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A Systematic Method for Calculating Volumes of Polyhedra Corresponding to Brillouin Zones*

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In problems involving the interpretation of crystal structures of metals and intermetallic compounds, the volumes of polyhedra (in wave-number space) corresponding to Brillouin zones, defined by crystallographic forms or groups of forms with large X-ray structure factors, are frequently calculated in order to ascertain how well the polyhedra accommodate the quantum states of assumed numbers of valence electrons per unit cell. This procedure depends upon a long-established apparent analogy between Brillouin zone stabilization and diffraction of the slow-moving valence electrons by the crystallographic planes corresponding to these forms, and upon the reasonable assumption that the structure factors for the diffraction of these slow electrons bear essentially the same qualitative relationships to one another as the structure factors for fast electrons or X-rays do. While the geometrical problems involved in calculating the volume of and number of quantum states contained in such a polyhedron are relatively simple when but one form is involved, the polyhedra corresponding to more than one form frequently truncate one another and the computation of the volume of the minimum truncated polyhedron for several forms is rather complicated. Methods for systematizing and simplifying these geometrical problems have been worked out, and are described here for the convenience of workers faced with the determination of the shapes and volumes of such polyhedra.

Introduction

In the study of the valences of metal atoms in crystals of certain metals and intermetallic compounds in this Laboratory, the necessity arose for calculating the volumes enclosed in wave-number space by polyhedra, simple and truncated (Pauling & Ewing, 1948). In this particular application the polyhedra are specified by the Miller indices of the forms which define them. Sometimes an effective polyhedron is bounded by planes corresponding to only one crystallographic form, but more often the polyhedron is the result of mutual truncation of polyhedra generated by two or more effective forms. Given the Miller indices of a number of forms with large structure factors, the geometric problem arises of determining among which forms, if any, truncation takes place; of determining the shapes of the resulting truncated or non-truncated polyhedra; and of computing the volumes of the polyhedra. A considerable saving in computational time over methods heretofore used has been obtained in the present work by the application of analytical geometry and by the systematization of the computations. Criteria have been formulated for classifying truncated polyhedra, and formulae have been derived for the calculation of the volumes of polyhedra of several types. The results of this approach to the problem are summarized here in the belief that further opportunities are likely to arise for their use in the theoretical treatment of metals and intermetallic compounds, and perhaps also in problems of other kinds.

The discussion here will be restricted to polyhedra that are everywhere convex (i.e. have no re-entrant angles); the smallest polyhedron that is bounded by the forms under consideration will be the only one treated. Moreover, since Friedel's law may be expected to hold in at least a reasonable approximation for slow electrons, only centrosymmetric polyhedra will be treated.

Theory

The reciprocal-lattice point in wave-number space corresponding to a set of crystallographic planes with Miller indices (hkl) is at the terminus of the vector

$$\mathbf{h}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \,, \qquad (1)$$

where $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are the reciprocal-lattice vectors

$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\times\mathbf{b}\cdot\mathbf{c}}\,, \text{ etc.}$$

It is well known from the work of Brillouin (1930 *a*, *b*, *c*, 1931, 1932, 1933*a*, *b*, 1936, 1946) and others

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(Seitz, 1940) that the energy eigenvalue $\varepsilon_{\mathbf{k}}$, corresponding to a one-electron eigenfunction $\psi_{\mathbf{k}}(\mathbf{r})$ representing a plane wave of wave number $\mathbf{k}$ travelling in a lattice-periodic potential function, deviates in general more and more from the 'free-electron' eigenvalue $\varepsilon^0_{\mathbf{k}}$ (corresponding to a constant potential) the closer the terminus of the vector $\mathbf{k}$ comes to a plane defined by the equation

$$(\mathbf{k}-\tfrac{1}{2}\mathbf{h}_{hkl}) \cdot \mathbf{h}_{hkl} = 0 \,, \tag{2}$$

and that when the terminus of $\mathbf{k}$ lies on such a plane $\varepsilon_{\mathbf{k}}$ is in general double valued, so that $\varepsilon_{\mathbf{k}}$ is a discontinuous function of $\mathbf{k}$ along any path that crosses such a plane.

The plane in wave-number space that corresponds to equation (2) is the one that perpendicularly bisects the reciprocal-lattice vector $\mathbf{h}_{hkl}$. It will be seen that this plane is also the locus of the centers of all possible Ewald spheres of reflection which correspond to crystallographic reflection from the (hkl) planes in the crystal (of the order implied by the given hkl). The physical situation may therefore be described approximately as diffraction of the travelling electron wave by the crystal lattice.

The plane described by equation (2) in wave-number space is parallel to the plane (hkl) in real space. It therefore appears convenient to describe it in terms of axes that are parallel to the real crystallographic axes and proportional to them in length, with a factor of proportionality that takes into account the different dimensionality. The planes in wave-number (reciprocal) space that correspond to the form $\{hkl\}$ describe a polyhedron which, aside from dimensionality factors, is geometrically similar to the polyhedron described in real space by all the planes in the form.

The apparent analogy with X-ray diffraction has led to the prediction (Jones, 1934*a*, *b*) that in general the energy discontinuity at the plane described by equation (2) will be large when the X-ray structure factor $|F_{hkl}|$ is large, and small when $|F_{hkl}|$ is small. In other words, the assumption is made that the energy discontinuity for a given plane is a function of the structure factor for the slow-moving electrons in the metal, and that the structure factors for slow electrons bear essentially the same qualitative relationships to each other as the structure factors for fast electrons or X-rays do. Hence the Brillouin polyhedra in which we are interested are those that correspond to forms with large X-ray structure factors.

If we take the Born–v. Kármán periodic boundary conditions, it is seen that (aside from spin) the density of quantum states in wave-number space ($\mathbf{k}$-space) is one per volume $1/V_c$, where V_c is the volume, in real space, of the super-unit-cell defined by these boundary conditions. (For practical purposes, V_c can be taken as the volume of the crystal.) One reciprocal cell (reciprocal, that is, with respect to the crystallographic unit cell) in $\mathbf{k}$-space therefore has a capacity of one quantum state per crystallographic unit cell, or, if we include spin, two states per unit cell. Hence we shall find it convenient to take the reciprocal cell as the unit of volume in $\mathbf{k}$-space for all of our work. In terms of this unit, the number N of quantum states per crystallographic unit cell, *including* spin, that are contained inside a polyhedron is numerically equal to twice the volume V of that polyhedron, and the number of states in the entire crystal that are contained in the polyhedron is equal to N multiplied by the number of crystallographic unit cells in the crystal.

