# PROCEEDINGS OF SOCIETIES

## ABSTRACTS OF PAPERS PRESENTED AT THE SPRING MEETING OF THE CRYSTALLOGRAPHIC SOCIETY AT SMITH COLLEGE MARCH 21–23, 1946

### TYPES OF ORDER IN PROTEIN FIBRILS

RICHARD S. BEAR,

*Massachusetts Institute of Technology.*

Evidence concerning the structure of certain animal protein fibrils reveals two more or less independent types of order in the arrangement of the constituent amino-acid residues: (1) a limited amount of structural regularity in the immediate neighborhood of individual residues, and (2) a surprising degree of order in the overall disposition of the residues, extending through large distances (hundreds of A) and specific for each protein. In the best known cases, collagen and paramyosin, the repeating large units of structure are, respectively, one- and two-dimensional in character. The remaining (transverse) dimensions of these fibrils apparently lack order of large size.

Structures of this type, which possess regular order in less than three directions and whose randomly constructed remaining dimensions are not too thick, should yield diffraction over a wide range of angles of incidence of the $x$-ray beam. The true fiber-axis spacings in such cases are given by $d_{\text{Bragg}/\cos oc}$, where $d_{\text{Bragg}}$ is an apparent spacing calculated using the Bragg Law, and $oc$ is the angle of departure from perpendicularity between $x$-ray beam and fiber axis. This relationship has been observed for myosin and collagen specimens.

### THE LATTICE IN CRYSTALLOGRAPHY

J. D. H. DONNAY,

*The Johns Hopkins University.*

The lattice is a geometrical concept which would be very useful in crystallography even if crystals had not been found to possess their triperiodic structure. Independently of any structural hypothesis, the primitive lattice built on the relative unit lengths obtained by goniometry enables one to give the fundamental laws of crystallography a most vivid expression: (1) *Faces* (and the other planes that are the evidence for the discontinuous vectorial properties) *are parallel to families of nets* (= Law of Constancy of Angles). (2) *These families of nets are among those characterized by large interplanar distances* (= Law of Small Rational Indices). If extinctions are taken into account—lattice extinctions due to various centerings and space-group extinctions due to the symmetry of the motif (cell content)—a lattice and an aspect (corresponding to one or several space-groups) can generally be found such that (3) *the families of nets parallel to which faces occur are precisely those with the largest effective interplanar distances and the larger this distance the more important the corresponding face* (= Generalized Law of Bravais, which coincides with the Classical Law of Bravais in the absence of glide-planes or screw-axes of symmetry).

The lattice was also made to express the triperiodicity of the crystal structure, at a time when such periodicity could only be postulated (*reticular hypothesis*). Haüy's concept of "decroissance" was in fact the first reticular hypothesis, his "formes primitives" being the cells of seven primitive lattices. Bravais postulated physical reality for his fourteen lattices. Friedel showed that the nonexistence of irrational three-fold axes of symmetry was, at the time, the only justification for the reticular hypothesis, since such axes are compatible with the Law of Small Rational Indices but are impossible in a lattice. $X$-ray diffrac-

tion proved the reticular hypothesis, previously based on negative evidence, and definitely established that irrational 3-axes would never be found in crystals.

The lattice determined from the Classical Law of Bravais has been called the *morphological lattice* (or Haüy-Bravais lattice) to stress the fact that, in many cases, it did not coincide with the *structural lattice* found by x-ray diffraction. In view of the generalization of the Law of Bravais, this distinction has lost most of its significance.

The first reciprocal lattice was Bravais' "reseau polaire." Subsequent varieties differ only as to scale. V. Goldschmidt's "Polarform" was the cell of a primitive reciprocal lattice, as Haüy's "forme primitive" was the cell of a primitive direct lattice. The reciprocal lattice is the tool par excellence for the analysis of crystal morphology as well as for the x-ray investigation of crystal structure by Ewald's method.

