

THE MORPHOLOGICAL COMPLEMENTS OF CRYSTAL STRUCTURES*

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ABSTRACT

Two complementary approaches to the study of crystallography, morphology (B) and structure (S), are related by a transformation operator (T); $B = T(S)$. Defining the inverse magnitude of a plane by its distance h_i from a central point (Wulff's point), and setting $h_i = 1/d_i F_i$, where d_i is the interplanar spacing of the i th plane (hkl) and F_i its structure factor, the smallest plane polyhedra about the Wulff point are designated *Wulff zones*. For all structure factors equal, the Wulff zones reduce to the first Brillouin zones of the physicists. For structure factors calculated for space-group equipoints, the Wulff zones reduce to polyhedra designated as Donnay-Harker zones because the serial order of their bounding planes is that given by the Donnay-Harker generalization of the law of Bravais. As the transformation is independent of physical or mineralogical theory, the form of the Wulff zones is determined by the physical or mineralogical assumptions employed in the calculations of the structure factors F_i . The computer has been used to model general and reduced zones for FCC, BCC, diamond and barite periodic arrays, the latter with the assumption that the specific surface energies σ_i of Wulff's theorem may be derived from the statistical persistences of the faces in natural occurrence.

SOMMAIRE

La morphologie (B) et la structure (S) constituent deux voies d'accès à l'étude du cristal; elles sont reliées par un opérateur de transformation (T): $B = T(S)$. Si l'on définit l'inverse de la grandeur d'un plan par la distance h_i de ce plan à un point central (point de Wulff) et qu'on pose $h_i = 1/d_i F_i$, où d_i est l'équidistance réticulaire du i ème plan (hkl) et F_i son facteur de structure, les polyèdres les plus petits centrés au point de Wulff sont les zones de Wulff. A facteurs de structure égaux, ces zones se ramènent aux premières zones de Brillouin. Lorsque les facteurs de structure sont calculés pour des positions de points homologues du groupe spatial, les zones de Wulff se réduisent à des polyèdres dits zones de Donnay-Harker parce que le numéro d'ordre des plans qui les limitent est celui que donne la première généralisation (Donnay-Harker) de la loi de Bravais. Comme la transfor-

mation ne dépend d'aucune théorie physique ou minéralogique, la forme des zones est déterminée par les hypothèses physiques ou minéralogiques qui ont présidé au calcul des facteurs de structure F_i . L'ordinateur fournit des modèles de zones, générales ou réduites, pour quatre distributions périodiques: cF (c.f.c.), cI (c.m.c.), D (diamant) et barytine, cette dernière dans l'hypothèse que les énergies spécifiques superficielles σ_i du théorème de Wulff peuvent se déduire de la persistance statistique des faces cristallines naturelles.

(Traduit par la Rédaction)

INTRODUCTION

Paradoxes inherent in the quantum approach to the physical chemistry of solids are reconciled in large part through the principle of complementarity. The systemic morphology of crystallographically symmetrical polyhedra and by contrast, what Friedel has designated the reticular hypothesis (crystal-structure analysis) are also complementary conceptual approaches that between them have given rise to modern mineralogical crystallography. Both members of the couple are valid systemic analyses of the mineral kingdom, although until the discovery of X-ray diffraction in 1912, little could be done with structures; since 1912 there has been a decline in interest in morphology.

The crystallographic dichotomy is, however, indirectly related to the continuity-discontinuity or the wave-particle duality for which the principle of complementarity was originally proposed by Niels Bohr in 1928. "A complete description of observable phenomena requires that these concepts be employed in turn," de Broglie wrote of the quantum contradiction, "but . . . these concepts nevertheless are in a sense irreconcilable, the images that they furnish never being simultaneously applicable *in toto* to a description of reality" (1953, p. 18). The first mathematical expression for the complementarity of matter was the de Broglie equation ($\lambda = h/mv$) expressing the equivalence of the length of a wave to the mass and velocity of a particle.

There is a long history of attempts to determine similar transformations between the external forms and internal periodicity of crystals. Modern theory began with the work of Bravais, established by Friedel as a law of nature.

*Dedicated to Professor J. D. H. Donnay on the occasion of his 75th birthday.

The lattice assigned to a particular mineral species must be "... the one which assigns to the various possible faces of the crystal reticular densities whose decreasing series represents as accurately as possible the decreasing series of ease of production, either naturally (through crystallization) or artificially (through cleavage) of these same faces" (Bravais 1851).

