# WEB MATERIALS FOR *STRUCTURE DETERMINATION BY X-RAY CRYSTALLOGRAPHY*

# *ANALYSIS BY X-RAYS AND NEUTRONS*

# *5TH EDITION 2013*

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# *Celebrating the Centenary of X-Ray Crystallography*

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# WEB APPENDICES

# Web Appendix WA1 Analytical Geometry of Direction Cosines

## WA1.1 Direction Cosines of a Line

In Figure WA1.1, let *P*1 be any point *x*1, *y*1, *z*1 referred to *x, y*, and *z* orthogonal axes. Draw lines from *P*1 perpendicular to the *x, y*, and *z* axes to cut them at *A, B*, and *C*, respectively. Thus, *OA = x*1, *OB = y*1, and *OC = z*1. The direction cosines of *OP*1 are given by cos *χ*1 = *x*1/*OP*1, cos *ψ*1 = *y*1/*OP*1, and cos *ω*1 = *z*1/*OP*1. Hence,

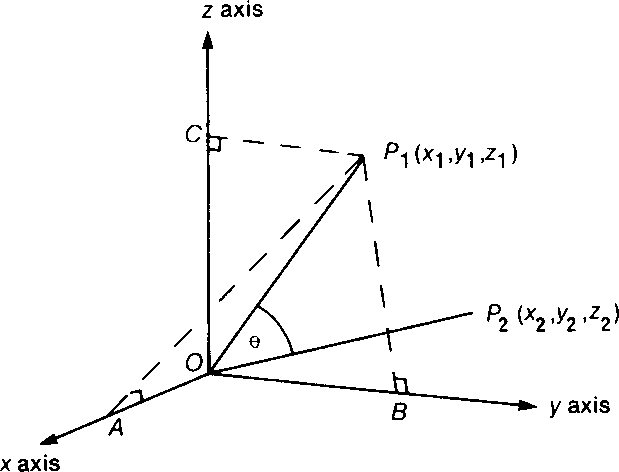
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FIGURE WA1.1. Direction cosines of a line referred to the rectangular axes *x, y* and *z*.

 (WA1.1)

Since *x*1, *y*1, and *z*1 are the projections of *OP*1 on to the *x, y*, and *z* axes, it follows that

 (WA1.2)

Hence,

 (WA1.3)

## WA1.2 Angle between Two Lines

On the line *OP*2, let a point *x*2, *y*2, *z*2 be marked off such that the lengths of *OP*2 and *OP*1 are equal, say *r*. We have for *OP*1, from above,



and for *OP*2,



where cos *χ*2, cos *ψ*2, and cos *ω*2 are the direction cosines of the line *OP*2.

If the origin is shifted from *O* to *P*1, then the coordinates of *P*2 become

 (WA1.4)

so that the length *P*1*P*2 is given by

 (WA1.5)

Using (WA1.3), we have

 (WA1.6)

In the isosceles triangle *OP*1*P*2

 (WA1.7)

Therefore,

 (WA1.8)

Comparing (WA1.6) and (WA1.8), we obtain

 (WA1.9)

The same result can be achieved by following the general vector method in Chapter 7, Section 7.5.1.

WEB APPENDIX WA2 Stereographic Projection

The study of crystal morphology in terms of the analytical description of planes and zones is inadequate for an overall appreciation of the many faces exhibited by a crystal. It is necessary to be able to represent a crystal by means of a two-dimensional drawing, while preserving certain essential properties. In crystal morphology, the interfacial angles, which are a fundamental feature of crystals, must be maintained in plane projection, and the *stereographic projection* is useful for this purpose. Furthermore, with imperfectly formed crystals, the true symmetry may not be apparent by inspection. In favorable cases, the external symmetry may be revealed completely by a stereographic projection of the crystal. We shall develop this projection with reference to the idealized crystal shown in Figure WA2.1.

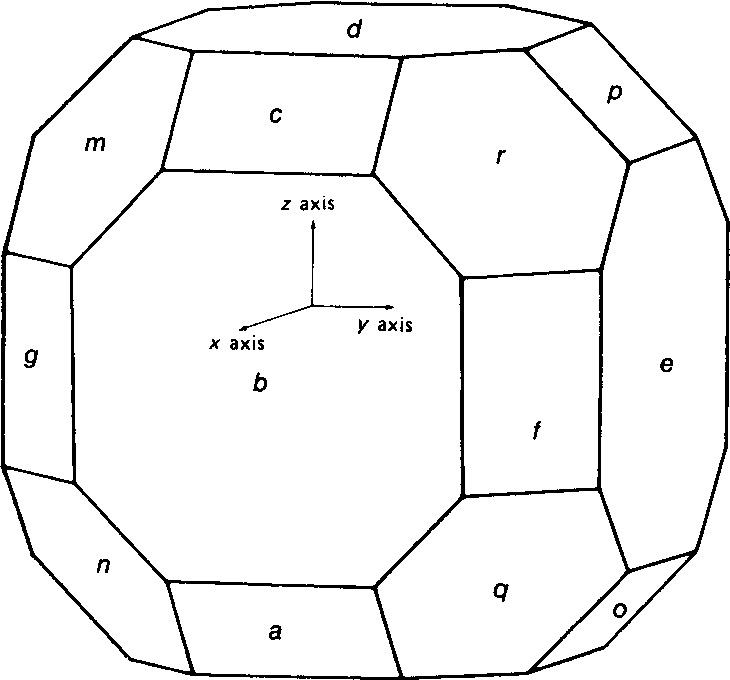


FIGURE WA2.1 Cubic crystal showing three forms of planes: cube—*b,e,d*, and parallel faces; octahedron—*r, m, n, q*, and parallel faces; rhombic dodecahedron—*f, g, p, o, c, a*, and parallel faces. The *x, y*, and *z* axes are parallel to important (symmetry) directions in the crystal.

