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The Society now has 230 members. Membership blanks may be obtained from the Secretary-Treasurer, c/o Philips Laboratories, Inc., Irvington-on-Hudson, N. Y.

Abstracts of papers presented at the Second Annual Spring Meeting held at Post-graduate School, U. S. Naval Academy, March 19-21, 1947, are given below.

**THE DETERMINATION OF THE UNIT CELLS AND SPACE GROUPS OF  
CHILDRENITE, LINDGRENITE AND PROBERTITE BY THE  
BUERGER PRECESSION METHOD**

WILLIAM H. BARNES, *McGill University.*

The unit cell constants and the space groups of childrenite, lindgrenite and probertite have been determined by the Buerger precession method, using copper and molybdenum radiations. The following results have been obtained:

Childrenite:  $\text{AlPO}_4 \cdot \text{Fe}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , orthorhombic,  
 $a = 10.35 \text{ kX}$ ,  $b = 13.34 \text{ kX}$ ,  $x = 6.90 \text{ kX}$ ,  
 $n = 8$ ,  $Bba(2)$

Lindgrenite:  $2\text{CuMoO}_4 \cdot \text{Cu}(\text{OH})_2$ , monoclinic,  
 $a = 5.60 \text{ kX}$ ,  $b = 14.03 \text{ kX}$ ,  $c = 5.39 \text{ kX}$ ,  
 $\beta = 98^\circ 23'$ ,  $n = 2$ ,  $P2_1/n$ .

Probertite:  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ , monoclinic,  
 $a = 13.85 \text{ kX}$ ,  $b = 12.54 \text{ kX}$ ,  $c = 6.60 \text{ kX}$ ,  
 $\beta = 107^\circ 40'$ ,  $n = 2$ ,  $P2_1/n$ .

This work was carried out in Professor M. J. Buerger's Laboratory of X-Ray Crystallography at the Massachusetts Institute of Technology during the tenure of a Fellowship from the John Simon Guggenheim Memorial Foundation.

## THE STRUCTURE OF DIGLYCINE HYDROBROMIDE

ELSA BARNEY, *Massachusetts Institute of Technology.*

The Weissenberg method was used to determine the space group,<sup>1</sup>  $D_2^4$ , and the unit cell of  $a = 8.21 \text{ \AA}$ ,  $b = 18.42 \text{ \AA}$ , and  $c = 5.40 \text{ \AA}$ . The cell contains 4 ( $\text{C}_4\text{H}_{11}\text{BrN}_2\text{O}_4$ ).

For the determination of the parameters, the intensities of  $hk0$ ,  $0kl$ , and  $h0l$  reflections were determined by Dawton's method. The Weissenberg method using  $\text{CuK}\alpha$  radiation was used to obtain the  $hk0$  and  $h0l$  reflections. The precession method, using  $\text{MoK}\alpha$  radiation, was used to obtain the  $0kl$  reflections. From Patterson summations the bromine atom was located and by assuming that the bromine atom determined the phases, electron density maps  $\rho(xy0)$ ,  $\rho(0yz)$  and  $\rho(x0z)$  were made. These gave the locations of other atoms. However, which of these locations were for oxygen, which for nitrogen, and which for carbon, could not be ascertained from the relative heights of the electron density peaks, as the difference of scattering power of oxygen, nitrogen, and carbon is small. The peaks that represented the O, N, and C were decided upon by assuming the diglycine structure to be built up of glycine molecules of known structure.<sup>2</sup>

Further refinement is necessary on the atomic positions listed.

	x	y	z
C	.089	.380	.833
C	.106	.430	.120
O	.470	.112	.317
O	.196	.333	.842
N	.268	.430	.158
Br	.178	.035	.833
C	.423	.283	.517
C	.065	.172	.373
O	.475	.213	.650
O	.423	.283	.350
N	.145	.193	.158

<sup>1</sup> Space group determined by M. J. Buerger.

<sup>2</sup> Albrecht, G., and Corey, R., *J.A.C.S.*, **61**, 5 (1939).

### AN ELECTRONIC METHOD OF FOURIER SYNTHESIS

L. S. BIRKS, *Naval Research Laboratory.*

Fourier synthesis by the Bragg method is accomplished using a television receiver for projection of the individual terms in the series. Continuous, rather than stepwise variation in the amplitude, phase, and wavelength of the cosine terms is possible with equipment consisting of a television receiver and a stable oscillator of continuously variable frequency. A rotatable camera mount makes possible the addition of the individual terms in the proper direction with respect to the unit cell axes. About one-half hour is required to sum up a hundred terms.