The translation of this hypothesis of mineralogy of Bravais into a formal mathematical relationship analogous to the de Broglie equation for the wave-particle duality is the problem posed in this paper. Bravais recognized at the outset that his lattices were degenerate modes of a more complex structure; his lattices were "the relative arrangements of the centres of gravity of the molecules of crystalline bodies." The complexities of crystal morphology provided the evidence for this. The problem of the complementarity relationship is therefore a more general one than that of a relationship between morphology and *lattice* alone. It is the problem of the relationship of the fully-detailed structure to the associated polyhedral morphology. This mathematical problem should be clearly distinguished from related problems of natural science such as the problem of the equilibrium form of a crystal, or the manifold problems of crystal growth, or even the Bravais problem of determining the lattice from the morphology of the species. Crystallography recognizes two systems of mathematical analysis, morphological and structural. What is the equivalence relationship between the two? This paper is concerned with the determination of a consistent relationship between three-dimensionally periodic arrays and crystallographic polyhedra. The extent to which such relationships are to be found in nature is a more difficult question which will be addressed in the future.

DERIVATION OF COMPLEMENTARITY RELATION

In the simplest version, the problem is to find the polyhedra complementary to the Bravais lattices. This problem was posed by Brillouin in 1931 and the polyhedra designated as Brillouin *zones* by Mott & Jones (1936). To avoid confusion with the physics literature, the complementary zones will hereafter be designated by the name(s) of the author(s) proposing the manner of determination, *i.e.*, the designation Brillouin zone for those polyhedra complementary to the Bravais lattices.

The Brillouin zones are found by the following method: determine the structure factors for the reciprocal lattice planes of lowest Miller indices excluding any planes for which the

structure factor is 0, and for the remainder, calculate the normal distances from the origin one half the vector from the origin to the reciprocal lattice point. The smallest polyhedron about the origin is the Brillouin zone (Mott & Jones 1936).

The extension of the Bravais law by Donnay & Harker (1937a,b) was a generalization to cover the repetitions of the motifs of space-group theory (equipooints) as well as the nodal points of the Bravais lattice (identipooints). In the original Donnay-Harker statement, face indices in the equations for the calculation of reticular densities are replaced by the multiple indices of the lowest order of X-ray reflection compatible with the space-group symmetry (Donnay & Harker 1937b). Using the method for the determination of the Brillouin zones, structure factors of the planes of lowest Miller indices are calculated for the assemblage of equipooints of the space group as distinct from the identipooints of the lattice. The structure factors for additional planes of low indices will vanish (space-group extinctions).

Structure factors for the planes of primitive lattices are all non-zero. Structure factors for other than primitive lattices, termed lattices *with basis* by physicists, are 0 for planes for which the interplanar spacings are halved. In the same way, structure factors for planes for which the interplanar spacings are divided by space-group translations may also cancel. In this case the magnitude associated with the reciprocal lattice points for the planes in question is 0. The planes must vanish and the zone is changed accordingly.

For example the lattice for the diamond structure is *Fcc*, face-centred cubic, for which the appropriate Brillouin zone is constructed of the (111) and (200) forms, the cuboctahedron of Figure 1. But the space-group symmetry is *Fd3m*. With the *d* glide, the structure factor for (200) vanishes and the zone for the diamond structure is therefore the octahedron (111) alone. Mott & Jones (1936) give the rhombic dodecahedron (220) (Fig. 2) for the Brillouin zone of the diamond structure because the structure factor of (111) is sharply reduced and they have defined their zones in part physically. The octahedron (111) about the origin of the reciprocal lattice is smaller than the dodecahedron (220) and the octahedron planes alone bound the smallest polyhedron with structure factor >0 . If we are to be consistent, the *Brillouin zone* for the diamond *lattice* *F* would remain the cuboctahedron of Figure 1, whereas the octahedron alone (Fig. 3) would be designated the Donnay-Harker zone for the diamond equipoint assemblage with space group *Fd3m*.