This crystal belongs to the cubic system (see Chapter 1, Table 1.3): the crystallographic reference axes *x, y*, and *z* are orthogonal, and the parametral plane (111) makes equal intercepts (*a = b = c*) on these axes. The crystal shows three forms of planes. In crystallography, a *form* of planes, represented by {*hkl*}, refers to the set of planes that are equivalent under the point-group symmetry (see Chapter 1, Section 1.4) of the crystal. The crystal under discussion shows the cube form {100}—six faces (100), (00), (010), (00), (001), and (00); the octahedron {111}—eight faces; and the rhombic dodecahedron {110}—12 faces. Each face on the crystal drawing has a related parallel face on the actual crystal, for example, *b* (shown) and *b'*. The reader may care to list the sets of planes in the cubic forms {111} and {110}; the answer will evolve from the discussion of the stereographic projection of the crystal.

From a point within the crystal, lines are drawn normal to the faces of the crystal. A

sphere of arbitrary radius is described about the crystal, its center *O* being the point of intersection of the normals, which are then produced to cut the surface of the sphere.

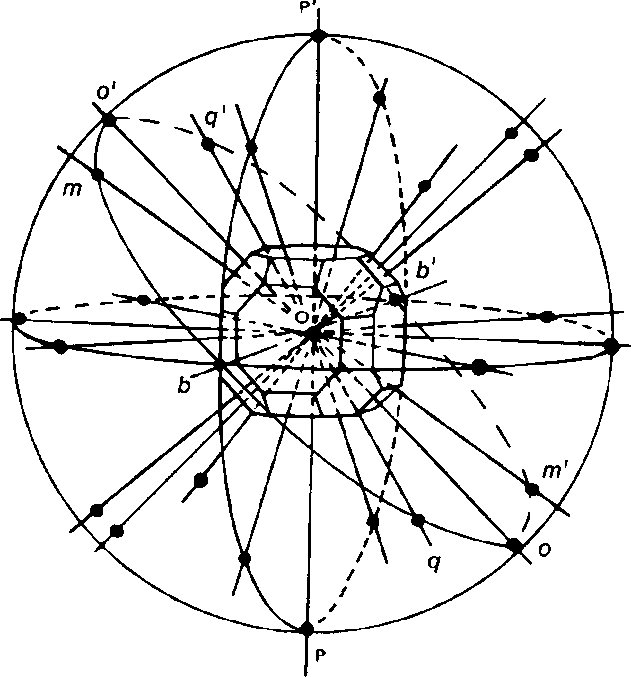


FIGURE WA2.2. Spherical projection of the crystal in Figure WA2.1; the radius (*ρ*) of the sphere is arbitrary. The inclined circle projects as  in Figure WA2.4.

In Figure WA2.3, the plane of projection is *ABCD*, and it intersects the sphere in the *primitive circle*. The portion of the plane of projection enclosed by the primitive circle is the *primitive plane*, or *primitive*. The point of intersection of each normal with the upper hemisphere is joined to the lowest point *P* on the sphere. The intersection of each such line with the primitive is the stereographic projection, or *pole*, of the corresponding face on the crystal, and is indicated by a dot on the stereographic projection, or *stereogram*. In particular, *R* is the intersection of the normal to the face *r* with the sphere, and *r* (in this figure) is the corresponding pole.

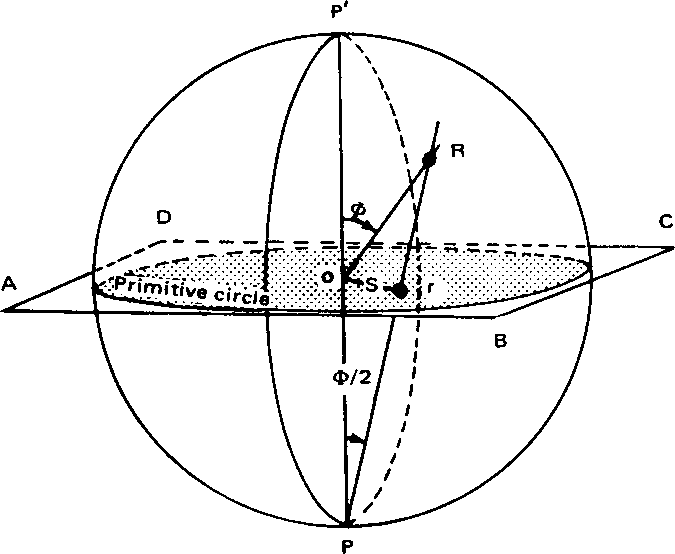


FIGURE WA2.3. Development of the stereographic projection (stereogram) from the spherical projection. Points on the upper hemisphere, such as *R*, are joined to the lowermost point, *P*.

If the crystal is oriented such that the normal to face *d* (and *d'*) coincides with *PP'* in the sphere, then the normals to the zone *e, f, b*, …, *g'* lie in the plane of projection and intersect the sphere on the primitive circle. In order to avoid increasing the size of the stereogram unduly, the intersections of the face normals with the lower hemisphere are joined to the uppermost point *P'* on the sphere and their poles are indicated on the stereogram by open circles.

The completed stereogram is illustrated by Figure WA2.4. The poles now should be compared with the corresponding faces on the crystal drawing. A fundamental property of the stereogram is that all circles drawn on the sphere project as circles. Thus, the curve  is an arc of a circle; specifically, it is the projection of a great circle that is inclined to the plane of projection. A great circle is the trace, on the sphere, of a plane that passes through the center of the sphere; it may be likened to a meridian on the globe of the world. Limiting cases of inclined great circles are the primitive circle, which lies in the plane of projection, and straight lines, such aswhich are projections of great circles lying normal to the plane of projection. All poles on a great circle represent faces lying in one and the same zone.