The geometrical method of calculating volumes to be here described consists in dividing the surface of the polyhedron into plane triangles, evaluating the coordinates x_i, y_i, and z_i of the vertices i of the triangles with respect to a convenient coordinate system, and then calculating the volume of each tetrahedron defined by the origin of coordinates (which is taken at the center of the polyhedron and hence at the origin of $\mathbf{k}$-space) and the corresponding ith plane triangle. The volume of the polyhedron is the sum of the volumes of the several tetrahedra.

Let us take a right-handed (not necessarily orthogonal) system of axes x, y, z in $\mathbf{k}$-space with basic vectors $\boldsymbol{\xi}, \boldsymbol{\eta}, \boldsymbol{\zeta}$. We shall find it convenient to define these vectors in such a way that they are parallel respectively to the crystallographic axes $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, and proportional to them in length. Hence

$$\mathbf{k} = x\boldsymbol{\xi}+y\boldsymbol{\eta}+z\boldsymbol{\zeta} \tag{3}$$

and

$$\mathbf{k} \cdot \mathbf{h}_{hkl} = K(hx+ky+lz) \,, \tag{4}$$

where

$$K = \xi/a = \eta/b = \zeta/c \,. \tag{5}$$

Equation (2) now becomes

$$hx+ky+lz = q_{hkl} \,, \tag{6}$$

where q_{hkl} is defined as

$$q_{hkl} \equiv \frac{1}{2K}\,|\mathbf{h}_{hkl}|^2 = \frac{1}{Kd^2_{hkl}} \,. \tag{7}$$

The quantity d_{hkl} is the Bragg spacing between planes (hkl) in the crystal. *Equation* (6) *is the equation for a plane that forms one of the faces of the polyhedron.*

Consider a given plane triangle on this face, the vertices of which are the termini of vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ which are numbered in such a way as to form a right-handed set. The volume of the tetrahedron corresponding to this face is one sixth of the volume of the parallelepiped defined by the three vectors, and hence is

$$\tfrac{1}{6}\mathbf{k}_1\times\mathbf{k}_2\cdot\mathbf{k}_3 = \tfrac{1}{6}\begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \cdot (\boldsymbol{\xi}\times\boldsymbol{\eta}\cdot\boldsymbol{\zeta}) \,.$$

Because of symmetry it will in general be necessary only to consider one nth of the polyhedron in computing the volume, where n is the multiplicity of the point group of the crystal. Hence we may write for the volume of the polyhedron

$$V = \frac{N}{2} = \frac{nK^3V_0^2}{6} \sum_j \Delta_j , \tag{8}$$

where

$$\Delta_j \equiv \Delta(1_j, 2_j, 3_j) \equiv \begin{vmatrix} x_{1j} & y_{1j} & z_{1j} \\ x_{2j} & y_{2j} & z_{2j} \\ x_{3j} & y_{3j} & z_{3j} \end{vmatrix} . \tag{9}$$

Here V is expressed in terms of the volume of the reciprocal cell as a unit, and is a pure number equal to one half the number N of quantum states (including spin) contained, per unit cell, in the polyhedron. V_0 is the volume of the crystallographic unit cell ($\mathbf{a}\times\mathbf{b}\cdot\mathbf{c}$). The sum in equation (8) is taken over all triangles (j) into which the nth part of the polyhedron is decomposed. The vertices of each triangle are taken in such order as to form a right-handed set, so that all terms in the sum will be positive.

The coordinates of each vertex of the polyhedron can be obtained by solving simultaneously the three equations (6) corresponding to the three planes intersecting at that vertex.

In each of the point groups O_h, D_{4h}, D_{6h}, and D_{2h} the sector of interest, comprising one nth of the polyhedron, is bounded by three mirror planes and can be defined by three axes x, u, and v formed by the intersection of these planes two at a time. The x axis is identical to the x axis of the polyhedron; the u axis is identical with the y axis in D_{2h}, the line $x = 2y$ ($z = 0$) in D_{6h}, and the line $x = y$ ($z = 0$) in O_h and D_{4h}; and the v axis is identical with the line $x = y = z$ in O_h, and in the other point groups is the z axis. We take the sector belonging in the positive octant. In a polyhedron bounded by one holohedral form only, the sector of interest contains a single triangular face (hkl) which does not extend beyond this sector except in special cases where it may be coplanar with faces belonging to one or more adjacent sectors. This face cuts the x axis at a point which we shall refer to by the number 1, the u axis at 2, and the v axis at 3. If there are m mutually truncating forms bounding a truncated polyhedron, the sector will contain m faces, not necessarily triangular. We shall here present criteria for the determination of the ways in which as many as three forms can intersect within this sector.

Where more than one form must be considered, they will be distinguished from one another by the use of primes. Here we shall consider the forms $\{hkl\}$, $\{h'k'l'\}$, $\{h''k''l''\}$. The primes will be so assigned that

$$x_1 \le x_1' \le x_1'' , \tag{10}$$

where x_1 is the x coordinate of point 1, x_1' that of point 1′, and x_1'' that of point 1″. Where an equality exists, e.g. $x_1 = x_1'$, the primes should be assigned on the basis of a corresponding inequality in the y_2's; in the case given we require $y_2 \le y_2'$, and so on. The coordinates of the points 1, 1′, 1″, 2, ... may be found by application of formulae which will be given in the sections dealing with particular point groups.

An intersection of an unprimed plane with a primed one and with one of the planes which bounds the sector of interest gives a point which will be denoted 4, 5, or 6 depending on whether the point lies on the $x\,u$ plane, the $x\,v$ plane, or the $u\,v$ plane. Where the intersection involves a primed and a doubly primed plane, it will be denoted 4′, 5′, or 6′, and if it involves an unprimed and a doubly primed plane it will be denoted by 4*, 5*, or 6*. A mutual intersection of an unprimed, a singly primed, and a doubly primed plane will be denoted 7. Coordinates of these points may be determined simply by the solution of the corresponding set of simultaneous linear equations (one equation for each plane, of the form given by equation (6)).

With three forms there are altogether seventeen general shapes possible (in a given one of the four point groups under discussion) for the smallest polyhedron, of which one (No. 1) is bounded by one non-truncated form, three (Nos. 2, 3, and 4) by two mutually truncating forms, and thirteen (Nos. 5–17 inclusive) by three forms each of which truncates at least one of the other two. For facility in identification and calculation a further breakdown into thirty-six cases has been made on the basis of the thirty-six possible combinations of inequalities among the coordinates of the points 2, 2′, 2″, 3, 3′, and 3″. These cases are presented schematically in Fig. 1. In a few cases it is convenient to make a further breakdown on the basis of the coordinates of points 5, 5′, 5″, 6, 6′, and 6″. Special cases (arising from equalities rather than inequalities in the selective criteria) are not given separately in Fig. 1, as they present no problems not covered by the general cases. Dashed lines denote intersection lines lying or extending outside the polyhedron. The particular case in Fig. 1 that corresponds to a given selection of three planes may be found by reference to Table 1.

