I. GEOMETRICAL CRYSTALLOGRAPHY

Why is "crystallography" important?:

Crystallography is a very old science. Its published beginnings have been traced back to the 1600s. (You may perhaps be interested in the very readable book by J. G. Burke, *Origins of the Science of Crystals* (1966)). By the end of the 19th century, all of the major concepts and structure of the classical theory were developed. Since the discovery of the diffraction of x-rays by crystals in 1912, these classical concepts of crystallography have been verified and used constantly over and over by scientists and engineers from many disciplines.

We will be concerned with the language and concepts of classical crystallography. It should be noted that, over the last ten years or so, a revolution in crystallography has been taking place. It has been found that the basic classical concepts can be extended to the description of the geometry of certain kinds of objects or structures in higher dimensional spaces and even curved spaces.

The structural arrangements of the atoms in solids are fundamentally important to the study of their properties. In addition, the design process for new materials depends intensely on the manipulations of the structural arrangements of the component phases. Shifting the positions of atoms in a solid material by one means or another, or substituting one chemical species for another, can dramatically alter the properties of that material. The complete understanding of many interesting, fundamental phenomena in solids cannot be accomplished without an appreciation of the atomic arrangements in those solids. This extends even to events in biological systems; for example, understanding how antibodies attach to viruses requires knowledge of the structural arrangements of the atoms in the viruses.

Most of the solids about which we are speaking are, or can be made **crystalline**, or at least partially **crystalline** (for example, polymeric materials). To be crystalline, a solid must consist of large regions (grains or crystals) in which identical groups of atoms are repeated periodically or regularly an almost infinite number of times (on an atomic scale), usually in three dimensions. An example is shown in figure 1.1a below.....The structure and the essence of its repetition are shown only in two dimensions because it is easier to visualize.

The number of ways in which crystalline repetition can take place is infinite...even in only two dimensions. This is because the directions along which the repetition can take place can vary, and the distances (the repeat periods) can take on any values. As an example, compare the structure in figure 1b with that in figure 1.1a; note that, in figure 1.1b, the two directions along which the repetition takes place are not orthogonal, and the repeat distances are different, and not equal.

While the possibilities for atom arrangements and repetition are, theoretically, infinite in number, the requirement of crystalline repetition imposes many rules on these possibilities, so that the study of the structural arrangements in solids is really a tractable endeavor. We must learn these rules. In order to understand the rules for the description of crystal structures, we must, at the same time, become familiar with the nomenclature of crystallography.

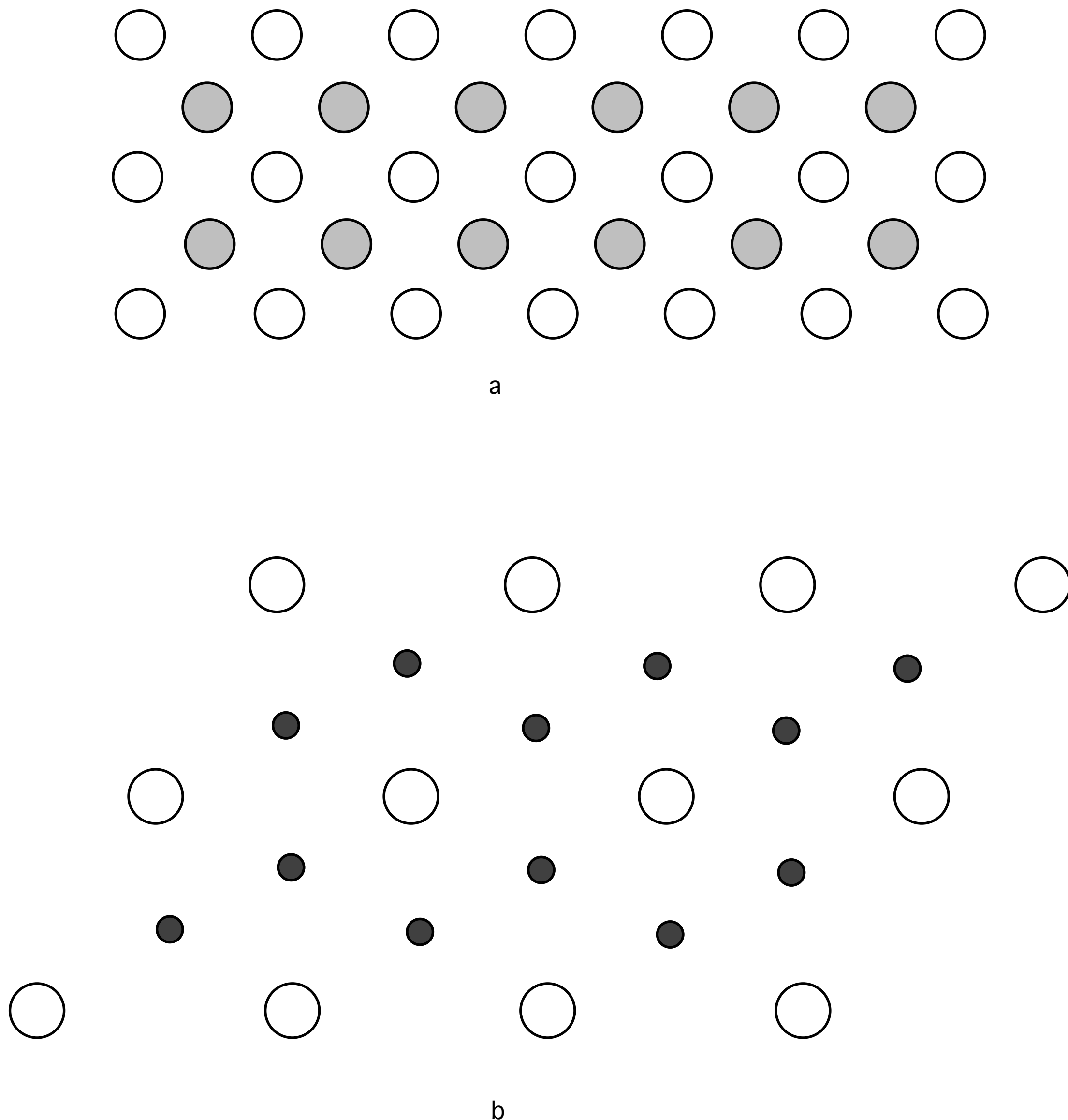


Figure 1.1. Portions of the two dimensional layers of two different crystal structures.

Crystal lattices:

It should be obvious now that to describe the atomic arrangement of a crystalline solid, it is not necessary to give the describe the coordinates and type of the nearly innumerable atoms in a crystal. Because of the repetition, it is only necessary to describe the arrangement of the atoms in the group that is repeated, and then to describe how the repetition takes place. Let us begin with a discussion of the ways in which repetition can take place. For this discussion, we can replace the (probably) large number of atoms in the repeating group with a **point**. This is a mighty simplification, but its usefulness will very soon become obvious.

So now we are faced with the relatively simpler task of discovering the ways in which a **point** can be repeated periodically in space. We call these assemblages of periodically repeated points **lattices**.

We adopt this formal definition of a lattice:

> A lattice is an n-dimensional, infinite, periodic array of **points, each of which has identical surroundings**.

So, a lattice is an abstraction of a crystal structure, with each **lattice point** representing an identical group of atoms; no atoms are ever shown in the drawing of a lattice......it consists only of points. The crystal structures of materials can be very complex, and to even just visualize them can be a monumental task, as we have suggested above. The lattice is much more easily visualized. Furthermore, use of the lattice concept will permit us to understand many of the characteristics of the crystal structures the lattices represent.

Note that a lattice can be defined in the space of any dimensions. We can have one dimensional lattices. There are many new synthetic materials whose structures are represented by one-dimensional lattices. The structures of surfaces and interfaces can be represented by two-dimensional lattices; two dimensional kinds of things are easy to visualize, as we have already seen. But, really, crystalline solids require three-dimensional lattices. There are some very interesting materials, recently discovered, whose structures can only be represented by lattices in, say, a six-dimensional space.....but such things are tough to draw.

Note also the requirement of infinity of extent. This avoids the problems associated with the edges of a space. A formality, really.

Finally, note the important qualifying phrase regarding **identical surroundings**. This is used as a test for the identification of lattice points when looking at a crystal structure. Compare the two portions of the crystal structures and their lattices shown in figure 1.2. In figure 1.2a, all of the atoms are identical, so that all can be represented by lattice points. In 1.2b, the atoms are not all the same; in this case, each lattice point has to represent one of each of the two different types of atoms.

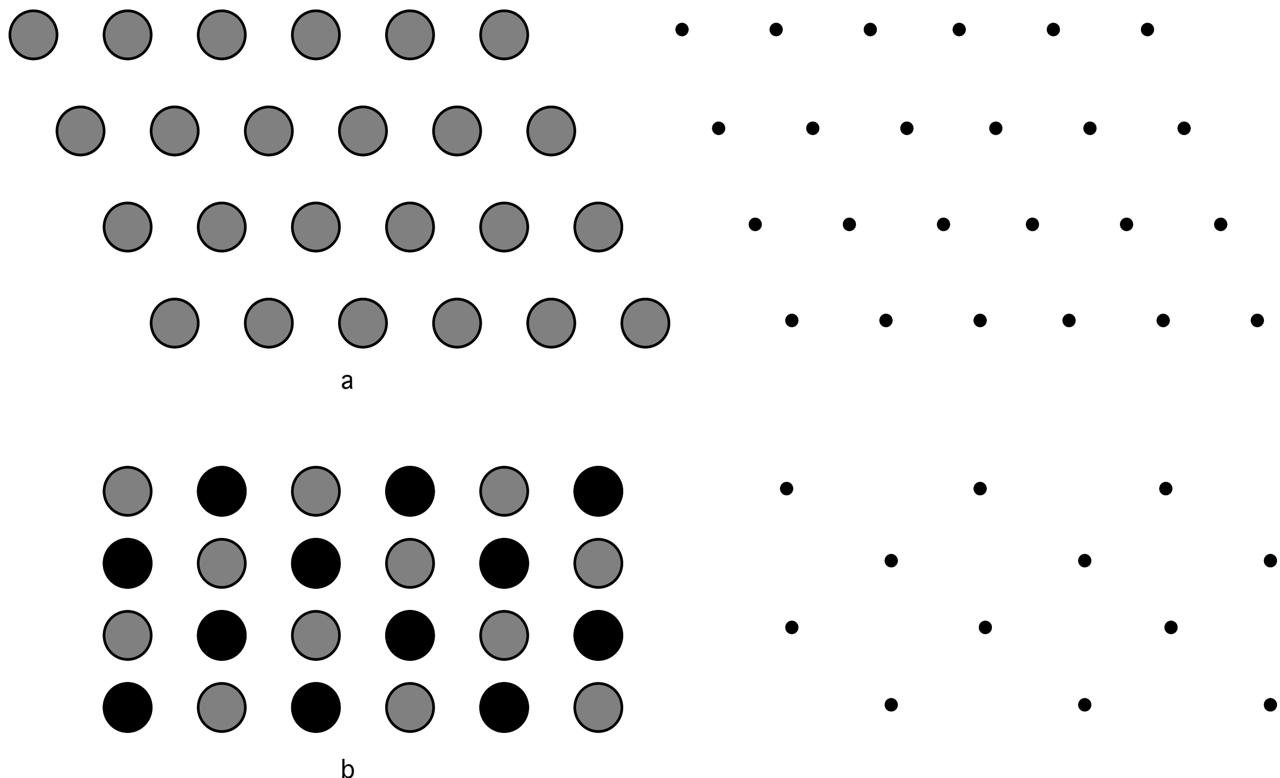


Figure 2. Portions of two simple crystal structures (left) and their lattices (right).

An error commonly made by many materials scientists and others involves the structure of CsCl, shown in figure 3. CsCl appears to be body-centered cubic (defined later) with atoms at the positions (000) and (1/2,1/2, 1/2) in the unit cell, but it is not, because Cs^+ is on one site and Cl^- on the other; thus, the surroundings of these 2 points, the cell origin and the "body-centered" position, are not identical, and the lattice is thus primitive cubic. On the other hand, if both atoms at (000) and (1/2,1/2, 1/2) are Cs atoms, then the structure is indeed body-centered cubic (Cs metal is body-centered cubic).

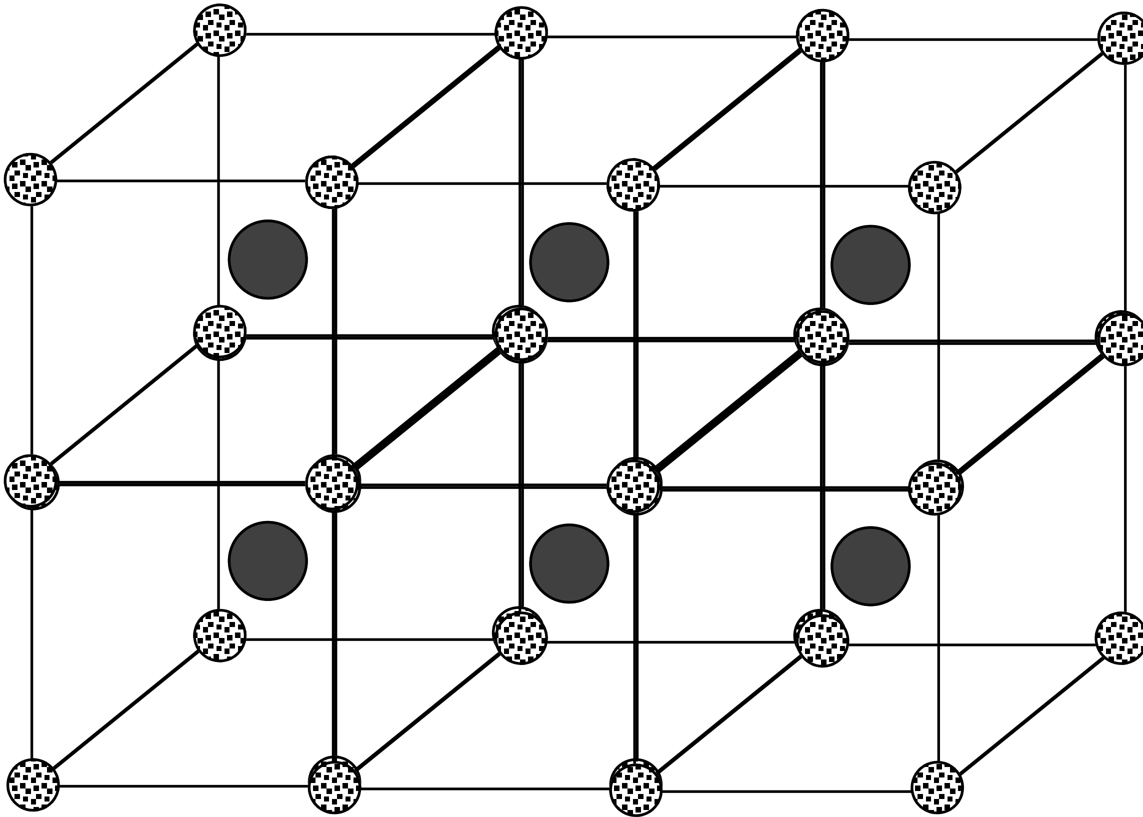


Figure 3. The crystal structure of CsCl. Lattice points can not be assigned to both the large (Cl^-) and small (Cs^+) ions. Here, the positions of the lattice points are shown at only the small ions (where the line segments intersect), and each lattice point must represent both a large and a small ion.