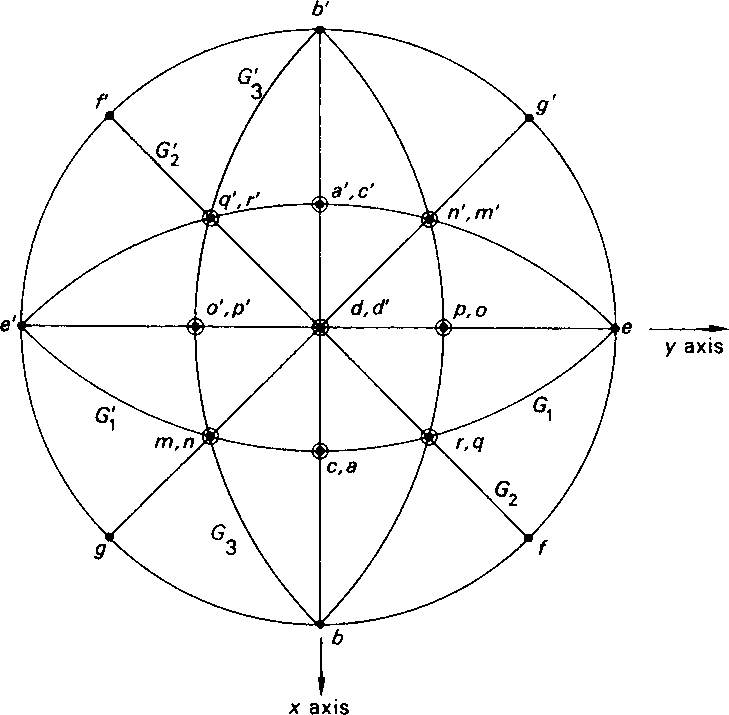


FIGURE WA2.4. Stereogram of the crystal in Figure WA2.1. The zone circle (great circle) , symbol [101], passes through *e*, *q*, *a*, *n*, *e*', *q*', *a*', *n*'; the zone circle  symbol [10], passes through *f*, *r*, *d*, *q*', *f*', *r*', *d*', *q*; the zone circle , symbol [011], passes through *b*, *m*, *o*', *q*', *b*', *m*', *o*, *q* (see Figure WA2.2).

Circles formed on the surface of the sphere by planes that do not pass through the center of the sphere are called small circles; they may be likened to parallels of latitude on the globe.

In order to construct Figure WA2.4, the following practical principles must be followed. The interfacial angles are measured in zones. If an optical goniometer is used, the angle Φ (see Chapter 1, Figure 1.15) is plotted directly on the stereogram. *Although* Φ *is the angle between the normals to planes, it is often called the interfacial angle in this context*. Next, the crystal orientation with respect to the sphere is chosen: for example, let zone *b*, *f*, *e*, … be on the primitive circle, and zone *b*, *c*, *d*, … run from bottom to top on the projection. Since , the angle between face *b* and *f*, is 45o, zone *f*, *r*, *d*, … can be located on the stereogram.

The distance *S* of the pole *r* from the center of the stereogram (Figure WA2.3) is given by

 (WA2.1)

where *ρ* is the radius of the stereogram and Φ is the interfacial (internormal) angle *dr* (cf. Figure WA2.1). A simple graphical method, employing a Wulff net1, is often sufficiently accurate to locate poles on a stereogram.

Triangles such as *dcr* can be solved by spherical trigonometry. If the angles *dc*, *cr* and *qd* are represented here by the letters *a*, *b*, and *c* respectively, and the angles within the triangle and opposite them by *A*, *B*, and *C* respectively, then from the sine and cosine rules in spherical trigonometry(see Appendix WA3), we have

 (WA2.2)

and

 (WA2.3)

Thus, in the triangle *dcr,* angle *cr = b =* 35.26o*, dc-dr = B =* 45o*, dr = c, dc-cr = C =* 90o . Hence, from Chapter 1, equation (1.2) or (1.3),

*c = dr =* 54.74o  (WA2.4)

or one half the tetrahedral angle.

The completed stereogram (Figure WA2.4) may now be indexed. The parametral plane is chosen as face *r* (the parametral plane must intersect all three crystallographic axes), and the remaining faces are then allocated *h*, *k*, and *l* values (Figure WA2.5). We may note here that if two zone axes are [*U*1 *V*1 *W*1] and [*U*2 *V*2 *W*2], then the face (*hkl*) that contains these two zone axes is given by solving two equations of the form of Chapter 1, equation (1.9), following Chapter 1, equations , (1.2) and (1.3). Thus, *h = V*1 *W*2 − *V*2 *W*1, and similarly for *k* and *l*. It is not necessary to write the indices for both poles at the same point on the stereogram. If the dot is *hkl*, then we know that the open circle is *hk*. Figure WA2.6 shows the crystal of Chapter 1, Figure 1.1 again, but with the Miller indices inserted for direct comparison with its stereogram.

We shall not be concerned here with any further development of the stereogram. The angular truth of the stereographic projection makes it very suitable for representing not only interfacial angles, but also symmetry directions, point groups, and bond directions in molecules and ions. For further discussion, see Bibliography.

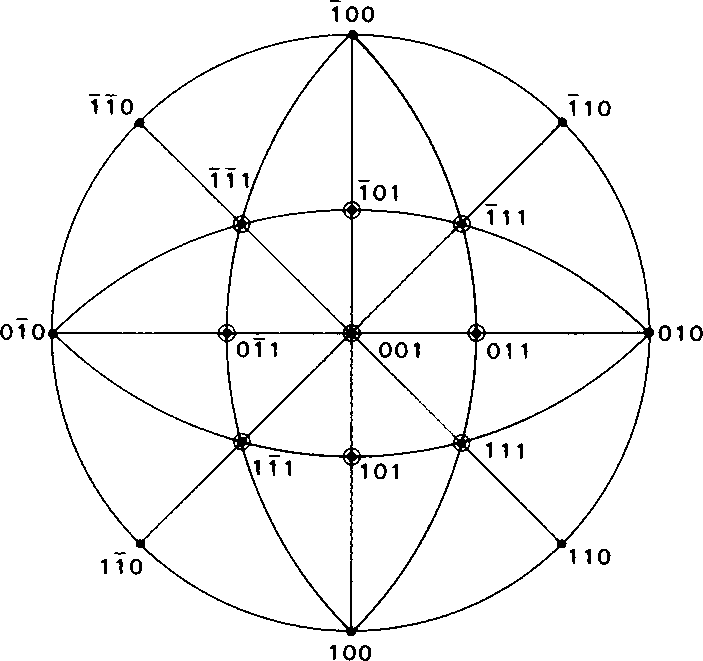


FIGURE WA2.5. Stereogram in Figure WA2.4 indexed, taking *r* as 111. The zone containing (100) and (111) is [01], and that containing (010) and (001) is [100]; from Chapter 1, equations (1.7) – (1.9), it follows that the face *p* common to these two zones is (011).