Cases involving more than three mutually truncating forms are too complicated to be treated here. When and if problems arise which require the consideration of such cases, it should be possible to solve these problems by taking the forms in various combinations, two or three at a time, and applying the methods described here. It may be helpful to point out that whether a point x', y', z' lies inside, on, or outside a plane (hkl) depends on whether $hx'+ky'+lz'$ is less than, equal to, or greater than q_{hkl}. A simple means exists for insuring that a form $\{h'''k'''l'''\}$ does not truncate a given polyhedron; this consists in ascertaining that

$$h'''x_i+k'''y_i+l'''z_i \le q''' \tag{11}$$

for every vertex i in the sector of interest.

For the hemihedral point groups T_h, C_{4h}, and C_{6h} the sector of interest, when defined conveniently with respect to the crystal axes, is not completely bounded by mirror planes and consequently contains in general

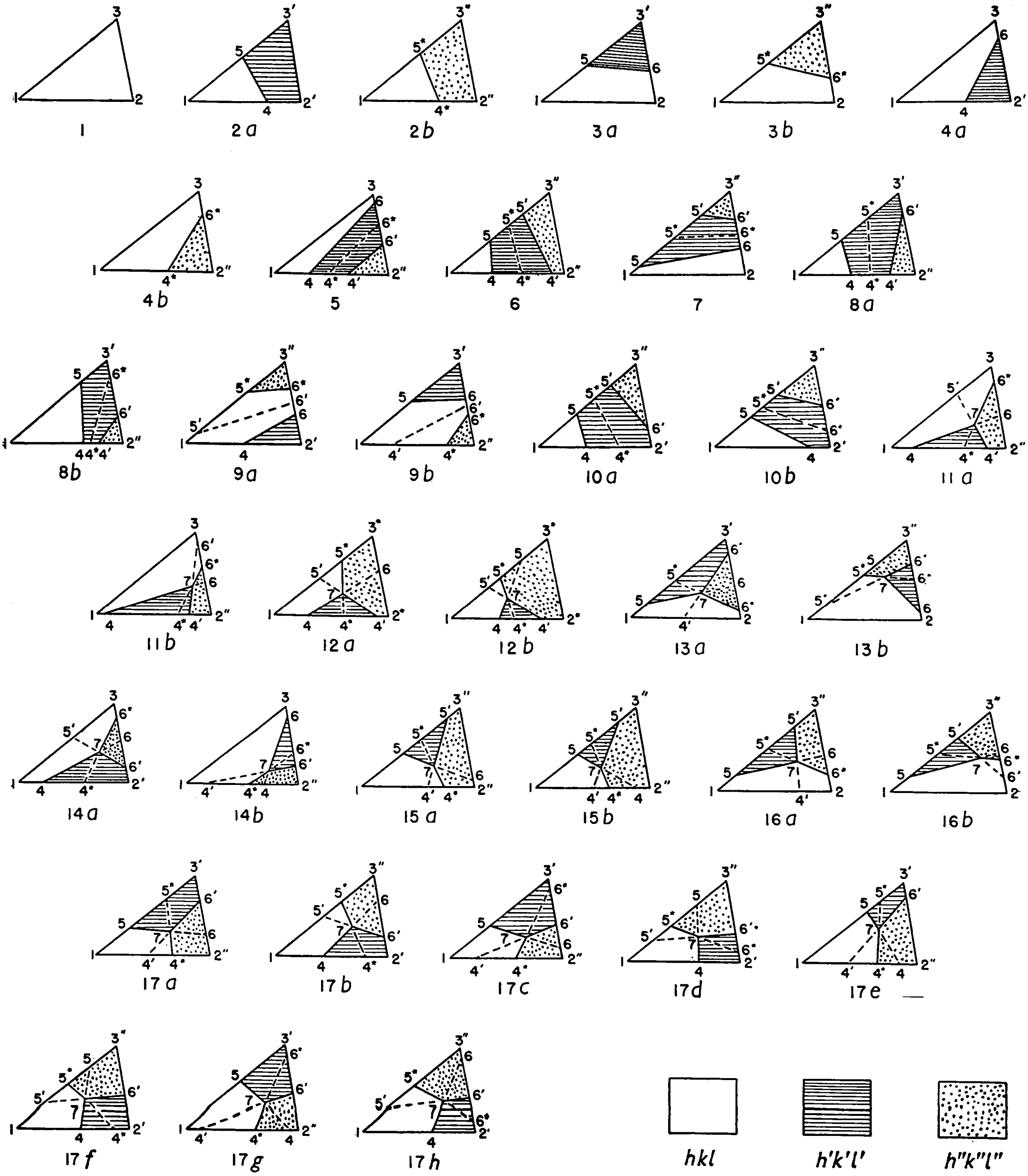

Fig. 1. Schematic presentation of thirty-six cases involving as many as three holohedral forms (see Table 1). (*Note added in proof.*—In 12 *a* and 12 *b*, 2* and 3* should read 2″ and 3″ respectively.)

two planes of each form, both of which extend outside the sector of interest. This fact complicates the problem of determining and classifying the types of truncated polyhedra and it will be worthwhile to consider here only cases involving one or two forms.

Let the sector of interest be defined by three axes x, x^*, and v. In T_h and C_{4h}, the x^* axis is identical to the y axis; in C_{6h} it is identical to the line $x = y$, $z = 0$. In T_h the v axis is identical to the line $x = y = z$; in C_{4h} and C_{6h} it is the z axis. Let the two planes to be

Table 1. *Selection criteria for truncated holohedral polyhedra obtainable with three forms (point groups O_h, D_{4h}, D_{6h}, D_{2h})*

		A		B	C	D	E	F	
		$z_6 \le z_6'$	$z_6' \le z_6$					$z_5 \le z_5'$	$z_5' \le z_5$
I	$z_6 \le z_6'$ $z_6' \le z_6$	1		1	3*a*	3*b*	3*a*	7 16*b*	13*b* 3*b*
II	$z_6^* \le z_6'$ $z_6' \le z^*$	1		1	3*a*	3*b*	13*a* 3*a*	16*a*	3*b*
III	$z_6 \le z_6^*$ $z_6^* \le z_6$	4*a*		4*a*	2*a*	9*a* 17*h*	2*a*	10*b*	17*d*
IV	$z_6^* \le z_6$ $z_6 \le z_6^*$	4*b*		4*b*	9*b* 17*c*	2*b*	17*a*	15*a*	2*b*
V	$z_6' \le z_6^*$ $z_6^* \le z_6'$	4*a*		14*a* 4*a*	2*a*	17*b*	2*a*	10*a*	17*f*
VI	$y_4 \le y_4'$ $y_4' \le y_4$	11*b* 4*b*	5 14*b*	11*a* 4*b*	8*b* 17*g*	12*a* 2*b*	8*a* 17*e*	6 15*b*	12*b* 2*b*

