

## MORPHOLOGICAL BASIS FOR THE RETICULAR HYPOTHESIS

CECIL J. SCHNEER, *The University of New Hampshire,  
Durham, New Hampshire 03824.*

### ABSTRACT

The persistence of the forms of a mineral species through the environmental variation represented in geological space and time ( $P_{hkl}$ ) is used to derive average specific surface energies  $\sigma_{hkl}$  as a function of the multiplicity,  $m$ , and the interplanar spacing,  $d$ ;  $\sigma_{hkl} = -C [\ln P'/m]/d^2$  with  $-C$  a constant proportional to the absolute temperature. Relative  $\sigma$  are of the order of magnitude of 0.5 kcal/mole at room temperature. The equation is one transform from an empirical morphological intensity space to an incomplete structure factor space. It is confirmed by Fourier transforms to the electron and vector densities, and by the comparison with calculated structure factors with residuals of 0.187, 0.274, and 0.360 for anglesite, barite, and celestite.

The ensemble of the forms of a mineral species should approach equilibrium (a statistical distribution invariant with time) throughout geological time and space. As it approaches equilibrium the observed distribution becomes a function of the structure and the structure is a Fourier transform of the distribution.

### INTRODUCTION

The aim of this research is to establish the functional relationship between the forms and the structure of crystals. It is based on the concept that the polyhedral envelope of a well-developed crystal results from a vectorial 'quantized' distribution of growth rates; and second, that these growth rates are a function of the potential energies to be associated with each point of the reciprocal lattice.

Some of the terms that enter into the calculation of these energies are dependent upon the geometric distribution of the particles making up the crystal structure and this paper is concerned with these structure-dependent terms. Other terms are either independent of the structure or dependent upon bulk properties. Such scalar terms do not effect the proportionate frequencies of occurrence or relative sizes of the individual faces of a crystal. The crystal or 'lattice' energy is an example of such a scalar term since it influences growth rate but is invariant with respect to the points of the reciprocal lattice. Curie (1885, p. 146) has considered the change in energy for a change in the shape of a body, the volume being held constant, as proportionate to the variation of the area. He defines specific surface energy as the energy required to increase the surface by one unit, the volume being held constant. The definition does not distinguish between a collective of many crystals and an individual crystal.

### THE MORPHOLOGICAL STRUCTURE FACTOR SPACE

*Definition.* The distribution of the forms of a mineral species in geological

time and space is the outcome of a world-experiment establishing the probability of occurrence of each particular form. These probabilities may be approximated by the  $P_{hkl}$ '—or persistence-values of Niggli (1941, 504, 523). Forms which persist through a wide range of conditions and time ought to be characterized by lower specific surface energy than forms which are rarely observed. Using the statistical-mechanical relationship between energy and probability (*cf.* equation 6 below) it is possible to derive relative average specific surface energies from the geological persistence of the crystal forms of a mineral species. These energies are the magnitudes associated with points of the reciprocal lattice.

The geometry and the proportions of the direct lattice and of the corresponding reciprocal lattice can be derived directly from the morphology (Friedel, 1905, p. 109). The absolute dimensions can be derived from the molecular weight and the specific gravity to within an integer multiple (number of formula molecules per unit cell). Therefore, a reciprocal lattice with points weighted by empirically determined energies may be derived from the crystal morphology.

If each point of the reciprocal lattice is assigned a weight proportional to an observed magnitude (as for example the intensity of the X-radiation reflected in the point), the reciprocal periodic space so defined may be termed the intensity space (*cf.* James, 1954, p. 349). The intensity space varies with the experimental procedure for weighting the lattice points, as for example, neutron diffraction, or X-ray diffraction (Ewald, 1921, p. 154) which give radically different sets of observed magnitudes. To obtain a space reciprocal to the direct crystal structure it is necessary to convert the intensity space obtained by a particular experimental technic to a reciprocal lattice with points weighted by empirical "structure factors" alone. This is the structure factor space. To be complete, the structure factor space should be very large (containing many points) and the weight of each point should include the phase as well as the magnitude of the structure factor. In practice, no single experimental method provides weights and phases for all conceivable points and therefore any structure factor space derived from experiment is more or less incomplete. If the values  $P_{hkl}$  are assigned to the appropriate points of the reciprocal lattice, a limited morphological intensity space is defined. A conversion from this morphological intensity space to the structure factor space is outlined below (equation 10).

*The Transform from Morphology to Structure.* A number of transforms between morphology and structure have been proposed in the past (Bravais, 1866; Barlow, 1883; Pope and Barlow, 1907; Niggli, 1920; Buerger, 1947; McLachlan, 1952, among others). The rule of Bravais

TABLE 1. PERSISTENCE VALUES AND  $\sigma \cdot d$  VALUES USED FOR FOURIER TRANSFORMS

| $hkl$<br>(Niggli) | $hkl$<br>(cell) | Anglesite |                  | Barite |                  | Celestite |                  |
|-------------------|-----------------|-----------|------------------|--------|------------------|-----------|------------------|
|                   |                 | $P'$      | $\sigma \cdot d$ | $P'$   | $\sigma \cdot d$ | $P'$      | $\sigma \cdot d$ |
| 102               | 101             | 73        | 66.87            | 86     | 67.54            | 85        | 70.65            |
| 011               | 011             | 73        | 84.33            | 86     | 86.70            | 94        | 91.19            |
| 100               | 200             | 38        | 85.77            | 61     | 92.66            | 37        | 86.37            |
| 122               | 111             | 52        | 67.30            | 27     | 49.00            | 17        | 38.39            |
| 001               | 002             | 67        | 120.84           | 98     | 128.20           | 67        | 122.44           |
| 110               | 210             | 81        | 110.98           | 92     | 111.23           | 68        | 107.02           |
| 104               | 102             | 28        | 81.98            | 37     | 87.96            | 25        | 79.51            |
| 111               | 211             | 65        | 92.70            | 69     | 91.82            | 43        | 79.94            |
| 010               | 020             | 32        | 128.37           | 71     | 156.27           | 8         | 77.69            |
| 112               | 212             | 21        | 68.87            | 16     | 55.90            | 9         | 34.11            |
| 120               | 220             | 25        | 110.90           | 11     | 73.36            | 11        | 75.62            |
| 144               | 122             | 2         | 0.0              | 2      | 0.0              | 14        | 61.20            |
| 210               | 410             | 2         | 0.0              | 39     | 144.55           | 2         | 0.0              |
| 113               | 213             | 1         | 0.0              | 26     | 95.50            | 6         | 21.57            |
| 012               | 024             | 6         | 75.12            | 4      | 46.35            | 6         | 76.02            |

All values were scaled to  $\sigma_{000}$ =no. of electrons in unit cell for the maps (Figures 1-4).

(1866) provided that the morphological importance of faces would be in the order of the reticular densities of planes of the direct lattice. The rule of Donnay and Harker (1937) substituted the reticular density of "equipooints" *i.e.*, points added by space group operations as well as true lattice points, for the reticular densities of Bravais. The reticular densities are proportional to the interplanar spacings  $d(hkl)$ . In the example of Donnay and Harker, the basal plane of quartz  $\{0001\}$  should be the most prominent according to the Bravais rule, but each lattice point is replaced by three "equipooints" as a result of the  $3_1$  or  $3_2$  screw operation. In the same way, the spacing  $d(0001)$  is divided by 3 and the plane under consideration is  $\{0003\}$ , rather than  $\{0001\}$ . But for this argument to have physical significance, the density under consideration ought to be related to the density of centers of force or material particles rather than geometric points. The electron density is a possible physical substitute for the densities of ideal points.