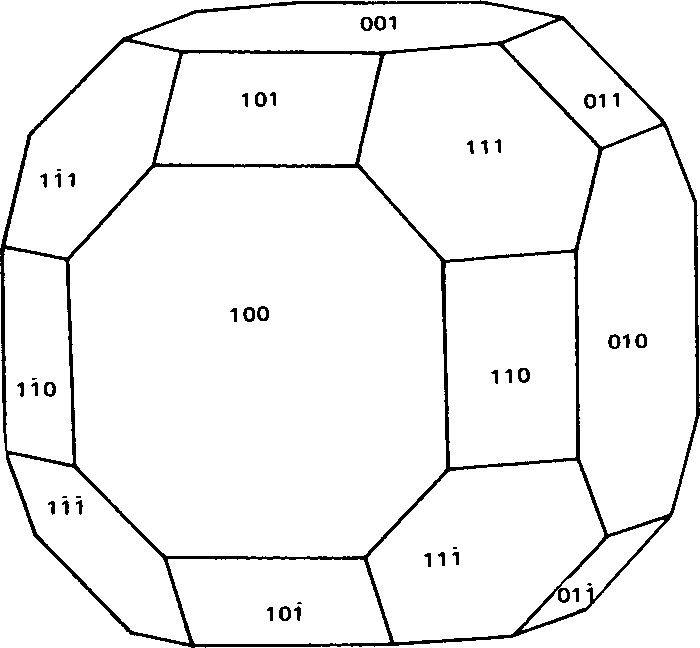


FIGURE WA2.6. Crystal of Figure WA2.1 with Miller indices inserted.

Bibliography WA2

PHILLIPS, F. C., *An Introduction to Crystallography*, Longmans, London (1971).

# Web Appendix WA3 Spherical Trigonometry

## WA3.1 Spherical Triangle

Figure WA3.1 shows a spherical triangle *ABC* formed on the surface of a sphere by the intersections of great circles of which *AB, AC*, and *BC* form parts; great circles pass through the centre of the sphere. The arcs *a, b*, and *c* are the *sides* of the triangle, and *A, B*, and *C* are its *angles*; side *a* is measured by the angle ∠*BOC*, and the angle *A* by the angle between the tangents at *A* to the arc *AB* and *AC*, that is, the plane angle ∠*PAQ*. Similar definitions apply to the other four elements of the triangle. The following equations apply to spherical triangles, and are easily proved with the aid of trigonometry applied to Figure WA3.1:

 (WA3.1)

 (WA3.2)

Other examples of (WA3.1) can be set down by cyclic permutation.

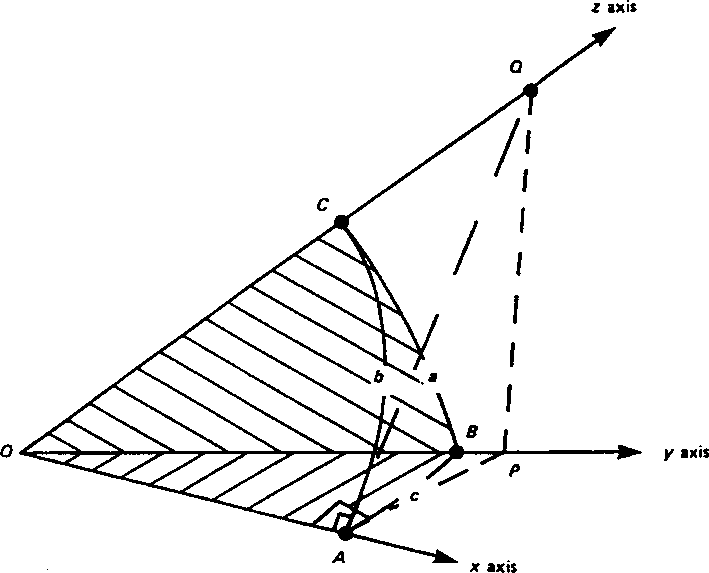


FIGURE WA3.1. Spherical triangle *ABC* formed by the intersections of three great circles on a sphere of centre *O; AP* and *AQ* are tangents to the sphere at *A*.

## WA3.2 Polar Triangle

The polar triangle and equations derived from it become important for the solution of triangles when applying Euler’s theorem on the combination of rotations to the elucidation of point groups (see Chapter 1, Section 1.4.2).

In Figure WA3.2, *ABC* is again a spherical triangle. The arc *B′C′* is drawn such that all points on it are 90o away from *A*; thus, *A* is the *pole* of the great circle of which *B′C′* is an arc. Similarly, *B* and *C* are the poles of the arcs *A′C′* and *A′B′* respectively: *A′B′C′* is defined as the *polar* triangle of triangle *ABC*. By reciprocity, *ABC* is the polar triangle of triangle *A′B′C′*.

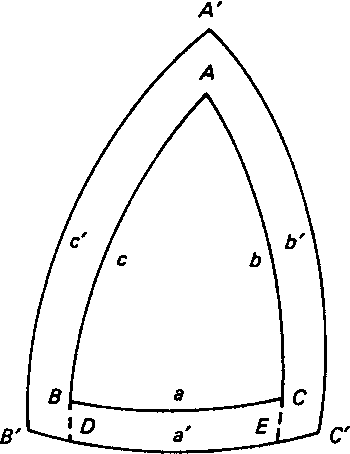


FIGURE WA3.2. Spherical triangle *ABC* (see Figure WA3.1) and its polar triangle *A′B′C′*: all points on the are *B′C′* are 90o away from *A*, the pole of the great circle represented by *B′C′*; similar relations apply to poles *B* and *C*.

The arcs *AB* and *AC* are produced to cut *B′C′* in *D* and *E*, respectively. Since *A* is the pole of *DE, DE* is a measure of the angle *A*. But *B′E + C′D = B′C′ + DE* and, because *B*′ and *C′* are the poles of *CE* and *BD* respectively, *B′E = C′D* = 90o. Thus, *B′C′ + DE = a′ + A* = 180o, so that

 (WA3.3)

and, since triangles *ABC* and *A′B′C′* are polar to each other,

 (WA3.4)

with similar relationships for *b, c, b*′, and *c*′. Using these relationships with (WA3.1), we obtain

 (WA3.5)

with similar results for the other four elements by cyclic permutation.