### AN ALINEMENT CHART FOR THE POLARIZATION CORRECTION IN THE EQUI-INCLINATION WEISSENBERG METHOD

W. L. BOND, *Bell Telephone Laboratories.*

An alinement chart is presented for use with the equi-inclination Weissenberg method. The chart gives the polarization correction directly from the layer line screen setting<sup>θ</sup> and the distance of the reflection from the zero line.

### MAKING ORIENTED CRYSTAL PLATES FOR PIEZOELECTRIC INVESTIGATIONS

W. L. BOND, *Bell Telephone Laboratories.*

Crystals the size of sand grains, and known to be of low symmetry, are tested by the Geibe and Scheibe method. If active they are grown to pea size and three mutually perpendicular plates cut (arc holder in conoscope). These are tested for electro mechanical coupling by a bridge method. If this is high, the crystal is grown to hazelnut size, and sets of plates are cut oriented with respect to the crystallographic axes using *x*-rays. These are used to determine the elastic constants, piezoelectric constants, and expansion coefficients.

### THE GENESIS OF CRYSTAL FORMS AND A RATIONAL EXPLANATION OF THE "LAW" OF BRAVAIS

M. J. BUERGER, *Massachusetts Institute of Technology.*

A number of rules have been proposed to correlate the relative importance of the several faces of a crystal with the geometrical features of the crystal lattice. Chief of these are the rule of simplest indices, Bravais' rule, and Donnay-Harker's rule. The latter has had considerable success in formulating the relative importance of the faces of a crystal, but it is completely empirical, as are the other rules. This paper suggests a rational explanation as to why the rule should work. It is shown that if the crystal grows by accretion of molecular chunks which are equivalent by an operation with a translation component, then Bravais' rule can be derived from crude surface energy considerations. These considerations also explain the stability of crystal faces and predict that crystals may sometimes form without faces when they grow from media of equal surface tension. The same theory accounts for the known deviations from Bravais' rule by ionic crystals.

### THE LATTICE CONSTANTS OF A SINGLE CRYSTAL OF BARIUM TITANATE

A. P. DEBRETTEVILLE AND S. BENEDICT LEVIN, *U. S. Signal Corps.*

Weissenberg moving film layer photographs were taken of a barium titanite crystal of about 1 mm. size. The crystal was synthesized by crystallization from a melt. The

zero-level photographs show barium titanite has a simple tetragonal lattice with one formula weight per unit cell, and with lattice constants  $a=3.99 \text{ kX}$ ,  $c=4.03 \text{ kX}$ , giving  $c/a=1.01$ . This provides direct confirmation of constants indirectly determined by Megaw on polycrystalline material, on the basis of an assumed  $c/a=1.01$  with  $a=3.9860 \text{ kX}$  and  $c=4.0259 \text{ kX}$ . The density calculated from  $x$ -ray data is 6.00. Direct measurement on the single crystal material yields 5.78. Our powder measurements give  $a=3.982 \text{ kX}$  on the basis of  $c/a=1.01$ .

Superposition of the  $a$  and  $c$  reflections on the same central layer lattice lines indicate that the apparent single crystal is actually composed of many small units whose  $c$  axes lie in all three directions formerly occupied by the  $a$  axes of the antecedent cubic barium titanite above  $120^\circ\text{C}$ . (the Curie point).

### PHYSICAL CHEMICAL PHENOMENA IN CRYSTAL GROWTH

PAUL H. EGLI AND PAUL L. SMITH, *Naval Research Laboratory*.

A useful picture of crystal growth which fits many of the experimental facts has been developed from the concepts of Kossel, Stranski and Landau.

Features of the crystallization process accounted for include supersolubility, superheatibility of nuclei effects of foreign ions, and the effect of temperature, etc.

Application of this picture to growth both from melts and from solution has suggested useful techniques in the preparation of large single crystals.

Although the picture is by no means complete, the success of these techniques developed from it contributes additional evidence concerning parts of the theory of crystal growth which are not yet settled.

### X-RAY CRYSTALLOGRAPHY OF SOME HETEROPOLYMOBYDATES

HOWARD T. EVANS, JR., *Massachusetts Institute of Technology*.

The heteropolymolybdates are ionic oxy salts of which the anion is generally very large and complex. The anion contains a number of highly condensed  $\text{MoO}_6^{8-}$  octahedra with a coordinated metalloid ion forming a nucleus. Three distinct structural types are well known: the 12-molybdates (i.e.,  $\text{SiMo}_{12}\text{O}_{40}^{8-}$ ), the 9-molybdates (i.e.,  $\text{PMo}_9\text{O}_{31}^{3-}$ ), and the 6-molybdates (i.e.,  $\text{IMo}_6\text{O}_{24}^{5-}$ ). Of all the iso- and heteropoly salts, the only type whose structure has been studied and worked out is the first of these. The subject of the present study is the structure of the hetero-6-molybdates.

