The growth and properties of large crystals of synthetic quartz.

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INTRODUCTION.

IN the last twenty years quartz has become of considerable importance to the telecommunications industry, one of its most important uses being the control of the frequency of oscillation of high-frequency transmitters. In this country alone the peak war-time demand for oscillator crystals was well over a million a year.

Although quartz is very abundant in the earth's crust it is usually found in the polycrystalline state or as small crystals. Large crystals, reasonably free from twinning and flaws, are relatively rare and most of the supply for piezoelectric purposes comes from Brazil.

Attempts have been made to grow synthetic quartz for over a century, but, except for the work of Spezia in 1900, they resulted only in the production of minute crystals. The scarcity of high-grade Brazilian quartz during the war presented a new aspect to this problem and in the early 1940's work began both in this country and in Germany, and more recently it has also been followed in the U.S.A.

HISTORY OF THE PREPARATION OF QUARTZ CRYSTALS.

Schafhäutl (1845) produced microscopic hexagonal crystals of quartz by heating freshly precipitated silica in Papin's digester for eight days. Many variants of this experiment were subsequently carried out by geologists and mineralogists. Mineralizers added, in an effort to improve quality and size, included hydrochloric acid (de Sénarmont, 1849, 1851), carbonic acid (de Sénarmont, 1851), and hydrofluoboric acid (von Chroustschoff, 1887). Most of these experiments were conducted at

temperatures between 200° and 300° C., and many lasted several months. Other hydrothermal methods that were tried included Daubrée's (1859) interesting experiment of heating glass tubes in water in an autoclave. He obtained a kaolin-like mass in which doubly-terminated, perfect quartz crystals were embedded. This result was confirmed by Bruhns (1889) who added ammonium fluoride as a mineralizer. All these experiments were successful in producing quartz crystals, often of good quality, but the crystals were invariably small and usually microscopic.

Spezia (1900–1909), however, carried out a series of experiments which showed that large crystals could be grown in the course of a few months provided an adequate source of raw material was available. His method was based on the fact that quartz is more soluble in a solution of sodium metasilicate at temperatures above 300° C. than below it. His apparatus consisted of an autoclave which was heated by gas at the top and cooled by water at the bottom. The extremes of temperature that he obtained on the outside of the autoclave in a typical experiment were between 326° and 337° C. at the top, and 165° and 178° C. at the bottom. A silver wire basket containing quartz chips was placed in the hot part of the autoclave and a truncated quartz crystal was suspended some distance below. As a result of the quartz chips dissolving the density of the solution around the basket increased and the heavy liquid flowed down past the seed crystal. This being at a lower temperature, the liquid became supersaturated, and the seed grew. After one typical experiment had been in progress some hundred days, Spezia quenched the bomb and opened it. He found the two truncated crystals he had inserted had grown complete rhombohedral terminations, and the crystals had increased in weight by 97 and 79 %. One of Spezia's crystals is shown in fig. 1. He found that quartz crystals grown in a simple sodium metasilicate solution were cloudy, but that if he added 'a handful' of sodium chloride, the quality was excellent.

Day and Shepherd (1906) published some experiments which showed that quartz could be obtained by heating magnesium ammonium chloride with sodium metasilicate and water in a steel bomb to 400° or 450° C. for three days. Only small crystals were obtained. Fenner (1912, 1914) heated silica glass or amorphous precipitated silica with water and sodium carbonate in a steel bomb at a temperature between 400° and 500° C. for two or three days, and obtained perfect doubly-terminated crystals 2 or 3 mm. long.

Two of the authors, Wooster and Wooster (1946), set up an apparatus

similar in all respects to that used by Spezia and carried out a number of tests on the growth and solution of silica in the form of quartz, silica glass, and soda glass. The result obtained by Spezia that quartz could be grown on a seed crystal in the cooler part of an autoclave when a source of quartz was present in the hotter part, was confirmed. The rate of growth obtained was so slow that the process did not appear promising. At the same time it was found that silica glass was considerably more soluble in sodium metasilicate than broken crystalline quartz. Minute crystals of quartz are readily obtainable from the devitrification of silica glass under these conditions, but attempts to grow large crystals by allowing only one nucleus to develop were unsuccessful. This work, however, led to a new process for growing large crystals of quartz, which depended on the greater solubility of silica glass compared with that of quartz under hydrothermal conditions. In an autoclave containing both silica glass as source material and quartz seeds, the solution could be saturated with respect to the vitreous phase and supersaturated with respect to the crystalline seed, on which growth of quartz would consequently ensue. The process could thus be carried out under isothermal conditions, the temperature gradient used by Spezia being unnecessary. Growths of up to 0·5 mm. on each side of a seed plate cut parallel to a major rhombohedral face (10$\bar{1}$1) were obtained in a run of about a day. Due to the very high supersaturation obtained in this isothermal process, spurious seeding occurred on the wall of the bomb and a large part of the source devitrified in situ. Increasing the amount of source only increased the amount that devitrified and did not increase the amount available for deposition on the seed. Thus the run could not be increased beyond a day and to grow a large crystal the autoclave had to be frequently recharged and the growth built up in layers. It has been found that during the initial stages of each cycle of growth there is a thin disordered layer which is clearly visible under the microscope.