The standard method of representing the structure is by mapping the electron density. Given the electron density the complete structure factor space can be calculated directly. The inverse process from the structure factor space to the electron density by Fourier transform is also well known. This transform, shares with the structure factor space, the property of complete independence of any experimental technique. If the transform from the morphologically-derived structure factor space

should yield an approximation to the electron density, the morphology would be a function of the electron density to the degree of the approximation, and the function would be to the same degree the inverse of the Fourier transform.

Ordinarily the detail and accuracy of the Fourier electron density map depends upon the inclusiveness and accuracy of the structure factor space. A space derived from diffraction is markedly more accurate as well as inclusive than the space derived from morphology. The morphologically-derived structure factor space is determined for only a single point of the lattice in any rational direction (a single order  $n$  for any  $nh$   $nk$   $nl$ ). In place of hundreds or even thousands of diffraction intensities, meaningful values for morphological frequencies may be two orders of magnitude fewer and of only approximate accuracy.

*Results.* The first attempt at a Fourier transform from a morphologically-derived structure factor space to an electron density, *i.e.* starting from the external forms of crystals and finishing with the crystal structure was shown at the 1966 meetings of the International Mineralogical Association in Cambridge, England (Schneer and Silva, 1966B).

In order to obtain a quantitative evaluation of the results, error factors were calculated as residuals in the comparison of morphologically derived specific surface energies with structure factors. The structure factors were calculated by weighting known atomic positions with 1) electron scattering factors; 2) neutron form factors (atomic numbers); 3) atomic weights; and 4) by using atomic numbers for metal and sulfur alone, omitting oxygens. Residuals varied from less than 0.20 to 0.40. The omission of oxygen atoms and the use of constant atomic number (neutron form factor) in place of electron scattering factors overweighted the metal ion and brought about the lowest residuals. The lowering of the residuals confirms the testimony of the maps in emphasizing the morphological role of the metal ion.

Although these calculated error factors are at least twice as large as those for the corresponding diffraction data, and relatively unamenable to the refinement procedures of diffraction analysis, the *a priori* probability of matching 15 structure factors with a residual of 0.2 or less is vanishingly small. The relationship cannot be coincidence.

Fourier maps, Figures 1 and 2, constructed from the morphologically-derived structure factor space, are crude but show clearly the location and relative magnitude of the metal ion in the barite group structures. They are only slightly less detailed than the Fourier maps made from X-ray data for the same sharply restricted Fourier series. They are greatly superior to the Fourier maps of the same selected terms with

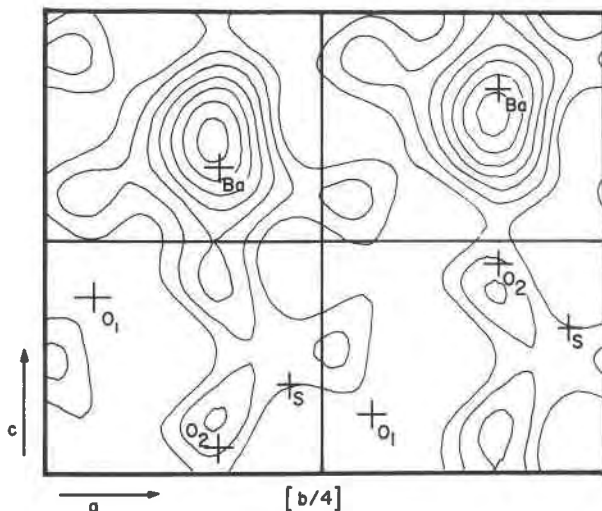


FIG. 1. Fourier transform (electron density map) of the  $y(1/4)$  plane of barite,  $\text{BaSO}_4$ , using the values of Table 1 as coefficients. All computations and graphs by computer. Positions of atoms located on the plane by diffraction procedures are marked for comparison. The *signs* of the Fourier coefficients were determined from the structure (diffraction); Schneer (1968).

random magnitudes. Using observed magnitudes (in the form of squared morphologically-derived structure factors) without phase or symmetry or other *a priori* additions to the reciprocal lattice, a preliminary Patterson-Harker (Buerger, 1959) transform from the barite data of Niggli, (Fig. 3a) may be compared with the equivalent map (Fig. 3b) prepared from the known structure data (Wyckoff, 1963). Figure 4 compares the morphologically derived Zn-Zn and S-S vector of sphalerite with the F-F and Ca-Ca vectors of fluorite. It underlines the physical significance of the morphological frequency data.

Wherever parallelism between morphological importance and diffraction intensities is observed, parallel analytic procedures should lead to the same structure. Such parallelism was remarked by Wells (1946) *cf.* Figure 5, and a correlation between Brillouin zones and morphology was pointed out by Schneer (1959). Working backwards, morphological significance should be predictable and calculable from the known structure. The detail of the Fourier map may reflect the relative importance of the different atoms in determining the morphology, as for example in locating the metal ion and ignoring the approximately close-packed anions. For polar crystals the absolute orientation of the structure with respect to the morphology should be obtainable (suggested by J. D. H.

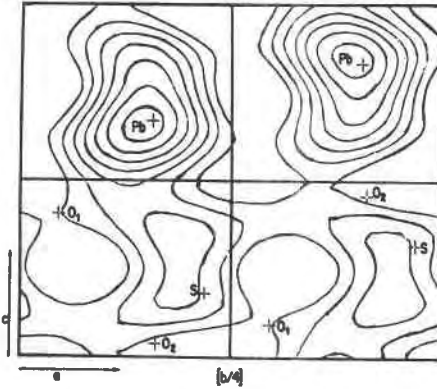


FIG. 2. Fourier transform as in figure 1, but for anglesite  $\text{PbSO}_4$ ; data of Table 1, after Schneer (1970).

Donnay). The morphological effects of diadochy, incorporated impurities, defect structures and stacking faults, as well as the complete morphological frequency distribution in geological time and space should be calculable *a priori*.

#### THE RELATIONSHIP BETWEEN MACROSCOPIC GROWTH AND THE FUNDAMENTAL LAWS OF CRYSTALLOGRAPHY

*Introduction.* If a crystal is grown uniformly from solution it is often morphologically a better crystal than if it is grown at arbitrarily variant rates. Not only is the body of the crystal clearer, but the external faces of the polyhedral surface approach ideal planes more closely and the edges and corners are more sharply defined, the more slowly the crystal is grown. These are observations made in our laboratory but also reported widely (Buckley, 1951, p. 129) and it is commonly accepted by mineralogists that well-developed single crystals are evidence of uniform growth under conditions permitting the barest minimum of excess saturation. It has also been reported that under these uniform conditions crystal growth is observed to proceed by mechanisms other than that of spiral growth (Egli, in Doremus *et al.*, 408, 409).

Regardless of the particular microscopic mechanism of growth, if the developing crystal is observed macroscopically at intervals of time as for example in time-lapse photography (Schneer and Silva, 1966A), and if the Wulff normals on each face<sup>1</sup> are measured as a function of time, then the

<sup>1</sup> Wulff, 1901, proposed that the face-normals from a particular point within the crystal are proportional to the velocities of growth. Such a velocity would be an average for the length of the normal over the total time of growth.