The Donnay-Harker generalization of the law of Bravais was presented as a law of nature and with its introduction, minor but embarrassing departures from the serialization of forms of the Bravais law were explained. The final generalization is to extend the analysis to the details of the motif. This was done in part by Niggli (1919), Donnay & Harker (1937b), Wells (1946), Buerger (1947), Donnay & Donnay (1961 a, b, c; 1962) and in detail by McLachlan (1952, 1977) and Schneer (1968, 1970). The equation for the structure factor is: $E_{hkl} = \sum f_j \exp(i\phi_j)$, where $\phi_j = 2\pi(hx_j + ky_j + lz_j)$. The summation is taken over the j components of the unit cell with each component assigned a specific magnitude f_j . For the Brillouin zones and for the Donnay-Harker zones, the f_j are specific to identipoints and equipoints, respectively. The f_j are therefore constant and equal. But in the general case, the f_j are functions of the specific cell components such as particular atoms, ions, neutrons or electrons. The scattering factors for the atoms in diffraction computations are an example. For the general case then, the f_j functions express the influence of the motif. The Brillouin zones express the effect of the Bravais translations, the Donnay-Harker zones, the effect of the space-group operations. Symmetry (and cell constants) alone determine the Brillouin and Donnay-Harker zones; these are therefore topologically alike for all mineral species of the same symmetry. The Wulff zones are the morphology of a mineral species and include expression of the individuality of the motif. Beyond this, specimens of the same species are also different. Their individuality, the particular, unique morphology of specimens of the same species, is a record of their conditions and history of growth, unique to every specimen.

The zones discussed above are the first zones, the smallest polyhedra about the origin of the reciprocal lattice. Zones of indefinitely higher order are taken by considering the next largest polyhedron formed about the origin by bounding planes of non-zero structure factors, the next largest, and so on. The relationship discussed above, namely the transform (T) from the structure to the zone (B) may be expressed as: $B = T(S)$. This in turn may be reversed by Fourier synthesis. The planes of the zones are the points of the reciprocal lattice. If a sufficient number of appropriately weighted points are used, the Fourier transform of the weighted reciprocal lattice is the crystal structure (Schneer 1968).

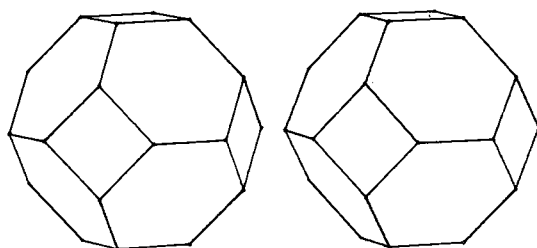


FIG. 1. The first Brillouin zone for the face-centred cubic lattice (F). Two-dimensional stereographic projection is by computer.

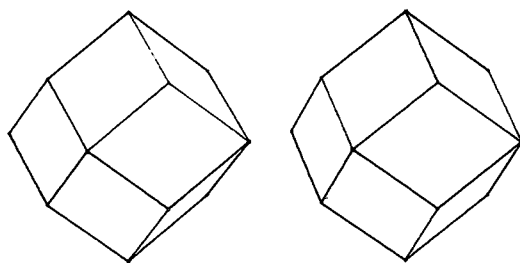


FIG. 2. The first Brillouin zone for the body-centred cubic lattice (I), or second zone for (F).

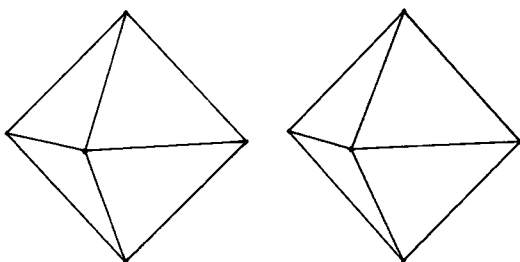


FIG. 3. The Donnay-Harker zone for the diamond structure, $Fd3m$. The (200) of Figure 1 is cancelled by the diamond glide d leaving the (111).

General zones

In the rule for the construction of the Brillouin zones, distances from the origin to the bounding planes were calculated solely on the basis of geometry, all distances being equal to $\frac{1}{2}$ the reciprocal of d_{hkl} , the interplanar spacings of the direct lattice. As the lattice points are identipoints, the coefficients for the structure factors are equal and all structure factors are either finite and equal or 0. As noted above in the case of diamond, the structure factors computed from the equipoints of the space group are no longer equal although the coefficients f_j for the structure factors remain the same. The problem is the same as that of the intensity of X-ray diffraction. Only the lattice

will determine the possible planes of diffraction (reciprocal lattice points); for the primitive lattices, these will be the points with indices given by all possible permutations of the integers, positive, negative and 0. The structure factors for all such lattices (identipoints) are non-zero. For the non-primitive lattices (lattices with basis) the planes of possible diffraction are sharply limited: those with $(h^2 + k^2 + l^2) = 2n$ are allowed for body-centred lattices, for example, with all others cancelled. If the sum of the squares is odd the structure factors for body-centred lattices are 0.