Unit cells:

While we have simplified the description of crystal structures considerably with the introduction of the concept of the lattice, we see immediately that the repetition thing leads to yet another tremendous simplification. We don't really need to visualize a complete lattice. Only one small portion of it, the **unit cell**, is sufficient.

Unit cell. Considering the above definition of a lattice in three-space, we can define a unit cell as follows:

A unit cell is a lattice cell defined by three unit lattice translation vectors.

The entire lattice can be formed by repetition of this unit cell. Some examples are shown in figure 1.3 for a two-dimensional lattice; the unit cells need be defined by only two unit translation vectors here since the lattice is two-dimensional.

Now it can be seen that even a consideration of the entire lattice is unnecessary since the whole of the lattice can be represented by one little box (in 3D)....the unit cell.

It should be obvious that since a lattice is infinite in extent there are an infinite number of choices of unit cells. Since there are so many choices of unit cell, which would be the best? When choosing a unit cell remember the following criteria:

a. A very small unit cell is desirable since the least amount of information is necessary to describe the contents of such a cell.

b. Whenever possible and reasonable, a cell with 90° angles (and in some cases 120°) should be chosen so that visualization and geometrical calculations are easier.

c. Choose a cell which reflects the symmetry of the lattice and the structure which it represents. In reality, this is the only real criterion for choosing the correct cell.

The shapes of unit cells in 2-D and 3-D must be parallelograms and parallelepipeds, respectively. Any polygons or polyhedra other than these will either result in open spaces between them or overlaps upon translation. Only these shapes can successfully "tile" a 2-D or 3-D space. In 2-D, for example, a triangle leaves holes in the tiling when translated, and a hexagon produces overlaps.

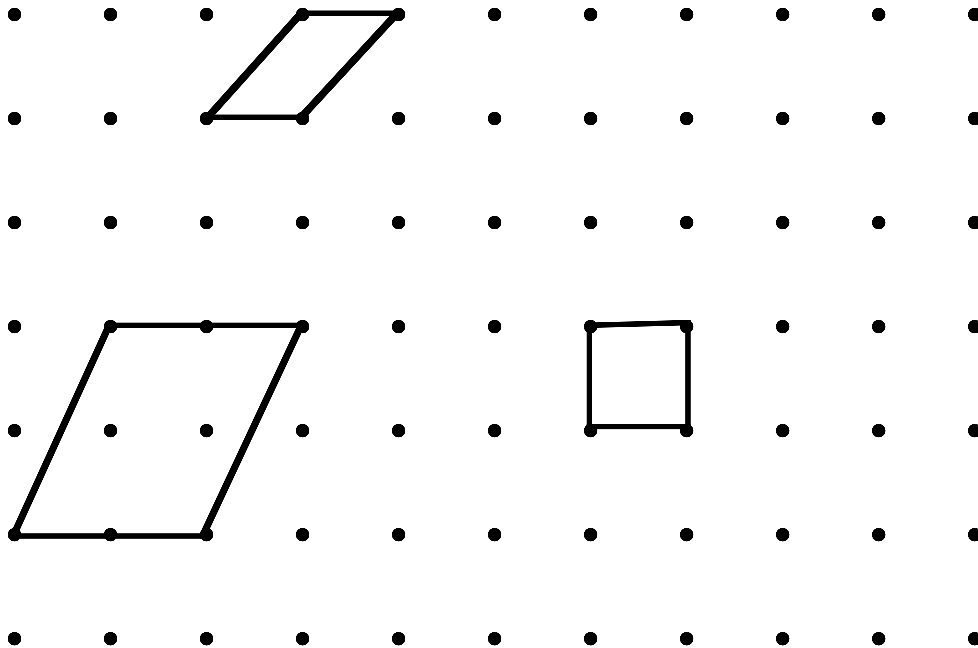


Figure 1.3. Some unit cells for a two-dimensional lattice.

C. Crystal systems. In crystallography, three-dimensional lattices are classified into seven crystal systems according to the shape of the unit cell that can be chosen for the lattice. These are listed in Table I; The column entitled Minimum Symmetry will be discussed in detail later, but is presented here in order to make the table complete. **The student will find it extremely beneficial to begin memorizing this table right away. This table will be used extensively throughout the course...even in the sections on microscopy.**

Table I. Characteristics of Crystal Systems

System	Interaxial Angles	Axes	Minimum Symmetry
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90°$	$a \neq b \neq c$	1 or $\bar{1}$
Monoclinic	$\alpha = \gamma = 90° \neq \beta$	$a \neq b \neq c$	2 or $\bar{2}$
Orthorhombic	$\alpha = \beta = \gamma = 90°$	$a \neq b \neq c$	three 2 or $\bar{2}$'s
Tetragonal	$\alpha = \beta = \gamma = 90°$	$a = b \neq c$	4 or $\bar{4}$
Cubic	$\alpha = \beta = \gamma = 90°$	$a = b = c$	four 3's or $\bar{3}$'s
Hexagonal	$\alpha = \beta = 90°, \gamma = 120°$	$a = b \neq c$	6 or $\bar{6}$
Trigonal	$\alpha = \beta = 90°, \gamma = 120°$	$a = b \neq c$	3 or $\bar{3}$

Crystal Symmetry:

Since the classification of three-dimensional lattices in crystal systems can also, as seen in Table I, be made according to the principal rotation axes present in the lattice, we now must discuss crystal symmetry.

A. Symmetry Elements. A symmetry element or symmetry operation is an operation which transforms a lattice or other point in the lattice into another point of like environment.

This is one of those apparently meaningless, formal definitions. Let's couch the definition in rather more familiar terms, which are actually more general:

A symmetry operation is something that can be done to an object, array, etc., which has the result that it appears that nothing was done.

The types of symmetry elements which are consistent with the periodic translations of a lattice are given in Table II.

Table II. Types of Symmetry Elements

	Element	Symbol
1.	Inversion	i
2.	Mirror	m
3.	Rotation	1, 2, 3, 4, 6
4.	Rotoinversion	$\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$
5.	Glide	(discussed in a
6.	Rototranslation	later section)

Note: the above definitions and discussion describe the symmetry observed for crystals and crystal lattices. In general, other symmetry elements, such as 5, 8, 10, 12, 16, do exist, but they do not conform to the translational requirements of a conventional lattice. Five-fold rotational symmetry, for example, is exhibited by a pentagon, a soccer ball, icosahedrally-shaped viruses, and many other shapes and objects. These types of symmetry axes do conform to periodic lattices in spaces of dimension higher than 3. The descriptions of such spaces are quite complicated, and are beyond the scope of this text. In what follows, we limit our considerations to lattices in 1, 2, and 3 dimensions.

B. The Stereographic Projection. Unfortunately, much of our intellectual world is, at the present time, flat. We get much of our information from the pages of a book, the TV or computer screen, paper, etc. Three-

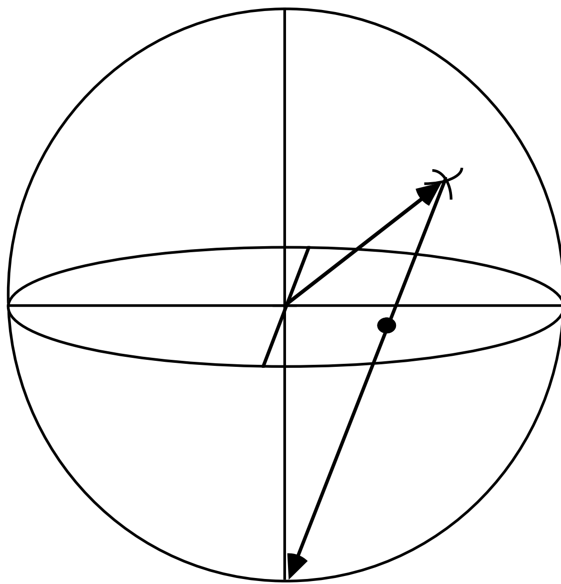
dimensional objects in these media are projected onto two-dimensions, and it is left to our minds to add depth to the projected images. We must also make projections in crystallography, but the usual type of projection, the stereographic projection, is constructed in a manner which is somewhat different from that to which you are probably accustomed. Our first use of stereographic projections will be to graphically represent symmetry operations and their results.

A stereographic projection is a means of showing a three-dimensional configuration in two-dimensions, and is drawn as described below.

Procedure

Refer to figure 1.4.

Draw a sphere and locate the north and south poles, and the equator. Place the object or configuration at the center of the sphere. For crystals, the symmetry elements and the poles of the crystal planes (the poles are the normals to the crystal planes; see the discussion on crystal planes below) are usually projected. The pole is extended from the center of the sphere to its surface. The resulting point on the surface, if in the northern hemisphere, is connected to the south pole with a line; where this line intersects the equatorial plane, a point is marked thus: • (If the point is in the southern hemisphere, the point is connected to the north pole and the projected point is shown as: 0.)



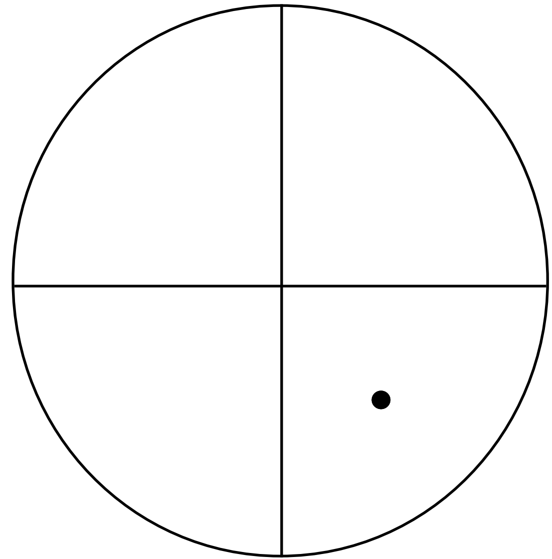


Figure 1.4. Procedure for drawing a stereographic projection. Only the projected point (right) for one pole (left) is shown.

Stereographic projections of various symmetry elements are shown in Figure 1.5 on the next page.

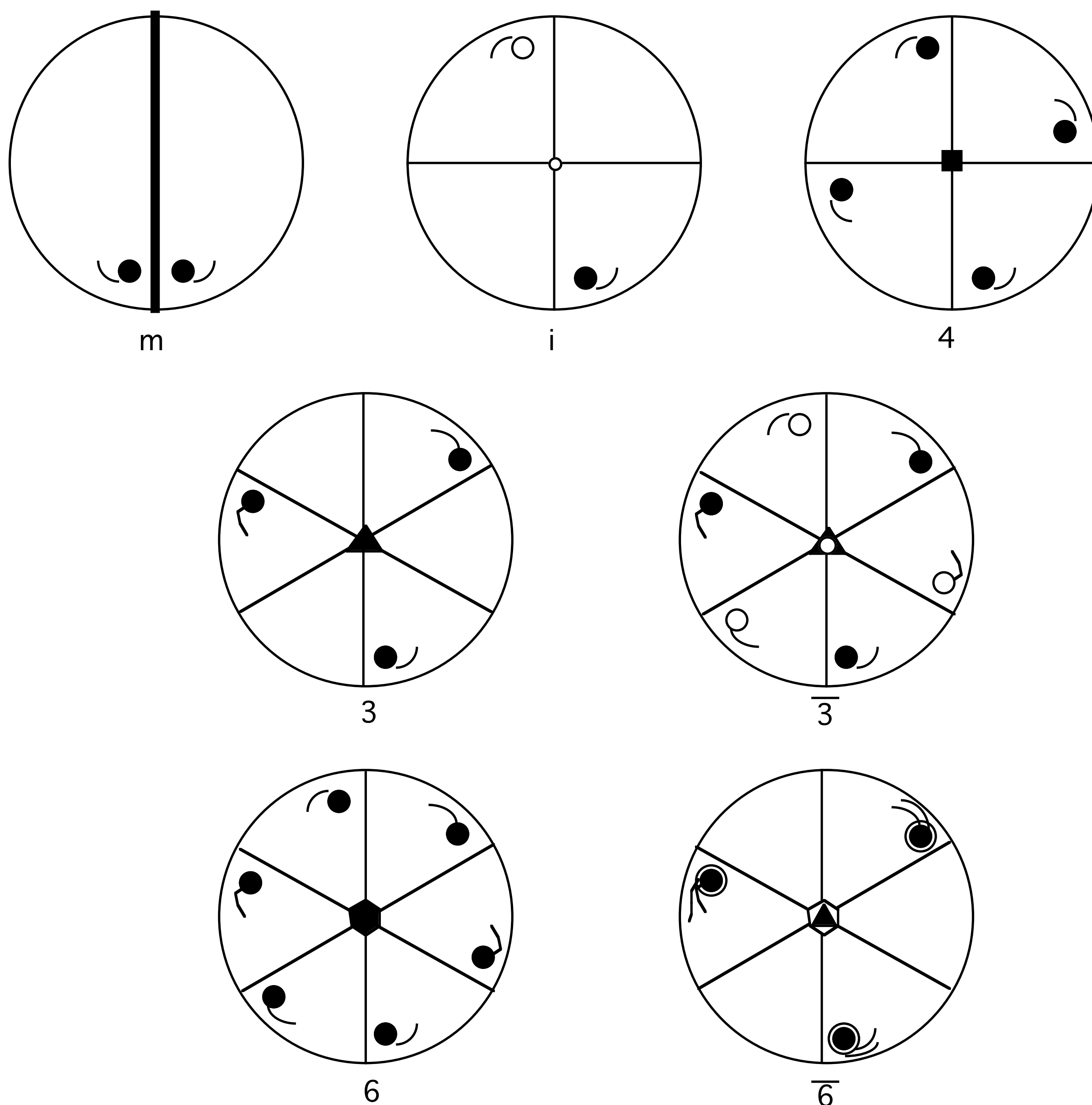


Figure 1.5. Stereographic projections of some symmetry operations. Both the equivalent points and the symmetry elements are shown on the same diagram to save space; however, they are conventionally shown in two separate diagrams. You should always present them as two separate diagrams.

Rotations which are 5-fold or greater than 6-fold are not valid symmetry operations for a lattice which is periodic in 3-dimensions.

C. Point Groups

Picture a cube. It is obvious that it has a four-fold rotation axis (4) because it can be rotated about an axis through its center into four "identical" positions in 360°. However, there is more than one such 4. In fact, there are three, all mutually perpendicular. Continued inspection of the cube shows that there are also 2's, 3's, and m's, all oriented in specific directions. Thus, we see that objects generally do not exhibit only one operation which describes its symmetry, but, in fact, the point symmetry elements listed in Table II can be

combined in specific ways to describe the symmetry of any object....or crystal structure. These combinations are called (crystal) classes or point groups.

There are 32 unique combinations possible, and each of these point groups describes all the symmetry around a point in the lattice for a particular crystal structure. The nomenclature for describing the point groups is given according to Table III; listed there are the crystallographic directions (described below) down which the various symmetry elements can be found. **This table should also be memorized as soon as possible.**

Table III. Point Group Nomenclature (Hermann-Mauguin system). The (usually) three symmetry symbols for a point group represent the symmetry observed down the various crystallographic directions listed for each crystal system.

