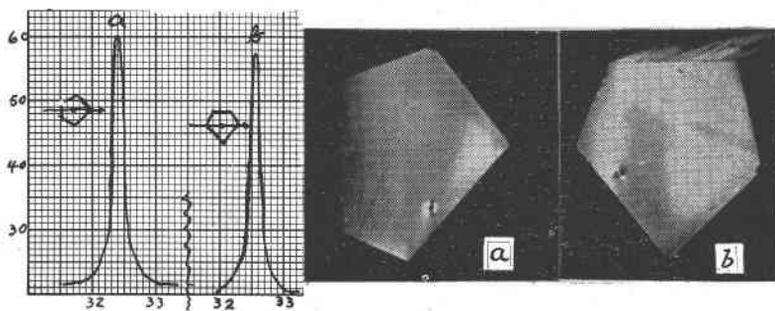


FIG. 8

made, and broken off material is forced into these, wedging them open thus causing strain over an extended area. This is possibly the main mechanism of disorientation of ground surfaces of non-plastic crystals. The material actually broken off and trapped in the fissures is of very small amount and is probably misoriented to a much greater extent. If it were randomly oriented the probability that any one particle would have a plane (01·1) within a minute of the reflecting position is one chance in four million. Hence it seems probable that the slight misorientations are in the still attached material put under strain by the impacted material.

Figure 8 shows the best face of a Bell Laboratories synthetic quartz crystal. The crystal, which is 32 millimeters long is shown in Fig. 9c, the face pictured in Fig. 8 being the lower right major rhombohedral face of Fig. 9c. There is a low pimple shaped mound near an edge of this face. There is local strain around this pimple but the rest of the face is nearly perfect.

Figures 9a and b show the upper rhombohedral face of Fig. 9c. This face is far from perfect. There is a central mound much more prominent than the mound of Fig. 8, no inclusions can be seen under either mound

at 360 magnification. Fifty minutes away from the main peak is a secondary peak that is due to ring shaped regions, picture 9*b*. It would be interesting to put this crystal back in the bomb and grow more quartz onto it to see if the face would become more perfect.

Figure 10 shows several views of a slice of a synthetic quartz crystal grown at the Bell Laboratories. A seed plate about $\frac{1}{8}$ inch thick and $1\frac{1}{2}$ inches square parallel to $(01\cdot1)$, was grown to about $\frac{3}{8}$ inches thick. A slice was cut out of the center and since it was too long to cover in one picture it was sawed in two. In cutting the slice the cuts were made along

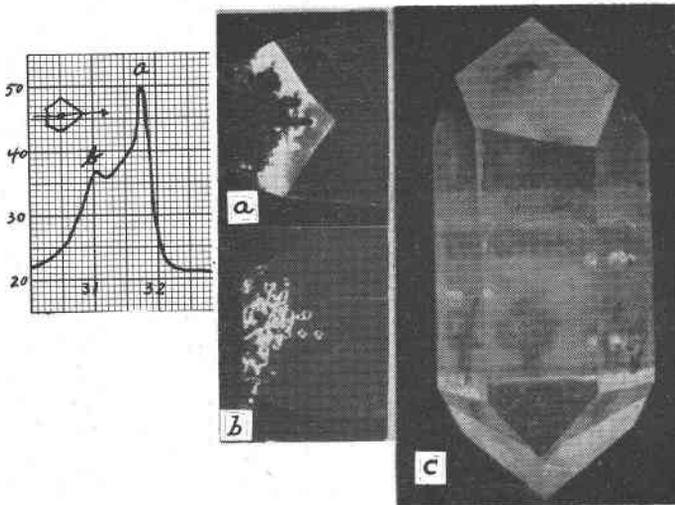


FIG. 9

$r(01\cdot1)$ planes which are $76^{\circ}26'$ from $z(01\cdot1)$, giving a surface nearly perpendicular to the growing face (see Fig. 10*a*) so the process of growth could be studied. The original seed was Brazilian quartz and shows diagonal stripes which are growth lines on prism faces. The new material shows stripes over the large face edges, growth on $(01\cdot1)$ faces. The joint between the old and new quartz shows a fair amount of misorientation. Under the microscope, one sees many fine radial crystal aggregates in the new material near the boundary with the old material. The aggregates are about 10 microns in diameter. They are much more numerous on one side of the seed than on the other. The side with the greatest number was probably uppermost during growth. They may be recrystallized material from the bomb wall. If, as is likely, the upper side of the seed was least dissolved back at the beginning of the growth run, it may