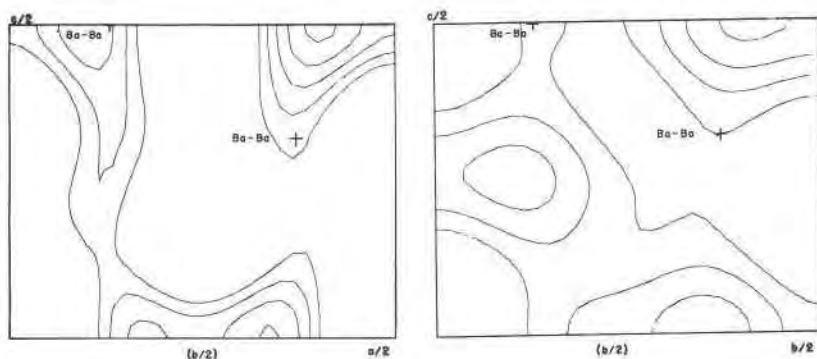


FIG. 3a. Fourier transform (Patterson-Harker map) showing the interatomic vector density for the  $y(1/2)$  plane of barite using the same values of Table 1 as in Figure 1 but squared (*without a priori* phase information or symmetry information). The positions of the Ba-Ba interatomic vectors calculated from the diffraction structure are marked (+) for comparison 2.

FIG. 3b. Fourier transform (Patterson-Harker map) for barite exactly as in figure 3a but computed from the diffraction determined structure with coefficients the squares of the calculated X-ray structure factors. The terms of the series were limited as in Figures 1-3a to the list in Table 1.

increments in length,  $\Delta l$ , of these normals, divided by the time difference of the observation,  $\Delta t$ , have the dimensions of velocity and approximate the instantaneous growth rate. We are concerned here solely with those *macroscopic* growth rates in directions perpendicular to the crystal faces  $\{hkl\}$ , in full awareness that this growth may in most if not all cases, proceed through microscopic processes such as the spiral, with orientation and geometry essentially independent of the crystallography. The crystal is considered to be a black box with a bounding polyhedron which is evidence of its relative growth rates in different directions averaged over the crystal's life-path.

In summary, the macroscopic growth of crystals may be referred to a set of vectors in the directions of the face-normals and identified by the face indices. They have the magnitudes of the rates of extension of the face-normals. These are the "Wulff vectors."

If crystals grew in all directions rather than in the directions of a discrete set of vectors, and if the rates of growth were equal, the resulting surfaces would approach spheres, *cf.* Curie, 1885, p. 147. If crystals grew in all directions and not solely in the directions of the vectors joining the origin to points of the reciprocal lattice, the resulting polyhedral surfaces (*cf.* Gibbs, 1961, p. 316) would contradict the laws of the constancy of interfacial angles and of rational intercepts. Crystals in general do not

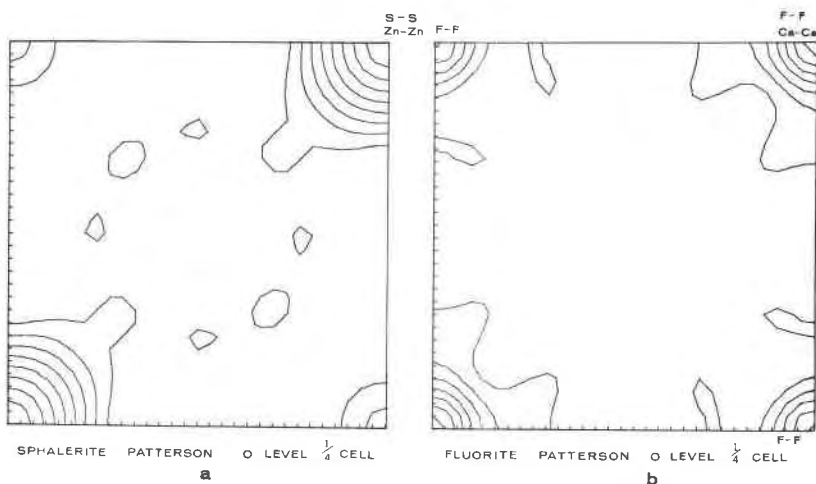


FIG. 4a. Patterson for Sphalerite from the morphological data of Gebhardt (1933). Interatomic vectors at the corners are labeled.

FIG. 4b. Patterson for fluorite from persistences measured on figures in Goldschmidt's *Atlas* (1923).

exhibit spherical surfaces, and do obey the two fundamental laws of crystallography. Therefore we conclude that *the macroscopic growth of a crystal may be represented by vectors in directions from the origin to the points of the reciprocal lattice, with the magnitudes of the rates of extension of the face-normals.*

*Environmental Influences on Growth.* Any environmental influence on the growth of crystals may be considered in two parts, the first random and the second crystallographically controlled. Random influences affect the persistence of one face as much as another. A property of the fluid medium in which the crystal is growing, such as viscosity, would be a random influence. If a crystal is growing with one face exposed to a current of supersaturated fluid, there is no reason to suppose that another crystal will grow in the same orientation with respect to the current—unless there is a crystallographic control.

Only if the differences in the vectorial growth rates are structurally determined should we expect statistical consistency in the forms and habits of crystals. The forms and habits of crystals may reflect microscopic mechanisms of growth such as spirals without as well as with consistent crystallographic orientation. But the forms and habits of crystals also exhibit the statistical consistency expressed in the surveys referred to below. This statistical consistency, this repeated preference



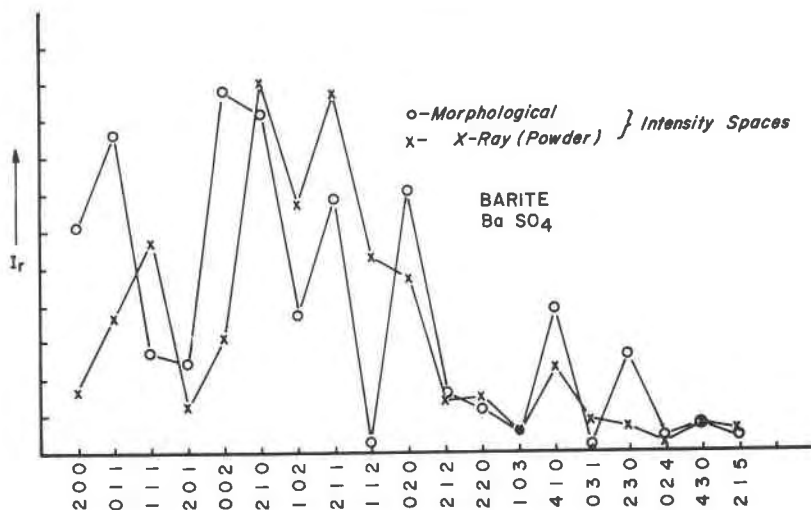


FIG. 5. Morphological and diffraction intensity spaces. The non-zero reciprocal lattice weights ( $P'$ ) for barite observed by Braun (1932) and the N.B.S. standard X-ray powder diffraction intensities compared. Magnitudes are plotted in order of decreasing interplanar spacings ( $d$ ).

of some forms over others throughout the very great diversity of habit and environment characteristic of the provenance of a mineral species, is evidence of a crystallographically oriented distribution of surface energies.