System	1st symbol	2nd symbol	3rd symbol
Triclinic	–	–	–
Monoclinic	[010]	–	–
Orthorhombic	[100]	[010]	[001]
Tetragonal	[001]	[100]	[110]
Cubic	[100]	[111]	[110]
Hexagonal	[001]	[100]	[210]
Trigonal	[001]	[100]	[210]

D. Lattice Directions

A lattice or crystallographic direction is given by the whole number components of the direction vector:

$$\underset{\sim}{D} = u\underset{\sim}{a} + v\underset{\sim}{b} + w\underset{\sim}{c}$$

where a, b, c, are the unit cell vectors. The direction is noted as [uvw]. See Figure 1.6 for an example.

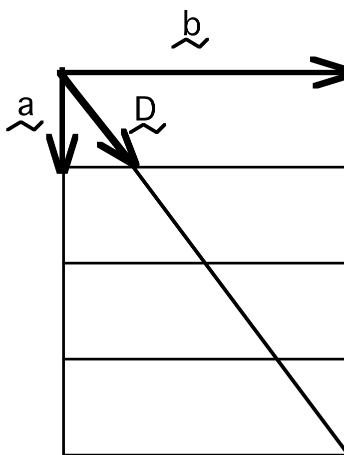


Figure 1.6. The rational direction [410] shown in relation to four orthorhombic unit cells.

{uvw} denotes a family of directions, which consists of all symmetry equivalent planes. The planes which are included in a family of directions thus depends upon the crystal system in question. For example, {110} for cubic consists of:

[110], [101], [011], [$\bar{1}$10], [1$\bar{1}$0], [$\bar{1}\bar{1}$0], [$\bar{1}$01], [10$\bar{1}$], [$\bar{1}$0$\bar{1}$], [0$\bar{1}$1], [01$\bar{1}$], [0$\bar{1}\bar{1}$]

while for orthorhombic {110} represents only:

[110], [$\bar{1}$10], [1$\bar{1}$0], [$\bar{1}\bar{1}$0].

Some very important directions in cubic are (see figure 1.7):

{100} - cube edges
{111} - cube body diagonals
{110} - cube face diagonals

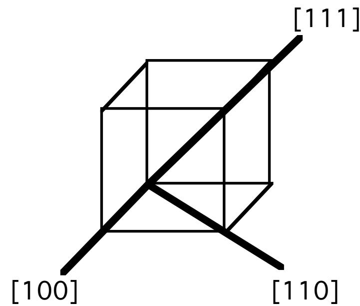


Figure 1.7. Principal directions in cubic

<u>E. Lattice planes</u>: This seems like a good point at which to introduce another very important nomenclature system. In crystallography it is very frequently useful, and for x-ray diffraction absolutely essential, to think of planes in a lattice.

A set of planes in a crystal lattice consists of an infinite number of parallel planes in a particular orientation. These sets of planes are designated by a set of three integers (hkl) known as Miller indices. The recipe for finding the (hkl) for a particular set of planes in a lattice follows:

1. Draw the lattice, designate an origin, and draw a right-handed set of basis vectors.
2. Draw a number of the members of the set of planes in question.
3. Pick the plane closest to the origin and determine its fractional intercepts on each of the three crystallographic axes (the basis vectors).
4. The reciprocals of these intercepts are h, k, and l.

Each set of planes has a unique interplanar distance, denoted d_{hkl}. d_{hkl} can be easily calculated from the lattice parameters; the equations used are, however, different for each crystal system.

<u>Families of planes</u> or planes of the same form, {hkl}, consist of all those planes, including negatives, that are related by symmetry, and have h, k, and l's which are negatives and/or permutations of one another. As in crystal directions, the planes included in a family depends upon the crystal system. For example, in cubic {100} represents:

(100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), (00$\bar{1}$)

whereas in orthorhombic it consists of only:

(100) and ($\bar{1}$00).

<u>Hexagonal-trigonal indices.</u> From time to time, a set of four indices (hkil) will be encountered for denoting planes in a hexagonal or trigonal lattice. Here, h, k, and l are derived from the intercepts on the $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$ axes, as expected, and i is derived from the intercept along an $\mathbf{a}_3$ axis where $\mathbf{a}_3 = -(\mathbf{a}_1 + \mathbf{a}_2)$. Since i = -

(h + k) always, and is therefore redundant, it will not be used here. Thus, three indices (hkl) will be used for all crystal systems, including hexagonal and trigonal.

Planes in centered lattices

For centered lattices, certain sets of planes do not exist. These are determined by so-called extinction rules, like:

P: no extinctions
I : $h + k + l \neq 2n$ are extinct
F: h,k,l mixed with respect to evenness or oddness are extinct

An infinite number of sets of planes can be passed through all the points of a lattice. These sets of planes are designated by Miller indices (hkl), where h, k, l are the whole number reciprocals of the intersections of the planes with the unit cell axes.

intercepts: 1/2, 1, ∞

(planes and c-axis are parallel, and perpendicular to the paper)

Miller indices: (210)

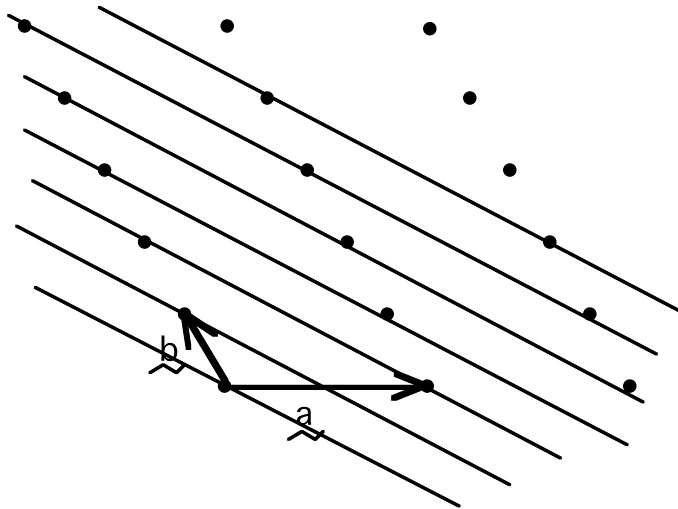


Figure 1.8. The set of planes whose Miller indices are (210). Note that there are really an infinite number of member planes in the set.

Back to point groups now.

Example: Consider the point group $\frac{4}{m}\frac{2}{m}\frac{2}{m}$ (also denoted D_{4h}) . This, according to Table I, must belong to the tetragonal system, since there is a 4-fold axis. According to Table III, we look down the following directions to see the symmetry indicated:

[001] - $\frac{4}{m}$ (4-fold rotation axis perpendicular to mirror)

[100] - $\frac{2}{m}$ (2-fold rotation axis perpendicular to mirror)

[110] - $\frac{2}{m}$ (2-fold rotation axis perpendicular to mirror)

Note that the notation $\frac{n}{m}$ means an n-fold rotation axis perpendicular to a mirror. The resulting stereographic projection is shown in Figure 7.

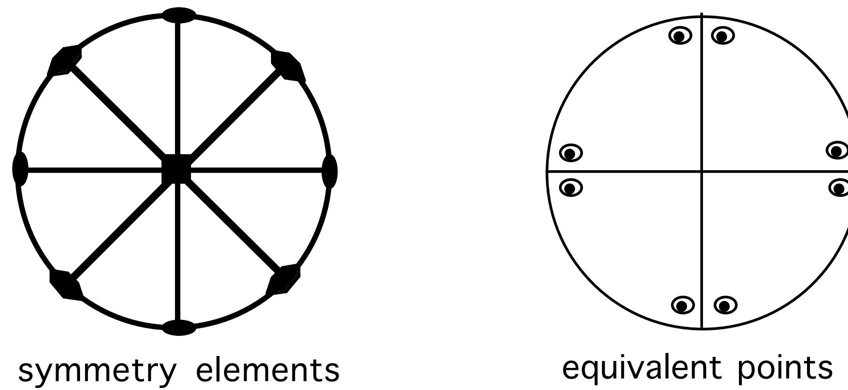


Figure 1.9. Stereographic Projections for the point group $\frac{4}{m}\frac{2}{m}\frac{2}{m}$.

A detailed study of the ways in which symmetry elements can be combined shows that the combinations are specific and limited. As stated before, there are only 32 possibilities, listed below.

The 32 point groups

System	**Groups**
triclinic	1, i
monoclinic	2, m, $\frac{2}{m}$
orthorhombic	222, mm2, $\frac{222}{mmm}$
tetragonal	4, $\bar{4}$, $\frac{4}{m}$, 422, 4mm, $\bar{4}$ 2m, $\frac{422}{mmm}$
cubic	23, $\frac{2}{m}\bar{3}$, 432, $\bar{4}$ 3m, $\frac{4}{m}\bar{3}\frac{2}{m}$
trigonal	3, $\bar{3}$, 32, 3m, $\bar{3}\frac{2}{m}$
hexagonal	6, $\bar{6}$, $\frac{6}{m}$, 622, 6mm, $\bar{6}$ 2m, $\frac{622}{mmm}$

G. <u>Bravais Lattices</u>. We have up to now considered only point symmetry operations and must now consider the types of translations which can occur in a lattice.

1. The 14 Bravais lattices. A unit cell for a particular lattice can be chosen in many ways. See Figure 1.10.

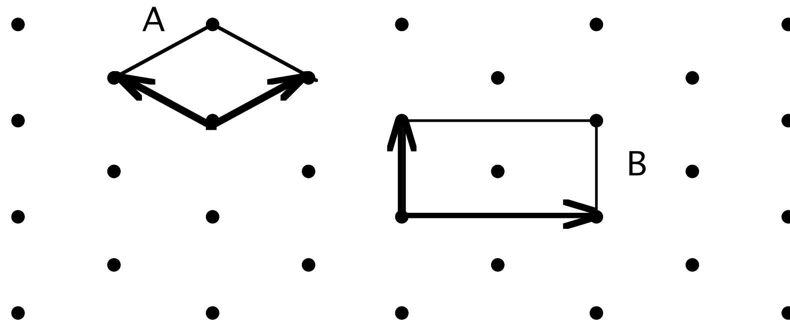


Figure 1.10. Choosing a unit cell.

In Figure 1.10, if cell A is chosen, we have picked a primitive unit cell. A primitive unit cell has no internal lattice points. However, the choice of the "centered" cell B may have several advantages:

(1) Orthogonal axes.

(2) The cell may belong to a higher symmetry class.

See Figure 1.11, where an oblique primitive cell picked in a body-centered cubic lattice is shown by light lines. This cell choice does not display the full symmetry of the lattice.

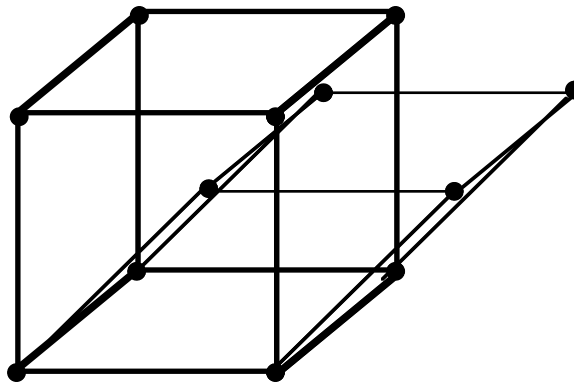


Figure 1.11. Primitive and body-centered cells for the same lattice.

The possible types of cells which can be chosen are given in Table IV.

Table IV. Centering Types.

Primitive - P
End-centered - A, B, or C
Body-centered - I
Face-centered - F
Rhombohedral - R

The types of lattices which each crystal system can have are listed in Table V. These are called Bravais lattices.

Table V. Bravais Lattices.

System	Bravais Lattice
Triclinic	P triclinic
Monoclinic	P monoclinic, I monoclinic
Orthorhombic	P orthorhombic, I orthorhombic A orthorhombic, F orthorhombic
Tetragonal	P tetragonal, I tetragonal
Cubic	P cubic, I cubic, F cubic
Hexagonal	P hexagonal
Trigonal	R rhombohedral

All the lattice types shown in Table IV do not occur for all systems because:

(1) Some are equivalent within the **same crystal system** by rechoice of unit cell.
(2) Some are eliminated by the symmetry requirements of the crystal system.

These two points are illustrated in Figures 1.12 and 1.13. In figure 1.12, we see that an A centered monoclinic cell is equivalent to an I centered cell in the same crystal system (monoclinic). In figure 1.13, we see that the 3-fold symmetry is no longer present when a point is placed at the center of the C face of a cubic unit cell. In this case, as in all others, it would be possible to rechoose the cell so that it is primitive, but the new cell would no longer have a cubic shape.

The best procedure, when examining combinations of centering types with crystal systems, is to check first to see that the symmetry requirements of the crystal system are met. If so, then try to rechoose the cell within the same crystal system.

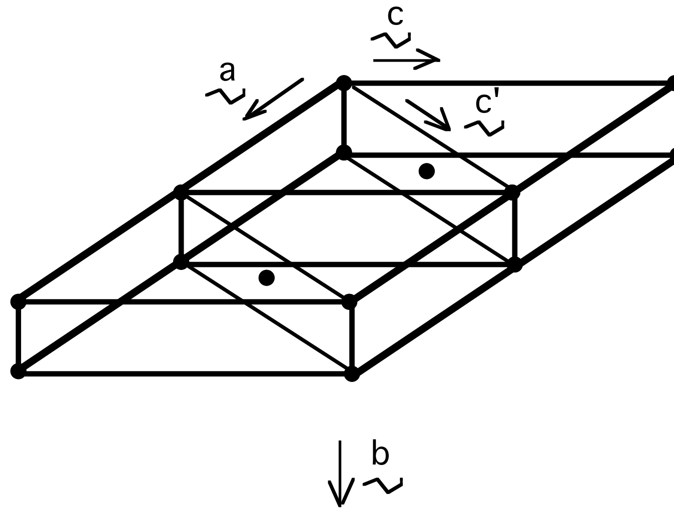


Figure 1.12. Equivalence of A monoclinic and I monoclinic cells.

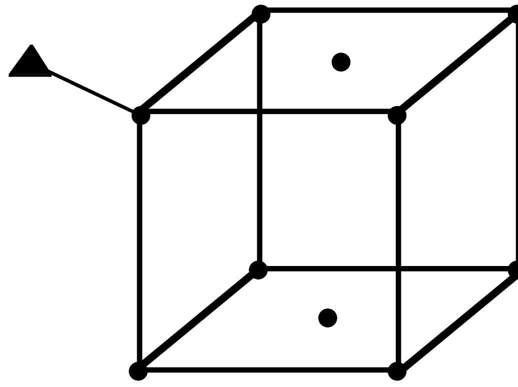


Figure 1.13. Elimination of end-centering in the cubic system.

H. Glide planes .

A glide operation is a combination of a translation and a reflection. See Figure 1.14.