The present report gives a preliminary account of a lattice study of several compounds of this type. The data found are as follows:

- (1)  $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24} \cdot \text{H}_6\text{TeO}_6 \cdot 7\text{H}_2\text{O}$ : monoclinic, space group  $A2/a=C_{2h}^6$ ;  $a_0=21.38 \text{ \AA}$ ,  $b_0=10.01 \text{ \AA}$ ,  $c_0=18.75 \text{ \AA}$ ;  $\beta=115^\circ 30'$ ;  $Z=4$ .
- (2)  $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24} \cdot 7\text{H}_2\text{O}$ : orthorhombic, space group  $Pnaa=D_{2h}^{10}$ ;  $a_0=14.64 \text{ \AA}$ ,  $b_0=14.92 \text{ \AA}$ ,  $c_0=13.96 \text{ \AA}$ ;  $Z=4$ .
- (3)  $\text{K}_6\text{TeMo}_6\text{O}_{24} \cdot 7\text{H}_2\text{O}$ : isomorphous with (2);  $a_0=14.26 \text{ \AA}$ ,  $b_0=15.04 \text{ \AA}$ ,  $c_0=14.53 \text{ \AA}$ . Space group  $Pnna=D_{2h}^{10}$ .

The pseudocubic habit of all these compounds is quite striking. The morphology of (2) and (3) has been studied previously by Donnay and Melon,<sup>1</sup> and the data above show some departure in detail from their results.

Four other isomorphous compounds have been incompletely studied in this series.  $(\text{NH}_4)_3\text{H}_6\text{XMo}_6\text{O}_{24} \cdot 12\text{H}_2\text{O}$ , where  $\text{X}=\text{Al, Fe, Cr, and Co}$ . These crystals are parallelogram plates showing symmetrical extinction.  $X$ -ray patterns show a twinned lattice which is

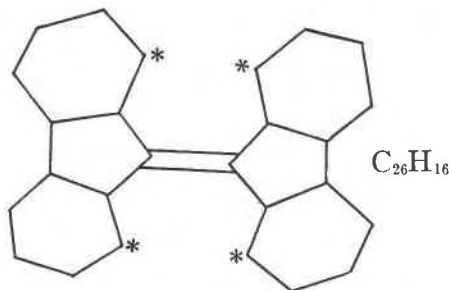
<sup>1</sup> *Proc. Nat. Acad. Sci.*, 20, 327 (1934).

apparently triclinic. The patterns also show some randomness of structure and seem to be entirely unsuited for accurate intensity measurements.

### PRELIMINARY REPORT ON THE STRUCTURE OF BIS-BIPHENYLENE ETHYLENE

C. P. FENIMORE, *Aberdeen Proving Ground.*

Bis-biphenylene ethylene possesses conjugated double bonds and should therefore be planar.



With the customary  $\bar{c}$  bond lengths and angles, however, the starred carbon and hydrogen atoms overlap. A large departure from the usual bond values would be required for planarity. This might be possible (in part at least) if the molecule were a diradical, for which there is some indirect chemical evidence. Other planar structures, not diradical, might be suggested, or the molecule may not be planar at all.

Bis-biphenylene ethylene crystals are acicular, untermated, orthorhombic, *Pcan*;  $a=17.2$ ,  $b=36.9$ ,  $c=8.23$ ;  $Z=12$ .

The decreasing order of interplanar distances  $d_{(hkl)}$  is 020, 110, 130, 200. According to the generalized law of Bravais this should be the order of the relative importance of the corresponding forms. The crystals are morphological anomalies, however, in that the single large form is (130) and the only other  $(hkl)$  face is a line face (200).

This anomalous predominance could be explained by placing molecules in

Position 4: (*a*), symmetry  $\bar{1}$ ; or 4: (*c*), symmetry 2, with  $x=0$

$$\text{giving } 00z_1, 00z_1 + \frac{1}{2}, \frac{1}{2}z_1, \frac{1}{2}z_1 + \frac{1}{2}$$

$$[z_1=0 \text{ or } \frac{1}{4} \text{ as position (a) or (c) is used}]$$

and in

Position 8: (*d*), symmetry 1, with  $x=0$ ,  $y=\frac{1}{3}$ ,

$$\text{giving } 0 \frac{1}{3}z, \frac{1}{2} \frac{1}{6}z + z, \frac{1}{2} \frac{5}{6}z, 0 \frac{1}{3}z - z, 0 \frac{1}{3}z, \frac{1}{2} \frac{5}{6}z - z, \frac{1}{2}z, 0 \frac{1}{3}z + z$$

thus forming in projection three centered pseudo cells. Then the order of  $(hkl)$  planes in decreasing importance could be (130), (200) as observed.