I	$y_2 \le y_2' \le y_2''$
II	$y_2 \le y_2'' \le y_2'$
III	$y_2' \le y_2 \le y_2''$
IV	$y_2'' \le y_2 \le y_2'$
V	$y_2' \le y_2'' \le y_2$
VI	$y_2'' \le y_2' \le y_2$

A	$z_3 \le z_3' \le z_3''$
B	$z_3 \le z_3'' \le z_3'$
C	$z_3' \le z_3 \le z_3''$
D	$z_3'' \le z_3 \le z_3'$
E	$z_3' \le z_3'' \le z_3$
F	$z_3'' \le z_3' \le z_3$

All cases: $x_1 \le x_1' \le x_1''$.

considered for a given form $\{hkl\}$ be denoted (hkl) and $(h^*k^*l^*)$; the relations among these indices will be given in the later sections dealing with individual point groups. The (hkl) face of the polyhedron is that which cuts the x axis, while the $(h^*k^*l^*)$ face cuts the x^* axis with an equal intercept. If two forms are to be considered, let the unprimed one be the one that cuts the v axis with the smaller intercept; i.e. we require that

$$z_3 \le z_3' . \tag{12}$$

The points of intersection of the various planes with each other and with the planes bounding the sector of interest are

1 : (hkl), x axis
1*: $(h^*k^*l^*)$, x^* axis
1′ : $(h'k'l')$, x axis
1*′: $(h^{*\prime}k^{*\prime}l^{*\prime})$, x^* axis
2 : (hkl), $(h^*k^*l^*)$, xx^* plane
2′ : $(h'k'l')$, $(h^{*\prime}k^{*\prime}l^{*\prime})$, xx^* plane
3 : (hkl), $(h^*k^*l^*)$, v axis
4 : (hkl), $(h'k'l')$, xx^* plane
4*: $(h^*k^*l^*)$, $(h^{*\prime}k^{*\prime}l^{*\prime})$, xx^* plane
5 : (hkl), $(h'k'l')$, xv plane
5*: $(h^*k^*l^*)$, $(h^{*\prime}k^{*\prime}l^{*\prime})$, x^*v plane
7 : (hkl), $(h^*k^*l^*)$, $(h'k'l')$
7*: (hkl), $(h^*k^*l^*)$, $(h^{*\prime}k^{*\prime}l^{*\prime})$
8 : (hkl), $(h'k'l')$, $(h^{*\prime}k^{*\prime}l^{*\prime})$
8*: $(h^*k^*l^*)$, $(h'k'l')$, $(h^{*\prime}k^{*\prime}l^{*\prime})$
9 : (hkl), $(h^{*\prime}k^{*\prime}l^{*\prime})$, xx^* plane
9*: $(h^*k^*l^*)$, $(h'k'l')$, xx^* plane

The coordinates of these points can be easily found by solving the corresponding sets of simultaneous linear equations (6) defining the intersecting planes.

With two forms there are six general cases, of which one (No. 1) involves one form only, and five (Nos. 2–6 inclusive) involve the mutual truncation of the two forms. Two of the latter, No. 5 and No. 6, apply only to the point group T_h. A further breakdown of

Table 2. *Selection criteria for truncated hemihedral polyhedra obtainable with two forms (point groups T_h, C_{4h}, C_{6h})*

				Case
$y_2/x_2 \le y_2'/x_2'$:				
	$x_1 \le x_1'$:			
		$y_9^* \le y_4$		1
		$y_4 \le y_9^*$:		
			$y_9^* \le y_2'$	2*a*
			$y_2' \le y_9^*$	5*a*
	$x_1' \le x_1$:			
		$x_9^* \le x_4^*$		4*a*
		$x_4^* \le x_9^*$:		
			$x_9^* \le x_2$	3*a*
			$x_2 \le x_9^*$	6
$y_2'/x_2' \le y_2/x_2$:				
	$x_1 \le x_1'$:			
		$x_9 \le x_4^*$		1
		$x_4^* \le x_9$:		
			$x_9 \le x_2'$	2*b*
			$x_2' \le x_9$	5*b*
	$x_1' \le x_1$:			
		$y_9 \le y_4$		4*b*
		$y_4 \le y_9$:		
			$y_9 \le y_2$	3*b*
			$y_2 \le y_9$	6

All cases: $z_3 \le z_3'$

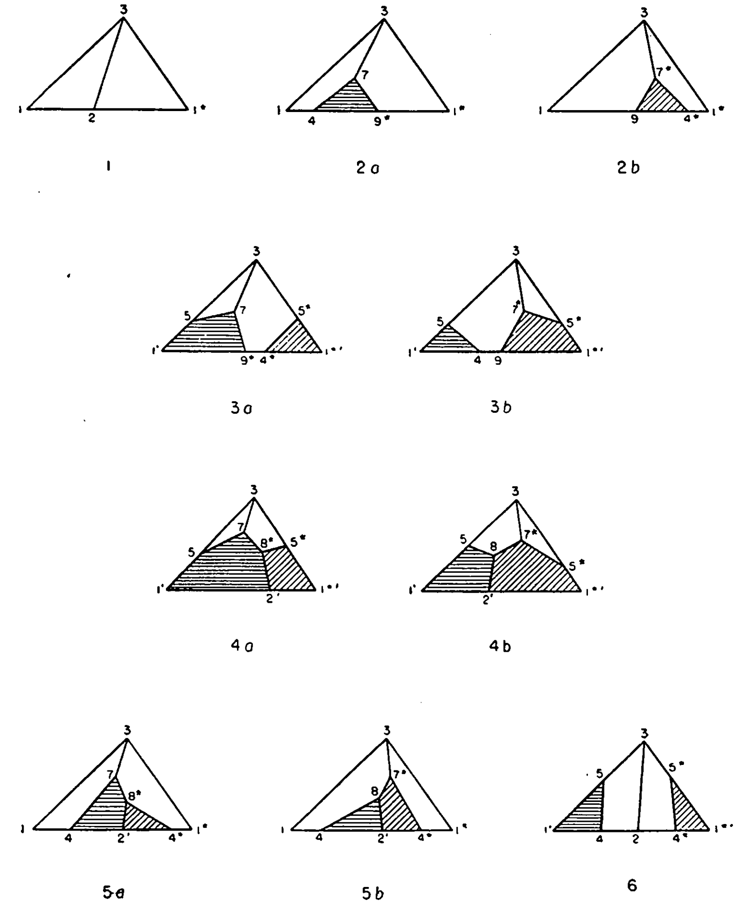

Fig. 2. Schematic presentation of ten cases involving as many as two hemihedral forms (see Table 2).

the six cases into a total of ten has been found convenient. These are shown schematically in Fig. 2, and criteria for their selection are given in Table 2.