If the forms and habits which admittedly vary widely within a mineral species, did not exhibit a statistical consistency but were as random as they appear to the nonmineralogist, then there would be no significant relationship between crystal form and crystal structure. Growth would be solely a function of microscopic mechanisms. If, on the contrary, significant patterns in the occurrence of crystallographic forms of a mineral species emerge through the study of crystals grown in a wide range of environments, then a mechanism *in species* is also in operation, and the environment is not the sole determinant of the crystal form. To decide the question we may seek such evidences in the laboratory, but in fact it already exists in the geological field and its examination falls within the science of mineralogy.

In the long geologic past and throughout the earth's crust, it may be assumed that a very wide range of experimental conditions, physical and chemical, have permitted the growth of crystals of all mineral species. In effect, the earth's crust is an enormous laboratory in which an experiment on a scale vast enough to provide a statistical basis for con-

clusions has already been carried out. The geological field is the result of this effort through geological time, which may be called the experiment of the world. As our record of the world-experiment becomes more complete it should form an increasingly close approximation to statistical equilibrium, *cf.* definition below.

*The Classical Conditions for Equilibrium.* J. W. Gibbs in 1878 (1961, p. 322) and P. Curie (1885), p. 147) proposed that the equilibrium shape of the crystal would be such as to minimize the sum of the surface energies. If  $\sigma_i$  is the specific energy of the  $i$ th face with area  $F_i$ , then the condition for equilibrium is that the sum  $\sum_i F_i \sigma_i$  shall be a minimum for the volume of the crystal. Sheftal and Gavrilova (1966) modified this to consider the equilibrium shape with respect to the bulk free energy. Wulff (1901), taking the velocities of growth represented by  $h_i$ , the face-normals from a central point, as directly proportional to the specific surface energies  $\sigma_i$ , proposed that for the equilibrium crystal shape:

$$h_i/\sigma_i = h_j/\sigma_j = h_k/\sigma_k = \dots = C. \quad (1)$$

The Wulff theorem was derived from first principles by von Laue in 1943. It should be emphasized that the shape referred to is a relationship between specific surface energies and the relative magnitudes of surface planes, and not necessarily the shape of a real crystal.

The Wulff theorem is applicable to a single crystal. Any rule or "law" of mineralogy (as contrasted with physical law) applies to an ensemble of crystals. If a very large quantity of a particular compound is crystallized as one huge crystal, the equilibrium morphology will be defined by Wulff's theorem. If the same quantity of material is crystallized as a very large number of individual crystals, experience, as well as statistical mechanics dictates that the probability of a variety of combinations of forms is overwhelmingly greater than the probability that all the crystals will have identical forms. The same high energy form which is prohibited by thermodynamic considerations, is virtually assured of appearance by probability calculations. The diversity which is *a priori* implicit in the second law is described *a posteriori* by the statistical surveys of crystal morphology.

Valid objections have been raised to the concept of growth as an equilibrium process, beginning with queries by Gibbs and Curie in the original papers in which the equilibrium shape was defined.

*Experimental Critique.* To try to determine the extent to which the forms of single crystals adapt during growth to achieve equilibrium, we undertook a number of elementary experiments. These experiments demon-

strated qualitatively that growth rates and therefore shapes are not obviously affected by the force of gravity, and therefore that thermodynamic equilibrium was not achieved for individual crystals.

Small seeds of Rochelle salts single crystals cut in the shape of cubes approximately 0.5 cm on a side with cube axes parallel to the orthorhombic crystallographic axes, were allowed to grow in a centrifuge under accelerations corresponding to as much as 1000 times normal gravity. Crystals were grown in various orientations with respect to the field so that the  $a$ ,  $b$ , and  $c$  axes were in turn vertical. In several trials, three seeds were mounted along the vertical axis of the same centrifuge tube so that adjacent seeds were subject to very different gravitational force. In no instance was a significant difference in growth rate observed which could be related to the gravitational field. A potential energy difference between the top and bottom cube surfaces of a seed growing at an acceleration of 500  $g$  ( $g$  is the normal force of gravity) is  $500 \Delta\rho gh$ , ( $h$  is the height of the cube,  $\Delta\rho$  is the difference in density between the crystal and the medium).<sup>1</sup> Reduction of the potential energy of this order of magnitude would be achieved if the crystal tended toward a plate-like habit. Nothing like this could be observed in our experimentation. The forces involved in crystal growth are evidently of a much greater order of magnitude. Thermodynamic equilibrium could not be demonstrated.

Wulff (1901) measured relative differences in growth rates from face to face from the total increments in the Wulff vectors in each experiment. Our own experiments measured lengths along the directions of the crystallographic axes quasi-continuously by time-lapse photography. In the curves of length vs time, growth began rapidly and somewhat erratically, slowed into constant rates (linear) and later curved as growth rates began to slow still further. But it is not clear that these results may not have been related to the particular conditions of the experimentation such as size of chamber, etc. We can only conclude that relative growth rates and therefore crystal shapes, do change during growth, *cf.* Figure 6, and that a single privileged shape was not determined.

#### *Statistical Equilibrium.*

*Definition.* In his memoir of 1875, Gibbs (1961, p. 56) defines the condition of thermodynamic equilibrium of a conservative system as “. . . necessary and sufficient that in all possible variations of the state of the system, the variation of its entropy shall either vanish or be negative.” The condition of statistical equilibrium stated by Gibbs in 1902 (1960, p. 8) for a conservative system is that the probability distribution shall be constant in time—a condition satisfied when the distribution is that of maximum probability, or for the velocities of classical particles, the Maxwell-Boltzmann distribution, Figure 7, curve a, (*cf.* Lindsay and

<sup>1</sup> This corresponds to a potential difference between the top and bottom of a 1 cm-high crystal in a 500  $g$  field of  $\simeq .01$  cal for each gram/ml of  $\Delta\rho$ ; *cf.* below and Appendix for relative specific surface energies.

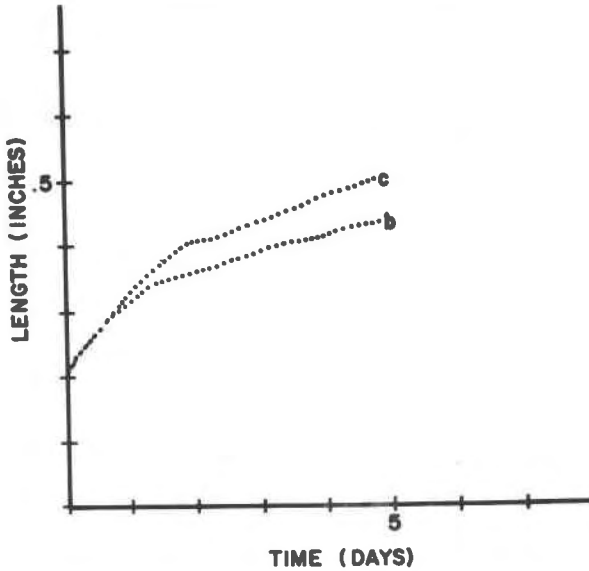


FIG. 6. Growth of Rochelle Salts crystal along  $b$  and  $c$  axes. A single crystal of Rochelle Salts growing freely at  $30^{\circ}\text{C}$  from a seed cut to a cube with axes parallel to the crystallographic axes, observed photographically at fifteen minute intervals; length in inches vs. time in days.

