the diffraction patterns of square and rectangular eyepieces and eye-pieces of triangular and circular form were well known, both geometrically and analytically. The effect on the diffraction pattern of repeating such shapes in regular arrays was also studied in the classical investigations of circular holes arranged on a triangle, and square holes arranged in a square, etc. (Airy 1834, Bridge 1858). Nowadays the relation between $g(xyz)$, a distribution of atoms, or more generally an electron density distribution, and $G(XYZ)$, its structure factor or Fourier transform (Hettich 1935, Wrinch 1946, Glaser and Wrinch 1953), is much used in crystal structure analysis and we recognize the analysis of the diffraction pattern of repetitions of various shapes on a lattice in the works of the astronomers in its modern form in which, for a distribution g, repeated on a lattice L, the structure factor is G, sampled at the reciprocal lattice L^*.

In Figs. 1 and 2 above, we have an illustration of the type of relation between a non-periodic distribution g and the square of its structure factor $[G]^2$. We may compare the edges of the small triangle in Fig. 3 forming a trigonal set of directions, with the preferential directions in the distribution, Fig. 1, and the direction of the rays of the star lying at right angles to these axes, in Fig. 3, with the preferential direction of the rays in the star of Fig. 2. Further analysis of cases of this kind, with special reference to such issues as the "spacing" between the parallel distributions in Fig. 1 and the detailed geometry of the star in Fig. 2 can be carried out in terms of the general relations (Wrinch 1946) between a distribution g and its Fourier transform G.

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HYDROTHERMAL GROWTH OF ALUMINUM ARSENATE CRYSTALS

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The growth of aluminum orthoarsenate crystals of sufficient size and quality for evaluation of their piezoelectric properties was undertaken because previous studies had shown that its crystal structure was

analogous to that of quartz with three of the silicon atoms of the elementary cell of quartz statistically substituted in a 1:1 ratio by Al^{+3} and As^{+5} ions (1). The *c*-axis is doubled in order to distribute properly the Al^{+3} and As^{+5} ions.

A number of attempts were made to synthesize aluminum arsenate crystals from various systems before it was determined that the system Al_2O_3-As_2O_5-H_2O would be most suited for the growth of this crystal. Initial experimentation indicated that aluminum arsenate had a retrograde solubility in arsenic acid solutions and that the alpha form could be grown above 200° C. in medium pressure stainless steel and tool steel autoclaves. Because of the corrosive nature of the arsenic acid at the crystallization temperature, glass containers were used to hold the solutions in the autoclaves. Highly concentrated viscous solutions of arsenic acid were used as solvents for the feed material. In the majority of experiments the feed material was a recrystallized aluminum arsenate but aluminum arsenate reagents were also used quite extensively.

Solutions for growing aluminum arsenate crystals were prepared by heating to 200° C. sufficient As_2O_5, H_2O and $AlAsO_4$ to make a 33N solution containing 1.2 moles of $AlAsO_4$. This preliminary heating period of sixteen hours was accomplished in a sealed autoclave. The solution obtained was clear and viscous. Further heating of it in a sealed autoclave at a temperature of 235–240° C. for an eighteen hour period produced small crystals of aluminum arsenate, 2–3 mm. long. They were generally prismatic in shape, clear and of good quality.

A number of techniques were tried to increase the size of the crystals to the point where they could be cut and tested. The first one involving the use of seeds suspended in the solutions by platinum wires was unsuccessful because the seeds always lost more weight in being brought up to the crystallization temperature (235° C.) than they would gain while being held at this temperature. The period of time required to reach equilibrium between the seed and solution at this temperature was eighteen hours. A similar dissolution of the seed occurred in experiments made at lower temperatures. The rate was somewhat slower than the rate at 235° C. but it was still sufficient to prevent the crystals from increasing in size.

To prevent the dissolution occurring during the heating up period, the seed crystals were placed on platforms above the solutions and dropped into them by tilting the autoclave when the crystallization temperature was reached. This temperature was predetermined for the particular concentration of aluminum arsenate in the 33N acid.

With this technique and by changing the solution every eighteen

hours, it was possible to grow $1\frac{1}{2}''$ long crystals in a period of sixty days. The daily growth rate was quite slow and the quality poor, being quite milky in appearance, although well faced. The seeds used in these experiments were clear prismatic single crystals without any apparent flaws or inclusions. As growth progressed from cycle to cycle, the quality of growth became poorer until the crystal became completely opaque. The prism faces also disappeared with continued growth, merging into rhombohedrons. Some of the crystals produced by this method are shown in Fig. 1.
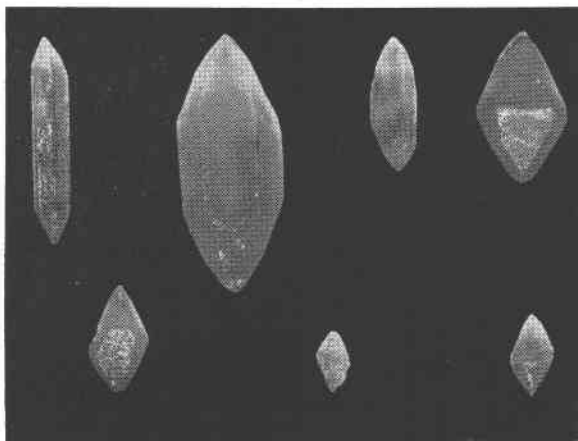

FIG. 1

Examination of a thin section of one of the crystals produced in this manner under the polarizing microscope indicated layers of microscopic bubbles corresponding to the cycles of growth. These layers of bubbles were believed formed as a result of etching during the heating up and cooling down portions of the cycle. Growth over these pits formed the bubble inclusions believed to be responsible for the milky appearance of the aluminum arsenate crystals grown in this manner.