There is some ground for supposing that cases will rarely be encountered in which the consideration of the hemihedral cases is necessary; first, because most metallic structures are holohedral, and second, because, if one form in a hemihedral structure constitutes an effective barrier to the existence of electrons in states outside it, it is unlikely that the Fermi surface will deviate so far from spherical shape as to extend beyond the planes defined by the other form which with holohedry would be equivalent to the first. Whenever in a hemihedral structure two forms truncate which in the corresponding holohedry would be equivalent to one another and together constitute a single holohedral form, the corresponding holohedral case 1 can be used so far as these two forms are concerned.

Inscribed sphere.—In the event that the Fermi surface is suspected to be capable of approximate representation by a sphere inscribed in and tangent to a polyhedron, the volume of the sphere, in terms of the unit we have chosen (the volume of the reciprocal cell), may be calculated by use of the equation

$$V = \frac{N}{2} = \frac{1}{\mathbf{a}^*\times\mathbf{b}^*\cdot\mathbf{c}^*}\frac{\pi}{6}\,|\mathbf{h}_{hkl}|^3 = \mathbf{a}\times\mathbf{b}\cdot\mathbf{c}\frac{\pi}{6}\,(2Kq)^{3/2}\,, \qquad (13)$$

since the radius of such a sphere, tangent to the planes in the form $\{hkl\}$, is $\frac{1}{2}|\mathbf{h}_{hkl}|$. When a sphere is inscribed in a polyhedron defined by more than one form, the form with the smallest value of q is the one which is tangent to the sphere, and that value of q is the one that should be used in equation (13).

Cubic system

A convenient choice of axes is

$$K = 1/2a^2,\ \xi = \eta = \zeta = 1/2a\,. \qquad (14)$$

We obtain from equation (7):

$$q = h^2+k^2+l^2\,. \qquad (15)$$

Symmetry O_h (multiplicity $n = 48$; for crystals of point group symmetry T_d, O, O_h).—The sector of interest is that subtended by the shaded triangle in Fig. 3. The volume of a polyhedron in this point group is

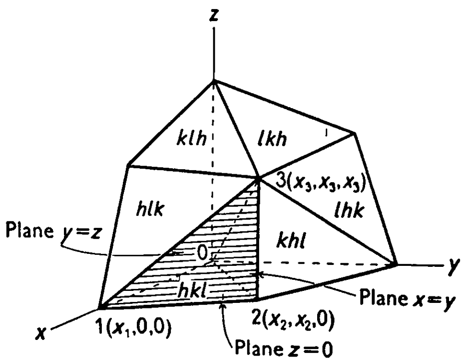

Fig. 3. Principal octant of general polyhedron of one form, symmetry O_h.

$$V = \frac{N}{2} = \sum_i \Delta_i\,, \tag{16}$$

where the sum is taken over all triangular faces in the sector of interest. Since the polyhedron is assumed to be convex, the particular plane of the form $\{hkl\}$ which receives the indices (hkl) and occupies the shaded position in Fig. 3 must be so designated that

$$h \geq k \geq l \geq 0\,. \tag{17}$$

The coordinates of the points shown in Fig. 3 are

$$\left.\begin{aligned} x_1 &= q/h,\ y_1 = z_1 = 0\,, \\ x_2 &= y_2 = q/(h+k),\ z_2 = 0\,, \\ x_3 &= y_3 = z_3 = q/(h+k+l)\,. \end{aligned}\right\} \tag{18}$$

The volume of a polyhedron bounded by one form $\{hkl\}$ is

$$V = \tfrac{1}{2}N = x_1x_2x_3 = q^3/\{h(h+k)(h+k+l)\}\,. \tag{19}$$

Cases involving two or three forms may be dealt with by reference to Fig. 1 and Table 1. In Table 1, y_2, y_2', y_2'' may be replaced by x_2, x_2', x_2'', and z_3, z_3', z_3'' by x_3, x_3', x_3'' by virtue of equations (18). Inequalities containing z_6, z_5, and y_4 may be replaced by ones in x_6, x_5, and x_4 written the other way around; e.g. for $z_6 \leq z_6'$ we may take $x_6' \leq x_6$.

As an example, let us consider the polyhedron corresponding to the strong powder line for which $q = 36$ in the γ alloys (e.g. Cu_5Zn_8). Here we have two forms, $\{600\}$ and $\{442\}$, both of which have large structure factors and are therefore assumed to give rise to strong perturbation discontinuities in the energy. These are already written in conformity with equation (17), and since $36/6 < 36/4$ we take (600) as the unprimed plane ($q = 36$, $x_1 = x_2 = x_3 = 6$) and (442) as the primed one ($q' = 36$, $x_1' = 9$, $x_2' = 9/2$, $x_3' = 18/5$). Reference to Table 1 leads us immediately to case $2a$, and the diagram in Fig. 1 reveals that we require the coordinates of points 4 and 5. The coordinates of points 4 and 5 are easily found to be (6, 3, 0) and (6, 2, 2) by solution of the corresponding sets of simultaneous linear equations, and we have

$$V = N/2 = \Delta(1,4,5)+\Delta(2',5,4)+\Delta(2',3',5)$$

$$= \begin{vmatrix} 6 & 0 & 0 \\ 6 & 3 & 0 \\ 6 & 2 & 2 \end{vmatrix} + \begin{vmatrix} 9/2 & 9/2 & 0 \\ 6 & 2 & 2 \\ 6 & 3 & 0 \end{vmatrix} + \begin{vmatrix} 9/2 & 9/2 & 0 \\ 18/5 & 18/5 & 18/5 \\ 6 & 2 & 2 \end{vmatrix}$$

$$= 36+27+324/5 = 127{\cdot}8 \text{ reciprocal cells.}$$

$N = 255{\cdot}6$ electrons per cubic unit cell (cf. Pauling & Ewing, 1948).

Symmetry T_h (multiplicity $n = 24$; for crystals of point group symmetry T and T_h).—The sector of interest is that subtended by the shaded area in Fig. 4.

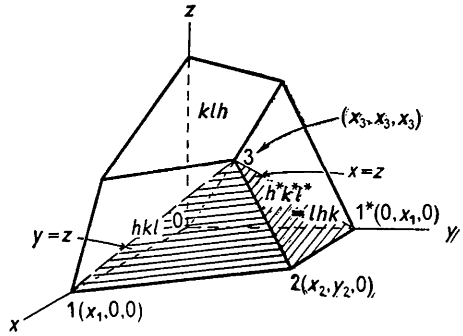

Fig. 4. Principal octant of general polyhedron of one form, symmetry T_h.