In the structure determination, using approximately these positions, the ethylenic bond in (*a*) or (*c*) is found to be parallel to the *a* axis, in (*d*) parallel to the *b* axis. The molecule appears to be more planar than the usual values for bond lengths and angles would permit.

## HIGH TEMPERATURE-PRESSURE CRYSTAL GROWTH

I. I. FRIEDMAN, *Naval Research Laboratory.*

Crystal synthesis under high temperature and pressure is complicated not only by the inherent difficulty of experimentation under these conditions, but also by the lack of data in the literature. Therefore, the first step in the synthesis of large single crystals under these conditions is to accumulate data concerning systems from which the crystal will crystallize.

The problem can be illustrated by the examples of quartz, aluminum phosphate, and barium oxide. In order to synthesize quartz the ternary system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  was chosen. The system was investigated from 200°C. to 400°C. In addition to equilibrium data, the rates of solution and growth of quartz under different conditions of temperature and composition was determined. The system exhibits liquid immiscibility which disappears below 200°C. Several methods of growth present themselves. Quartz can be grown by saturating a solution of NaOH with  $\text{SiO}_2$  at 350°C. and lowering the temperature to 250°C., or it can be grown in the quaternary system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ . A discussion of both the ternary and the quaternary system will illustrate the methods.

The aluminum phosphate problem is quite similar and it can be grown in the ternary system  $\text{AlPO}_4-\text{H}_2\text{O}-\text{P}_2\text{O}_5$  by several methods.

Several systems from which beryllium oxide may be grown are discussed.

## REPLACEMENT OF CALCITE IN COPPER CHLORIDE

ROBERT M. GARRELLS, *Northwestern University.*

Calcite is covered quickly by a green film when exposed to hot solutions of cupric chloride. The rate of thickening of the film is a logarithmic function of time and of the concentration of the reacting solution. Studies of film formation as a function of temperature yielded data which indicate a possible change of composition of the film. The green film formed under most conditions is atacamite; thus the replacement represents an interesting case in which the replacing substance has no common ions with the original material but in which the rate of replacement is chemically controlled by the original material. Studies also were made of colloidal loss, and curves have been determined for the change in replacement rate for cases intermediate between a completely stable film and a film which is lost as rapidly as it is formed.

## KINETICS OF D.D.T. CRYSTALLIZATION FROM THE MELT

VICTOR GILPIN, *Armour Research Foundation.*

As an outgrowth of the work described in the paper by W. C. McCrone, quantitative measurements were made of the linear crystallization velocity of D.D.T. as a function of temperature, and amount of added impurity. From these data equations were derived which predict growth rates with considerable accuracy at the lower temperatures. Some impurities lower the activation energy of crystallization, others do not. A survey of earlier work shows the dependence of the linear crystallization velocity on the fluidity of the supercooled melt, in the low temperature ranges where the fluidity activation energy is abnormally high. At higher temperatures, where the fluidity activation energy falls to more normal values, fluidity is no longer the rate determining step in crystallization.

### AN X-RAY METHOD OF IDENTIFYING GEMSTONES

SAMUEL G. GORDON, *The Academy of Natural Sciences in Philadelphia.*

The random manner in which gemstones are usually cut, as well as their mounting, has precluded use of conventional X-ray techniques for identification purposes. By simply rotating and oscillating a gemstone in a beam of X-rays with automatic shifting through all possible  $2\theta$  values, reflections should be obtained from a sufficient number of planes to identify it by comparison with a series of standards prepared from the few dozen minerals found in jewelry.

### CHALLENGING PROBLEMS IN CRYSTALLOGRAPHY

DAVID HARKER, *General Electric Research Laboratories.*

Almost all the realms of crystallography present challenging problems. A partial list of problems includes the following:

The development of new methods for crystal structure determination, experimental and theoretical.

A correlation of the properties of crystals with their structures and the application of such correlations to related materials.

A study of crystal imperfections; their origins and their theoretical and practical implications.

The problems of crystal plasticity.

The problems of crystal growth and degrowth.

The problems connected with the nature of solid-solid reactions.

The problems of electrical and thermal conductivity.

The problems connected with piezoelectricity.

The question as to the nature of ferro-magnetic and ferro-electric materials.

The surface properties of crystals: catalysis and electron emission.

All these fields contain unsolved problems inviting the interest and effort of crystallographers. In addition to these problems, there must be many others that have not as yet been even studied.

There is obviously a glorious future in crystallographic research.