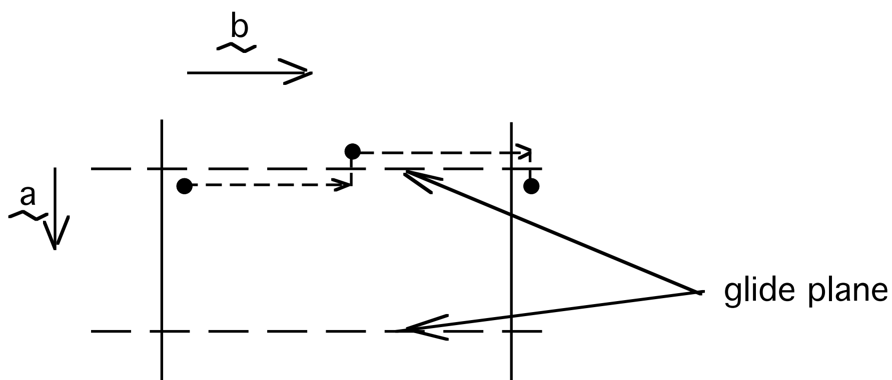


Figure 1.14. b-glide

Note that only a translation of b/2 is possible, since b/3, b/5, etc., translations would not result in the same pattern for each lattice point (the lattice points are not shown in Figure 1.14, but are located at the intersections of the solid lines with the upper long dashed line), and b/4, b/6, etc., translations would generate new lattice points at b/2, b/3, etc., respectively.

A convention on directions and type of glide (a, b, c, n, d) is required so that the orientation of the glide plane and the direction of the glide translation are specified. For Figure 1.14, we say that this is a b-glide with the glide plane perpendicular to the a axis, or a b-glide in the c-direction.

I. Screw axes

A screw operation is a combination of a rotation and a translation. See Figure 1.15.

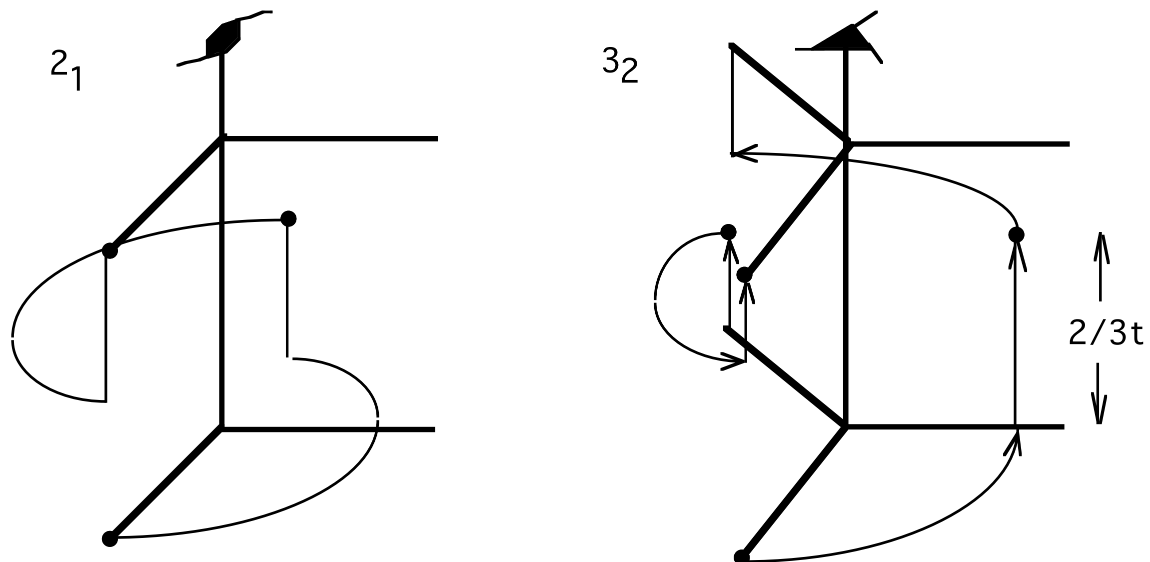


Figure 1.15. 2_1 and 3_2 screw axes.

For the notation n_m, the subscript m indicates the amount of translation after (or before) a rotation of $2\pi/n$, according to the relation:

$$\tau = \frac{m}{n} t$$

These are the only possible translations for a screw axis which are consistent with lattice periodicity requirements.

The 230 Three-dimensional Space Groups:

By extending the 32 point symmetry groups with the translational operations, i.e., the 14 Bravais lattices and the various glide planes and screw axes, it is possible to derive only 230 unique three-dimensional symmetry groups known as space groups. The characteristics and drawings for the 230 3-dimensional space groups are given in International Tables for X-ray Crystallography, Vol 1 or Vol A. The symmetry of the crystal structure of any crystalline substance must be described completely by one and only one of these space groups. Examples are:

$P2_12_12_1$
P4cc
$P\bar{3}m$
$P\bar{4}3m$

The nomenclature for these space groups is the same as for the point groups (see Table III) except that the symbol for the lattice centering precedes the other symbols.

The drawings which represent the space groups are projections like those for the point groups, but they are orthographic projections, not stereographic projections. In these projections, the cell origin is in the upper left, the **a** axis is drawn downwards, and the **b** axis is drawn horizontal to the right; the **c** axis comes out of the page or screen. The rotation axis and mirror plane symbols are different from those used in the point group diagrams when they lie in the plane of the projection. New symbols are introduced for glide planes and screw axes.

As an example of the use of space groups and equipoints (explained below), consider the example of the structure description of the compound $HoZn_2$: Imma with a = 4.456, b = 7.039, c = 7.641 Å, and Ho in 4e, z = 0.5281, and Zn in 8h, y = 0.0410, z = 0.1663. Imma can be dissected as: I-centering + orthorhombic (from the point group mmm, which changes to mma through the addition of a translational operation known as a glide plane). Imma is looked up in the Tables, and it is found that 4e is (0 1/4 z).......... and 8h is (0yz)..........., plus body-centering. Since the values of z, and y,z are given, a plot or model of the structure can now be constructed, from which any number of crystal chemical calculations and considerations can be made.

Constructing a plot or model of this or any structure is really no more complicated than plotting (x,y,z) points on a three-dimensional axis system.

A. Atom Positions

We have discussed lattice types and point symmetries; the object of those discussions is to point out that, when building a model of a particular crystal structure, the positions of atoms placed in a unit cell of a lattice are entirely dependent upon the lattice type and point symmetry which describe that structure.

1. A lattice point is a hypothetical thing. We are actually interested in some grouping of atoms which can be associated with a lattice point. A real crystal, then, actually consists of a configuration created by the repetition of this group or "pattern"; the lattice can be superimposed on this configuration (or vice versa) so that each pattern belongs to a lattice point.

A particular atom placed in a unit cell has a certain relation to the lattice point(s) of the cell. It may be located at the lattice points or at some distance from it. Referred to the cell origin, its position is given by the fractional coordinates (x, y, z). For example, in Figure 1.16, atoms, if placed on the lattice points, would have the positional coordinates:

(000) (1/2,1/2,0) (1/2,0,1/2) (0,1/2,1/2)

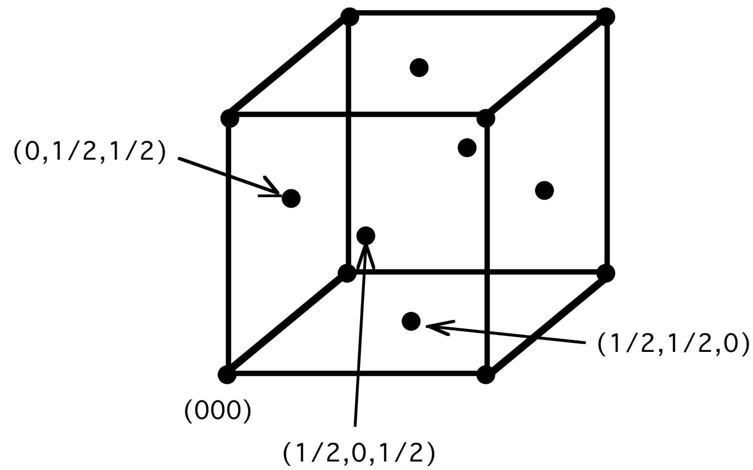


Figure 1.16. One set of atom positions in an F cell.

2. A particularly simple example is the space group P222 (P orthorhombic), which is presented in figure 1.17. As with point groups, there is a symmetry diagram and an equivalent points diagram. The coordinates of the equivalent points are (xyz), $(\bar{x}\bar{y}z)$ $(x\bar{y}\bar{z})$, and $(\bar{x}y\bar{z})$. This set of positions is known as an equipoint - a set of symmetry-related positions - and is denoted as 4u, where 4 indicates the number of positions in the equipoint, and u is an arbitrary letter designation peculiar to the space group P222. 4u is the most general equipoint in this space group, but there are others, such as the one-fold special position 1a (000) (the most special equipoint), 2i (x00) and $(\bar{x}00)$, 2r (1/2 0 z) and $(1/2\ 0\ \bar{z})$, etc. In general, if an atom is placed in one position of an equipoint, it must be also placed in all the other positions. If we choose to place atoms in the general position (x, y, z) in, for example, the space group P222, we can see from the space group diagrams how the symmetry controls the atom positions. All of the equipoints for the space group P222, and for the other 229 space groups, are listed in International Tables for X-ray Crystallography, Vol. I, and in the recently updated Vol. A.

P222 means:

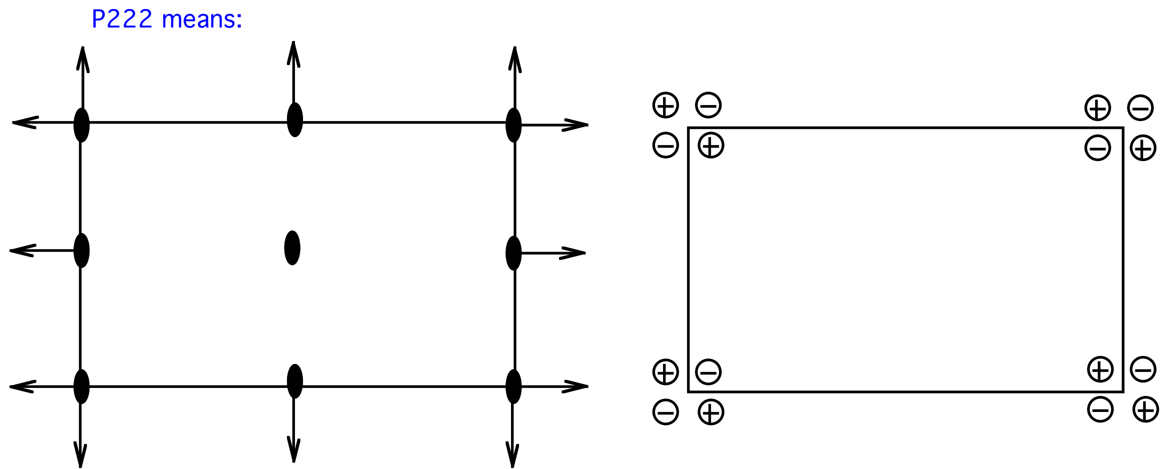


Figure 1.17. Symmetry elements and equivalent positions (for the most general equipoint) in P222.

Point and Space Group Nomenclature:

Question: How are mirrors oriented?

1. First note that m = $\bar{2}$ as shown below.

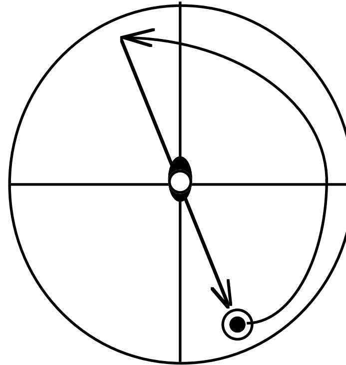


Figure 1.18.

A two-fold rotation followed by an inversion gives rise to a mirror perpendicular to the $\bar{2}$ axis.

2. In point group symbols, there are three possibilities for two-fold axes, viz., (1) a 2 exists, (2) a $\bar{2}$ exists, and (3) both 2 and $\bar{2}$ exist down a particular direction.

3. The first possibility has already been explained.

4. The second possibility is the $\bar{2}$ or mirror. To get the orientation of the mirror in a point group diagram:

a. Replace each symbol m by $\bar{2}$ in the point group.

b. Draw the symmetry elements and equivalent points in the usual manner.

Example: m = $\bar{2}$ (monoclinic-second setting)

The b axis has $\bar{2}$ symmetry.

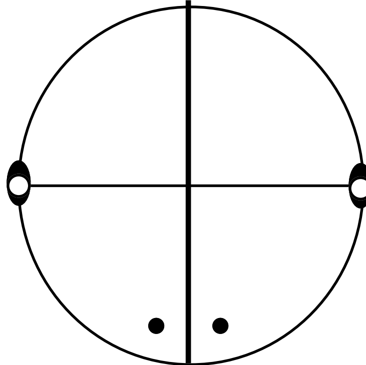


Figure 1.19.

Thus, the a - c plane is a mirror plane.

5. The third possibility, both 2 and $\bar{2}$, is written 2/ $\bar{2}$ or 2/m. The procedure is the same as in part 4 above.

Example: 2/m = 2/ $\bar{2}$ (monoclinic - second setting)

The b axis has 2 and $\bar{2}$ symmetry.

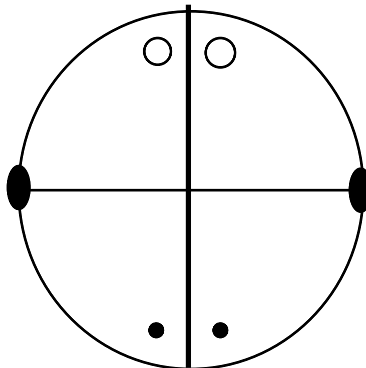


Figure 1.20.

Again, the a - c plane is the mirror plane, but in this case, there is a 2-fold axis perpendicular to it.

Some Miscellaneous Comments:

A. Plane normals

Plane normals are useful in stereographic projections. Note, however, that the plane normals are not the same as crystallographic directions. These are only equivalent for the cubic crystal system. Crystallographic directions [uvw] are rational directions, i. e., directions along lines which must pass through at least two lattice points.

B. Zones

Any two planes intersect along a line which is called a zone axis. A number of planes may have the same zone axis, which means that each plane is parallel to the same line. The zone axis [uvw] is calculated as ui + vj + wk from:

$$\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \end{vmatrix}$$

A plane (hkl) belongs to the zone [uvw] if hu + kv + lw = 0. If (h_1 k_1 l_1) and (h_2 k_2 l_2) are in the same zone then (h_1+h_2 k_1+k_2 l_1+l_2) is also in the same zone.

C. Stereographic projections

The purpose of the stereographic projection is to describe a 3-D object, array, etc. in two dimensions such that quantitative measurements of solid angles can be made from the projection. Plane normals (poles) are usually plotted in crystallography. The object to be described is placed at the center of a sphere in the desired orientation. The poles are extended until they hit the sphere. Then a line is drawn from each point where a pole hits the sphere to the south (or north) pole. Where these lines pass through the equatorial plane, the projected points are marked.

D. Symmetry stereograms

The stereographic projection can be used to describe symmetry operations about a point. For each separate set of operations (a point group), two stereographic projections are given - one which shows the symbols for the symmetry operations, and one which shows the equivalent points.

The diagrams for the 32 point groups are given in the International Tables; both proper and improper rotations, the mirror operation, and combinations of all of these are shown.

II. THE PRODUCTION AND PROPERTIES OF X-RAYS

X-rays were discovered by W. Rö ntgen in Würzburg, Germany, in 1895. The modern x-ray tube, a diagram of which is shown in figure 2.1, operates in the same manner as the one that Rö ntgen used. Electrons are "boiled" off of a heated thoriated tungsten filament and accelerated toward a target or anode where the x-rays are produced. The Coolidge-type x-ray tube is sealed and operates under a relatively high vacuum. The focusing cup, held at a negative potential, helps to direct the electrons toward the anode. To adjust the x-ray beam intensity, the tube current and/or the tube voltage can be changed, but the IV power is limited because of the extensive heat development in the target material. About 99% of the energy input is converted to heat. As a result, the anode must be water-cooled. The energy of the electrons as they hit the target is given by $eV = hc/\lambda$ because of their dual wave-particle nature. $\lambda = hc/eV = 12.4/V$ (V in kV and λ in Å).