To prevent the formation of these inclusions in aluminum arsenate crystals, a method was developed for their growth in an extended single cycle. The method involved the use of a temperature gradient in combination with a tilted autoclave. Small aluminum arsenate crystals were used as feed material and 33N arsenic acid as the solvent. The seed was suspended $\frac{1}{2}''$ to $\frac{3}{4}''$ above the surface of the solution to keep it from dissolving while being heated to the crystallization temperature. The seed, solvent and feed material in a pyrex tube were then sealed in a $12''$ long stainless steel autoclave and heated in a furnace designed to produce a

20° C. temperature difference between the bottom (240° C.) and middle (260° C.) of the bomb. Because of the retrograde solubility of the material the feed material was placed at the bottom of the bomb (cooler portion) and the seed at the middle (hotter portion). When the crystallization temperature is reached (260° C.), the autoclave and furnace are tilted at an angle of 45° to immerse the seed into the solution. The feed material dissolves in the cooler bottom portion of the autoclave and is carried up by thermal currents to the middle section of the bomb where it deposits on the seed near the interface of the liquid and vapor phases. This is just the reverse of the procedure used to grow synthetic quartz at the Clevite Research Center (4) and Bell Telephone Laboratories (5).

Development of this technique was an outgrowth of many unsuccessful attempts to grow aluminum arsenate crystals in vertical autoclaves with temperature gradients. The growth obtained was very clear and free of the microscopic bubbles that were causing the cloudiness in these crystals. Some idea of the conditions used in various runs by this technique and the rates of growth obtained under these conditions may be had from the data listed in the following table.

	Runs		
	1	2	3
Crystallization temp. (° C.)	254	263	285
Gradient (° C.)	20	17	25
Type of seed	Faced xtal	Faced xtal	Faced xtal
Initial seed wt. (grams)	6.81	9.00	0.40
Final seed wt. (grams)	14.26	14.90	2.80
Wt. increase (grams)	7.45	5.90	2.40
Length of run days	22	11	7
Quality of growth	Excellent	Good	Good

In the course of investigating methods for the continuous growth of aluminum orthoarsenate, a hydrated form was prepared from 280 cc. of a 33N arsenic acid solution containing 29 grams of undissolved aluminum oxide. The solution was heated in a sealed vertical autoclave in a furnace containing a fire brick diaphragm. Controlled heat was supplied to the portion of the furnace above the diaphragm while that below was unheated. The autoclave was positioned in the furnace so that the seed would be just above the diaphragm (225° C.) and the feed material below it (177° C.). The diaphragm was used to provide a sharp temperature

gradient between the seed and feed. After seven days of these conditions, the autoclave was quick cooled and opened. The seed had partially dissolved but at the bottom there was an aggregate of fibrous crystallites in parallel arrangement. The fibrous nature of this aggregate is illustrated in Fig. 2. X-ray examination of these crystals and other tests indicated that they were a hydrated form with the probable composition $Al_2O_3 \cdot 3As_2O_5 \cdot 10H_2O$ (2).

FIG. 2

The alpha to beta inversion of aluminum orthoarsenate was checked by differential thermal analysis and found to be 571° C., approximately that of quartz. Crystals of the order of 1–2 mm. were used for this determination.

Small prismatic aluminum orthoarsenate crystals produced as described herein were tested for piezoelectricity in the Giebe-Schiebe "Click" tester. The response obtained was of the same order of magnitude as that obtained from aluminum orthophosphate. Confirmation of this effect was obtained by testing X-plates of aluminum orthoarsenate in the electrometer. Full evaluation of its piezoelectric properties was prevented by the occurrence of sporadic electrical twinning throughout plates cut normal to the X-axis and at the same angle (35°15') as that of the AT-cut in a quartz crystal. Twinning was detected by etching in phosphoric acid.

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CALCULATED ATOMIC SCATTERING FACTORS FOR SILICON AT 25° C.

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Despite the central position of silicon in the inorganic world and its singular importance in inorganic crystallography, no accurate atomic scattering factors at room temperature have been published for this element. Our recent studies of the crystallography of silicon have necessitated the calculation of these f values at 25° C. as a function of $\sin \theta/\lambda$; we feel that this information will be a convenient reference for crystallographers.

Bragg and West (1928) have published semi-empirical scattering factors for silicon at room temperature as a function of $\sin \theta/\lambda$; their f value for $\sin \theta/\lambda = 0.2$ is actually greater than the corresponding f_0 value calculated by Hartree's method (1928). Using Hartree's method, James and Brindley (1931) have compiled accurate f_0 values for silicon.

Recently, Pearlman and Keesom (1952) have determined the characteristic temperature of silicon, 658° K, thus allowing calculation of the temperature factor and atomic scattering factors for temperatures above 0° K. Therefore, the formula $f = f_0 \exp(-B \sin^2 \theta/\lambda^2)$ given in the Inter-

ATOMIC SCATTERING FACTORS FOR SILICON

$\sin \theta/\lambda$	0.0	0.1	0.2	0.3	0.4	0.5
f_0 Hartree	14.0	11.35	9.4	8.2	7.15	6.1
f_{298} calculated	14.0	11.3	9.3	8.0	6.8	5.6
f_T Bragg & West	14.0	11.2	9.6	8.0	6.6	5.5

$\sin \theta/\lambda$	0.6	0.7	0.8	0.9	1.0	1.1
f_0 Hartree	5.1	4.2	3.4	2.95	2.6	2.3
f_{298} calculated	4.55	3.6	2.8	2.3	1.9	1.6
f_T Bragg & West	4.4	3.6	2.9	2.4	1.9	1.6

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