### SURVEY OF INORGANIC PIEZOELECTRIC CRYSTALS

LEWIS R. JOHNSON, *Naval Research Laboratory.*

Inorganic crystals reported anywhere in the literature to be in symmetry classes permitting piezoelectricity have been reviewed unless they were obviously valueless because of poor stability or undesirable electrical properties. Most emphasis has been devoted to those compounds which have the most promising composition and electronic configuration. A variety of water-soluble materials have been grown to a stage where semiquantitative measurements of their merit factors could be made using techniques specially devised for measurement of tiny specimens. Oxygen bearing compounds with highly electropositive cations and highly electronegative anions exhibit the most activity, but rigorous correlation of property and structure await extension of our present concepts.

## A NEW CRYSTALLOGRAPHIC FORM OF RED PHOSPHORUS<sup>1</sup>

GILBERT E. KLEIN, *Massachusetts Institute of Technology.*

When ordinary red phosphorus is heated at various temperatures for varying lengths of time, several distinct crystalline modifications are formed. At a temperature in the neighborhood of 600° C. a new crystallographic form appears. The material is in the nature of hard lumps which are almost opaque under the microscope. No single crystals of size sufficient for measurement could be found.

An  $x$ -ray powder photograph of this new crystalline form contains some 26 lines and shows the material to have a simple cubic lattice. The indices of the planes producing the powder lines run out to values as high as (931). Since the indices assigned to the lines show no systematic missing reflections, the possible space groups for this form are:  $P23$ ,  $P43$ ,  $Pm3$ ,  $P43m$ , or  $Pm3m$ , of which only the space group  $P23$  may be ruled out by other considerations.

The size of the unit cell edge is calculated to be equal to 11.29  $kX$ , and using the measured value for the density of the material as being 2.38, the number of atoms per unit cell is calculated to be 66.

<sup>1</sup> Published with permission of the War Department. This work was conducted under research contract with the Chemical Corps, United States Army.

## THE EPSILON FORM OF SOME SODIUM 1-ALKANESULFONATES

E. C. LINGAFELTER AND L. H. JENSEN, *University of Washington.*

Six distinct crystalline hydrates of the sodium 1-alkanesulfonates have now been recognized. The  $\epsilon$  form has been found for sodium 1-tetradecane-, 1-hexadecane-, and 1-octadecanesulfonate, by crystallization from solutions in carbon tetrachloride-ethanol-water or 1, 4-dioxane-ethanol-water at *ca* 30°. The triclinic crystals are extremely small, very thin tabular parallel to {001} and outlined by {101} and {011}. The unit cell contains 8 molecules of  $RSO_2Na$  and probably some water of crystallization. The general features of the structure are discussed and compared with the forms previously investigated.

## THE APPLICATION OF CRYSTAL CHEMICAL PRINCIPLES TO THE PROBLEM OF GLASS STRUCTURE

JOSEPH S. LUKESH, *Massachusetts Institute of Technology.*

The structural characteristics of silicate glasses cannot be determined by the usual methods available to crystallographers. The information that can be obtained from  $x$ -ray analysis is limited. However, when one applies knowledge of silicate crystals, much useful information may be deduced. Huggins<sup>1</sup> has shown, for instance, that the densities of a series of glasses such as sodium silicate can be represented by straight lines with changes in slope at compositions which have crystal chemical significance. If the densities are plotted as functions of the ratio of silicon atoms to oxygen atoms, the changes in slope appear at the ratios which characterize the different silicate crystalline structural types. A further change in slope occurs for which there is no known type. By considering the densities of the various atomic species, it is seen that this break has a different character. It is deduced that the break represents the point at which the essentially cristobalite-like network of silicon and oxygen becomes saturated with sodium atoms.

If one plots the densities of sodium calcium silicate glasses on a three-dimensional

<sup>1</sup> Huggins, M. L., *Jour. Opt. Soc. Am.*, **30**, 420 (1940).



graph as functions of the ratios Na/O and Ca/O, the surface is found to be made up of a group of planes. A tentative structure-phase diagram can be constructed from published data. The boundaries of the planes appear to follow the crystalline silicate type compositions.

### AN EASILY MADE TWO-CIRCLE GONIOMETER

A. S. MAKAS AND C. D. WEST, *Research Laboratory, Polaroid Corporation.*

Modern crystal measurement consists primarily in first determining the *x*-ray elements, diffraction symbol, and possible space groups for a given single crystal, and then showing that the measured angular coordinates of all of the observed growth faces are consistent with these elements and space groups. The crystals used are small and often have faces of poor quality. A goniometer is a practical necessity, first for shortening the time needed to set up the crystal for the *x*-ray measurements, second for determining the two angular coordinates of each growth face, and third because the facial symmetry may contribute to the correct choice of space group. American crystallographers are at a disadvantage because a rational instrument has not been previously designed for these purposes and made in this country.