The region on the target where the electrons hit and the x-rays are produced is "viewed" at a small angle through a Be window by an x-ray diffraction instrument. This "take-off angle" is measured relative to the surface of the anode and is typically 2-6°. While it is possible to get more intense x-ray beams at higher take-off angles, there is generally a loss in resolution since the larger cross-sectional area of the beam viewed permits greater crossover of the rays of x-radiation.

Since the filament is linear in shape, the "focal spot" on the anode, the area bombarded by the electrons, is roughly a long and very narrow rectangle. Thus, since the take-off angle is low, the focal spot will appear to be a line or a spot, depending upon whether the view direction is perpendicular or parallel, respectively, to the line of the filament.

White or continuous radiation:

White or continuous radiation is produced by the deceleration of electrons as they hit the target. (Decelerating charged particles give up their energy in the form of radiation.) This radiation is also called Bremstrahlung or "braking" radiation. A spectrum of continuous radiation is obtained since the electrons can exchange any or all of their energy upon interaction with the atoms in the target. The shortest wavelength (λ_{SWL}) in the spectrum arises from an exchange of all the energy of an electron, which is a function of the applied voltage. The total intensity of the continuous radiation is $I_{conts} = AiZV{\sim}^{2}$, where A is a constant, i is the tube current, and Z is the atomic number of the target. There is only one common technique that specifically employs this type of radiation - the Laue technique for single crystals; an x-ray tube with a target of high atomic number is generally used for Laue photographs.

Characteristic radiation:

Characteristic radiation is produced through the ejection, upon collision, of an electron from one of the energy levels of the atoms of the target material; the x-rays are produced when the empty level is filled again by a transition of an electron from a higher level to the empty level. (Decelerating charged particles give up their energy in the form of radiation.) This type of radiation is characteristic of the target material. Different target materials give off characteristic x-rays of different wavelengths according to Moseley's law - $\sqrt{\nu} = C(Z - \sigma)$,

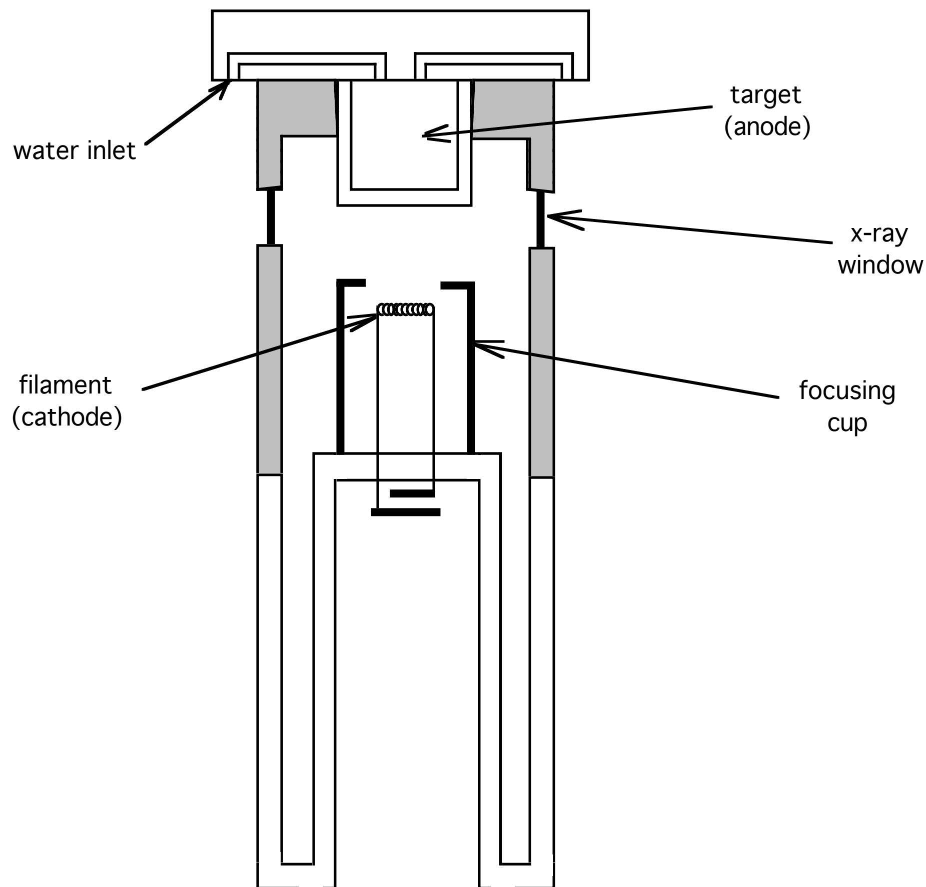


Figure 2.1. Coolidge type sealed x–ray tube

Target	Atomic No.	Wavelength for Kα (Å)
Cr	24	2.29100
Fe	26	1.937355
Cu	29	1.541838
Mo	42	0.710730

where C and σ are constants. Transitions that terminate on the K level (and in a few cases the L levels) give rise to x-rays with wavelengths in the useful range of about 0.5-5 Å. There are two L→K transitions (which give $K\alpha_1$ and $K\alpha_2$ x-rays) and one M→K transition (which gives Kβ x-rays) allowed transitions which are important. $I_{\alpha_1} = 2I_{\alpha_2}$ and $I_\beta \approx 0.2I_{\alpha_1}$.

The wavelengths of the $K\alpha_1$ and $K\alpha_2$ x-rays are so close together that they are frequently not very well resolved in the peaks in x-ray diffraction patterns, and therefore, to interpret such measurements, a weighted average of the wavelengths ($\lambda_\alpha = (2\lambda_{\alpha_1} + \lambda_{\alpha_2})/3$) is used.

A minimum voltage ($V_{crit} = 12.4/\lambda_K$, where λ_K is the wavelength of the "K edge", defined later) on the x-ray tube is required in order to obtain emission of the characteristic radiation since the incoming electrons must have an energy great enough to eject the electrons from the atoms of the target material. For example, to calculate the minimum voltage at which a copper target x-ray tube must be operated in order to produce the characteristic x-rays for copper, we look up the K edge for copper and calculate:

$$\frac{12.4\ \text{Å/kV}}{1.38\ \text{Å}} = 8.99\ \text{kV}.$$

The intensity of the characteristic radiation is given by $I_{char} = Ai(V-V_{crit})^{\sim 1.5}$. This equation shows that the intensity of the characteristic radiation at $V \leq V_{crit}$ is zero, and that it increases as V increases above V_{crit}.

The characteristic and continuous spectra superimpose upon one another, and the resulting wavelength distribution is what the sample usually sees.

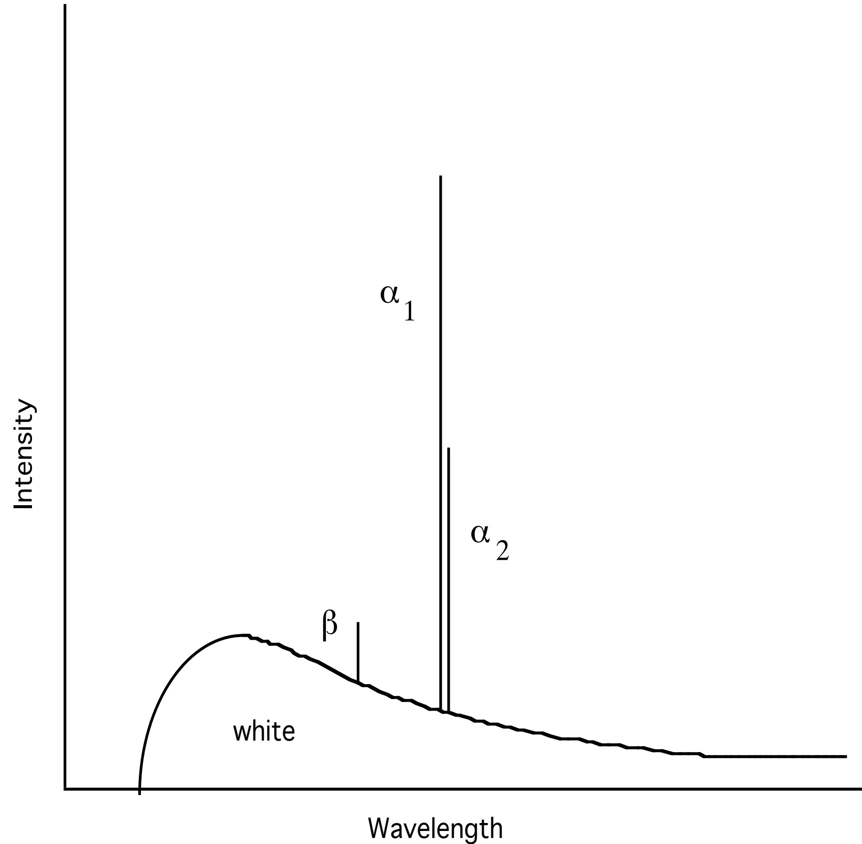


Figure 2.2. Typical x-ray spectrum from a standard x-ray source.

Absorption

Absorption coefficients

X-rays interact with a material by transmission, scattering or diffraction, and absorption. The effect of absorption is to decrease the intensity of the transmitted x-ray beam as it travels through the absorbing medium. The equation which describes this effect is $I/I_o = e^{-\mu^* x}$, where I is the intensity at point x along the path of the beam, I_o is intensity of the incident beam, and μ^* is the linear absorption coefficient. It is also common to use the mass absorption coefficient μ^*/ρ $(=\mu)$, where ρ is the density, to characterize the absorption of a material. Values of μ^*/ρ for the elements are tabulated in International Tables, Volume III. The absorption coefficients for compounds or mixtures must be calculated from these values. The procedure for the calculation of μ^*/ρ for a compound or mixture is to sum up the products of the weight fraction and μ^*/ρ for each atomic species. For example, we can calculate the mass absorption coefficient μ for $NiSO_4$ as follows:

$NiSO_4$........μ's: 45.7, 89.1, 11.5, resp., for $Cu_{K\alpha}$ radiation; AW's: 58.69, 32.064, 16, resp.

Example calculation for ZnS for $Cu_{K\alpha}$ and $Mo_{K\alpha}$ radiations:

$$\mu_{compd} = \Sigma \text{ (wt. fraction)}_{element} \times \mu_{element}$$

	Atomic weight	Weight fraction	μ ($Cu_{K\alpha}$)	μ ($Mo_{K\alpha}$)	$\mu_{ZnS}(Cu_{K\alpha})$	$\mu_{ZnS}(Mo_{K\alpha})$
Zn	65.38	0.671	59.51	55.46	70.37 cm^2/gm	40.38 cm^2/gm
S	32.064	0.329	92.53	9.625		

The linear absorption coefficient μ^* for a mixture can be calculated only if the density of the compound or mixture is known.

Note: recently, the IUPAC decided that μ^* = linear absorption coefficient and μ = mass absorption coefficient......this is just the opposite of what you will find in most texts and handbooks printed up to about 1987. We will use the IUPAC convention.

Through an examination of the dependence of the mass absorption coefficient for an element upon the x-ray wavelength λ, it is possible to discover several important trends.

$$\mu = \mu^*/\rho = k\lambda^3 Z^3$$

K is a constant, and Z is the atomic number of the absorbing element. μ increases with the radiation wavelength and the atomic number of the absorbing material.

One example of the use of this equation for μ^*/ρ is the determination of the best material to use for windows in x-ray tubes. The absorption by the window material should be extremely low, and thus an element with a very small atomic number is best. Beryllium is the metal used.

The absorption edge

When the energy of the incident x-rays becomes sufficiently large (wavelength sufficiently small) to eject the electrons in the K level in the sample, the mass absorption coefficient rises dramatically. This value of the x- ray wavelength is called the K absorption edge. At energies higher than that corresponding to the absorption edge, the mass absorption coefficient decreases again because of the "red rover effect". See the absorption curve in Figure 2.3.

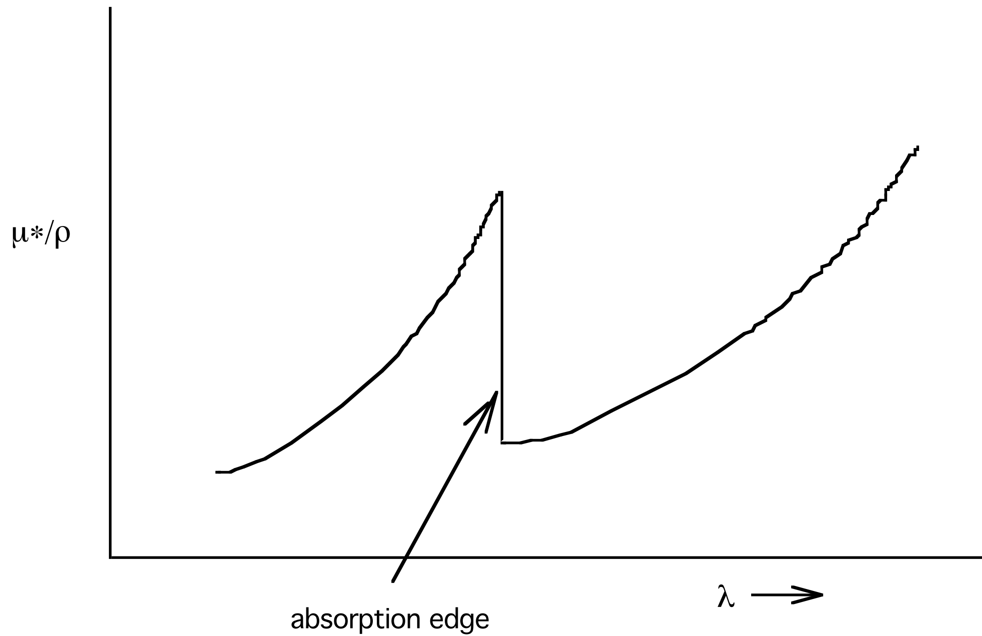


Figure 2.3. The variation of the mass absorption coefficient with radiation wavelength.

What happens to the absorbed energy? The vacant energy levels are quickly filled with electrons from higher energy levels, resulting in the emission of x-radiation which is characteristic of that atom. This emitted radiation is called fluorescence. It does not have the same wavelength as the radiation incident on the sample, and it is emitted from the sample in all directions. It will be detected in a diffraction measurement at all diffraction angles. For this reason, fluorescent radiation can make a significant contribution to the background of a diffraction pattern and therefore may cause serious problems in diffraction studies.

A particularly common example in which this effect is very noxious is the study of iron-bearing materials with Cu x-radiation. Figure 2.4 shows the reason. The absorption edge for iron atoms is at a wavelength which is somewhat larger than that of the incident CuKα radiation. There is considerable absorption of the incident radiation by the iron atoms, with the subsequent formation of extensive FeK fluorescent radiation. This fluorescence significantly increases the background levels for the diffraction pattern, and in some cases has been observed to completely "swamp out" the diffraction peaks or reflections. FeKα radiation, however, has a wavelength which is above the wavelength value of the iron absorption edge; if used to obtain diffraction patterns from an iron-bearing sample, very little fluorescence from the iron atoms in the sample is observed.