## EXPERIMENTAL STUDY OF THE CHANGE IN HABIT OF SODIUM NITRATE CRYSTALS GROWN FROM WATER SOLUTION

HOWARD T. EVANS, JR.,

*Massachusetts Institute of Technology.*

The mechanism of the change in habit of a growing crystal due to the presence of impurities in the solution is usually considered from the point of view of the effect of distortion introduced on the surface of the crystal by the implanting of the impurity particle. This mechanism requires, among other things, a relationship between the size of the impurity particle and the dimensions of the crystal structure. A study of the behavior of sodium nitrate crystals (rhombohedral, isostructural with calcite) yields new information, but still not enough to completely elucidate the mechanism. Iodides produced an effect that varied with the cation, LiI having the least effect, and $NH_4I$ the greatest. A large variety of other cations and anions gave negative results. The effect of hydroxyl was profound, producing great distortion, and in high concentration, effecting a complete change of habit. The prevailing theories are applied to these observations as far as possible. Experimental work on sodium nitrate is limited by the great solubility of this salt.

## CRYSTALLOGRAPHY, A COMMON GROUND IN MANY SCIENCES

I. FANKUCHEN,

*Brooklyn Polytechnic Institute.*

The scientific study of crystals may be said to have started in the latter half of the 18th century with the introduction of the goniometer, although the constancy of interfacial angles was known at an earlier time. Haüy enumerated the Law of Rational Indices and made a thorough study of crystals found in nature (minerals). Particularly with the development of the polarizing microscope, crystallography took a firm place as a tool in chemistry. Biology too proved an attractive field to apply the ideas of crystallography. With the discovery and development of x-ray diffraction an entirely new world of structural studies was opened and very rapidly the old fields and many new ones like metallurgy were invaded. The influence of crystallography in all these fields was great but perhaps the reaction on crystallography was even greater. The interesting materials often proved to be not the perfect crystals that delighted the early crystallographers but rather the imperfectly organized structures of metallurgy, biology and even mineralogy. The crystallographers of today can no longer pun as Tutton did that "unlike women, the beauty of crystals lies in the planeness of their faces."

## TWINNING IN LEADHILLITE

SAMUEL G. GORDON,

*The Academy of Natural Sciences of Philadelphia.*

A recent find of leadhillite crystals at the Mammoth Mine, Arizona, showed three types of crystals in a single vug: I. bipyramidal (trigonal, uniaxial "susannite"); II. prismatic crystals composed of biaxial sectors of monoclinic symmetry, but resembling aragonite sections in twinning; and III. pseudo-rhombohedral or tabular crystals composed of 2, 3, or 6 individuals, twinned according to the Artini law.

## GRAPHICAL SUMMATION OF FOURIER SERIES IN CRYSTAL STRUCTURE ANALYSIS

JOSEPH S. LUKESH,

*Massachusetts Institute of Technology.*

The contribution of each plane to the electron density throughout the projected unit cell is in the form of a cosine surface whose shape depends only on the geometry of the plane. The amplitude of the surface only is a function of crystal structure. Graphical computation of the product of F or $F^2$ by the cosine function can be accomplished rapidly by use of a cosine curve and a variable scale. If the points in the unit cell for which computation is to be made are located by a semi-polar coordinate system, the form of the computations is considerably simplified and the Fourier series reduces to the following form

$$\rho_{(x,c)} = \Sigma \Sigma F_{(hk0)} \cos \frac{2\pi x}{N} K$$

where $x$ is an integer from one to $N$ and $K$ is a constant whose value depends on the indices and the slope of the line from the origin to the point. With the computations in this form, it is possible to sum the entire series using one curve, one compact table and a scale. The scale is variable and can be adjusted for any F or $F^2$ value from one to one thousand. The contributions of a reflection to all of the points along a given radial line can be computed and recorded in a minute or less. The electron density of diopside projected on (100) has been computed using this method and was found to be identical with published diagrams.

## CRYSTAL PATTERN SYNTHESIS BY AN APPROXIMATE SUMMATION OF FOURIER SERIES

JOSEPH S. LUKESH,

*Massachusetts Institute of Technology.*

An accumulation of electron density in a projected unit cell can occur only when the positive solutions of the Fourier series exceed the negative solutions. A large peak can occur only when most of the planes, $hk0$, are contributing nearly their maximum amplitudes. This suggests that a faithful indication of the positions of important peaks might be obtained quickly by determining for each point in the cell the difference between the sums of the maxima and minima which occur at each point. Since the maxima and minima do not, in general, fall on the points of the coordinate system, it is necessary to assume that a plane contributes its full amount when its amplitude is within a certain amount of the maximum. Fifty per cent has been chosen arbitrarily as the amount. Similarly, the plane

is assumed to subtract its full amount when fifty per cent or more of its minimum. Using this concept, it is possible to perform an approximate summation with no computations other than addition. In the approximate summation of the density of diopside projected on (001), estimated intensities were found to give peak parameters which compare favorably with those obtained when the complete summation is performed in the conventional manner. The approximate method, although perhaps not to be trusted in actual structure analysis, can be used to eliminate areas where atoms will not be found and as a guide in deciding if an assumed structure is possible.