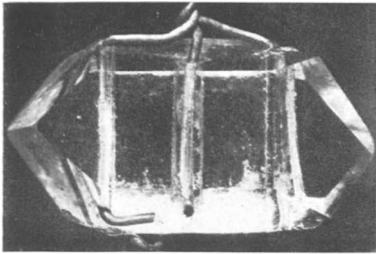Numerous attempts have been made to overcome the discontinuous

FIG. 1. Quartz crystal showing pyramidal terminations, grown by G. Spezia in 1906, on a truncated prism of natural quartz as seed (with supporting wire). ×4. (Kindly loaned by the University Museum, Oxford.)

nature of the isothermal process but these have met with little success. In one of these attempts, a method of circulating a silica-saturated solution at high pressure from one chamber containing the source to another containing the seed crystals was tried.

The high supersaturation encountered in the isothermal process gives rise to very variable results and it has been found to be extremely
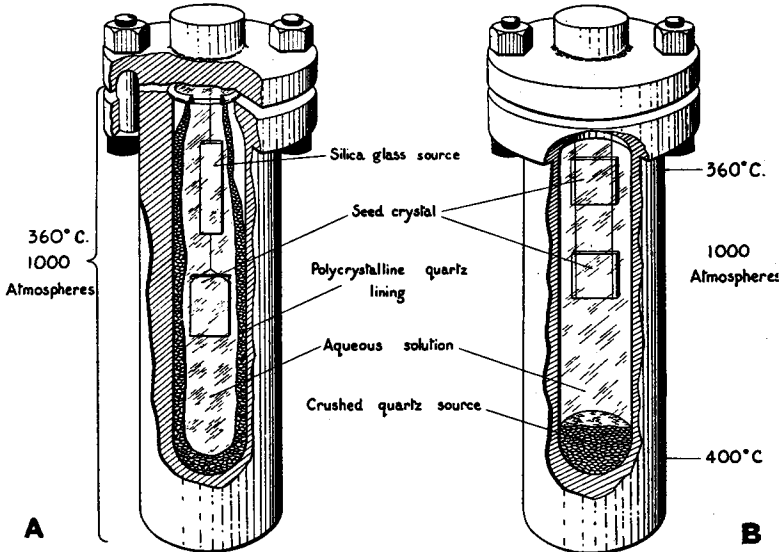

FIG. 2. Autoclaves showing the difference of arrangement in the isothermal (A) and temperature-gradient (B) methods.

difficult to produce a thick layer of quartz which shows no imperfections (Thomas, Wooster, and Wooster, 1949). This variability and the discontinuous nature of the process have led to a method based on the temperature-gradient process of Spezia being preferred. This possesses the advantages of a readily controllable supersaturation and gives a continuous growth of high quality. A diagram comparing the arrangements in the autoclaves in the isothermal and temperature-gradient methods is shown in fig. 2.

Independent of the work carried out in this country, Nacken (1945) devised a process similar to the isothermal method which we had used. Nacken's work ceased in 1944 but was taken up by workers in the U.S.A. After their early attempts at overcoming the difficulties of the isothermal technique had failed, Hale (1948, 1949) and Walker and

Beuhler (1950) started using a form of temperature-gradient-technique which, although similar to that described in the following section, possesses certain significant differences. These have been briefly discussed by Brown et al. (1951).

GROWTH OF LARGE CRYSTALS.

The work reported here has been carried out using autoclaves 10 inches long with an internal diameter of 2 inches and walls a little over $\frac{3}{4}$-inch thick. Mild steel, durahete steel, and S.80 stainless steel have all been used successfully, although the superior strength of the two latter materials has proved advantageous. The autoclaves are sealed using a mild steel lens ring. When the lid is bolted to the body of the autoclave with eight bolts of high tensile steel, a line contact occurs between the spherical surfaces of the lens ring and the conical surfaces turned on the lid and body. In this manner the autoclaves have been sealed to withstand pressures approaching 2000 atmospheres.