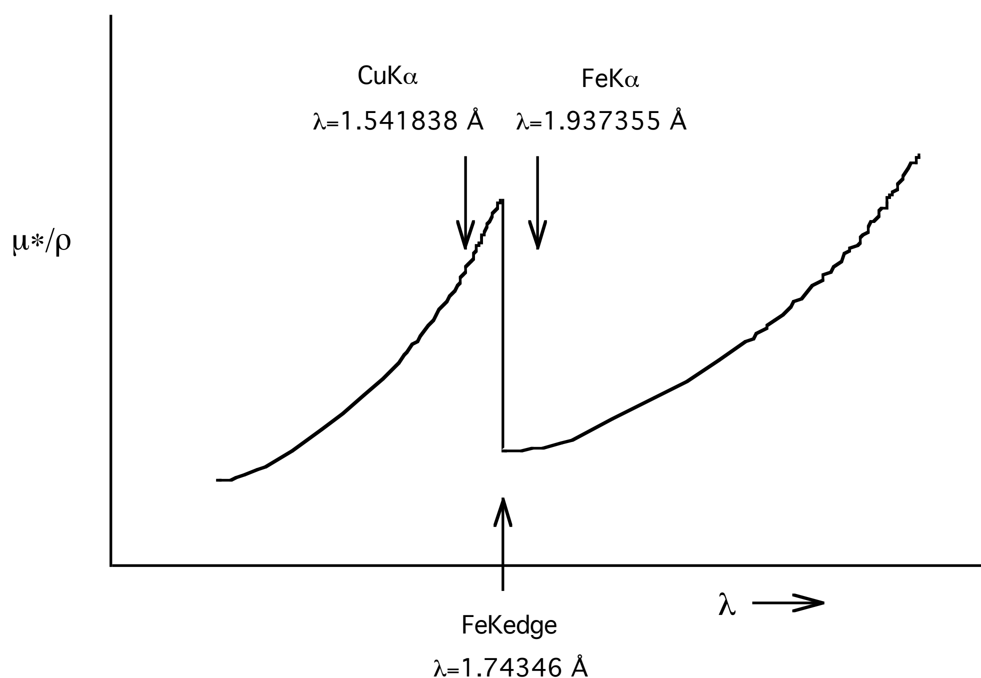


Figure 2.3. Choice of x-radiation for diffraction samples containing iron.

The use of a diffracted beam monochromator (described later) also solves the fluorescence problem. However, when such a device is not used, the absorption edges for all of the known atomic species in the sample should be examined to determine what type of x-ray tube would be the best to use to obtain the diffraction patterns with the least amount of fluorescence.

On the other hand, fluorescence is used as the basis for a very popular analytical tool for chemical analysis - the x-ray fluorescence spectrometer.

β filters

We can make use of this differential absorption character of materials. Remember that the characteristic radiation coming from x-ray tube has both β and α components. The presence of the Kβ radiation in the x-ray beam incident on the sample being studied by x-ray diffraction complicates the interpretation of the resulting diffraction pattern considerably. Each set of planes gives two diffraction maxima, one corresponding to the β component and one corresponding to the α component of the incident radiation. When interpreting such a diffractogram, it is necessary to determine which peaks arose due to the β radiation and which are due to the α radiation, often a laborious task. The β component of the radiation can be almost completely removed through the use of a so-called β filter. This β filter is composed of a material whose K absorption edge lies between the Kα and Kβ wavelengths of the x-rays coming from the x-ray tube. The Kα x-rays are reduced in intensity by a factor of about 2. It is a simple matter to choose an appropriate β filter: use tables of x-ray wavelengths and absorption edges to locate the element with a value of the absorption edge between the β and α wavelengths. Also, there is a rule of thumb: for a β filter, use a material whose atomic number is one or two less than the atomic number of the target material.

The filter can be placed anywhere in the incident or diffracted beam paths; most commonly, a β filter is placed before the collimator (in the incident beam) of a camera device, and near the receiving slits (in the diffracted beam) in a counter device. β filters are rarely used in present-day powder x-ray diffractometers since other diffracted beam devices have been developed which not only reduce the intensity of the β radiation reflections to essentially zero, but also discriminate against any fluorescence radiation coming from the sample. These are discussed in the chapter on instrumentation. However, in camera instruments, incident beam β filters are almost always employed.

III. X-RAY DIFFRACTION

The diffraction of x-rays by crystals was first demonstrated by Max von Laue at the University of München in Germany in 1912. A single crystal of $CuSO_4$ was placed in an x-ray beam and diffraction patterns were recorded on flat films placed around the crystal. This experimental arrangement has since been known as the Laue technique. von Laue described the nature of the diffraction effect in terms of equations taken from the theory of diffraction, now known as the Laue conditions. However, soon after this discovery William and Lawrence Bragg, in England, described x-ray diffraction by crystals in extremely simple terms.

Getting familiar with Bragg's law:

We now consider this simple formulation of the geometry of the diffraction of x-rays by crystalline materials. The main equation which describes the geometry of the diffraction of x-rays by crystalline materials is:

$$\lambda = 2d_{hkl}\sin\Theta_{hkl}$$

This equation is easily derived by considering t**he x-rays to be reflected from a set of lattice planes** and calculating the condition on the reflecting angle (the Bragg angle) when the rays reflected from two adjacent, parallel planes in the set have a path length difference of λ for total constructive interference. This is seen in figure 3.1, where only a few planes in a single crystal are shown.

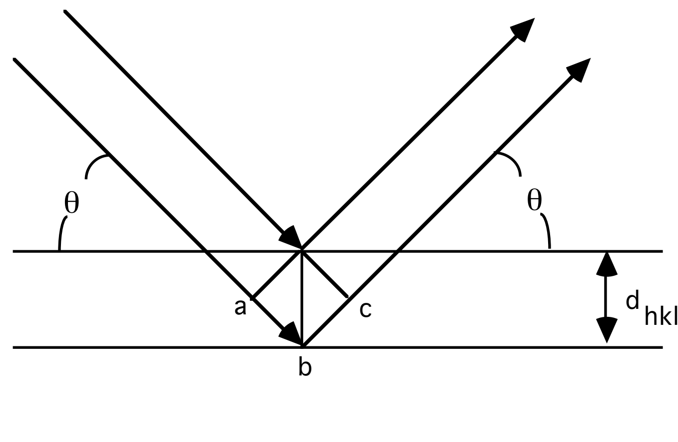


Figure 3.1. Geometrical derivation of Bragg's law.

In order for the two outgoing or reflected waves to be in phase (constructive interference), the path length difference **abc** has to be equal to one wavelength. The same relationship has to be true for any two adjacent planes in the set. Expressing this relationship leads directly to Bragg's law.

<u>What does a diffraction pattern look like?</u>
In a diffraction measurement, the instrument detects diffraction maxima, or reflections, being emitted from the sample at a particular angle 2θ to the direction of the incident beam when the reflecting or diffracting planes make an angle with the incident beam of θ. Through the use of Bragg's law, the interplanar spacings for the sets of planes which give these reflections can be calculated since λ is known. This equation can, of course, also be used to predict the Bragg angles θ for diffraction from a substance for which the d_{hkl}'s are known, along with λ.

The general appearance of a diffraction pattern can be obtained through the following considerations. First we note that, since we have reflection only, θ will range from 0° to 90°. Next, we investigate the corresponding possible values for the d's. We remember from Bragg's law that as the Bragg angle θ

increases, the value of d decreases. Thus it is possible for the d's to range from ∞ to $\lambda/2$. There must be a maximum value of d which depends upon the material in the diffraction sample. For an orthogonal crystal axis set, this maximum value is for the set of planes which is perpendicular to the crystal axis with the greatest repeat distance. No set of planes exists which has a larger interplanar distance. A similar situation exists for materials with non-orthogonal basis vectors. Thus, the first peak (lowest θ or 2θ) in the pattern will occur at a specific non-zero angle.

Next we note that the values for d are discrete, not continuous. This means that the diffraction maxima in the pattern occur at specific angles, separated from one another. In some cases, the values of some d's are close enough that the diffraction maxima overlap, but, in general, the pattern consists of discrete peaks.

Finally, we note from Bragg's law that, while the lower limit of the values of d is zero, there is a limit $d_{min} = \lambda/2$ below which no diffraction maxima can be observed. The specific limit on the value of d depends upon what type of x-ray tube is being used to produce the diffraction pattern. In fact, the configuration of all diffraction instruments imposes a practical limit of about 160° (in some specialized instruments, the maximum 2θ value is much less). From the expression $d_{min} = \lambda/2$, it can be seen that when more diffraction maxima must be observed, a smaller wavelength radiation must be employed.

The nature of the tube spectrum also influences the appearance of the diffraction pattern. We expect to see diffraction maxima in the pattern for every component of the radiation including the white or continuous radiation, the β, α_1, and α_2 components, and the characteristic lines for any target contaminants. For a new tube, used with a β-filter or a monochromator, the only radiations which the sample should see are the α_1 and α_2. While these have two different wavelengths, the values are so close to one another that separate reflections from the two are frequently unresolved in the diffraction pattern at low angles. The separation between the α_1 and α_2 peaks increases (this can be easily demonstrated by calculating Bragg angles for large and small values of d) until they are frequently completely resolved at high 2θ angles. The ability to resolve these "α_1-α_2 doublets" also depends upon how well the diffractometer is aligned, and the nature of the sample.

<u>X-ray fluorescence spectrometry</u>

It is also possible to use Bragg's law to calculate the wavelength of the radiation being used when the diffraction angle θ measured for a substance for which the interplanar spacing d_{hkl} is known. By choosing a particular value for the interplanar spacing, λ can be determined by measuring the Bragg angle in an <u>x-ray spectrometer</u>. Characteristic fluorescence radiation from the sample is incident upon a <u>single crystal</u> (the analyzer crystal) which has a particular set of crystallographic planes parallel to its surface. As the analyzer crystal is rotated, the incident radiation hits it at varying angles. When the angle of incidence corresponds to a Bragg angle for that characteristic wavelength, the analyzing crystal reflects those x-rays into a counter. λ is determined for the Bragg angle, and thus the identity of the fluorescing atom is known.

It is important for the student to differentiate between these two uses of Bragg's law. The experimental setups for the two techniques may <u>appear</u> to be similar but they are really different. The objectives of the two techniques are also quite different; x-ray diffraction is tool for studying the structural aspects of a material, while x-ray fluorescence is used to determine the elemental composition of a material.

X-ray diffraction - overview:

The general procedure in many diffraction studies is the following. A sample is placed in an x-ray diffraction instrument and a measurement of the angular positions of the diffraction maxima, or reflections, is made. These are the Bragg angles. From these angles, the d's are calculated from Bragg's law. The next task is to determine the hkl's for the planes with these d's; this indexing procedure results in a determination of the crystal system which the substance exhibits. Since the crystal system is determined, it is then possible to calculate the lattice parameters for the material using the appropriate relationship between d, h, k, l, and the lattice parameters. These relationships are:

Cubic

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$$

Tetragonal

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal, trigonal

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\,\frac{h^2+k^2+hk}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic

$$\frac{1}{d_{hkl}^2} = \text{complex}$$

In summary, to interpret an x-ray diffraction pattern:

Measure θ's for the sample
Calculate d's from the θ's
Index the reflections - assign hkl's to each
Calculate lattice parameters

We will discuss only diffraction from polycrystalline samples since it is much more common. Many of the principles carry over into single crystal diffraction studies; one of the major differences is that the procedures for indexing the reflections and finding the symmetry of the material are much, much easier in single crystal diffraction techniques. On the other hand, experimental techniques for the measurement of x-ray diffraction patterns from polycrystalline materials is generally much less involved than for single crystal measurements; powder diffraction techniques have become quite routine in most analytical laboratories.

Cubic powder patterns:

We begin our discussion of x-ray powder diffraction patterns with the description of those from cubic materials. Cubic diffraction patterns are discussed first because the appearance of these patterns is quite simple and their interpretation is very easy. This is because there is only one lattice parameter involved, and the geometric relationship given above:

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2} = a/s^{1/2}$$

is particularly simple in form. In general, indexing a cubic powder diffraction pattern essentially amounts to scaling a set of predicted d's for all possible hkl's to the values of the observed d's. In this way, the lattice parameter **a** is determined.

It should be pointed out that the peaks on an x-ray diffraction pattern cannot always be indexed by simply assigning all possible indices to them as they occur. In fact, the pattern may not be cubic; or, some of the peaks in a cubic pattern may accidentally be missing or of such low intensity that they are undetected. In all cases, the indexing should be checked by calculating the lattice parameter(s). The lattice parameter(s) should all agree within experimental error. For example, the following indexing, based upon cubic, would not be satisfactory....only 2.156 and 2.158 agree to within the usual limits of error. For this indexing, the **a** values vary far too much:

d(Å)	(hkl)	s	a(Å)

2.023	100	1	2.023
1.762	110	2	2.492
1.245	111	3	2.156
1.063	200	4	2.126
1.018	210	5	2.276
0.882	211	6	2.158

Let us now examine what hkl's will be possible for any particular powder diffraction pattern. For starters, the largest value of d that can be observed is determined by the value of the lattice constant. This can be seen by examining the expression

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$$

where it can be seen that a large d corresponds to a large **a** for any hkl. Then from Bragg's law

$$\lambda = 2d_{hkl} \sin\theta_{hkl}$$

we see that the lowest Bragg angle θ corresponds to the largest d_{hkl}. Finally we also note that, for a fixed **a** value, the largest d's are calculated from hkl's with the smallest integer values. Thus, the lowest angle reflections should correspond to those planes with the smallest hkl values.

The minimum interplanar spacing that can be observed in any diffraction pattern depends upon the wavelength λ of the x-radiation used. Since $\lambda = 2d_{hkl} \sin\theta_{hkl}$, the smallest possible value of d_{hkl} corresponds to the largest possible value of θ_{hkl} , i. e., 90°, where $\sin\theta_{hkl} = 1$. For example, using CuKα radiation, the smallest d_{hkl} which can be observed for any substance is (theoretically) $d_{min} = \lambda/(2\sin 90°) = 1.542/2 = 0.771$Å. Practically, because of equipment limitations, d_{min} is larger than the theoretical minimum, sometimes much larger.

Now if $s = h^2 + k^2 + l^2$ for cubic, the possible reflecting planes can be listed in order of increasing s, which we note is also in order of increasing θ. The s values, and thus the hkl's, are simply matched in order to index the reflections. From the d's and the hkl's, a value for the lattice constant can be calculated for each reflection. If the indexing is correct, these values should agree with one another very closely. One of the most common errors students make here is to assume that an indexing is correct based upon an agreement between the values of the calculated and observed lattice parameters only to the first and second decimal place......or sometimes worse. Calculations which lead to these kinds of indexing should be reevaluated. To be fair, there are systematic errors which show up in the observed data which can be large at low Bragg angles; we will examine the nature of such errors later.

The only complicating factor in the indexing of cubic powder patterns arises from the fact that, initially, the Bravais lattice type for substance being examined is unknown. This must be determined during the course of the indexing. As noted In the chapter on crystallography, there are three types of Bravais lattices for cubic: P cubic, I cubic, and F cubic. Because of the different centering in these lattices, certain planes can be considered to not exist. The systematic extinction rules, which we will derive later, that describe the non-existence of the planes in these three cases are given below.