## THE USE OF SAND IN MAKING FOURIER PROJECTIONS OF CRYSTAL STRUCTURES

DAN McLACHLAN, JR., AND E. F. CHAMPAYGNE,

*American Cyanamid Company.*

This paper presents a method of using sand in building models of two dimensional Fourier projections in crystal structure analysis. The machine for producing these models is described and the results are illustrated by projections of known structures.

The mathematical principle of this method of summing Fourier series is identical to that which Bragg[1] developed in England and which Huggins[2,3] so ably perfected in this country. The chief difference is in the use of sand instead of photographic film as the medium for producing contrasts in electron density throughout the projection.

When a diffraction pattern of a single crystal is taken on any of the moving film types of cameras, each spot presents three measurable parameters: two of position and one of density. These three parameters may be used to calculate three corresponding parameters: (a) the interplanar spacing, (b) an angle which might be called $\psi$ and (c) the structure factor. Since it happens that each term in a Fourier series (as used in crystal structure work) is the equation of a two-dimensional wave having four properties $(a^1)$ wave length, $(b^1)$ direction, $(c^1)$ amplitude, and $(d^1)$ phase, and since there is a one-to-one relationship between $a, b, c$ and $a^1, b^1,$ and $c^1$, it follows that aside from $(d^1)$ the diffraction pattern furnishes all the data that is desired for making a Fourier projection. It only remains to find means of assimilating the proper wave for each term in the series and means for adding the waves. In the Bragg method the waves were represented by sinusoidal transparencies having two properties (a) wave length, which corresponded to interplanar spacing, and (b) direction. These waves are added photographically and the third property (c) or amplitude of each wave is related to the time of exposure.

In the present method the waves are produced by mechanically spreading sand into a grid from a moving hopper. The hopper has a sinusoidal template below it which causes a wave-like distribution of sand; the wave length of this template corresponding to the interplanar spacings of the crystal with a scale of one centimeter per Angstrom. The angle is adjusted by rotating the collecting grid, and the amplitude is established by the rate by which the sand is mechanically driven from the hopper. The phase is controlled by shifting the collecting grid the proper fraction of a wave length perpendicular to the direction of the wave crests. The electron density at any point in the projection is proportional to the elevation of sand in the corresponding point in the grid. The simple method for photographing the result is described.

[1] Bragg, W. L., *Zeits. Krist*; **470,** 475 (1929).

[2] Huggins, M. L., *J, Am. Chem. Soc.*, **63,** 66 (1941).

[3] Huggins, M. L., *J. Chem. Phys.*, **12,** 520 (1944).

## VARIATION IN CRYSTAL HABIT OF PYRITE IN THE COLLINS HILL PEGMATITE NEAR MIDDLETOWN, CONNECTICUT

BENJAMIN M. SCHAUB,
*Smith College.*

The pegmatite on Collins Hill has been worked chiefly for feldspar during the past several decades and for 15 years the writer has collected specimens from the dumps of waste material containing small pyrite crystals from microscopic size up to a quarter of an inch through the crystals.

The crystals usually occur in the small cavities and are associated with a variety of minerals or they may be located in the polyhedral cavities of cleavelandite.

The crystal forms are sometimes unmodified cubes or octahedrons or a combination of these. In some cavities the crystals in addition to the cube and octahedron are modified by the pyritohedron, trisoctahedron and dyakisdodecahedron. The more complex crystals are associated with calcite which is encountered usually in crystals but occasionally in masses partly filling some of the cavities.

The minerals usually associated with the pyrite in various amounts and combinations are fluorite, cookeite, lepidolite, albite, quartz, various multi-colored tourmalines, siderite, bertrandite, beryl, apatite, etc.