The furnaces used are simple but effective and consist of a hot plate on which the autoclave stands, completely surrounded by broken refractory material for thermal insulation, as shown in fig. 3.

The temperatures at various points of the autoclave are measured by strapping on thermocouples. The temperature at the base is controlled to within $\pm 1°$ C. using a mechanical temperature-regulator, whilst the top is allowed to attain an equilibrium temperature some 40° C. lower than that at the base. Detailed measurements of the temperature distribution have shown that a large part of this temperature drop occurs in the metal forming the base of the autoclave and that the temperature gradient in the liquid is certainly less than $\frac{1}{2}°$ C./inch. This small gradient in the liquid enables crystals of comparable size to be grown throughout the length of the autoclave.

The pressure developed under working conditions is controlled primarily by the temperature and the initial degree of filling of the liquid in the autoclave. The liquid used is a 10 % sodium carbonate solution in water.

The source material which maintains the supersaturation of the liquid with respect to silica in the vicinity of the seed crystals is in the form of melting-quality quartz which has been crushed in a mechanical ore crusher. The size of the particles of the source material is an important factor affecting the rate of growth and hence the quality of the synthetic crystals. The quartz used as source is of comparatively low cost since it can be of small size and the presence of flaws and twinning is immaterial.

The seed crystals are cut in the form of rectangular plates, approximately 2 mm. thick, and are suspended from the lid of the autoclave by fine platinum wires looped round the seeds near the edges. The seeds hang with the major surfaces vertical to avoid the deposition of rubble on the growing faces. The orientation of the seed plate with respect to
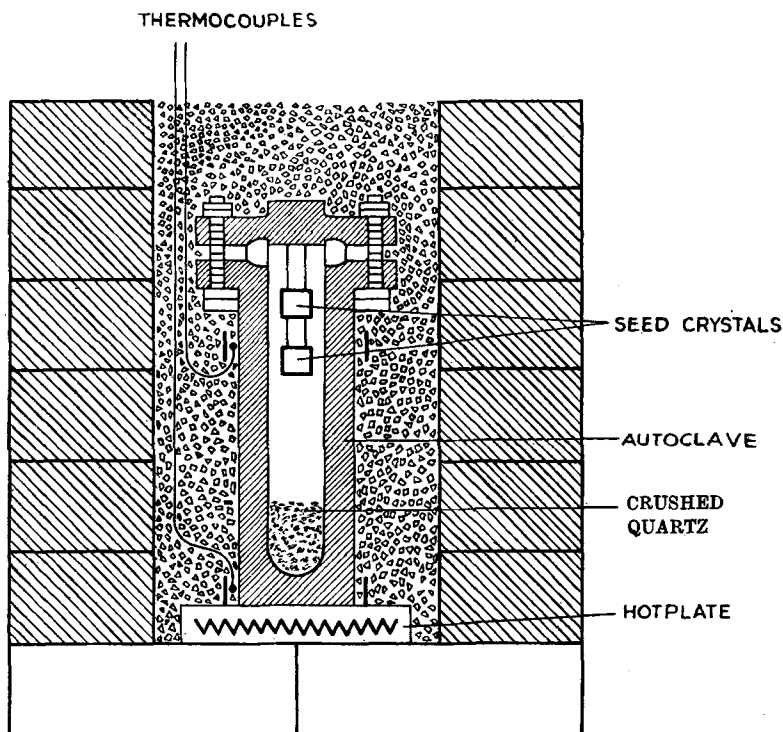
THERMOCOUPLES

FIG. 3. Furnace arrangement in the temperature-gradient method.

the crystallographic axes is of considerable importance, the form of the final crystal and the rate at which it grows being dependent upon it. The majority of the experiments have been carried out using plates cut parallel to the basal plane (0001), although plates cut parallel to both positive and negative rhombohedral faces have been used.

Early experiments, using the temperature-gradient process, soon showed that the growth on the basal plane, although not a natural form face, can be of good quality as long as the growth rate is controlled to be less than a critical value. This contrasts with the results published by Hale (1948) and Walker and Beuhler (1950) who have reported that

the growth is usually misoriented and filled with inclusions until the crystal is completely 'capped', that is, until the pyramid has fully developed and the basal plane has disappeared. This poor quality capping is similar to that which occurs in the growth of water-soluble crystals, such as ethylene diamine tartrate and ammonium dihydrogen phosphate. Much of the work since these early experiments has been directed towards an understanding of the factors affecting the quality and rate of growth of crystals grown in this manner. It has been found that the walls of the autoclave must be scrupulously clean before the start of an experiment or else small crystals of quartz will develop on the walls and result in a considerably reduced rate of growth. (In the earlier isothermal method the presence of a thick lining of polycrystalline quartz was essential for clear growth.) If the supersaturation is too high, spontaneous nucleation will occur on the wall of the autoclave however clean it is and the quartz deposited on the seed crystals will tend to become less perfect. The reproducibility of the process is such that the time and conditions of a growth run to produce a given size of crystal can be predicted reasonably accurately as long as the growth rate is kept below the critical value. The crystals grown under optimum conditions are free from all flaws and twinning.