# Web Appendix WA4 Rotation Matrices

We derive here a matrix for the rotation of a point *X, Y, Z* by an angle *φ* about an axis normal to the plane of *x* and *y*, with an angle *γ* between the *x* and *y* axes. Since the rotation axis is normal to the plane, the *z* coordinate of the point is unchanged.

In Figure WA4.1, ∠*PQN = π − γ*, and ∠*QPN = γ − π*/2. Then, we have the ensuing analysis:

 (WA4.1)

It follows that

 (WA4.2)

Expanding (WA4.2), substituting for *r* sin *θ* and *r* cos *θ* from (WA4.1), and rearranging leads to

 (WA4.3)

 (WA4.4)

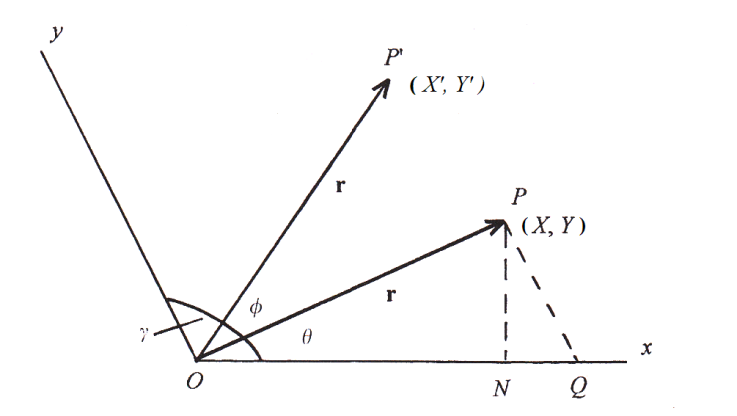


FIGURE WA4.1. Vector *OP* of length |**r**| at a general angle *θ* to the *x* axis; *OP*′ is the same vector after being rotated by an angle *φ* from *OP*. The general angle between the *x* and *y* axes is *γ*; for 3-fold and 6-fold symmetry, it has the value 120o.

Thus, we can write concisely,

 (WA4.5)

where the matrix **S** is given by

 (WA4.6)

EXAMPLE What are the coordinates obtained from *x*, *y*, *z* by a right-handed 6-fold rotation about the *z* axis in the hexagonal system (** = 120o)?

For a 6-fold rotation, * =* 60o. Hence,

 (WA4.7)

Then, from WA4.5

 (WA4.8)

so that the column vector **X (***X, Y, Z*) is rotated to **Xʹ** (*X − Y, X, Z*).

Matrix (WA4.6) will suffice for all rotational operations that we meet in studying point groups where the rotation axis is normal to the *x*, *y* plane. For 3-fold rotation in the cubic system, we can see from the stereogram for point group 432 (Chapter 1, Figure 1.32) that a 4-fold anticlockwise rotation about the *x* axis followed by an anticlockwise rotation about the *z* axis is equivalent to a 3-fold anticlockwise rotation about the direction [111].

Thus, from (WA4.6) for a 4-fold rotation **R***x* about the *x* axis in the cubic system (*γ* = 90o), by interchange of axes, we obtain

and for rotation about the z axis,

  (WA4.9)

Hence, **R**[111] = **R***z* · **R***x*, that is,

# Web Appendix WA5 Formulae in Plane Trigonometry

The following formulae are often useful in manipulating a structure factor equation so as to obtain the geometrical structure factor equation.

 (WA5.1)

 (WA5.2)

 (WA5.3)

 (WA5.4)

 (WA5.5)

 (WA5.6)

 (WA5.7)

 (WA5.8)

 (WA5.9)

 (WA5.10)

 (WA5.11)

 (WA5.12)

cos 2*π*(*θ + n*/2) is crystallographically equivalent to cos2**(*n*/2) (WA5.13)

where *n* is an integer.

Any coordinate *x* can always be changed by ±½ to a crystallographically equivalent value *x*.

Web Appendix WA6  Reciprocal Lattice: Analytical Treatment

We considered a geometrical derivation of the reciprocal lattice in Chapter 2, as we believe that that treatment forms a straightforward introduction to the concept. Here, we discuss the reciprocal lattice in greater detail.

In considering the stereographic projection, we showed that the morphology of a crystal could be represented by a bundle of lines, drawn from a point, normal to the faces of the crystal. This description, although angle-true, lacks linear definition. The representation may be extended by giving each normal a length that is inversely proportional to the corresponding interplanar spacing in real space, and applying it to all possible lattice planes, so forming a reciprocal lattice.

Let a Bravais (real-space) lattice be represented by the unit cell vectors **a, b, c.** The reciprocal lattice unit cell is defined by the vectors **a**\*, **b**\*, **c**\*, such that **a**\* is perpendicular to **b** and **c**, and so on. Then,

 (WA6.1)

The magnitudes of the reciprocal unit cell vectors are defined by

 (WA6.2)

In Figure WA6.1, the *z*\* (*c*\*) axis is normal to the plane *a*, *b*. Since  = *cc*\* cos *COR*, that is, taking *κ* = 1 in this discussion,

 (WA6.3)

where *κ* is a constant, normally equal to unity in theoretical discussions, and to an x-ray wavelength in practical applications, where the size of the reciprocal lattice is important.