Margenau, p. 224). The probability of a mechanical distribution and the entropy of a thermodynamic system are related.

$$S = k \ln P; \quad (\text{Whittaker, 1960, p. 82}) \quad (2)$$

In curve a, Figure 7, the vertical axis represents the number of particles with velocities between the abscissa values  $v$  and  $v + \Delta v$ . According to classical statistical mechanics, it is the most probable distribution and the distribution toward which any system tends with increasing time and number of samples. It is therefore the form toward which the distribution of energy among the external forms of a crystal species must tend.

#### *Niggli's Method of Measuring Persistence.*

Niggli (1941) defined the persistence- or  $P$ -value of a crystal form  $\{hkl\}$ , as the number of combinations of forms in which it appeared in the specimens of a given mineral species.

Braun (1932, p. 208) reported one specimen of barite with only forms  $\{101\}$ ,  $\{210\}$ ; another with these two forms plus  $\{001\}$ ,  $\{010\}$ , and  $\{102\}$ ; another with  $\{101\}$ ,  $\{210\}$ ,  $\{001\}$ ,  $\{010\}$ , and  $\{011\}$ . Each of the three specimens is enclosed by a distinct combination

of forms. The first two forms are counted three times;  $\{001\}$ , and  $\{010\}$  are counted twice;  $\{102\}$  and  $\{011\}$  are counted once each. If another specimen is found with only the first two forms,  $\{101\}$ , and  $\{210\}$ , this will increase the value for the frequency of occurrence of the two forms, but it does not count for the  $P$ -value. In this way the statistics are less likely to be effected by bias in the selection of specimens, by the quantities of specimens collected, or the size of the deposit, etc.

The persistence-value so defined does not take into account the relative development of the faces, counting a single minute facet and a fully

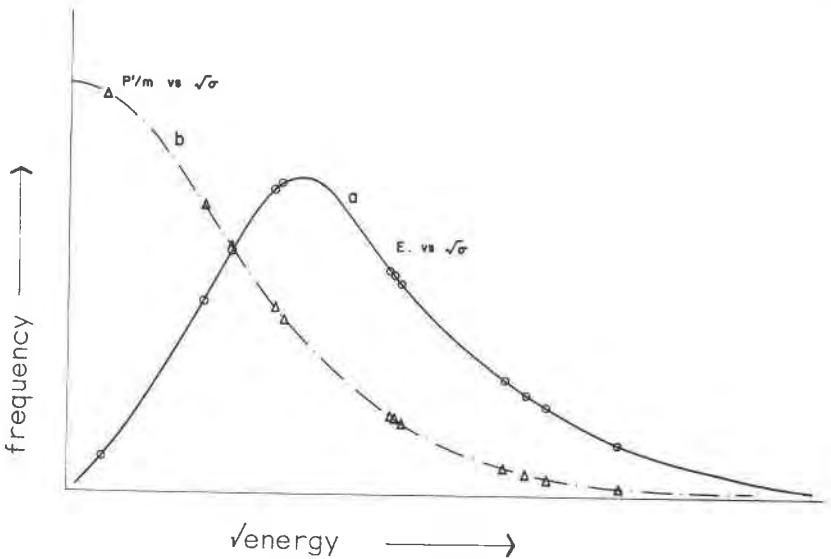


FIG. 7. The Maxwell-Boltzmann frequency distribution. Curves for the proportion of particles vs.  $\sqrt{\text{kinetic energy}}$ . The barite  $P'/m$  vs.  $\sqrt{\sigma}$  from equation (8) is shown on curve b and the total energy for each form  $E_{hkl}$  from equation (4) vs.  $\sqrt{\sigma}$  is shown on curve a. Points are coincident with the curve because the values of  $\sigma$  and therefore  $\sqrt{\sigma}$  are obtained from the equations.

developed prism equally as a single occurrence. To take this partly into account, Niggli used an amended type of persistence-value which he designated  $P'$ , and which is the value used in this research. The  $P'$ -value counts a form once for each time that it appears in a distinct combination of forms in any habit (habits distinguished qualitatively). Since a markedly different development of forms means a distinct habit, forms persist through changes of habit in proportion approximately relative to their size.

Braun (1932, p. 200) reports the same combination of forms  $\{001\}$ ,  $\{010\}$ ,  $\{011\}$ ,  $\{010\}$ ,  $\{210\}$  in the habit which he designates Rechteckig Tafeliger-Typ I as well as in his habit,

Erz-Typ IIIa. Each of these forms is counted twice for the  $P'$ -value because the combinations though the same, are in different habits. They would be counted only once for the  $P$ -value. In order to visualize the effect of the unequal development of forms on the  $P'$ -values, consider a graph in which the proportionate surface area of each form is plotted along a different Cartesian coordinate axis. If a crystal combination consisted of a pinacoid ( $x$ ) and a hexagonal prism ( $y$ ), a plate or tabular habit would be represented by a point on the  $x$ - $y$  plane with the value for the surface of the pinacoid ( $x$ ) high and the value for the surface of the prism ( $y$ ) low. A needle-like habit would be represented by a point far out along the prism ( $y$ ) axis but relatively close to the origin of the pinacoid ( $x$ ) axis. A stubby prismatic habit would be represented by a point somewhere along a line bisecting the two axes. If a third face is to be considered, a third axis would be added. For the complete system *in species* of  $n$  possible forms, each habit would be represented by a small region in an  $n$ -dimensional graph. Minor modifying facets would not displace the point representing the crystal from the small region of the habit. A major development however would mean a new habit and the form would be counted again. Restricting attention to a limited number of defined habits is essentially using a grab sample procedure for the  $n$ -dimensional graph. The graphs of snow crystals in environmental coordinates (Nakaya, 1954, p. 244) resemble projections on a plane through the  $n$ -dimensional space of such a graph (Fig. 8).

In any event, when statistical surveys of both sizes of faces and their persistence are reported, there is little difference (*cf.* Gebhardt, 1933).

*Results.* Figure 9, after Niggli (1941) represents the persistence values of the forms of ferberite arranged in order of decreasing magnitude. In 12 other examples given by Niggli, curves of the forms of various mineral species arranged in the order of descending values of  $P'$  also approximate the curve of Figure 9. Obenauer (1932) found the same curve for his surveys of 101 and 131 galena crystals. Nine individual frequency curves given by Braun (1932) for 9 distinct habits of barite show close adherence to the same curve. Also the order of the frequency of the particular forms in the 9 curves is almost identical. It would make little difference if any of the individual 9 curves or if the initial  $P$ -values were substituted for the  $P'$ -values used in the Fourier transform.

It is characteristic of all of these curves that there are few forms of high persistence, more forms of intermediate persistence and indefinitely many forms of low persistence. The number of forms in a given range of persistence increases as the persistence decreases. The same relationship characterizes an equilibrium distribution of particles among energy states. But if random numbers are assigned to forms which are then arranged in order of decreasing magnitude, there should be as many forms within a range of high magnitude as within a range of low magnitude. As an example, in selecting  $n$  random numbers between 1 and  $10^6$ , the ratio of  $n_a$  picked between  $9 \times 10^5$  and  $10^6$ , to the number  $n_b$  picked between  $1 \times 10^5$  and  $2 \times 10^5$ , should approach unity as the sample  $n$  gets larger. I conclude that the distribution of Figure 9 is not random.