The critical rate of growth, above which the quality of the quartz deposited is no longer perfect, is itself a function of the process variables and has been considerably increased since the beginning of this work. In a full-length run it is now possible to deposit quartz at an average rate of 0·6 mm./day in the direction of the optic axis on each side of the seed without any visible defects occurring. The characteristics of the process are such that this involves a maximum rate of growth in excess of 1·0 mm./day. In this manner crystals weighing up to 150 grams and with growths up to 16 mm. on each side of the seed have been grown in about four weeks. Fig. 4 shows such a crystal, together with a similar growth on a seed crystal of somewhat smaller area. This growth is the largest that can be obtained in the 2-inch bore autoclaves without the crystal coming into contact with the wall. However, it is remarkable that the growth is still of good quality even when the fully-grown crystal nearly fills the bore of the autoclave. Crystals more closely resembling the development of natural crystals can be obtained by growing on to seeds of smaller area. Two crystals grown on 2 cm. square seeds are shown in fig. 5 and these crystals have been very nearly completely capped.

The quality of a typical synthetic crystal is shown in fig. 6 by a

photograph of a crystal immersed in benzene, which was chosen because its refractive index differs sufficiently from that of quartz for some relief to be visible. There is no sign of any flaws or inclusions and the seed/ growth interface cannot be discerned. A similar photograph (not repro- duced here) was taken in methyl salycilate. This liquid very closely
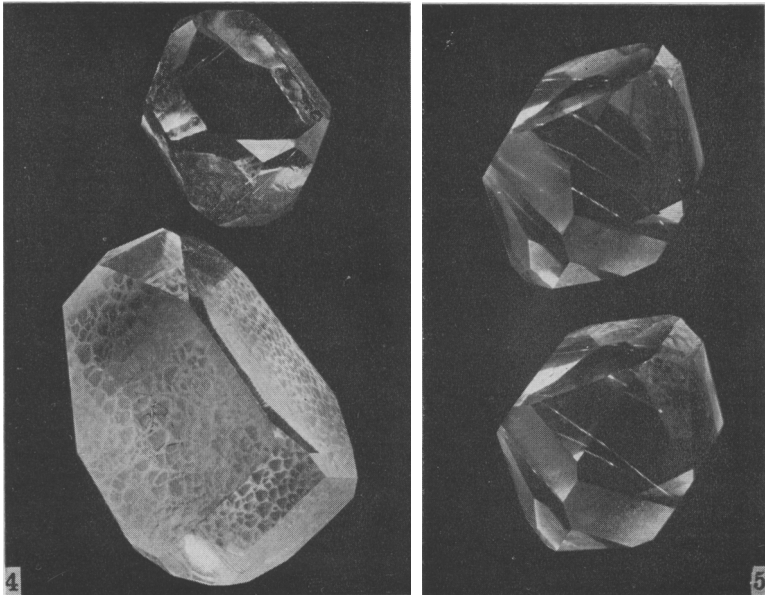

FIG. 4. Synthetic quartz crystals (150 and 70 grams). The mottling is due to the large cobbled surfaces approximating to basal planes. ×0·6.

FIG. 5. Synthetic quartz crystals almost completely capped by rhombohedral faces. ×1·2.

matches the mean refractive index of quartz and all that could be seen were the supporting wires and the reference number written on the crystal surface.