## CRYSTALLOGRAPHY OF THE SEVEN MODIFICATIONS OF SILICON CARBIDE

NEWMAN W. THIBAULT,
*Norton Company.*

In 1928 Ott, entirely from $x$-ray studies, described a modification of silicon carbide containing 17 formula weights in the rhombohedral unit cell, and designated it type V. During the author's comprehensive study of the crystallography of SiC (*Am. Mineral.*, **29**, pp. 249–278, 327–362, 1944), this modification was not encountered. Recently, however, a large crystal of this type was found, and studied by optical and $x$-ray goniometrical methods. The results of this investigation were outlined, and a comparison made with the other six known modifications of this compound.

Alpha-SiC, type V, is ditrigonal pyramidal, $c:a=41.71:1$, yielding a simple arithmetical series of forms characteristic of crystals with rhombohedral lattices. Equi-inclination Weissenberg studies indicated a rhombohedral unit cell containing 17 formula weights; space group, $R3m$. Referred to hexagonal axes: $a_0=3.073$Å, $c_0=128.17$Å. An $x$-ray powder photograph showed a unique pattern, but some of the lines were precisely or nearly equivalent in position to certain lines in the powder photographs of the other SiC modifications, particularly type VI.

## PLASTIC DEFORMATION AND RECRYSTALLIZATION OF NON-METAL CRYSTALS

EDWARD WASHKEN,
*Massachusetts Institute of Technology.*

Experiments have been carried out on plastically deformable substances to determine the effect of deformation on recrystallization. The basis for this work is the theory that increased energy due to plastic deformation, promotes recrystallization and grain growth.

Fluorite and anhydrite were chosen as experimental materials because structurally they possess a large number of glide planes.

Pressures of the order of 10,000 atmospheres have been used to compress the powdered minerals which were subsequently heated at temperatures below the melting point. The rate of grain growth is found to increase with temperature as demonstrated by measurement of grain sizes of polished sections.

*X*-ray patterns proved that increased strain reduces the temperature at which recrystallization starts, which is in accord with the proposed theory. It is concluded that for each substance there is a critical recrystallization temperature dependent on initial molding pressure.

Time has been found to be of secondary importance in affecting the critical temperature of recrystallization.

## OPTICAL ACTIVITY IN CRYSTALS: CRYSTALLOGRAPHY OF *l*-CYSTINE

C. D. WEST AND W. F. AMON, JR.,

*Polaroid Corporation.*

Optical activity along axes of optical isotropy can be detected in some transparent crystals with relatively simple optical systems available to many crystallographers. The presence of optical activity in a given crystal is a help in choosing or confirming its symmetry class and space group, where morphology and *x*-ray diffraction alone are often inadequate.

A new tetragonal crystal form of the amino-acid *l*-cystine, whose solutions have a large levo rotation, is reported and its lattice and optical constants are set out in a table along with those of the previously known hexagonal form of the same substance. The two crystals are shown to have opposite rotations along their isotropic axes, the hexagonal crystal has a levo rotation of about 18° per mm. while the tetragonal crystal has a dextro rotation of about 25° per mm. for white light.

## BIOLOGICAL PROBLEMS AND CRYSTALLOGRAPHIC PRINCIPLES

DOROTHY WRINCH,

*Smith College.*

A number of "structural" problems are of basic importance for biology, physiology and medicine. Foremost among these is the nature of protein synthesis. The suggestion is put forward that synthesis is a question of orderly propinquity. The problem is therefore discussed in the light of the application of crystallographic principles to arrangements of molecules in orderly propinquity, i.e. molecular crystals. A possible mechanism of synthesis is proposed for consideration. It is explained in terms of the crystal which seems most illuminating, namely the 5-hydrate of phosphotungstic acid, which has the space group $O_h^4$. Reference is also made to the crystal of hexamethylene tetramine. According to this picture, the autocatalytic native protein is necessarily a surface structure built on a framework of high symmetry: further the surface is self-complementary in a crystallographically satisfactory sense. The self-complementary of a surface resides in the complementarity of pairs of fragments of the surface and it is not justifiable or indeed necessary to assume the self-complementarity of all the individual fragments. The far-reaching implications of this viewpoint are indicated and a brief account of the essential importance of crystallographic ideas and principles in a wide variety of biological structure problems is given.