Students' spectrometers allowing readings to 1' on a horizontal circle are however readily available in this country at moderate prices. Representative optics of such instruments include objective lenses of 150 mm. focal length and an autocollimating Ramsden eyepiece of 25 mm. focal length, the combination being a 6 × telescope. Such instruments could be simply converted to one-circle goniometers by replacing the collimator slit with an interchangeable signal system, by adding a short-focus flip-out lens in front of the telescope objective that will change it at will to a microscope magnifying about 30 ×, and by providing a holder for the goniometer head used in Weissenberg cameras. It is also desirable to make an alternative eyepiece of lower power, say 100 mm. focal length to give a lower magnification with crystal faces of poor quality.

Since it is generally agreed that one-circle goniometers are inadequate for modern crystal measurement, we have converted the spectrometer just specified directly into a two-circle instrument. This requires only the extra steps of placing the microscope-telescope system on a fixed post so that its axis intersects that of the collimator at an angle of about 60°, and putting in its place on the moving arm a properly counter-weighted vertical circle assembly, preferably reading also to 1' and carrying the goniometer head. This system can be put and kept in adjustment without difficulty, and appears to be adequate for the purposes stated in the first paragraph. Further elaborations such as the telescope systems of V. Goldschmidt could be incorporated without difficulty if desired, but they do not seem necessary at present.

### SOME OBSERVATIONS ON CRYSTAL GROWTH FROM THE MELT

W. C. McCrone, *Armour Research Foundation.*

This paper will summarize the data on the use of the crystallization rate of DDT for the quantitative analysis of technical mixtures. The assumption was made in the course of this early work that synthetic mixtures of the two principal isomers of DDT would be equivalent to mixtures of technical DDT containing the same amount of *p,p'*-isomer. In other words, that *o,p'*-DDT would have the same effect on the rate of crystallization of *p,p'*-DDT as an equivalent amount of the various isomers and by-products known to be present in the technical products. Although this turned out to be correct, on the basis of comparative analyses, the question naturally arises as to whether the decrease in growth rate on addition of impurity is, in general, independent of the nature of the impurity.

The present study was undertaken, therefore, in an effort to determine the effect of the nature of the impurity on the rate of crystallization of *p,p'*-DDT. These studies have shown that the nature of the impurity has a very large effect on the rate of crystallization. For example, at 34° C. a mixture of 80% *p,p'*-DDT—20% *p'*-DDT grows at a rate of 80 microns in 5 minutes; a mixture of 80% *p,p'*-DDT—20% thymol at a rate of 2440 microns in 5 minutes; and a mixture of 80% *p,p'*-DDT—20% triphenylbenzene at a rate of 35 microns in 5 minutes.

Further work has been done to determine what physical properties (of the impurity) are significant in their effect on growth rates. A number of properties such as heat of crystallization, heat conductivity, molecular shape and size, and viscosity were investigated with the result that viscosity has been shown to be the principal factor in this particular case, that is, the crystallization of *p,p'*-DDT from the melt.

### THE OSCILLOGRAPHIC FOURIER SYNTHESIZER<sup>1</sup>

R. PEPINSKY, *Alabama Polytechnic Institute.*

The design and operation of an electronic synthesizer for two-dimensional Fourier series is discussed and illustrated. Operation of the synthesizer is based upon Bragg's early method for photographic summation of simulated interference fringes. The required sinusoidal light intensity variations are produced on the screen of a cathode ray tube by means of a television scan and intensity modulation of the CR tube grid, and the light pattern is locked in position by complete synchronization of modulation and sweep signals.

Amplitudes of Fourier coefficients are supplied to the machine as settings of individual volume controls, and phases (0° and 180°) are entered by means of double-throw switches for each term. A complete centro-symmetric planer projection of electron densities, corresponding to a specific set of amplitude and phase values, appears on the screen once each scanning frame. The projection remains on the screen as long as is desired. Effects of changes in phase of one or any number of terms, by changing the switch position for each term involved, are immediately observable on the screen—as are effects of individual amplitude changes.

Projections of any desired axial ratio or angle are readily attainable.

The synthesizer is designed to facilitate the deduction of general features of a structure, through alleviation of the tediousness of trial-and-error stages of an analysis. Because of the rapidity with which the effects of phase changes are observable, systematic variations of Fourier coefficient signs becomes possible in the search for a self-consistent structure.

<sup>1</sup> This is a development of the technique first reported by the writer at the Lake George, N. Y., meeting of the *A.S.X.-R.E.D.*, June 11, 1946.