The general expression for the volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{1}{2}\sum_i \Delta_i\,. \tag{20}$$

For the particular plane of the form which is designated (hkl), we require that

$$h \geq k \geq 0,\quad h \geq l \geq 0\,. \tag{21}$$

We also find that

$$h^* = l,\quad k^* = h,\quad l^* = k\,. \tag{22}$$

The coordinates of the points shown in Fig. 4 are:

$$\left.\begin{aligned} x_1 &= q/h,\ y_1 = z_1 = 0\,, \\ x_2 &= q\,\frac{h-k}{h^2-kl}\,,\ y_2 = q\,\frac{h-l}{h^2-kl}\,,\ z_2 = 0\,, \\ x_3 &= y_3 = z_3 = \frac{q}{h+k+l}\,. \end{aligned}\right\} \tag{23}$$

The volume of the polyhedron bounded by one form is then

$$V = \tfrac{1}{2}N = \tfrac{1}{2}\{x_1y_2x_3+x_1x_3x_2\} = \frac{q^3(2h-k-l)}{2h(h+k+l)(h^2-kl)}\,. \tag{24}$$

For the special case $k = l$ this result reduces to the result obtained for the volume enclosed by a single form in symmetry O_h (equation (19)), and equations (23) reduce to equations (18).

Polyhedra bounded by two forms may be treated as described previously with the use of Fig. 2 and Table 2.

Inscribed sphere.—In the cubic system the expression for the volume of an inscribed sphere becomes particularly simple:

$$V = \frac{N}{2} = \frac{\pi}{6} q_{hkl}^{3/2} . \tag{25}$$

Tetragonal system

We find it convenient here to take

$$K = 1/2a^2,\ \xi = \eta = 1/2a,\ \zeta = c/2a^2 . \tag{26}$$

Hence

$$q = h^2+k^2+(a^2/c^2)l^2 . \tag{27}$$

Symmetry D_{4h} (multiplicity $n = 16$; for crystals of point group symmetry C_{4v}, D_{2d}, D_4, and D_{4h}).—The sector of interest is that subtended by the shaded triangle in Fig. 5.

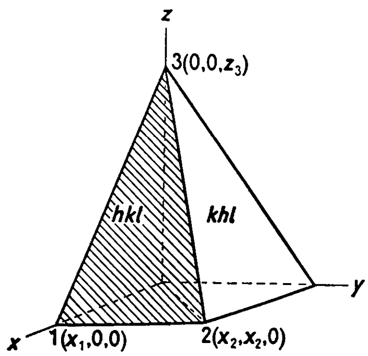

Fig. 5. Principal octant of general polyhedron of one form, symmetry D_{4h}.

The general expression for the volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{1}{3}\frac{c^2}{a^2}\sum_i \Delta_i . \tag{28}$$

For the particular plane of the form which is designated (hkl) we require that

$$h \geq k \geq 0,\ l \geq 0 . \tag{29}$$

The coordinates of the points 1, 2, and 3 shown in Fig. 5 are

$$\left.\begin{aligned} &x_1 = q/h,\ y_1 = z_1 = 0 ,\\ &x_2 = y_2 = q/(h+k),\ z_2 = 0 ,\\ &x_3 = y_3 = 0,\ z_3 = q/l . \end{aligned}\right\} \tag{30}$$

For a single form the volume of the polyhedron is

$$V = \frac{N}{2} = \frac{c^2}{3a^2}\frac{q^3}{h(h+k)l} . \tag{31}$$

The treatment of polyhedra bounded by two or three forms can be carried out with the aid of Fig. 1 and Table 1.

Symmetry C_{4h} (multiplicity $n = 8$; for crystals of point group symmetry C_4, S_4, and C_{4h}).—The sector of interest here is the positive octant shown in Fig. 6.

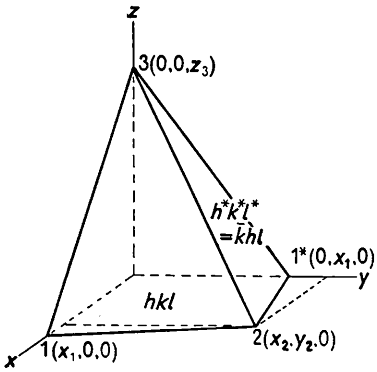

Fig. 6. Principal octant of general polyhedron of one form, symmetry C_{4h}.

The general expression for the volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{1}{6}\frac{c^2}{a^2}\sum_i \Delta_i . \tag{32}$$

For the particular plane in the form to be designated (hkl) we require that

$$h \geq 0,\ h \geq |k|,\ l \geq 0 . \tag{33}$$

We also find that

$$h^* = -k,\ k^* = h,\ l^* = l . \tag{34}$$

The coordinates of the points shown in Fig. 6 are

$$\left.\begin{aligned} &x_1 = q/h,\ y_1 = z_1 = 0 ,\\ &x_2 = \frac{q(h-k)}{h^2+k^2},\ y_2 = \frac{q(h+k)}{h^2+k^2},\ z_2 = 0 ,\\ &x_3 = y_3 = 0,\ z_3 = q/l . \end{aligned}\right\} \tag{35}$$

The volume of a polyhedron bounded by one form is

$$\begin{aligned} V = \frac{N}{2} &= \frac{1}{6}\frac{c^2}{a^2}(x_1y_2z_3+x_1z_3x_2)\\ &= \frac{c^2}{3a^2}\frac{q^3}{l(h^2+k^2)} . \end{aligned} \tag{36}$$

For cases involving two forms Fig. 2 and Table 2 may be used.

Inscribed sphere.—In the tetragonal system the volume of the inscribed sphere tangent to the planes of a form $\{hkl\}$ is

$$V = \frac{N}{2} = \frac{\pi}{6}\frac{c}{a} q_{hkl}^{3/2} . \tag{37}$$

Hexagonal system

In this system we find it convenient to take hexagonal axes throughout, with

$$K = 2/3a^2,\ \xi = \eta = 2/3a,\ \zeta = 2c/3a^2\,. \quad (38)$$

Hence

$$q = h^2+hk+k^2+(3a^2/4c^2)l^2\,. \quad (39)$$

For the most part, the designation $(hkil)$, where $i = -h-k$, will be abbreviated to (hkl).

Symmetry D_{6h} (multiplicity $n = 24$; for crystals of point group symmetry D_{3h}, D_6, C_{6v} and D_{6h}).—The sector of interest is that subtended by the shaded area in Fig. 7.