If Gibbs' assumption of a particular and morphologically significant

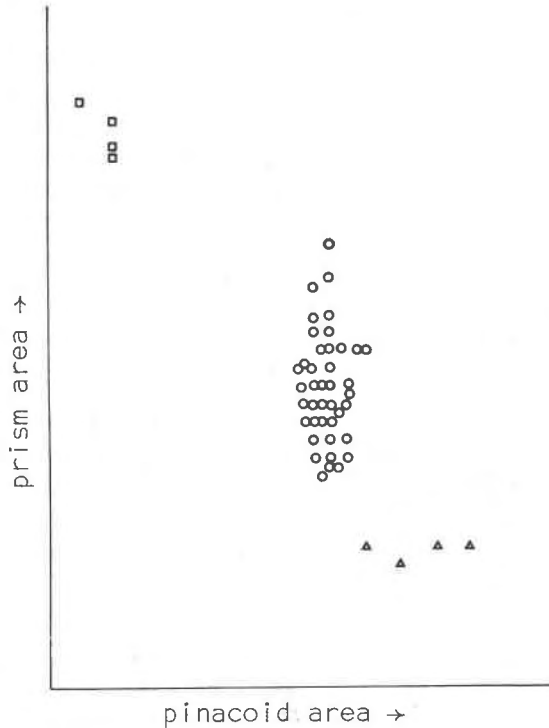


FIG. 8. Crystal habits represented on a prism vs. pinacoid surface graph. The effect of markedly differential development of forms is represented by this projection on a prism surface vs. pinacoid surface for snow. The points for three different snow crystal habits are taken from the temperature water vs. air graph of Nakaya (1954). Needles (prisms) are represented by  $\square$ ; plates (pinacoids) by  $\Delta$ ; and dendrites with more equal development of side and upper and lower bounding faces (prisms and pinacoids) by  $\circ$ . A major change in the proportionate development of a form carries it into a new habit and changes its persistence-value.

value for the specific surface energy (our  $\bar{\sigma}$ ) of a form of a mineral species was wrong, there would be no significant differences in values of  $P'$  for different forms, since on the average one would be as likely to occur as another. If there were no structural control over the occurrence of the forms of crystals, curves such as Figure 9 would not be repeated closely for 9 different habits of barite, or for the three minerals of the barite group examined.

#### *Derivation of Relative Surface Energies from Persistence Values*

*Theory.* Following the precedent of Gibbs (1961, pp. 224, 316) I have considered that there is a particular value of the specific surface energy

$\sigma_{hkl}$  associated with each form  $\{hkl\}$  of a mineral species. It is equal to the energy required to increase the surface  $\{hkl\}$  by one unit of area, the volume being held constant. Environmental effects, variations in the pressure, temperature, and chemistry of the system in which the crystal is growing should cause the observed surface energies to cluster about mean values, much as any suite of measurements of a physical quantity scatters about a mean. Any consistent sampling of the world-experiment represents such a suite of measurements. The  $P_{hkl}$  values correspond to the probability of occurrence of a form  $\{hkl\}$  through the ranges of pressure, temperature, chemistry, and time of growth of crystals of the mineral species. They are either functions of the crystal structure which is invariant for the species, or else they are random numbers. The effects of environment may be separated into two categories: those effecting all forms equally therefore not effecting relative persistence ( $P'$ ), and those selectively effecting particular forms because of interaction with internal factors such as the chemistry and structure of the crystal.  $P'$  values have been regarded as functions of internal factors and independent of external factors by Niggli (1920) and his followers, by Donnay and Harker (1937), and recently by Hartmann and Perdok (1955), who have used the same  $P'$ -values used here. Results from laboratory measurements suggest that synthetic crystals may obey the same laws of distribution as natural crystals. The relative growth rates of synthetic quartz were reported to correlate sensibly with the relative preponderance of the forms in nature (Laudise, 1958, p. 460).

Let the abscissa of Figure 7 represent the  $n$  possible forms of a mineral species, plotted in the order of increasing relative specific surface energies,  $\sigma_{hkl}$ . Then if the total surface energy is distributed by chance among the  $n$  possible forms of the crystal and if the sample space is large enough, the curve of the total energy associated with each form vs.  $\sqrt{\sigma_{hkl}}$  should

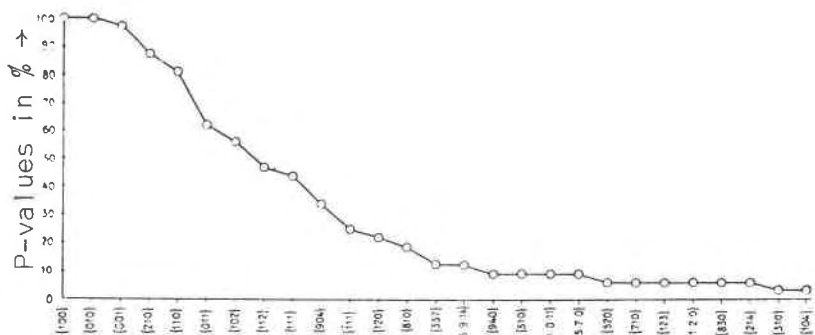


FIG. 9. Niggli's (1941) persistence-value curves for ferberite.



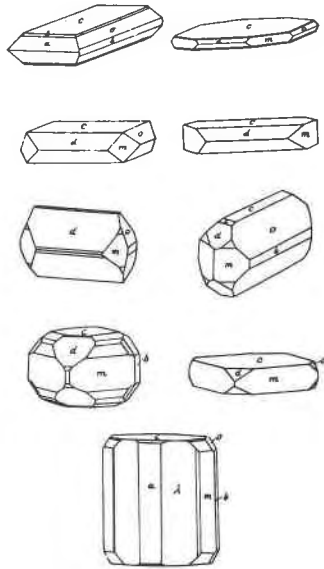


FIG. 10. The nine habits of barite crystals distinguished by Braun (1932). Fourier coefficients derived from the persistence values of these forms (Table 1) were used for the maps of Figures 1–3a. The nine habits illustrate the source morphology for the transforms to the structure.

be the familiar skewed curve of the Maxwell-Boltzmann distribution.<sup>1</sup> Let  $F_i$  be the surface area of the  $i$ th specimen of the form  $\{hkl\}$ . Then the total surface energy  $E_{hkl}$  associated with the  $P'$  occurrences of the form is given by;

$$E_{hkl} = \sum_1^{P'} F_i \sigma_{hkl} \quad (3)$$

Replacing  $F_i \sigma_{hkl}$  by an average value over  $P'_{hkl}$  for the surface energy,  $\bar{\sigma}_{hkl}$  (the average energy associated with the form  $\{hkl\}$  per crystal of the sample population) then;

$$E_{hkl} = P'_{hkl} \bar{\sigma} \quad (4)$$

and;

$$P'_{hkl} = E_{hkl} / \bar{\sigma} \quad (5)$$

<sup>1</sup> For comparison with the kinetic-molecular curves of frequency vs. velocity, the abscissa should have proportional dimensions. Therefore total energy and persistence are plotted against  $\sqrt{\bar{\sigma}}$  rather than  $\bar{\sigma}$

Divide each value of  $E_{hkl}$  of curve a, Figure 7, by the corresponding value of  $\sigma$  to obtain  $P'$  values for curve b. Curve b is the ideal frequency distribution curve corresponding to curve a. It is the curve to expect as the distribution of total surface energy among the forms of a mineral species approaches equilibrium. The empirical values of  $P'/m$  for barite vs. the values for  $\sqrt{\bar{\sigma}}$  obtained from equation 10 (below) have been marked on curve b. Multiplying  $\bar{\sigma}$  by  $P'/m$  gives  $E_{hkl}$  (Equation 4) plotted on curve 7a as a function of  $\sqrt{\bar{\sigma}}$ . The curves are ideal. The observed  $P'$ -values are an exact fit because the  $\bar{\sigma}$  are obtained from Equation 10 below which expresses the equilibrium relationship. That is, the assumption was made that the observed statistical persistence ( $P'$ ) could be equated with the theoretical probability of occurrence. On this assumption of an equilibrium distribution, the relative  $\bar{\sigma}$  are easily determined.