### MICROSCOPIC IDENTIFICATION OF TWO "LIQUID CRYSTALLINE" SOAP PHASES: NEAT SOAP AND MIDDLE SOAP

F. B. ROSEVEAR, *The Procter & Gamble Company.*

Neat soap and middle soap are two "liquid crystalline" (anisotropic liquid, mesomorphic, paracrystalline) aqueous solution phases which are important in the manufacture of soap and synthetic detergents.

Over the twenty years since McBain and Langdon announced middle soap as a phase distinct from the neat soap of soap boiling operations, ultimate distinction between the two has depended almost solely upon the comparative fluidity of neat soap and the strikingly

stiff plasticity of middle. There are, however, cases where the fluidity test is not adequate, as, for example, where the two phases are mixed with each other or with other phases. Apparently because both are considered to be typical "conic anisotropic liquid" or "smectic" phases, no generally applicable method for distinguishing them optically has been proposed.

In the work here reported, examination with the polarizing microscope has shown that while middle soap is characterized by the relatively coarse and well developed focal conic structure recognized since McBain's earliest papers on this phase, neat soap characteristically exhibits the texture described in the liquid crystal literature as "oily streaks," or a related texture consisting of individual or densely packed liquid spherulites. Almost always, considerable portions of the neat phase are isotropic because of orientation of the soap molecules perpendicular to slide and cover glass. The neat-middle distinctions are illustrated by photomicrographs, including some of the compositions generally accepted as being representative of each phase.

There is a phase termed neat soap occurring in many anhydrous soaps near 200–300° C. The work of McBain, the Volds, and their colleagues indicates that this phase is not continuous with "soap boiler's neat," as had been assumed in earlier work. Since there is sufficient evidence already published to show that the anhydrous neat soap is characterized by well developed focal conic structure, the properties here presented for "soap boiler's neat" serve as additional evidence for discontinuity between these two phases.

### SENSITIZED LUMINESCENCE

JAMES H. SCHULMAN, *Naval Research Laboratory.*

The ultraviolet excited luminescence of most inorganic crystalline phosphors is due to small amounts of impurity (activator) in solid solution in the host crystal. In the simplest case the activator may be considered to act like a dilute gas of atoms or ions, which absorb ultra-violet radiation incident upon them from an external source and re-emit the absorbed energy as luminescence. In other cases the absorption of the exciting energy takes place in the atoms of the host crystal and this energy is subsequently transferred to the activator, which then emits luminescent radiation.

A situation of particular interest arises if two impurities are built into the crystal, one of which functions as the absorber ("sensitizer") of the exciting radiation, and the other as the emitter. In this way phosphors can be built which are excited by selected regions of the ultraviolet. Examples of phosphors showing "sensitized" luminescence are the manganese-activated alkali halides and calcite, and certain rare earth activated sulfides.

### HARDNESS VARIATION AND THE MICROSTRUCTURE OF THE DIAMOND

C. B. SLAWSON, *University of Michigan.*

Microscopic twinning lamellae and polysynthetic twinning are characteristic of the diamond. Because of the differential hardness, twinning lamellae stand out in relief on a polished surface when examined with the reflecting microscope, if the direction of polishing is properly oriented. A diamond megascopically twinned on (111) may have other twinned structures on ( $\bar{1}11$ ), (1 $\bar{1}1$ ), and (1 $\bar{1}\bar{1}$ ). The apparent greater hardness of some diamonds as observed by diamond cutters may be explained by twinning lamellae. Contrary to the general practice in industry these so-called hard diamonds will be undesirable for tools. The twinning lamellae will become zones of inferior hardness on the working surface of the tool.

## TWINS AND INTERGROWTHS

DOROTHY WRINCH, *Smith College.*

The possibility that twins and intergrowths of crystals, supplementing crystalline form and atomic composition, may yield indications regarding their internal structure, is suggested. This approach is being developed for use in extremely complicated crystals where *x*-ray intensity data are not available. To demonstrate it, staurolite is chosen as an example, since its atomic structure is well-known.<sup>1</sup>

From measurements of angles between faces, Dana derives an orthorhombic unit cell, with axial ratio  $a:b:c=0.4734:1:0.6828$  and 032,232,230 and 130 as twinning planes.<sup>2</sup> Since the ratios differ from 2:3, 2:2 by less than 2.5 per cent, we introduce a submultiple cube of edge  $k$  (following many precedents) and write as an approximation