Above the critical rate of growth, the quality of the quartz deposited becomes steadily worse. At very rapid rates of growth the quartz is deposited as a large number of small pyramids having the appearance of a drusy mineral. Liquid may be included in gaps in the deposit so as to give the crystal an opaque appearance. However, far less obvious flaws can occur and these may still be sufficient to make the crystal unsuitable for the manufacture of oscillator plates. Some crystals which

appear to be visually perfect show marked Tyndall scattering in a high-intensity light beam. From the distribution of the intensity of the scattered light it has been inferred that the flaws causing the scattering are less than $0 \cdot 1\lambda$ and may even be of the order of molecular dimensions. These minute flaws have been found sufficient to spoil the performance of high-frequency oscillator plates. Slight reduction in the rate of growth has overcome this defect.
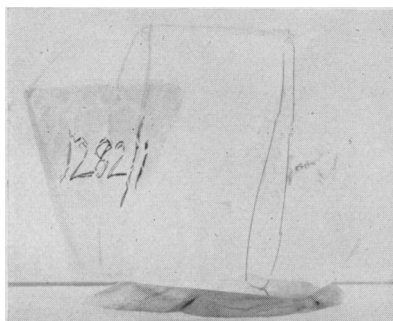

FIG. 6. Synthetic quartz crystal (no. 1282) immersed in benzene, showing freedom from flaws and inclusions. (Dark lines are the wires which suspended the seed plate.)

Under optimum conditions, using single-crystalline seeds, twinning is never found, but when the rate of growth exceeds the critical value Dauphiné twinning may occur. This normally results in the appearance of a major rhombohedral face where the minor rhombohedral face should occur. No examples of Brazilian twinning have been observed. Growth on a twinned seed (whether Brazilian or Dauphiné) results in a similarly twinned growth, the twin boundary being propagated parallel to the optic axis.

MORPHOLOGY.

The morphology of synthetic quartz grown on to Z-cut seeds follows closely that of natural quartz in most respects. The forms which commonly occur on natural quartz are: $m\{10\bar{1}0\}$, $R\{10\bar{1}1\}$, $r\{01\bar{1}1\}$, $s\{11\bar{2}1\}$, $x\{51\bar{6}1\}$. Trapezohedra other than x are recorded, e.g. $\{41\bar{5}1\}$ and $\{31\bar{4}1\}$, but forms other than m, R, r, s, x are very rarely observed. The R face is often bright and smooth and larger than the complimentary r face which is frequently dull or even matt. The m faces are usually striated in a direction perpendicular to the optic axis.

The forms which occur on synthetic quartz depend on the orientation and shape of the seed plate and on the amount of quartz which has been deposited on it. When growing on a square seed plate cut parallel to (0001) having sides parallel to ($1\bar{1}00$) and ($11\bar{2}0$) the following association of forms develops: $m\{10\bar{1}0\}$, $R\{10\bar{1}1\}$, $r\{01\bar{1}1\}$, $a\{11\bar{2}0\}$, $o\{11\bar{2}2\}$, and the trapezohedron of indices $\{h1\bar{h+1}1\}$ where h is not greater than 8.

The stereographic projections of right-handed natural and synthetic quartz crystals are shown in fig. 7. Due to the square shape of the seed plate on which the quartz has been deposited, it will be seen that a new zone of faces has appeared on the synthetic crystal. The zone axis for these faces is [1$\bar{1}$0] and it contains the forms $a\{11\bar{2}0\}$ and $o\{11\bar{2}2\}$. Not
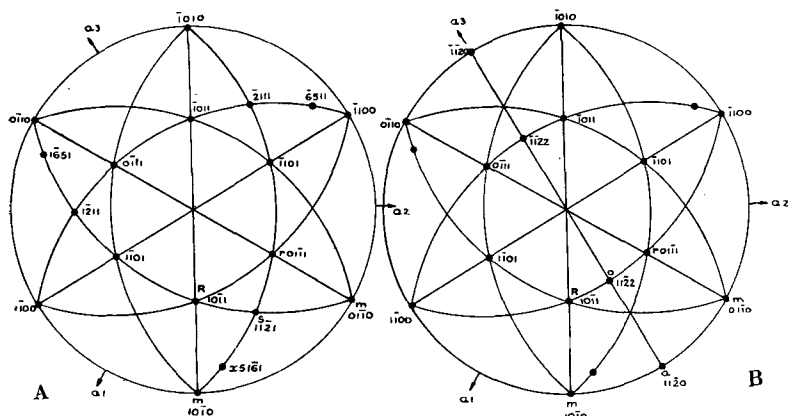

FIG. 7. Stereographic projections of right-handed quartz crystals: A, natural; B, synthetic.

all the faces corresponding to the forms a and o appear but only those which are parallel to one of the edges of the original plate, i.e.

$$a\ (11\bar{2}0),\ (\bar{1}\bar{1}20),$$
$$o\ (11\bar{2}2),\ (11\bar{2}\bar{2}),\ (\bar{1}\bar{1}2\bar{2}),\ (\bar{1}\bar{1}22).$$

These forms show an interesting difference at the two ends of the diad axis, a_3. Quartz is more rapidly deposited at the end of the diad axis at which the trapezohedral faces do not develop and hence the ($\bar{1}\bar{1}20$) face is smaller than the ($11\bar{2}0$) face at the opposite end of the axis. The trigonal pyramids o are considerably more developed at the fast-growing end of the diad axis and in many cases the faces ($11\bar{2}2$) and ($11\bar{2}\bar{2}$) are completely absent. The forms o and a are only intermediate forms in the development of the crystal and tend to disappear as the crystal grows. This is shown by the drawing of a typical fully-grown crystal in fig. 8. It may be noticed that the s form $\{11\bar{2}1\}$ which frequently occurs on natural crystals and which is in the same zone as o and a has not been observed on synthetic quartz.