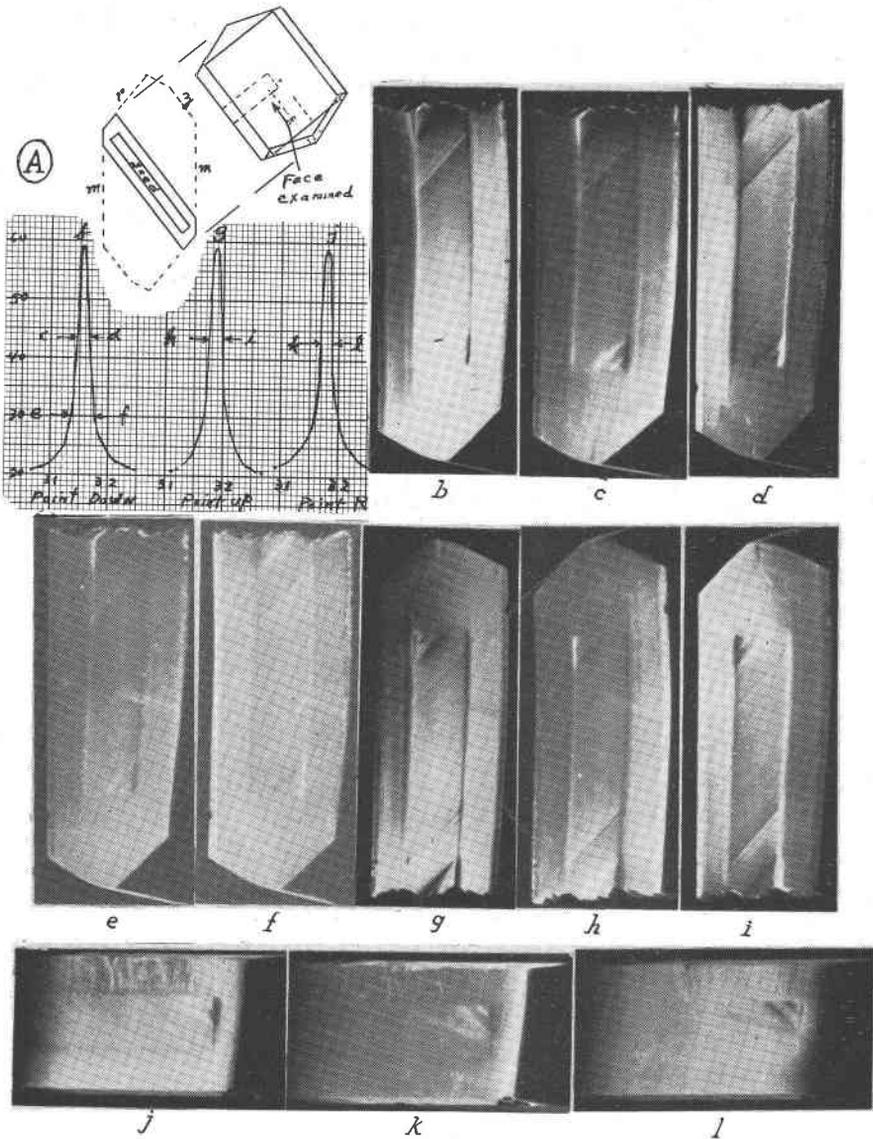


FIG. 10

have kept a region strained from grinding. This region could cause a pimple.

In the *old* material near the boundary there were three small voids, about 20μ in diameter, 60μ long, perhaps 40μ apart and parallel to each

other. Exactly opposite, near the other boundary were three more quite similar, also in the old material. Each was full of liquid except for a gas bubble. Probably there were three submicroscopic holes through the seed or three submicroscopic rutile needles. These etched out a short distance at the beginning of the growth run, then sealed over. No line connecting each with its opposite could be seen at 100 magnification of the microscope. Pictures, *j*, *k*, *l* taken with the *x*-ray beam traveling along the length of the slice shows a slight rumpling in the new material above the seed. Better "joins" of old to new material are now being made, at least better by the criterion of joint visibility but these newer crystals have not been tested by this *x*-ray test.

H. D. Keith (*op. cit.*) finds that the cell size of synthetic quartz varies with the temperature at which it was grown. Crystals grown at 390° C. have smaller cells than crystals grown at 280° C., smaller by 1 part in 10,000 along the (*a*) axes, by 1 part in 17,000 along the (*c*) axis. This is probably due to the effect of temperature on impurity content. The growth lines could be due to such a temperature effect.

Five *AT* quartz blanks were examined. One was found to have a *V* shaped twinned portion. This twinned portion showed perfect alinement with the rest of the plate. There was no strain at the boundary. Since $(0\bar{1}\cdot 0)$ reflects more strongly than $(01\cdot 1)$ this part merely reflected more strongly than the rest of the plate at all orientations near the peak. One of the five blanks showed stripes like those of Fig. 5 across a corner of the plate.

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