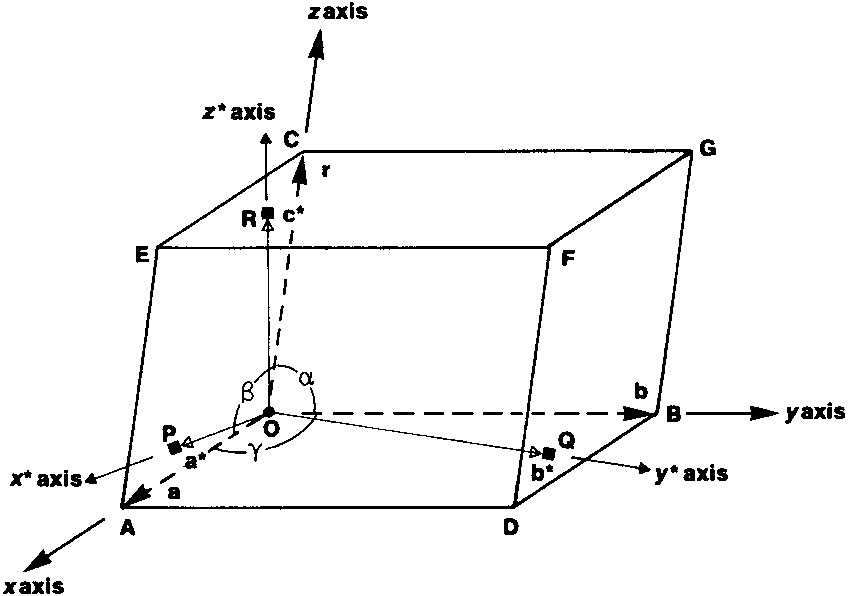


FIGURE WA6.1. Triclinic unit cell, showing its vectors **a, b,** and **c,** and the corresponding reciprocal unit-cell vectors, **a**\*, **b**\*, and **c**\*.

Thus, the magnitude of **c**\*, in reciprocal space, is inversely proportional to the *c*-spacing in real, or Bravais, space; similar deductions can be made for both **a**\* and **b**\*. Since **c**\* is normal to both **b** and **c,** it lies in the direction of their vector product:

 (WA6.4)

where *η* is a constant. Let *V* be the unit cell volume in real space. Then,

 (WA6.5)

Now **a × b** is a *vector* of magnitude *ab* sin *γ*, the area of *OADB*, directed normal to the plane of *a*, *b* and forming a right-handed set of directions with **a** and **b**. Then,

 (WA6.6)

Hence,

 (WA6.7)

with values for *a*\* and *b*\* obtained by cyclic permutation.

The angle *β*\* between **c**\* and **a**\* can be obtained by the equations of spherical trigonometry (see Web Appendix WA3). In Figure WA6.2, the spherical triangle *ABC*, where *OA*, *OB*, and *OC* are the directions of the *x*, *y*, and *z* axes respectively, has sides equal to the interaxial angles in real space *α*, *β*, and *γ*. The directions *OA*\*, *OB*\*, and *OC*\* are along **a**\*, **b**\*, and **c**\* respectively; *OC*\* is normal to the great circle through *A* and *B*, and similarly with *OA*\* and *OB*\*. Hence, *A*\**B*\**C*\* is a spherical triangle polar to *ABC*, so that *β*\* is the angle between the great circles through *AB* and *BC*, or *π − B*, where *B* is the angle of the spherical triangle *ABC* at *B*. Then, from the formulae of spherical trigonometry,

 (WA6.8)

with corresponding expressions for *α*\* and *γ*\* obtained by cyclic permutation. Simplified expressions obtain for (WA6.7) and (WA6.8) when the crystal symmetry is higher than triclinic.

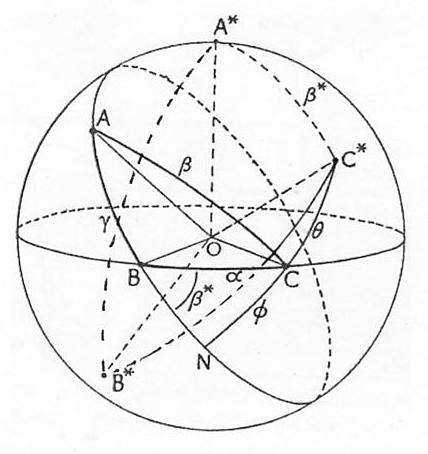


FIGURE WA6.2. Spherical triangle *ABC* and its polar triangle *A*\**B*\**C*\*.

WA6.1 Unit Cell Volumes in Real and Reciprocal Space

We may use (WA6.5) to evaluate an expression for the volume of a unit cell in terms of scalar quantities. Let **a**, **b**, and **c** be expressed in terms of a set of orthogonal unit vectors **i**, **j**, and **k**:

 (WA6.9)

Then, using (WA6.5) with expansion of the vector product **a × b**, the volume may be written

 (WA6.10)

which, after simplification, may be expressed as the determinant

 (WA6.11)

Since rows and columns of a determinant can be interchanged without altering its value, we can write

 (WA6.12)

Multiplying the determinants, according to the rules for matrices, leads to

 (WA6.13)

which may be expressed in vector notation as

 (WA6.14)

Evaluating (WA6.14), we obtain

 (WA6.15)

which simplifies to

 (WA6.16)

Now *V V*\* follows from (WA6.12) as

**** (WA6.17)

Hence,  (WA6.18)

WA6.2 Some Properties of the Reciprocal Lattice

The reciprocal lattice is particularly useful in that it enables the geometry of planes to be represented by the simpler geometry of points. We shall consider here some properties of the reciprocal lattice that are useful in calculations on crystal structures.

Interplanar Spacings

Let the plane (*hkl*) in Figure WA6.3 be that in the family of such planes that is nearest to the origin. Then it intercepts the *x, y*, and *z* axes in *A, B*, and *C* as shown. The vector **d**\*(*hkl*) in reciprocal space is defined by

 (WA6.19)

The vector **AB** (we use **AB** to represent the vector *A* → *B*) is equal to (**a**/*h* − **b**/*k*), so that, with (WA6.1) and (WA6.2), the scalar product **d**\*(*hkl*) (**b**/*k* − **a**/*h*) becomes



so that **d**\*(*hkl*) is normal to **AB**. Similarly **d**\*(*hkl*) is normal to **BC** and **CA**.