The trapezohedral form which occurs on a right-handed synthetic quartz crystal is prominent only at the negative end of the diad axis

which is parallel to an edge of the seed plate. It is often rounded or striated, but where goniometric measurements have been possible it has been found that it has indices varying between $\{51\bar{6}1\}$ and $\{81\bar{9}1\}$.

The face (0001) is never found, but the growing surface of the crystal remains approximately perpendicular to the optic axis. It develops a characteristic cobbled appearance as shown in fig. 9. The bounding edges often project above the mean (0001) plane which passes through the centre of the growing face.
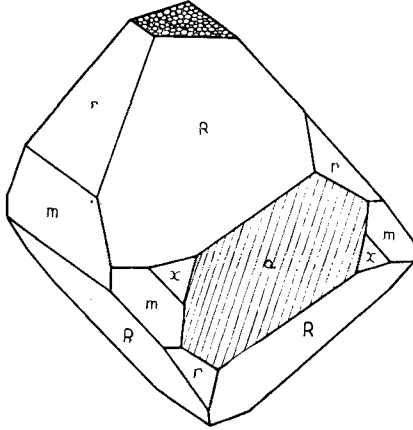
The surfaces of the rhombohedral faces on natural quartz show many varied growth features, but those shown on synthetic crystals are, on the whole, of a very simple nature. The partial development of vicinal faces gives rise to conical hills; a particularly clear example found on a R face is shown in fig. 10. On the other hand, the prism faces of synthetic crystals are rarely found to be striated.

FIG. 8. Habit of a typical synthetic crystal.

Where optical measurements could be made without serious disturbance due to vicinal faces, the interfacial angles have been found to correspond with those of natural quartz within the usual accuracy of measurement.

PHYSICAL PROPERTIES.

To assist in the appraisal of the synthetic quartz which has been grown by the temperature-gradient method a number of the physical properties have been measured and compared with the best-grade natural quartz from Brazil.

Optical properties.—Measurement of the refractive indices on an Abbe refractometer employing a total-reflection method has shown no differences in the indices of natural and synthetic quartz to within the experimental error of ± 0.0002. A prism has been cut from a crystal so that when used on a spectrometer part of the light from the collimator passes through synthetic quartz and the remainder through natural quartz. In this way it has been found that the chromatic dispersion is the same for the two materials.

Measurement of the absorption curves in the ultra-violet and infra-red regions has shown some very interesting results. Ultra-violet measurements have been made in the Schumann region from 220 mμ using a vacuum grating spectrograph. In the infra-red, measurements have been made from 1–5 μ using both a Perkin-Elmer spectrometer and a Grubb-Parsons automatic recording spectrometer.
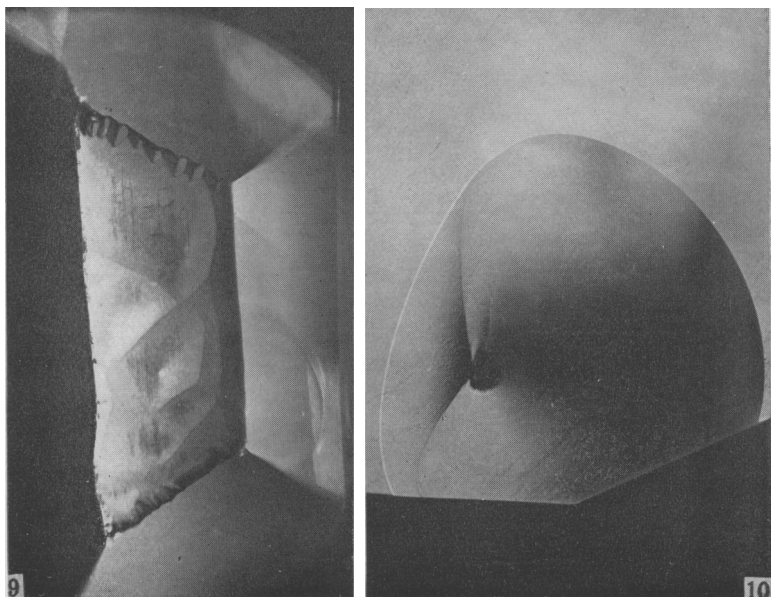

FIG. 9. Cobbled surface approximating to (0001) with adjacent rhombohedral faces. ×5.
FIG. 10. Growth feature on a major rhombohedral face R (10$\bar{1}$1). ×6·3.