In addition to the rules for finding the planes having lattice extinctions, rules also exist for the determination of planes with structure factors cancelled by the space-group operations. But what is the situation for planes with structure factors that approach 0 but are not 0? These rules do not distinguish between magnitudes of structure factors but only between 0 and non-zero. If the coefficients f_i used in the calculation of the structure factors are not all equal the structure factor for a given plane, such as the (100) of the primitive cube, for example, could vary from 0 to $\sum f_i$. At 0, the face vanishes from the Brillouin zone, now transformed from cube to rhombic dodecahedron.

In the case of β -brass, CuZn, the disordered alloy has the structure of the body-centred cube, with Cu and Zn distributed randomly at corners and centres of a cubic lattice. With ordering, there is a separation so that the probability of finding a Cu in one of the two positions varies quasi-continuously from 0.5 to 1 whereas the probability of finding it in the other position varies concomitantly from 0.5 to 0. In the state of complete order, as the probability of finding copper in the two positions reaches 1 and 0, the structure is wholly primitive cubic with a CuZn motif ($Pm\bar{3}m$). The zone is therefore a cube. In the state of complete disorder with probabilities for Cu = Zn = 0.5 in both positions, the structure is $Im\bar{3}m$. At all intermediate stages it is $Pm\bar{3}m$ as the positions are distinguishable. The structure factor coefficients f_{corner} and f_{centre} are directly proportional to the order parameters.

The problem of finding a general zone is therefore that of determining a morphology that in the example above would express the diminishing magnitude of the cube relative to the dodecahedron as the structure factor $F(100)$ approaches 0 and conversely the diminishing importance of the dodecahedron, which would vanish as $F(100)$ approaches $F(100)_{\text{max}}$.

As we are defining a general zone, the problem is purely mathematical and considerations of natural history or physics are not involved. The function we are seeking is that of the magnitude of the plane. Such a function was proposed by Wulff (1901). From a centre point designated the Wulff point (origin), poles called Wulff vectors are drawn to the faces of the crystal (toward the points of the reciprocal lattice). For the lengths of the Wulff vectors $\bar{h}_i$ and a set of specific surface magnitudes σ_i (Wulff used specific surface energies) and for a given volume, $\sum \sigma_i / \bar{h}_i$ is minimum when

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \frac{\sigma_3}{h_3} = \dots = C.$$

This minimum polyhedron has the properties desired for the general zones. To be consistent these should be referred to as *Wulff zones*. Let the magnitude for the reciprocal lattice point i be designated as σ_i and defined as a function of the structure factor F_i . For these equations to hold, the Wulff vectors h_i or poles to the faces from the Wulff point are set equal to the reciprocals of the product of the interplanar spacings and structure factors: $h_i = d_i F_i$.

To construct the Wulff zone, planes perpendicular to the lines from the origin to the points of the reciprocal lattice are constructed at distances proportional to half the h_i . This construction has the properties desired, in that for $d_i F_i / h_i = d_k F_k / h_k = d_j F_j / h_j = \dots = d_n F_n / h_n = 2C$; $\sum d_i F_i / h_i$ is a minimum.

The factor of two on the right-hand side of this equation is entered to bring the expression $h_i = 1/d_i F_i$ into agreement with the Brillouin zone construction. For the Brillouin zones, $F_i = F_k$. The distance $1/h_i$ of a plane from the origin of the reciprocal lattice is $1/2d_i$ or $1/2$ the vector to the lattice point, as in the Brillouin-Jones constructions above.

For the Donnay-Harker zones, the non-zero structure factors may no longer be equal. The general (Wulff) zone for the diamond structure is the octahedron (111) with polar distance 0.306, faceted by the rhombic dodecahedron (220) with polar distance 0.354 (Fig. 4).

CONCLUSION

In the preceding pages the construction of crystallographically symmetrical polyhedra complementary to the Bravais lattices, called Brillouin zones, and the construction of the complements of the equipoint assemblages of the space groups, here referred to as the Donnay-

Harker zones, has been demonstrated. For the general case of the three-dimensionally periodic repetition of a motif of components with effective magnitudes f_i , a construction of complementary polyhedra here referred to as Wulff zones was derived from Wulff's theorem and the Brillouin zone theory. In the simple case of the Bravais lattices the Wulff zones were shown to degenerate to the Brillouin zones. The Wulff zones for the equipoint assemblages modify the Donnay-Harker zones as defined *sensu stricto*. Finally, the Wulff zones were shown to conform to the requirements of Wulff's theorem: by weighting each surface with a specific surface magnitude σ_i , the total surface magnitude becomes a minimum when $\sigma_i/h_i = \sigma_k/h_k = c$ (von Laue 1943). The agreement (or lack of it) between the morphologies of real crystals and the zone complements of their structures remains to be demonstrated.