$$a=2k, b=3k\sqrt{2}, c=2k\sqrt{2},$$

thus taking cubic axes XYZ defined by

$$X=2x, Y=3y-2z, Z=3y+2z,$$

with the unit cell of volume  $24k^3$ . The unit cell faces are then translated into  $(100)_c$ ,  $(011)_c$  and  $(0\bar{1}1)_c$  of the cubic system and the twinning planes correspondingly into  $(001)_c$ ,  $(101)_c$ ,  $(211)_c$  and  $(111)_c$ . Let us call a cube face an X-plane, a face of the icositetrahedron, the rhombic dodecahedron and the octahedron of the cube, a U-, a V- and a W-plane. The staurolite twins are then seen to be expressible in terms of the cube as X, U, V and W twins. Their existence confirms what is already suggested by the cell ratios; namely, that—to some high degree of approximation—the crystal contains some *major cubic theme*, that this theme is of the scale and in the orientation of the submultiple cube and that there is also present some *minor non-cubic theme*, which so far as the cube is concerned is referred to a super or multiple lattice. According as the major theme lies on a cubic network or on a body-centered or face-centered cubic network, the cube contains 1, 2 or 4 repetitions and the orthorhombic cell 24 times as many. The major theme provides sites for the members of the minor theme in cubes, in octahedra and in octahedra and tetrahedra respectively: not all these sites are tenanted, when they are the surrounding polyhedra are slightly distorted.

If information regarding composition is now added; namely, Dana's suggestion of  $\text{HFeAl}_6\text{Si}_3\text{O}_{13}$ , in which we see that  $\text{O}_{13}$  must be corrected to  $\text{O}_{12}$ , we identify the cubic theme as an oxygen network. We select the face-centered network in order to provide tetrahedral sites for silicon and deduce 8 such units for Dana's unit cell. The X- and V-twins have an undisturbed network: the U- and W-twins adjoin the face-centered cubic networks in hexagonal closest packing. In all, the minor non-cubic theme is disturbed and the existence of twins is explained. The data have thus suggested what is known from *x*-ray studies to be the correct structure so far as it goes, leaving undetermined only the selection of positions from among the octahedral and tetrahedral sites for the minor theme. (This step follows from the space-group which also further corrects the composition into  $\text{H}_2\text{FeAl}_4\text{Si}_2\text{O}_{12}$ . It may be mentioned that the *x*-ray studies show that Dana's  $c$  should be  $c/2$  and that the absolute scale of any cell edge length; e.g.,  $a=7.81\text{Å}$  at once gives the absolute scale of the oxygen network, placing them at distances  $k/\sqrt{2}=a/2\sqrt{2}=2.76\text{Å}$  apart on the average.)

Similar treatments of other minerals are given, indicating the scale and orientation of their cubic themes and identifying various X-, U-, V- and W-twins.

<sup>1</sup> Bragg, *Atomic Structure of Minerals*, Cornell University Press, pp. 170-181 (1937).

<sup>2</sup> Dana's *Textbook of Mineralogy*, 3d edition, Wiley & Sons, 1922, pp. 162, 164, 170, 543-544.

## FRACTOGRAPHY

CARL A. ZAPFFE, *Baltimore, Maryland.*

Fractography is the study of the detail seen on nascent cleavage facets at high magnification. Applicable to any substance, crystalline or noncrystalline, this technique leads to observations of special significance because the fracture face, which becomes the plane of observation, is intimately involved with the points and planes of weakness within the structure. In crystalline material, the facet is a crystal face, which offers further advantages and which makes the technique of special interest to crystallographers.

## SOLID PHASE INVERSION IN CALCIUM ORTHOSILICATE

SAMUEL ZERFOSS, *Naval Research Laboratory.*

Calcium orthosilicate shows two types of solid-phase inversions—a sluggish inversion at 675° C. ( $\beta$ - $\gamma$ ) accompanied by a 10% positive volume increase, and a high-low quartz type inversion at 1435° C. ( $\alpha$ - $\beta$ ) of a quite rapid character. The sluggish inversion ( $\beta$ - $\gamma$ ) is inhibited by the introduction of 1% of  $\text{PO}_4$ ,  $\text{BO}_3$ ,  $\text{AsO}_4$ , or  $\text{VO}_4$  ions into the lattice. Work of the writer and recent work of Newman and Wells of the Bureau of Standards showed that these same ions also produce a lowering of the  $\alpha$ - $\beta$  inversion temperature. An attempt is made to explain the inhibition of the sluggish inversion on the basis of our knowledge of the structure of  $\text{Ca}_2\text{SiO}_4$ .

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Dr. James H. C. Martens has resigned his position of Professor of Geology at the University of West Virginia and accepted the appointment of Associate Research Specialist at the Bureau of Mineral Research, Rutgers University, New Brunswick, New Jersey.

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Dr. Terence Thomas Quirke, professor of geology at the University of Illinois, died August 19 of a heart attack at the age of 61 years.

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Dr. Vincent L. Ayres, associate professor of Mineralogy at the Michigan College of Mining and Technology, died at his home in Houghton, Michigan, on October 14, 1947, at the age of 55 years. He had been in ill health for several years and retired from teaching in the spring of 1947.