Lattice centering	Extinction rule	Allowed s values
P	none	1, 2, 3, 4, 5, 6, 8, 9,......
I	h + k + l = even no.	2, 4, 6, 8, 10, 12,.......
F	h,k,l all even or all odd	3, 4, 8, 11, 12, 16, 19, 20,.......

All three types of cubic patterns have a rather different appearance (see Figure 3.2), but they are still simple enough that, with a little practice, you should be able to index almost any powder pattern for any of the three lattice types essentially by sight, without any calculating. Of course, the final verification of the indexing should always be done by calculating the lattice parameters for each reflection as described above. There are some instances when the indexing may appear somewhat ambiguous, and a more laborious procedure must be adopted.

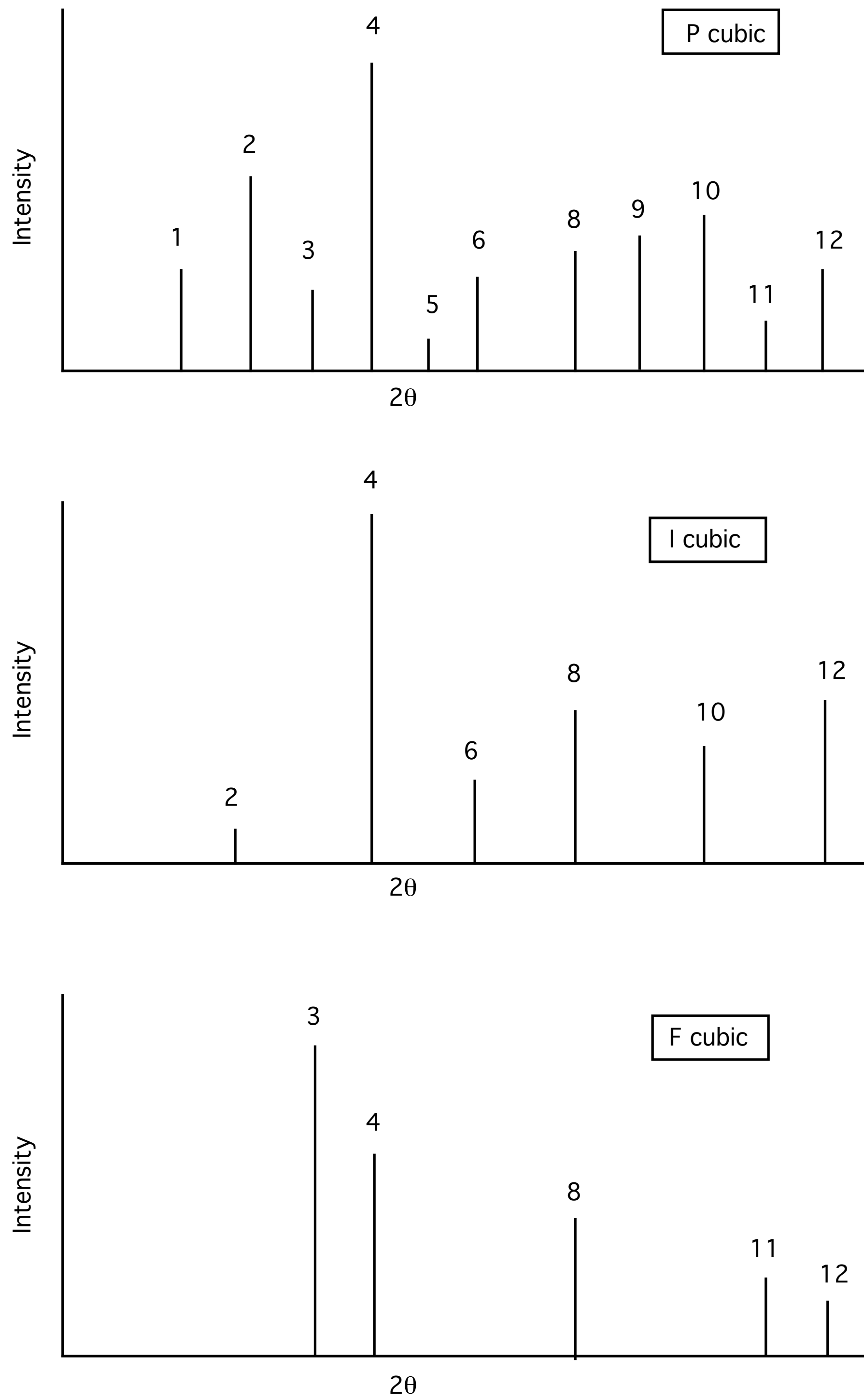


Figure 3.2. Diagrams of the appearance of powder diffraction patterns for P cubic, I cubic, and F cubic materials.

Indexing non-cubic powder patterns:

However, for lower symmetry systems, indexing is much more difficult and more involved than for cubic patterns. Manual indexing of polycrystalline patterns can be done relatively easily for tetragonal and hexagonal patterns. But for orthorhombic, monoclinic, and triclinic systems, it is frequently more convenient to obtain the symmetry and unit cell from single crystal measurements for which indexing is generally very easy.

Nowadays, a considerable number of x-ray diffraction patterns for polycrystalline materials are indexed with the aid of one of a number of computer programs designed specifically for indexing. We can understand something about how these programs carry out the indexing by studying the procedures for manual indexing. Manual indexing is usually accomplished using $1/d^2$ or $\sin^2\theta$ values (these differ only by the constant factor $\frac{4}{\lambda}$) because of the obvious multiplicative and additive relations between these quantities for the various reflections in the pattern. For hexagonal, $\sin^2\theta$ ratios of 3 can be found, while for tetragonal, $\sin^2\theta$ ratios of 2 can be found; this leads to immediate recognition of the pattern being for either a tetragonal or a hexagonal substance.

As an example, consider the relationships:

Hexagonal

$$\frac{1}{d^2} = \frac{4}{3}\,\frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}$$

Tetragonal

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Combining these with Bragg's Law:

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{3a^2}\left(h^2+k^2+hk\right) + \frac{\lambda^2}{4c^2}\, l^2$$

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a^2}\left(h^2+k^2\right) + \frac{\lambda^2}{4c^2}\, l^2$$

or:

$$\sin^2\theta_{hkl} = AM + CN$$

$$\sin^2\theta_{hkl} = AM + CN$$

Possible values of M, N:

M	hk	N	l
1	10	1	1
3	11	4	2
4	20	9	3
7	21	16	4
9	30	25	5

M	hk	N	l
1	10	1	1
2	11	4	2
4	20	9	3
5	21	16	4
8	22	25	5
9	30		

Note the differences in the M values!

Now:

$\sin^2\theta_{110} = 3 \sin^2\theta_{100} = 3A$

$\sin^2\theta_{200} = 4 \sin^2\theta_{100} = 4A$

etc.

$\sin^2\theta_{110} = 2 \sin^2\theta_{100} = 2A$

$\sin^2\theta_{200} = 4 \sin^2\theta_{100} = 4A$

etc.

And:

$\sin^2\theta_{101} = \sin^2\theta_{100} + \sin^2\theta_{001} = A+C$

$\sin^2\theta_{111} = \sin^2\theta_{110} + \sin^2\theta_{001} = 3A+C$

etc.

$\sin^2\theta_{101} = \sin^2\theta_{100} + \sin^2\theta_{001} = A+C$

$\sin^2\theta_{111} = \sin^2\theta_{110} + \sin^2\theta_{001} = 2A+C$

etc.

The recognition of these multiplicative and additive relationships between the $\sin^2\theta$'s leads to an "intuitive" indexing procedure. A computer program for indexing probably number-crunches all possibilities to look for these relationships, but we should be able to, at least in relatively simple diffraction patterns, pick them out really quickly. Let us index this pattern:

No.	$\sin^2\theta$	hkl	
1	0.097	001 ---------------------------------------→	002
2	0.112	100	100
3	0.136		101
4	0.209	101	102
5	0.332	110	110
6	0.390	002 ---------------------------------------→	004

First, we list the multiplicative relationships. They are calculated out somewhat systematically here for clarity; in reality, the determination of which relationships exist is easily done in your head.

2 x .097 = .194

3 x .097 = .291

4 x .097 = .388 ⇒ 4 x ① = ⑥

Here, we can guess C
C = 0.097

.112 x 2 = .224

.112 x 3 = .336 BINGO! ⇒ 3 x ② = ⑤

↑
LOOKS HEXAGONAL!
(see table of M values)

Here, we can guess A
A = 0.112

What we see is that two $\sin^2\theta$'s are related by a factor of 3. This tells us that the pattern can probably be indexed as hexagonal rather than tetragonal, and that the A value is probably 0.112. 0.097 must give us the C value. We list the corresponding hkl's next to the $\sin^2\theta$ values in the table.

Then note that 112 + 097 = 209! Another hit!

② + ① = ④

(100) + (001) = (101)

However, this leaves us with a problem with line 3. There are no possible, available indices. We have several choices as to how to proceed. We could ignore line no. 3 and say that we have successfully indexed the pattern. However, we are more than likely bound to have a sleepless night, worrying about line no. 3, since this is a good pattern of a single phase material with reflections from one x-radiation only. The alternative is that we have made a mistake in our indexing. One or both of the assumptions, our guesses for A and C, is/are wrong.

So, change one and try again. Which assumption to change is arbitrary; if we choose the wrong one to change, we will again run into a problem with the indexing. Some experience here is helpful. In this case, we guess that maybe we are dealing with a material whose structure exhibits a screw axis such that the (00l) reflections with l odd are extinct. This situation is, in fact, common in many hexagonal structures. So, let's change C.

Note that $4 \times \sin^2\theta_{002} = \sin^2\theta_{004} = 16C$ if so $C = \frac{097}{4} = 024$

Then, for line 3: 112 + 024 = 136

A + C = A + C

↓

(101) FINI!!

These points should be noted in indexing powder patterns:

1. All of the reflections must be indexed (or explained somehow...impurity phase reflections, β reflections, etc.)
2. A pattern is not correctly indexed if there are a lot of missing reflections. There are only three reasons why reflections may be missing from a diffraction pattern:
   a. systematic extinctions due to lattice centering, glide planes, or screw axes
   b. **occasional** "accidental" absences because the reflection intensities are too weak to be observed
   c. the d's for two planes may be so close that the reflections overlap

   It is possible to index any diffraction pattern (incorrectly) really easily if sufficiently large values of the lattice parameters (i.e., very small values of A, B, C) are chosen. However, there will be lots of missing (hkl)'s.
3. **ATCF**......Always try to index a pattern as cubic first because cubic indexing is very easy.
4. Be careful about additive relations. While, in hexagonal or tetragonal, the following is true:

$$A + C = \sin^2\theta_{101} = \sin^2\theta_{100} + \sin^2\theta_{001} = A + C$$

this is not:

$$A + 9C = \sin^2\theta_{103} = \sin^2\theta_{101} + \sin^2\theta_{002} = A + C + 4C$$

Precision determination of lattice parameters:

There are a number of applications of x-ray diffraction in which it is necessary to determine very precise values of the lattice parameters. We first consider how such a determination is carried out for a cubic material.

Suppose we have obtained the cubic x-ray diffraction pattern shown below.

d(Å)	hkl
3.155	111
2.7314	200
1.9316	220
1.6471	311
1.5771	222
1.3656	400
1.2533	331
1.2216	420
1.1152	422
1.0514	333
0.9658	440
0.9234	531
0.9105	600
0.8638	620
0.8331	533
0.8236	622

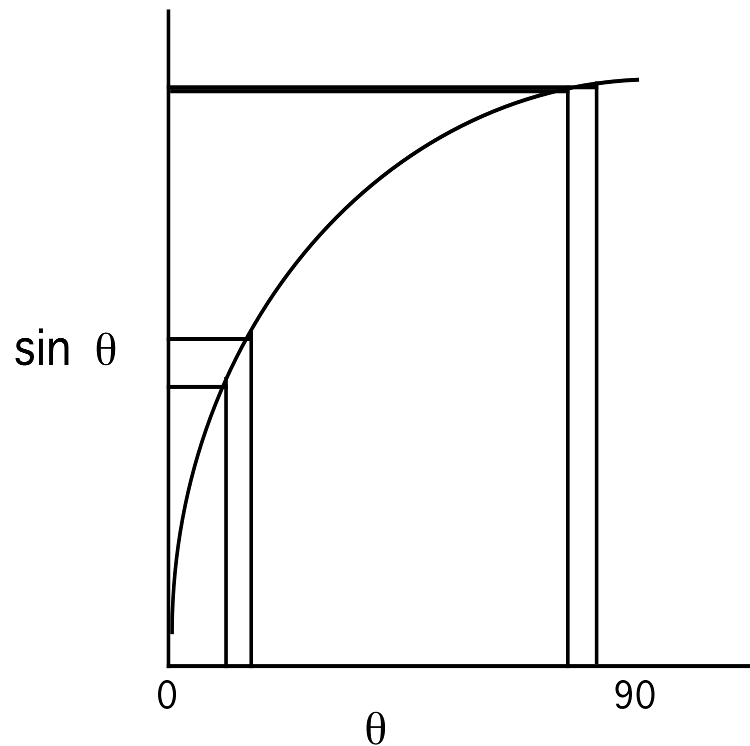
We note that we can use any of the reflections to calculate a value for the lattice parameter **a**. The d's listed have been calculated from measurements of the θ's:

$$\lambda = 2d_{hkl} \sin\theta_{hkl}$$

For each of the d values we can calculate a value for **a**:

$$a = d_{hkl} \cdot (h^2 + k^2 + l^2)^{1/2}$$

The question is, which reflection, if any, will result in a more precise value for **a**? We note from the above equations that the error in **a** depends directly upon the error in d, which in turn depends directly upon the error in sin θ. Suppose we make a constant measurement error Δθ in the determination of the positions of the reflections in the above x-ray diffraction pattern. From the plot below, we see that the resulting error in sin θ varies with θ. The error in sin θ is large at low θ, small at high θ, and zero at θ = 90°. Thus, we see that the best reflection to use would be the probably non-existent and certainly unobservable one at θ = 90°. An alternate approach is to use the **a** values for all of the reflections and extrapolate to θ = 90° to obtain the most precise value for **a**.



To obtain precise results in the determination of lattice parameters, special techniques are employed to calculate them. As we have seen above, the most precise values of the lattice parameters are those obtained for reflections which occur at high angles. In fact, all errors can be eliminated at $\Theta = 90°$, and so the lattice parameter values generally reported are those obtained from an extrapolation of the data to $\theta = 90°$ against some function intended to make the lattice parameter variation linear. Two such functions, obtained through an extensive evaluation of systematic experimental errors, are the Bradley and Jay function, $\cos^2\theta$ (frequently used for diffractometer data, and linear only over the range $\theta = 60\text{-}90°$) and the Nelson-Riley function ($\cos^2\theta/\sin\theta + \cos^2\theta/\theta$, linear over the range 30-90°θ, and used for other instrument geometries).

The extrapolation can be accomplished through the use of the least squares method. A function (in the above cases, a straight line) is fit to the data according to the criterion that the sum of the squares of the differences between the observed and calculated values is a minimum. The normal equations are obtained by setting the derivatives, taken with respect to the appropriate variables (functions of the lattice parameters), equal to zero; these equations are solved to obtain the lattice parameters.