Three synthetic crystals have been examined and compared with a specimen of high-quality natural quartz. Specimen 1 was a crystal showing no sign of Tyndall scattering in a high-intensity light beam, specimen 2 showed scattering of medium intensity, and specimen 3 showed strong scattering. The results for the infra-red region are shown by the curves for percentage transmission against wave-length given in fig. 11. Specimen 1 has a curve similar to that of the natural quartz crystal including the characteristic absorption band at 2·95 μ. Specimens 2 and 3 show a broad absorption band centred about 3·2 μ, this band being more intense in specimen 3. This absorption band and the

associated Tyndall scattering could be explained by the presence of sub-microscopic liquid inclusions. For example, if the resultant absorption of these inclusions was equivalent to a thin film of water, say 0·01 mm. thick, this would give rise to an absorption band extending from about 2·75 μ to 3·5 μ.
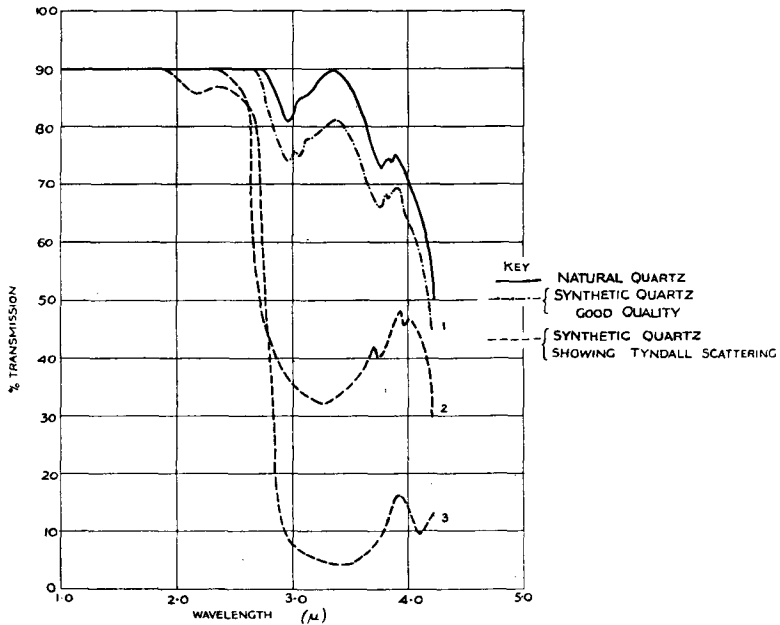

FIG. 11. Infra-red transmission curves through 1 mm. of natural and synthetic quartz.

A somewhat similar trend in the behaviour of the three specimens is shown by the measurements in the ultra-violet region, the cut-off extends farther into the ultra-violet as the degree of scattering lessens. Table I shows approximate wave-lengths for 50 % transmission through 1 mm. of quartz.

TABLE I. Ultra-violet transmission through 1 mm. of quartz.

Specimens.	Wave-length for 50 % transmission.
High quality natural Brazilian quartz	150 mμ
Synthetic specimen 1	165 mμ
,, ,, 2	180 mμ
,, ,, 3	193 mμ

Remembering the variations that occur in natural quartzes, synthetic

quartz free from Tyndall scattering would appear to be broadly similar to natural quartz in regard to its spectral transmission.

Using a half-shadow polarimeter, it has been shown that the rotary polarization of natural and synthetic quartz is the same to $0 \cdot 01°$/mm. for the sodium D lines.

Electrical properties.—The performance of piezoelectric oscillator plates cut from the synthetic crystals is not only of practical importance, but it is perhaps the best guide to the overall quality of the material.

Early measurements were carried out on small low-frequency bars which were the only type that could be fabricated from the crystals available at the time. These were found to compare favourably with similar natural quartz bars. A thorough comparison has been carried out more recently using very thin high-frequency plates which provide the most stringent test. The latest of these synthetic oscillator plates are as good as natural quartz, but earlier plates cut from crystals showing Tyndall scattering were considerably poorer than their natural counterparts.