*Calculation of  $\bar{\sigma}$  from Persistence Values.* Following the precedent for analysis of the intensities of X-rays diffracted by a powder, the observed values for  $P'$  were divided by a multiplicity factor ( $m$ ) for the number of faces of a particular form generated by the operations of symmetry.

The symmetry of minerals of the barite group is described by the point group  $mmm$ ; the general form is the orthorhombic dipyrmaid of 8 faces. There are 8 possibilities for the observation of a pyramid face as compared with 2 for the observation of a pinacoid or 4 for a dome or prism. The multiplicity of the probability of observation is a sampling factor having nothing to do with the relative surface energies and the multiplicity correction is therefore made as an adjustment to the  $P'$ -value before using it to derive an observed potential energy.

According to classical statistical mechanics, the proportionate numbers of particles  $n_1/n_2$  in two energy states  $\sigma_1, \sigma_2$  of a system in statistical equilibrium, is given by;

$$n_1/n_2 = e^{-\Delta\bar{\sigma}/kT} \quad (6)$$

$\Delta\sigma$  is the difference in energy between the two states  $\sigma_1$  and  $\sigma_2$ ,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature or in this case, average temperature. If  $n_2$  is the total number of distinct combinations of forms in distinct habits, and  $n_1$  is the number of times the form  $\{hkl\}$  was counted;

$$n_1/n_2 = P'_{hkl}. \quad (7)$$

$$\sigma_{hkl} = -kT \ln P'_{hkl}. \quad (8)$$

Equation (8) is (6) rewritten in logarithmic form with substitution of equation (7);  $\sigma_{hkl}$  is now the potential energy of the form  $\{hkl\}$  with

respect to the potential energy of a form occurring in all specimens counted ( $P' = 100$ ).

As an example if the average temperature of growth of barite crystals was 202°C or 475°K, the difference in  $\sigma$  between a prism like  $\{210\}$  and the pinacoid  $\{001\}$  would be 0.718 kcal/mol (Appendix). The value for room temperature would be about 0.5 kcal/mol. This means that a single *gram-molecule* of barite in solution would effect a reduction of potential energy of about 0.7 kcal by adhering to the surfaces of prisms  $\{210\}$  rather than pinacoids  $\{001\}$ , at a temperature of 202°C. The same process for a crystal growing at room temperature, would effect a lowering of potential of half as much. Therefore the diversity of forms on a crystal should be greater for crystals grown at low temperature relative to those grown at high temperature since at low temperature there is less driving energy for one form to be chosen over another. In addition there is an entropy of mixing of forms which favors diversity in the forms of the crystal.

Niggli (1941) and Braun (1932) counted the numbers of forms per combination and the numbers of combinations with every number of forms, ( $z$ -value). In a survey of more than 62 forms in 185 combinations for barite, Braun found that  $z$ , the number of combinations plotted against the number of forms per combination, is a curve roughly approximating the Maxwell-Boltzmann distribution curve. Twenty-four combinations were observed with 6 forms; only 2 with 2 forms, 1 each with 18 and 21 forms. In our experiments with the growth of Rochelle salts at temperatures from 0°C to 35°C we obtained a distinctly richer morphology from the crystals grown at 0°C.

In order to convert observed surface energies to morphological structure factors, it is necessary to take into account the interplanar spacings,  $d_{hkl}$ .

For ordinary copper with atoms in the face-centered cubic arrangement, structure factors are 4 for  $\{111\}$ ,  $\{200\}$ ,  $\{220\}$ ,  $\{311\}$ , etc. and 0 for planes of intermediate spacings. The effective surface energies for the planes, conceived as the energy required to extend a surface by one unit, cannot be the same for planes of different interplanar spacings. The Bravais and Donnay-Harker rules provided that morphological importance would be proportional to interplanar spacing. Surface energy would therefore be inversely proportional to interplanar spacing.

To obtain  $\sigma$  in appropriate units (energy per unit of area)  $d_{hkl}$  should be squared;

$$\sigma_{hkl} = - C/d_{hkl}^2 \quad (9)$$

Combining (9) with (8), including the correction for multiplicity ( $m_i$ ), with  $C'$  as a constant of proportionality, the expression for the observed morphological structure factor for the  $i$ th form of a species is:

$$\sigma_i = - C'(\ln P_i'/m_i)/d_i^2. \quad (10)$$

It is these values of  $\sigma_{hkl}$  which were used as the coefficients of the Fourier transforms with phases supplied a priori for the electron density transforms. For the Patterson (Harker) transforms, the  $\sigma_{hkl}$  were squared and no a priori information was required.<sup>1</sup> It should be emphasized that equation 9 is one possible modification of equation 8, and not necessarily the only way in which to transform surface energies to structure factors.

#### CONCLUSION

The contradiction between thermodynamic equilibrium which specifies a sharply limited number of simple forms for the polyhedral envelope of a single crystal, and statistical equilibrium which may encompass forms of unusually high specific surface energy, is only apparent. The persistence values of forms are a measure of their specific surface energies. The proportionate energies are in qualitative agreement with general observations of the growth of crystals under different conditions. They are in quantitative agreement with potential energies calculated as structure factors, as is demonstrated by the calculated residuals. Their validity and significance for further studies is warranted by their use in the two kinds of Fourier transforms from morphological space, first to the electron density and second, to the vector space. The transforms to the structure suggest the inverse,—the calculation of the morphological distribution from the known structure.

The factors of error are high when compared to those for diffraction methods. Does this result from deficiencies in the procedures for sampling, or does it represent the degree of departure from the state of statistical equilibrium? Better methods of proceeding from the morphological intensity space to the structure factor space are now under consideration.

The significance of the transform is not in the possibility of a return to morphological methods for the determination of crystal structures but in the understanding that emerges of the relationship between form and structure and in the further elucidation of what Friedel (1905) termed "the reticular hypothesis." The analytic techniques of diffraction which developed after 1912 were greatly indebted to the mineralogical studies which preceded them. The application of these techniques to the

<sup>1</sup> The  $\sigma_i$  used for the maps were calculated with the factor  $1/d_i$  rather than  $1/d_i^2$ . The residual calculated for anglesite with equation (10) was 0.187 as compared to a residual of 0.205 with the earlier factor. McLachlan (1952) expressed "the dominance of the crystal faces" by a laminarity factor,  $L_{hkl}$  proportional to  $d_{hkl}$  times a function of the structure factor. If each atom in the calculation of the laminarity is weighted with the atomic number, then these residuals are the agreement of the set of  $\sigma$  with  $\sqrt{Ld}$  and  $\sqrt{L/d}$  respectively.

problems of the experiment of the world is an operation of symmetry. In effect, the geologic distribution of a form of a mineral species is determined by a specific energy which is a function of the structure factor. The rule at which we finally arrive is this: *The morphological probability distribution is a function of the structure, and the structure is a Fourier transform of the morphological probability distribution.*

## ACKNOWLEDGEMENTS

Ruben Silva, Allen Hayes, and Robert Couture assisted with this research. The Graduate School and the Computation Center of the University of New Hampshire, and the National Science Foundation provided material support. A modified Busing-Levy ORFLS (1962) program was used. Professor G. Busch and the Institute for Solid State Physics of the E.T.H. of Zürich provided hospitality in the initial stages of this work. Professor G. Schiavinato and the Istituto di Mineralogia of the Università degli Studi di Milano provided me with the facilities for completing this paper.