The empirical verification of the Bravais and Donnay-Harker laws and the modification of the serial order of reticular densities by structure-factor calculations has been discussed in detail by Mallard (1879), Friedel (1904, 1911), Baumhauer (1904), Fedorov (1920), Ungemach (1934), Niggli (1941), Braun (1932), Wells (1946), Buerger (1947), Donnay & Donnay (1961a, b, c; 1962) and Phillips (1946) among others. The extent to which the morphology of natural crystals conforms to the zones complementary to their structures should be the object of future investigation. It is sufficient to point out here that the rationale for such conformity lies in equating the σ_i of Wulff's theorem with the product $d_i F_i$ above (McLachlan 1952 and in Schner 1977; Schner 1968) deriving in turn from the assumption of Bravais in 1851 that the interplanar bonds should be inverse functions of the interplanar distances. Barite, BaSO_4 , may be used as an example of the determination of Wulff zones for more complex structures. The writer has made use of computer graphics. For comparison with the Brillouin zone (Fig. 5) a modified Wulff zone has been constructed (Fig. 6) using the first ten most frequently observed forms 002, 200, 011, 210, 020, 211, 101, 410, 102 and 111 (Friedel 1904; Braun 1932; Schner 1970, Table 1). The planes as shown are plotted with Wulff vectors h_i determined from structure factors calculated from the observed frequencies of occurrence (P_i) of the faces, i.e., observed structure factors (Schner 1970): $F_i = \ln P_i/m_i$, where m_i is the multiplicity factor. Of the first ten faces, all those which would have been eliminated because of the greater structure factors of intersecting faces have been retained as facets with h_i 3%

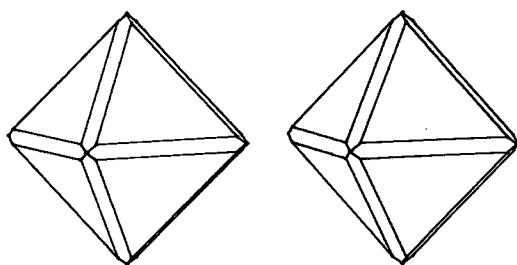


FIG. 4. The Wulff zone for the diamond structure. The forms (111) and (220) are constructed at distances from the Wulff point inversely proportional to the product of their interplanar spacings and structure factors. The structure factors are calculated for the 8 carbon atoms of the unit cell.

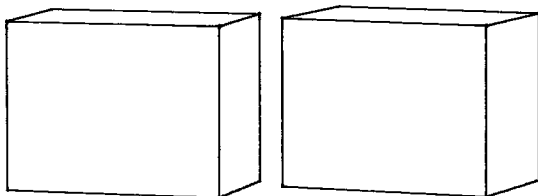


FIG. 5. The first Brillouin zone, for barite, BaSO_4 , $Pnma$; $a:b:c::1.627:1:1.311$; $Z=4$. If constructed with structure factors from persistences, the pinacoid (001) is slightly larger in proportion; otherwise the zone is unchanged.

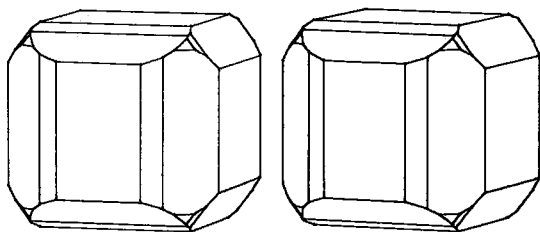


FIG. 6. The Wulff zone for barite with empirical structure factors for the ten planes of greatest persistence. Planes that would have been eliminated are shown as minor facets; these are (211), (002), (102) and (111).

less than the values at which the faces would have disappeared. The relation $h_i = 1/d_i F_i$ defines the transform operator T from the structure to the zone. Figure 6 may be regarded as a graphic expression of Braun's data for barite morphology, or alternatively as the mean (not modal) average barite crystal. It is clear that the Wulff zone will vary according to the proportionate values of the structure factors F_i and that these in turn will depend upon the coef-

ficients used for the components of the structure and upon the means by which they enter into the determination of the structure factors F_c .

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