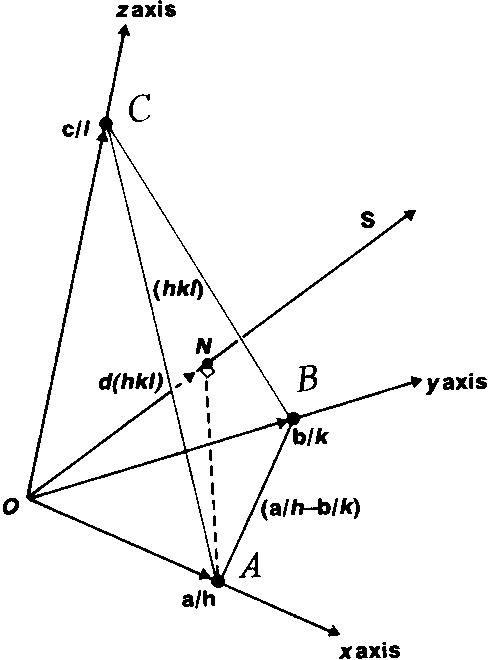


FIGURE WA6.3. A plane (*hkl*) in a Bravais lattice, showing the unit-cell vectors **a, b**, and **c**; *N* is the foot of the perpendicular from the origin *O* to the plane, so that *ON* is the interplanar spacing *d*(*hkl*).

The interplanar spacing in the Bravais lattice *d*(*hkl*) is the distance *ON*. If the unit vector along *d*(*hkl*) is **n**, then *d*(*hkl*) = **OA n**. But **n = d**\*(*hkl*)/|*d*\*(*hkl*)|; so that

 (WA6.20)

For *κ* = 1,



that is, the magnitude *d*(*hkl*) is equal to 1/*d*\*(*hkl*). In this discussion, the indices *h, k*, and *l* are unique, and any or all of them may contain a common factor (see Chapter 3, Table 3.1). From (WA6.19), we have

 (WA6.21)

whence *d*(*hkl*) and *d*\*(*hkl*) can be calculated. As before, simplifications of (WA6.21) arise in the presence of symmetry higher than triclinic (see also Chapter 2, Table 2.4).

Introducing the Bragg equation, Chapter 3, equation (3.43,

 (WA6.22)

where *d*\*2(*hkl*) is given by (WA6.21), so that (WA6.22) can be used to express sin *θ* for a reflection *hkl* in terms of the reciprocal unit cell parameters.

Angle between Planes

Given any two planes *h*1*k*1*l*1 and *h*2*k*2*l*2, the angle between them can be found as the supplement of the angle between the two normals, *d*\*(*h*1*k*1*l*1) and *d*\*(*h*2*k*2*l*2); this angle is the *interfacial angle* of the stereographic projection (see Chapter 1, Section 1.3).

In general, the angle *φ* between the forward directions of two vectors **p** and **q** is given by

 (WA6.23)

Following (WA6.21)

 (WA6.24)

Equation of a Plane

Consider any plane (*hkl*) and a point **r**(*x*, *y*, *z*) in it; the normal to the plane is **d**\*(*hkl*). If the unit vector along **d**\*(*hkl*) is ***δ***, the equation of the plane is *p* = **r*δ***, where *p* is the perpendicular distance from the origin to the plane. We may rewrite this equation as

 (WA6.25)

where (*hkl*) is the *n*th plane, in the family, from the origin. It follows from (WA6.25), since , that

 (WA6.26)

When *n* = 0, the plane passes through the origin, and when *n* = 1 it is the first plane in the family from the origin. These results may be compared with those derived in Chapter 1, Section 1.2.3.

Reciprocity of *F* and *I* Unit Cells

In Figure WA6.4, we select a primitive unit cell from the face-centered unit cell by the transformation

 (WA6.27)

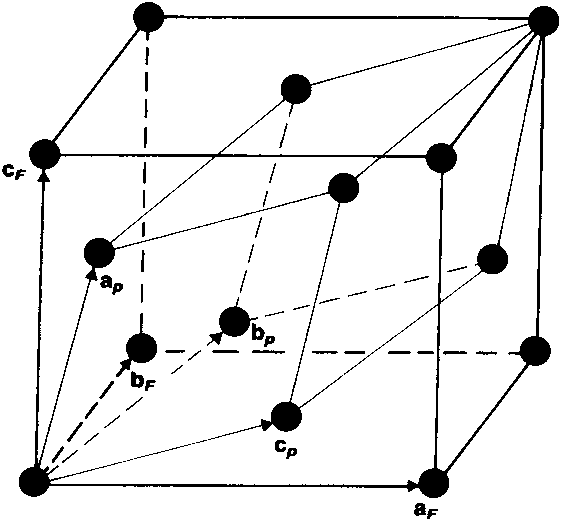


FIGURE WA6.4. An *F* unit cell, with a *P* unit cell outlined within it. The number of lattice points per unit cell shows that *V*F/*V*P = 4.

Using (WA6.4) and (WA6.5), with appropriate cyclic permutation



since *VF* = 4*VP*. Hence, we obtain

 (WA6.28)

with similar expressions for  and . The negative sign in front of  in (WA6.28) is introduced in order to preserve right-handed axes from the product (**c***F* × **b***F*).

In the case of the body-centered unit cell, the equations similar to (WA6.27) are

 (WA6.29)

with similar expressions for **b***P* and **c***P*. Writing (WA6.28) as

 (WA6.30)

We see that an *F* unit cell in a Bravais lattice reciprocates into an *I* unit cell in the corresponding reciprocal lattice, where the *I* unit cell is defined by the vectorsand . If, as is customary in practice, we define the reciprocal of an *I* unit cell by vectors  and , then only those reciprocal lattice points for which each of *h + k*, *k + l* (and *l + h*) are even integers belong to the reciprocal of the *I* unit cell. In other words, Bragg reflections from an *F* unit cell have indices of the same parity (see also Chapter 3, Section 3.7.1 and Table 3.2).

Web Appendix WA7 Gamma Function

The gamma function is useful in handling integrals of the type

 (WA7.1)

where *a* is a constant; they occur in studying *inter alia* atomic scattering factors and intensity statistics. The gamma function Γ(*n*) may be represented by the equation

 (WA7.2)

The following three results are useful:

1. For *n* > 0 and integral

 (WA7.3)

2. For *n* > 0

 (WA7.4)

and if *n* is also integral

 (WA7.5)

3.  (WA7.6)

EXAMPLE. Consider the solution of the integral

I 

Let *x*2/2 = *t*, so that *x* = (2*t*)1/2 and d*x* = (2*t*)−1/2d*t*. Then

I 

A reduction formula is also useful when working with these integrals:



Web Appendix WA8 Orthogonal Functions

Two functions *fi*(*x*) and *fj*(*x*) are said to be orthogonal over a given range *a* to *b* if



where *ij* is the Kronecker delta, and has the value unity if *i* = *j* and zero otherwise.