This research was based on the early studies of Professors J.D.H. and G. Donnay, David Harker, the work on transforms of Professor M.J. Buerger and an essay by A. Lande. I am particularly indebted to these individuals and institutions for inspiration and support.

## REFERENCES

- BARLOW, W. (1883) Probable nature of the internal symmetry of crystals. *Nature*, **29**, 186-188, 205-207.
- , AND W. J. P. POPE (1907) The relation between the crystalline form and the chemical constitution of simple inorganic substances. *Trans. Chem. Soc. (London)*, **91**, 1150-1214.
- BOLTZMANN, L. (1964) *Lectures on Gas Theory*. Univ. Calif. Press, Berkeley.
- BRAUN, F. (1932) Morphologische, genetische und paragenetische Trachtstudien an Baryt. *Neues Jahrb. Mineral.* **65A**, 173-222.
- BRAVAIS, M. A. (1866) *Études Cristallographiques*. Gauthier-Villars, Paris.
- BUCKLEY, H. E. (1951) *Crystal Growth*. John Wiley and Sons, New York.
- BUERGER, M. J. (1947) The relative importance of the several faces of a crystal. *Amer. Mineral.* **32**, 593-606.
- (1959) *Vector Space*. John Wiley and Sons, New York.
- BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a fortran crystallographic least-squares program. *U. S. Clearinghouse Fed. Sci. Tech. Info. Doc.* **ORNL-TM-305**.
- CABRERA, N., AND D. A. VERMILYEA (1958) The growth of crystals from solution. In R. H. DOREMUS, B. W. ROBERTS, AND D. TURNBULL, (eds.) *Growth and Perfection of Crystals*. John Wiley and Sons, New York, 393-408.
- CURIE, P. (1885) Sur la formation des cristaux et sur les constantes capillaires de leurs différentes faces. *Bull. Soc. Fr. Mineral.* **8**, 145-150.
- DONNAY, J. D. H., AND D. HARKER (1937) A new law of crystal morphology extending the law of Bravais. *Amer. Mineral.* **22**, 446-467.
- EWALD, P. P., (1921) Das "reziproke Gitter" in der Strukturtheorie. *Z. Kristallogr.* **56**, 129-156.

- FRIEDEL, G. (1905) Sur les bases expérimentales de l'hypothèse réticulaire. *Bull. Soc. Fr. Mineral.* **18**, 95-149.
- GEBHARDT, T. (1933) Über Zinkblende. *Neues Jahrb. Mineral.* **42A**, 1-52.
- GIBBS, J. W. (1960) *Elementary Principles in Statistical Mechanics*. Dover Press, New York.
- (1961) *The Scientific Papers*. Dover Press, New York.
- GOLDSCHMIDT, V. (1923) *Atlas der Kristallformen*. Winter, Heidelberg.
- HARTMAN, P. AND W. G. PERDOK (1955) On the relations between structure and morphology of crystals. *Acta Crystallogr.* **8**, 49-52, 521-524, 525-529.
- JAMES, R. W. (1954) *The Optical Principles of the Diffraction of X-rays*. Bell, London.
- LANDE, A. (1949) The physical significance of the reciprocal lattice of crystals. *Amer. Sci.* **37** (3), 414.
- LAUDISE, R. A. (1958) Hydrothermal crystallization. In R. H. DOREMUS, B. W. ROBERTS, AND D. TURNBULL (Ed.) *Growth and Perfection of Crystals*. John Wiley and Sons, New York, p. 458-464.
- LAUE, M. VON (1943) Der Wulffsche Satz für die Gleichgewichtsform von Kristallen. *Z. Kristallogr.* **105**, 124-133.
- LINDSAY, R. B., AND H. MARGENAU (1957) *Foundations of Physics*. Dover Press, New York.
- MCLACHLAN, D., JR., (1968) *Statistical Mechanical Analogies*. Prentice-Hall, Englewood Cliffs.
- , C. J. CHRISTIANSEN, AND A. CARLSON (1952) Some factors in the growth of crystals. *Bull. Univ. Utah Exp. Sta.* **57**, 1-12.
- NAKAYA, U. (1954) *Snow Crystals*. Harvard Univ. Press, Cambridge.
- NIGGLI, P. (1920) Beziehung zwischen Wachstumsformen und Struktur der Kristalle. *Z. Anorg. Chem.* **110**, 55-81.
- (1941) *Lehrbuch der Mineralogie und Kristallchemie, I* Borntraeger, Berlin.
- OBENAUER, K. (1932) Zur Tracht und Paragenese des Bleiglanzes. *Neues Jahrb. Mineral.* **67A**, 87-117.
- SCHNEER, C. J. (1959) Proposed rule of crystal habit. [Abstr.] *Bull. Geol. Soc. Amer.* **70**, 1670.
- (1968) Crystal form and crystal structure. *Helvetica Phys. Acta* **41**, 1151-1155.
- (1970) *Mind and Matter*. Grove Press, New York.
- , AND R. SILVA (1966A) A method of determination of relative surface energies for crystal growth. [Abstr.] *Geol. Soc. Amer. Spec. Pap.* **87**, 149.
- (1966B) Vectorial growth rates, statistical morphology, and the internal structure of minerals. [Abstr.] *Symposium I Int. Mineral. Ass., Cambridge*. Unpagged.
- SHEFTAL, N. N., AND I. V. GAVRILOVA (1966) Equilibrium shape of a crystal in relation to the bulk free energy. In N. N. Sheftal and A. V. Shubnikov (eds.) *Growth of Crystals*. **4**, Consultants Bureau, New York.
- SWANSON, H. E., R. K. FUYAT, AND G. M. UGRINIC (1954) Standard X-ray diffraction powder patterns. *Nat. Bur. Stand. [U. S.] Circ.* **539**, Vol. 30.
- WELLS, A. F. (1946) Crystal habit and internal structure. *Phil. Mag.* **37**, 184-199, 217-235, 605-630.
- WHITTAKER, E. (1960) *Aether and Electricity*. Harper, New York.
- WYCKOFF, R. W. G. (1963) *Crystal Structures*. Vol. 3. Interscience, New York.
- WULFF, G. (1901) Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Kristallflächen. *Z. Kristallogr.* **34**, 449-530.

APPENDIX: CALCULATION OF SPECIFIC  
SURFACE ENERGIES

Niggli (1941) gives  $P'_{001}=98$  and  $P'_{110}=92$  for barite. Using the structural cell (Wyckoff, 1963),  $\{110\}$  becomes  $\{210\}$ . The multiplicity of  $\{210\}$  is twice that of  $\{001\}$  and therefore  $P'_{210}$  is halved and becomes 46. The Boltzmann factor  $k$  per mole becomes  $R$  (the gas constant  $\simeq 2$  cal/mol-deg). A temperature of  $202^\circ\text{C}$ . is  $475^\circ\text{K}$ . From (8),  $|\sigma_{001}-\sigma_{210}| = RT(\ln 98-46) \simeq 718$  cal/mol.