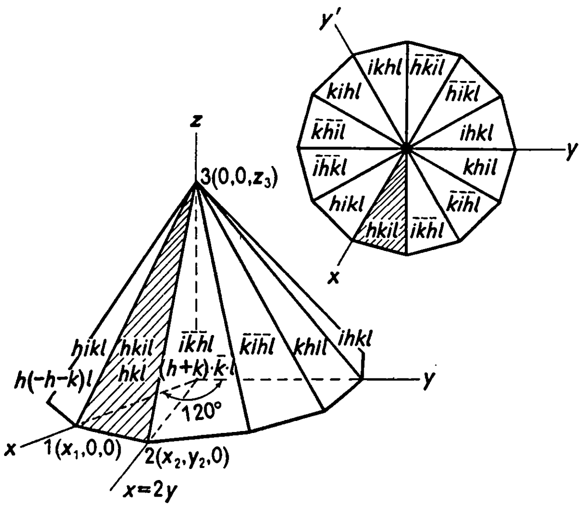

Fig. 7. Part of general polyhedron of one form, symmetry D_{6h}.

The general expression for the volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{8}{9}\frac{c^2}{a^2}\sum_i \varDelta_i\,. \quad (40)$$

For the particular plane in the form which is designated (hkl) we require that

$$\tfrac{1}{2}h \geq -k \geq 0,\ l \geq 0\,. \quad (41)$$

The coordinates of the points shown in Fig. 7 are

$$\left.\begin{aligned} &x_1 = q/h,\ y_1 = z_1 = 0\,, \\ &x_2 = \frac{2q}{2h+k},\ y_2 = \frac{q}{2h+k},\ z_2 = 0\,, \\ &x_3 = y_3 = 0,\ z_3 = q/l\,. \end{aligned}\right\} \quad (42)$$

The volume of a polyhedron bounded by one form is

$$V = \frac{N}{2} = \frac{8c^2}{9a^2}x_1y_2z_3 = \frac{8c^2}{9a^2}\,\frac{q^3}{h(2h+k)l}\,. \quad (43)$$

For cases of truncation involving two or three forms Fig. 1 and Table 1 can be used.

As an example of the application of these methods to a hexagonal crystal, let us consider hexagonal closest packing. The first zone for a hexagonal crystal is ordinarily that bounded by {100} and {001}, but in h.c.p. the latter form is extinguished, and the forms {101} and {002} may have to be considered.

$$\{100\}\colon\ q = x_1 = x_2 = 2y_2 = 1,\ z_3 = \infty\,.$$
$$\{101\}\colon\ q' = x_1' = x_2' = 2y_2' = z_3' = 1+3a^2/4c^2\,.$$
$$\{002\}\colon\ q'' = 2z_3'' = 3a^2/c^2,\ x_1'' = x_2'' = 2y_2'' = \infty\,.$$

The axial ratio for an ideal h.c.p. crystal is $c/a = 2\sqrt{2}/\sqrt{3} = 1{\cdot}633$, so that $z_3' = 41/32$ and $z_3'' = 9/16$. H.c.p. structures found in nature do not deviate from this axial ratio by more than about 15% at the most, and as long as $c/a > \sqrt{3}/2 = 0{\cdot}866$ we see that

$$y_2 < y_2' < y_2'',\ z_3'' < z_3' < z_3\,.$$

Reference to Table 1 shows that the possible cases are 3*b*, 7, 13*b*, and 16*b*, and application of the given criteria to the calculated intersection-point coordinates leads uniquely to case 7:

Point	x	y	z
1	1	0	0
2	1	$\frac{1}{2}$	0
3″	0	0	Z
5	1	0	$\frac{1}{2}Z$
5′	$1-\frac{1}{2}Z$	0	Z
6	1	$\frac{1}{2}$	$\frac{1}{2}Z$
6′	$1-\frac{1}{2}Z$	$\frac{1}{2}(1-\frac{1}{2}Z)$	Z

where $Z = z_3'' = 3a^2/2c^2$.

We have

$$\begin{aligned}\sum_i \varDelta_i &= \varDelta(5,1,2)+\varDelta(2,6,5)+\varDelta(5',5,6) \\ &\qquad +\varDelta(6,6',5')+\varDelta(3'',5',6') \\ &= Z/4+Z/4+(Z/4)\,(1+Z/2)+(Z/4)\,(1-Z^2/4) \\ &\qquad +(Z/2)\,(1-Z/2)^2 \\ &= (3Z/2)(1-Z/4+Z^2/24) \\ &= \frac{9}{4}\frac{a^2}{c^2}\left(1-\frac{3}{8}\frac{a^2}{c^2}+\frac{3}{32}\frac{a^4}{c^4}\right).\end{aligned}$$

$$V = \frac{N}{2} = 2-\frac{3}{4}\frac{a^2}{c^2}+\frac{3}{16}\frac{a^4}{c^4} \quad (44)$$

(cf. Mott & Jones, 1936).

Since there are two atoms per unit cell, the quantity given in equation (44) is equal to the number of electrons *per atom* that can be accommodated in the polyhedron. For a crystal with the ideal axial ratio $c/a = 2\sqrt{2}/\sqrt{3}$ this number is

$$V = N/2 = 1787/1024 = 1{\cdot}745\,,$$

and for a crystal with the 'minimum' axial ratio $\sqrt{3}/2$ the number is

$$V = N/2 = 4/3 = 1{\cdot}333\,.$$

One might ask if there are not other forms with low indices, e.g. $\{2\bar{1}0\}$ and $\{2\bar{1}1\}$, which might truncate the polyhedron further. For the first, $q''' = 3$, and for the second $q''' = 3+\frac{1}{2}Z$. If we apply equation (11), with each of these forms, to each of the vertex points above listed in turn, we see that the inequality is satisfied in all cases, and therefore that these planes do not truncate the polyhedron.

Symmetry C_{6h} (multiplicity $n = 12$; for crystals of point group symmetry C_{3h}, C_6 and C_{6h}).—The sector of interest ist that subtended by the shaded area in Fig. 8.

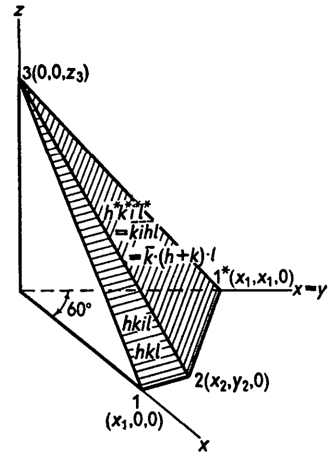

Fig. 8. Part of general polyhedron of one form, symmetry C_{6h}.