Although a complete study has not yet been carried out to determine the elastic constants, the above work has shown that the frequencies of synthetic and natural quartz oscillators of identical size are the same to within one part in a thousand.

Direct static measurements of the piezoelectric constant d_{11} has shown that the values for natural and synthetic quartz are the same to within 1%.

Other properties.—A comparison of the densities of specimens of natural and synthetic quartz has been carried out using a very sensitive suspension method capable of detecting a difference of two parts in a hundred thousand between two specimens (Douglas and Jones, 1948). Measurements to date on a number of specimens do not indicate any significant difference between the mean densities of natural and synthetic quartz, or in the spread of values about the mean figure.

Comparative hardness figures were obtained using a Vickers micro-hardness tester using a load of 20 grams. It is difficult to obtain accurate hardness measurements on a crystalline material like quartz. Large loads (about 1 kg.) cause brittle fracture to occur, whereas with small loads such as were used in these measurements elastic recovery may occur giving results which are too high. The results obtained agree to 5%, which is within the experimental error for this type of measurement.

Preliminary measurements have been carried out on the inversion temperature between α- and β-quartz for natural and synthetic powders.

Samples of crushed natural quartz and of a mixture of natural and synthetic quartz were heated simultaneously in a twin calorimeter of a differential thermal analysis apparatus. No difference in the inversion points has been detected to within $\pm 1^\circ$ C.

In addition to the observation of Tyndall scattering, the perfection of the synthetic quartz has been studied using the X-ray topograph technique (Wooster and Wooster, 1945). No difference has been observed in the quality of the best natural and synthetic quartz. At the same time comparison of the lattice spacings has shown no difference to within one part in six thousand.
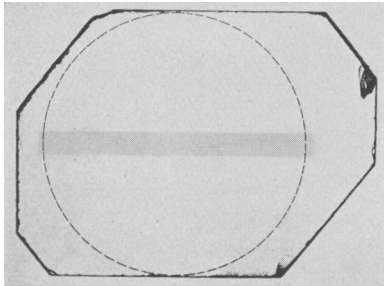

Fig. 12. Section through a synthetic quartz crystal after X-ray irradiation over the area bounded by the broken circle. The darkened region corresponds to the natural quartz seed.

Synthetic quartz grown by the standard temperature-gradient process does not darken when exposed to X-rays even when quite long exposures are used. This result is illustrated by fig. 12, which shows a section of a synthetic crystal grown on a seed plate of natural quartz. Only the central part of the section, corresponding to the natural seed, shows any darkening (Brown and Thomas, 1952).

Work on the removal of Dauphiné twinning from quartz had previously shown that the degree of darkening of natural quartz when exposed to X-ray irradiation was dependent on its perfection and the deeper the darkening the more difficult the crystal was to untwin (Wooster, Wooster, Rycroft, and Thomas, 1947). Synthetic quartz grown under conditions which do not produce the highest quality crystals does darken when exposed to X-rays, but the type of darkening may be different to that found in natural quartz. For instance, quartz grown by the isothermal method darkens to a purple colour similar to that of amethyst. Quartz into which impurities such as copper and arsenic have been introduced is found to darken in a non-uniform manner which is presumably related to the distribution of impurities in the crystal.

CONCLUSIONS.

The work reported here has led to the development of a process capable of producing synthetic quartz crystals which are, in every way,

as good as the best Brazilian quartz crystals. Crystals, weighing up to 150 grams and with growths of up to 16 mm. in the direction of the optic axis on each side of a seed crystal cut parallel to the basal plane, have been grown in about four weeks. The quality of these crystals is dependent on the rate of growth, and below a certain critical value the crystals are completely free from all flaws and twinning.

The physical properties of synthetic quartz have been compared with high-quality natural quartz and it has been found that, except for the behaviour under X-ray irradiation, the properties of the two materials are very similar. The non-susceptibility of synthetic quartz under X-ray irradiation is the only known means of distinguishing the two materials and may be evidence for the supposition that the best synthetic material is more perfect than most natural quartzes.

The present work may throw some light on the rate of growth of large natural quartz crystals. The conditions for the production of flawless synthetic quartz crystals are critical, and it would therefore appear that the best natural crystals must have grown under conditions which did not vary over a wide range.

To estimate the time taken for natural quartz crystals to grow would require a knowledge of the supersaturation and temperature of growth, both of which are very difficult to estimate. It can, however, be concluded from this work that in nature quartz may have grown relatively rapidly; a large natural crystal may have taken only a few years to grow. These conclusions, of course, apply only to natural crystals which have grown under hydrothermal conditions and not to crystals which have been grown from the melt or from vapour.

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