In the particular functions that we need to consider, *fi* and *fj* are cosine and/or sine functions. Consider the following integrals:



From trigonometrical relations, we know that . Hence, we write the integral as



since *h* is an integer. A second integral of importance is



From trigonometrical relations, we have . Thus, we write *I*2 as



which is clearly zero, since both *h* and *k* are integral. But if *h* = *k*, then because of the indeterminacy that would arise in the second term, we return to the original integral, which now becomes



which is again *a*/2.

# Web Appendix WA9 The Integral

This integral was encountered in the study of Fourier transforms in Chapter 6. It is an important integral in diffraction theory, and we derive its value here.

We need to integrate the function over a semicircular path, such as *−R, −r*, 0, *r, R, S, −R*, where *R* is an arbitrary radius and *z* is a variable in the complex plane, Figure WA9.1. However, we cannot integrate through the singularity at zero, so we excise a semicircular path *−r*, 0, *r, s, −r*, where *r* is another arbitrary radius.

Since *z* = 0 lies outside the now defined contour,

 (WA9.1)

so that

 (WA9.2)

If we replace *x* in the first integral by *−x*, negate its limits, and combine it with the second integral, we can write

 (WA9.3)

We now let *r* → 0 and *R* → ∞. In the limit, the second integral on the right-hand side tends to zero (Cauchy’s theorem), whereas the first integral, putting *z = r* exp(i*θ*), becomes

 (WA9.4)

Hence,

 (WA9.5)

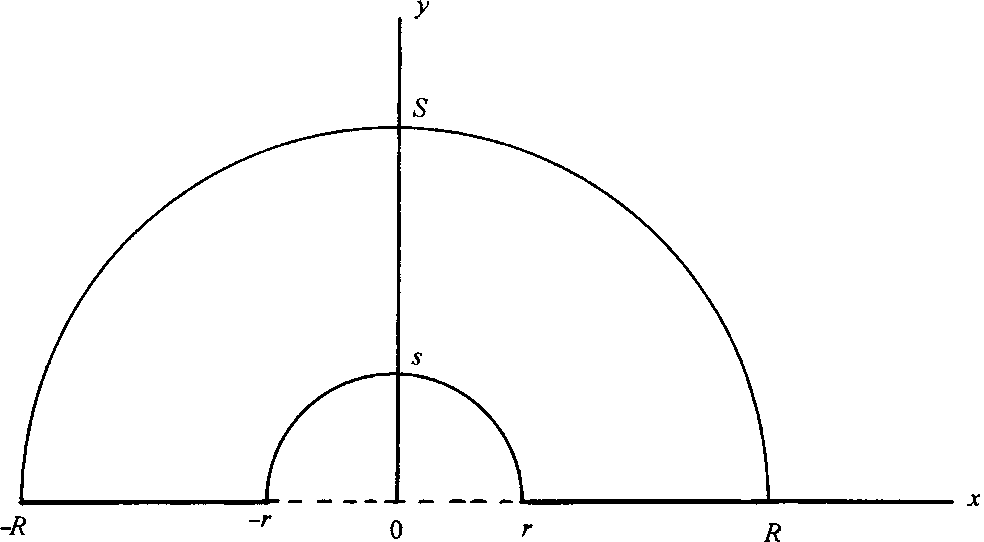


FIGURE WA9.1. Path of integration in the complex plane.

# II) WEB PROGRAM SUITE

The programs in this suite are **Version 1 2013**. Any changes to or revisions of these programs will form the next version under the same web reference. The programs ITO12, LEPAGE and ESPOIR will not be subject to revisions, unless so directed by the authors of these programs. The programs are presented as executable .EXE files in four folders.

**GNSYST**

EULR Derivation of point groups

FOUR1D One-dimensional Fourier summation

FOUR2D Two-dimensional Fourier summation (Also, source code FOUR2D.F90)

INTXYZ Cartesian coordinates from molecular geometry

LSLI Linear least squares

MATOPS Matrix operations on one or two 3 × 3 matrices

MOLGOM Molecular geometry from Cartesian or crystallographic coordinates

SYMM Interactive point group recognition

TRANS1 One-dimensional Fourier transform

ABDAT Sample data for TRANS1

CART Sample data for INTXYZ

MOLDAT Sample data for MOLGOM

**PDSYST**

ITO12 Powder indexing by Ito’s method

LEPAGE Unit cell reduction

QVALS Calculation of Q values from unit cell data

RECIP Real cell to reciprocal cell and *vice versa*

ITOINP Sample data for ITO12

PAGE Sample test data for LEPAGE

**POWDER**

ESPOIR Powder indexing and structure determination (Le Bail’s method)

RASMOL Plotting program (linked to ESPOIR)

Al2O3A Aluminium oxide A (dat and hkl)A Sample input data for ESPOIR

Al2O3B Aluminium oxide B (dat and hkl)B Sample input data for ESPOIR

Al2O3C Aluminium oxide C (dat and hkl)C Sample input data for ESPOIR

Methyl 1-Methylfluorene (dat and hkl) Sample input data for ESPOIR

**XRSYST**

XRAY Interactive x-ray crystal structure analysis simulation program

MAKDAT Data preparation program for input to XRAY

GINO FILES Plotting data (**On no account must these files be changed**)

BSTO Bis(6-sulphanyloxy-1,3,5-triazin-2(1*H*)-one data file for input to XRAY

CL1P 2-Amino-4,6-dichloropyrimidine data file for input to XRAY

CL2P 2-Amino-4-methyl-6-chloropyrimidine data file for input to XRAY

MTOL *m*-Tolidine dihydrochloride data file for input to XRAY

NIOP Nickel *o*-phenanthroline complex data file for input to XRAY

NO2G Nitroguanidine data file for input to XRAY

SMTX 2-*S*-methylthiouracil (y*, z)* data file for input to XRAY

SMTY 2-*S*-Methylthiouracil data (x*,* z) file for input to XRAY