The general expression for volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{4}{9}\frac{c^2}{a^2}\sum_i \Delta_i\,. \tag{45}$$

For the particular plane in the form which we designate as (hkl) we require that

$$h \geq -k \geq 0,\ l \geq 0\,. \tag{46}$$

We also find that

$$h^* = -k,\ k^* = h+k,\ l^* = l\,. \tag{47}$$

The coordinates of the points shown in Fig. 8 are

$$\left.\begin{aligned} &x_1 = q/h,\ y_1 = z_1 = 0\,,\\ &x_2 = \frac{qh}{h^2+hk+k^2},\ y_2 = \frac{q(h+k)}{h^2+hk+k^2},\ z_2 = 0\,,\\ &x_3 = y_3 = 0,\ z_3 = q/l\,.\end{aligned}\right\} \tag{48}$$

For a polyhedron bounded by one form,

$$V = \frac{N}{2} = \frac{4}{9}\frac{c^2}{a^2}x_1x_2z_3 = \frac{4}{9}\frac{c^2}{a^2}\frac{q^3}{l(h^2+hk+k^2)}\,. \tag{49}$$

Symmetry D_{3d} (multiplicity $n = 12$, for crystals of point group symmetry D_3, C_{3v}, D_{3d}).—The sector of interest is that subtended by the shaded area in Fig. 9. It could also be taken as the sector subtended by one of the faces (i.e. 3, 5, 5*) but in such a case there is likely to be considerable complication in the event of truncation.

There are two cases (*a*) and (*b*), depending on which of the following two criteria can be made to apply to some plane in the form $\{hkl\}$:

$$(a)\ \tfrac{1}{2}h \geq -k \geq 0,\ \ l \geq 0\,; \tag{50}$$

$$(b)\ h \geq k \geq 0,\qquad l \geq 0\,. \tag{51}$$

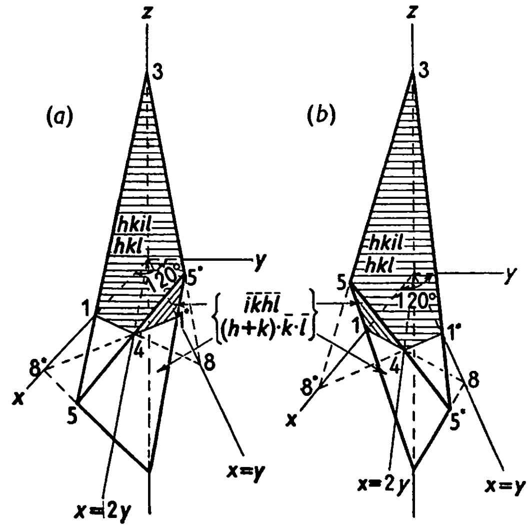

Fig. 9. Part of general polyhedron of one form, symmetry D_{3d}.

Among the planes in the form there must be one for which one or the other of the two sets of criteria apply. If only one form is to be considered, one of the cases, say (*a*), can always be obtained by an appropriate choice of axes, but where two or more forms intersect the distinction must in general be made.

The general expression for volume for this symmetry is identical with equation (45). The coordinates of the points shown in Fig. 9 are:

Case (*a*)	Case (*b*)
$x_1 = q/h,\ y_1 = z_1 = 0$	$x_1 = q/(h+k),\ y_1 = z_1 = 0$
$x_1^* = y_1^* = q/h,\ z_1^* = 0$	$x_1^* = y_1^* = q/(h+k),\ z_1^* = 0$
$x_8 = y_8 = q/(h+k),\ z_8 = 0$	$x_8 = y_8 = q/h,\ z_8 = 0$
$x_8^* = q/(h+k),\ y_8^* = z_8^* = 0$	$x_8^* = q/h,\ y_8^* = z_8^* = 0$

Either case:

$$\begin{aligned} &x_4 = 2q/(2h+k),\ y_4 = q/(2h+k),\ z_4 = 0\\ &x_3 = y_3 = 0,\ z_3 = q/l\\ &x_5 = 2q/(2h+k),\ y_5 = 0,\ z_5 = kq/\{l(2h+k)\}\\ &x_5^* = y_5^* = 2q/(2h+k),\ z_5^* = -kq/\{l(2h+k)\}\end{aligned} \tag{52}$$

For a polyhedron bounded by a single form

$$V = \frac{N}{2} = \frac{16c^2}{9a^2}\frac{q^3}{l(2h+k)^2}\,. \tag{53}$$

Cases involving intersections of two or more forms are too involved to be discussed in detail here.

Symmetry C_{3i} (multiplicity $n = 6$; for crystals of point group symmetry C_3 and C_{3i}).—This point group will not be treated here because polyhedra of this symmetry are not likely to be encountered more than rarely in practical work.

Inscribed sphere.—In the hexagonal system the volume of an inscribed sphere is

$$V = \frac{N}{2} = \frac{2\pi}{9}\frac{c}{a} q_{hkl}^{3/2}. \qquad (54)$$

Orthorhombic system

We shall take

$$K = \tfrac{1}{2},\ \xi = \tfrac{1}{2}a,\ \eta = \tfrac{1}{2}b,\ \zeta = \tfrac{1}{2}c. \qquad (55)$$

Hence

$$q = h^2/a^2 + k^2/b^2 + l^2/c^2. \qquad (56)$$

Symmetry D_{2h} (multiplicity $n = 8$; for crystals of point group symmetry D_2, C_{2v}, D_{2h}).—The sector of interest is that contained in the positive octant ($x \geq 0, y \geq 0, z \geq 0$).

For the plane in the form to be designated (hkl) we require that

$$h \geq 0,\ k \geq 0,\ l \geq 0. \qquad (57)$$

The general expression for the volume of a polyhedron of this symmetry is

$$V = \frac{N}{2} = \frac{a^2b^2c^2}{6} \sum_i \Delta_i. \qquad (58)$$

The coordinates of the vertices of the sector of interest are

$$\left.\begin{aligned} x_1 &= q/h,\ y_1 = z_1 = 0, \\ x_2 &= 0,\ y_2 = q/k,\ z_2 = 0, \\ x_3 &= y_3 = 0,\ z_3 = q/l. \end{aligned}\right\} \qquad (59)$$

The volume of a polyhedron bounded by one form is

$$V = \frac{N}{2} = \frac{a^2b^2c^2}{6} x_1y_2z_3 = \frac{a^2b^2c^2q^3}{6hkl}. \qquad (60)$$

For the analysis of polyhedra bounded by two or three forms, Fig. 1 and Table 1 can be used.

Inscribed sphere.—In the orthorhombic system, the volume of an inscribed sphere is

$$V = \frac{N}{2} = abc\frac{\pi}{6} q_{hkl}^{3/2}. \qquad (61)$$

Monoclinic and triclinic systems

These systems will not be treated here.

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