For non-cubic materials, in order to make use of all of the reflections in the determination of the extrapolated values of the lattice parameters, Cohen's least squares method may be used. Cohen's method uses the criterion that the sum of the squares of the differences between $\sin^2\theta$'s of the observed and calculated values, and includes one of the correction functions, in $\sin^2\theta$ form, for the systematic errors.

IV. INTENSITIES OF X-RAY REFLECTIONS

A crystal structure is completely described by giving:

Lattice parameters
Space group
Equipoints occupied
Positional parameters

From this information, it is possible to pinpoint the positions of each and every atom in the substance.

Up to this point, we have discussed only how the lattice parameters and space group (symmetry description) are obtained for a material from x-ray diffraction patterns. To get the parameters and symmetry, we inspect and measure only the positions of the x-ray reflections. There is no way, except for unusually simple crystal structures, to derive the positions of the atoms from this information alone. However, there is other information contained in the diffraction peaks - their intensities. The intensities are used to derive the atom positions. The following discussions show the relationship between the intensities and atom positions.

The atomic scattering factor:

It is the electrons in the atoms of the material in the sample that interact with the incident x-rays. Each atom has its own x-ray scattering power, called the atomic scattering factor, f, and f varies with θ because of increased destructive interference at higher angles due to greater path length differences. Values for f are obtained from quantum mechanical calculations, and are listed in tables of f vs. $\sin \theta/\lambda$ in, for example, International Tables for X-ray Crystallography, vols 3 & 4.

The structure factor:

A somewhat similar calculation is made for the scattering power of a unit cell. Here, each atom, j, produces a scattered wave of the form $f_j \exp(2\pi i(hx_j + ky_j + lz_j))$. The path length differences vary, depending upon the (x_j, y_j, z_j) of the atoms in the unit cell, and upon the direction of the scattered beam, accounted for here by the inclusion of h, k, and l in the phase factor in the exponent. Thus, the general expression for the scattering from all the atoms in the unit cell, called the structure factor, F_{hkl}, is:

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j)).$$

This important equation represents the amplitude of the total scattered wave from the N atoms in the unit cell, and thus $I_{hkl} = \text{constant} \cdot |F_{hkl}|^2$, since the contributions from all the other unit cells are the same and in phase. Thus, if the positions of the atoms in the unit cell are known, the F_{hkl}'s, and the I_{hkl}'s, can be calculated.

Structure factor calculations

Several important properties of this complex (meaning that it contains $i = \sqrt{(-1)}$) function are given below.

1. In general, F is an imaginary quantity, and:

   $F = A + iB.$

2. The absolute value of the complex quantity F_{hkl} is the square root of the sum of the squares of the real and imaginary parts:

   $|F_{hkl}| = ((A + iB)(A - iB))^{1/2} = \sqrt{(A^2 + B^2)}.$

3. In evaluating the expression for F_{hkl}, many shortcuts can be taken if we remember that:

$$e^{i\phi} = \cos\phi + i\sin\phi \quad \text{(Euler's rule).}$$

Thus:

$$e^0 = 1,\ e^{n\pi i} = 1 \text{ (n even) or } -1 \text{ (n odd), and } e^{i\phi} + e^{-i\phi} = 2\cos\phi.$$

Some sample F calculations:

A simple example.
Our first structure factor calculations will be done for a very simple structure.....Cu. The crystal structure of this material is described as follows:

a = 3.614Å

$Fm3m = F\ 4/m\ \bar{3}\ 2/m$

4 Cu atoms in 4a → (000) $(\frac{1}{2}\frac{1}{2}\ 0)$ $(\frac{1}{2}\ 0\ \frac{1}{2})$ $(0\ \frac{1}{2}\frac{1}{2})$

(Note that no values of positional parameters are required here.)

Start with:

$$F_{hkl} = \sum_{j=l}^{N} f_j\, e^{2\pi i(hxj + kyj + lzj)}$$

Since there are four atoms/unit cell , we expect to get four terms in the summation for F_{hkl}, when we substitute the four sets of atom coordinates:

$$F_{hkl} = f_{Cu}\,(e^0 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)})$$

When we simplify this expression, using Euler's rule:

$$e^{i\theta} = \cos\theta + i\sin\theta$$

noting thence that:

$e^{in\pi} = -1$ n odd
$e^{in\pi} = +1$ n even

we find that F_{hkl} is either zero or 4 f_{Cu} depending upon (hkl). Then, for specific reflections, we obtain:

s	hkl	F_{hkl}
1	100	0
2	110	0
3	111	$4f_{Cu}$
4	200	$4f_{Cu}$
5	210	0
6	211	0
7	-	-

Note that while F_{hkl} = 4 f_{Cu} for all allowed (hkl), F is not the same, since f_{Cu} is a function of $\sin\theta/\lambda$.

Derivation of extinction rules.

Note that, in the calculation of F_{hkl} for Cu, all of the unallowed reflections have F = 0. This suggests that the expression for F_{hkl} can be used to determine extinction rules, since the calculation predicts that all reflections with h, k, and l not all even or all odd will be extinct. All extinct reflections, of course, must have F = 0. For example, for an I orthorhombic substance, one can write immediately that $F_{100} = F_{311} = F_{234} = 0$, since $h + k + l \neq 2n$ for all these reflections.

In the general calculation, the atom positions are unknown.....the atoms are not, in general, located on the lattice points of an F lattice, for example, as they are in Cu. There is a procedure for deriving the extinction rules in general.

The extinction rule for F-centering

An example derivation for F - centering, for **any crystal system**, follows.

For F - centering, any atom at some (xyz) must yield equivalent atoms at:

$$(x + \frac{1}{2}, y + \frac{1}{2}, z), (x + \frac{1}{2}, y, z + \frac{1}{2}), \text{ and } (x, y + \frac{1}{2}, z + \frac{1}{2})$$

(This is the meaning of F-centering!)

Substituting into the structure factor expression, we obtain:

$$F_{hkl} = \sum_{j=l}^{N/4} f_j \left(e^{2\pi i(hxj + kyj + lzj)} + e^{2\pi i(h(xj+\frac{1}{2}) + k(yj + \frac{1}{2}) + lzj)} + e^{2\pi i(h(xj + \frac{1}{2}) + kyj + l(zj + \frac{1}{2}))} + e^{2\pi i(hkj + k(yj + \frac{1}{2}) + l(zj + \frac{1}{2}))}\right)$$

Note the change in the range of the summation; in reality, there are still N terms in the summation. Factoring out $e^{2\pi i(hxj + kyj + lzj)}$, we get:

$$F_{hkl} = \sum_{j=l}^{N/4} f_j \, e^{2\pi i(hxj + kyj + lzj)} \left(e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)} + 1\right)$$

Now, when does F_{hkl} go to zero?

(h + k) odd	→	h even k odd →	(k+l) odd	→ h even k odd l odd	F→0
		h odd k even →	(k+l) even	→ h odd k even l even	F→0
(h + k) even	→	h even k even →	(k+l) odd	→ h even k even l odd	F→0
		h odd k odd →	(k+l) even	→ h odd k odd l odd	F≠0
				→ h even k even l even	F≠0

The extinction rule is:

For all (hkl), h,k,l mixed w.r.t. evenness and oddness ←(absent)

It is possible to derive the extinction rule for any translational symmetry operation, including lattice centering, and glide planes and screw axes, in a similar fashion.

The extinction rule for I-centering

An example derivation for I-centering, for **any crystal system**, follows.

For I-centering, any atom at some (xyz) must also have equivalent atoms at:

$$(x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2})$$

(This is the meaning of I-centering!)

Substituting into the structure factor expression, we obtain:

$$F_{hkl} = \sum_{j=l}^{N/2} f_j \left(e^{2\pi i(hx_j + ky_j + lz_j)} + e^{2\pi i(h(x_j+\frac{1}{2}) + k(y_j + \frac{1}{2}) + l(z_j + \frac{1}{2}))}\right)$$

Note the change in the range of the summation; in reality, there are still N terms in the summation. Factoring out $e^{2\pi i(hxj + kyj + lzj)}$, we get:

$$F_{hkl} = \sum_{j=l}^{N/2} f_j \, e^{2\pi i(hxj + kyj + lzj)} \left(1 + e^{\pi i(h+k+l)}\right)$$

Now, when does F_{hkl} go to zero?

$$h+k+l \neq 2n$$

The extinction rule is:

For all (hkl), $h+k+l \neq 2n$ ←(<u>absent</u>)

<u>F_{hkl}'s for centric structures.</u>

It is frequently possible in manual structure factor calculations for centrosymmetric structures to reduce the amount of calculation which must be done. An important simplification results for materials which exhibit the symmetry operation i. To do this:

1. the structure must be recognized as centric. In this regard, it helps to learn to recognize from the space group symbol that the corresponding point group is centric. An example: the space group I4/mcm corresponds to the point group 4/m 2/m 2/m which is centric.

2. the atom positions must separated into two groups, one whose coordinates are the negatives of one of the atom positions in the other.

As usual, we start with expression for F_{hkl}:

$$F_{hkl} = \sum_{j=l}^{N} f_j \, e^{2\pi i(hxj + kyj + lzj)}$$

In centric structures, for every atom at (x_j, y_j, z_j) there is an identical atom at $(-(x_j, y_j, z_j))$. When these are substituted into the expression for F_{hkl}:

$$F_{hkl} = \sum_{j=l}^{N/2} f_j \left(e^{2\pi i\,(hxj + kyj + lzj)} + e^{-2\pi i\,(hxj + kyj + lzj)}\right.$$

From the well-known identity ($\cos\theta = \frac{(e^{i\theta} + e^{i\theta})}{2}$), or Euler's rule:

$$F_{hkl} = 2 \sum_{j=1}^{N/2} f_j \cos(2\pi(hx_j + ky_j + lz_j))$$

Note that F_{hkl} is no longer an imaginary quantity (= A + iB), but a real one. The evaluation of F_{hkl} now involves one-half the original number of terms. In addition, this expression has some important implications in the solution of unknown crystal structures, discussed below.

F_{hkl} 's for more complex structures.

We have, so far, discussed the calculation of the structure factor is some relatively simple cases. In general, however, crystal structures are rather more complex, so that the calculation becomes considerably more involved. Note that the resulting numbers for F_{hkl} may be real and positive, real and negative, or imaginary. Several examples are given below. Both structures are centric, so the values for F_{hkl} are real.

$HoZn_2$:

The description of the structure of $HoZn_2$ is:

a = 4.456 ± 0.001   b = 7.039 ± 0.003   c = 7.641 ± 0.005 Å

Imma $\equiv I \frac{2}{m}\frac{2}{m}\frac{2}{a}$

4 Ho in 4e $(0\ \frac{1}{4}\ z)\ (0\ \frac{3}{4}\ \bar{z})$ + I   z = 0.5281 ± 4

8 Zn in 8h $(0yz)\ (0\bar{y}\bar{z})\ (0, \frac{1}{2} + y, \bar{z})$ y = 0.0410 ± 9, z = 0.1663 ± 8

$(0, \frac{1}{2} - y, z)$ + I

When the atom positions are substituted into the expression for F_{hkl}, a rather complex expression results:

$$F_{hkl} = f_{Ho}\,(e^{2\pi i(k/4 + l(0.5281))} + e^{2\pi i(3/4k + l(-0.5281))} + e^{2\pi i(1/2h + 3/4k + l(0.0281))} + \text{1 more term})$$

$$+ f_{Zn}\,(e^{2\pi i(k(0.0410) + l(0.1663))} + \text{7 more terms}).$$

MoB:

In this example, you are to complete your notes by answering the questions and filling in the correct numbers.

MoB is $I4_1/amd$ with a = 3.110, c = 16.95 Å, and Mo and B atoms in 8e, z = 0.196 and 0.352, respectively.

Calculate F_{001} and F_{004}.

$F_{001} = 0$ ....the lattice is I-centered and therefore, when $h + k + l \neq 2n$, $F = 0$.

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j)).$$

F_{004} = ?

$$F_{004} = \sum_{j=1}^{16} f_j \exp(2\pi i(4z_j)).$$

What are the quantities that must be calculated in order to get F_{004}?

d_{004} = _______
$(\sin\theta)/\lambda$ = ________

	0.1	0.2
Mo	38.2	32.6
B	3.5	2.4

f_{Mo} = _______

f_B = _______

8e: (00z) $(0,\frac{1}{2},\frac{1}{4}+z)$ $(\frac{1}{2},0,\frac{3}{4}-z)$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2}-z)$

F_{004}=

Intensities:

The intensity of an x-ray reflection is obtained from its structure factor. The structure factor is an **amplitude**; to get the intensity, then, we must square the amplitude. However, the intensity, being a measurable quantity, must be a positive, real number, whereas, as we have seen, the structure factor can be a complex number (non–centric structures only). Thus, to calculate the intensity from the structure factor, we must perform this squaring operation in a particular manner:

$$F^*F = |F|^2 = (A-iB)(A+iB) \Rightarrow I$$

$F^* = (A-iB)$ is the complex conjugate of F.

In the calculation of reflection intensities, certain "correction factors" must be applied. For x-ray diffraction patterns from polycrystalline samples:

$$I_{hkl} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hkl}|^2 \, e^{-2M}$$

where:

p = multiplicity
LP = Lorentz-polarization factor
A = absorption correction
e^{-2M} = temperature factor, where

$$2M = 16\pi^2\mu^2\frac{\sin^2\theta}{\lambda^2}$$; μ^2 = mean square amplitude of thermal vibration of the atoms in a direction normal to the planes (hkl)

All of these correction factors, except the scale factor, vary with θ (or, equivalently, with (hkl)). The multiplicity factor p accounts for the differing probabilities that symmetry equivalent planes (hkl) will reflect. The polarization factor accounts for the polarization state of the incident beam (in most powder x-ray diffractometers, it is unpolarized). The Lorentz factor corrects for the geometrical broadening of the reflections as 2θ is increased. Thus, LP is usually:

$$LP = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos\theta}$$

The absorption factor accounts for the change in the absorption by the sample of the incident and reflected x-ray beams. In x-ray diffractometers with fixed divergence slits, this factor is constant over the complete 2θ range. Finally, the correction factor due to thermal motion of the atoms is quite difficult to evaluate, and must frequently be ignored.

Intensity calculations - an example:

Again, answer the questions and fill in the correct answers.

β-Np is $P42_12$ with a = 4.897, c = 3.388 Å, and Np in 2a ((000) and $(\frac{1}{2}\frac{1}{2}0)$) and 2c ($(0\frac{1}{2}z)$ and $(\frac{1}{2}0Û)$), z = 0.375. Find I_{101} for CuKα radiation.

f calculation:

(sin θ)/λ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
f	93	87	78	69	60	53	48	44

F calculation:

What is p?

Lp calculation:

I calculation:

Crystal Structure Analysis:

Essentially, the only experimental technique for the determination of the crystal structures of solids (i.e., finding the positions of all of the atoms in the unit cell) is that which uses the positions and intensities of the of x-ray (or also neutron) reflections. How do we use the intensity data to find the atom positions?

<u>The problem of locating atoms from x-ray intensity data.</u>
There is a technique for locating the positions of the atoms in a structure from intensity information. The Fourier transform of the F_{hkl}'s yields the electron density at any selected point (XYZ) in the unit cell:

$$\rho(XYZ) = 1/V \sum_{hkl}\sum\sum F_{hkl}\, e^{2\pi i(hX + kY + lZ)}$$

By calculating this Fourier transform at points (XYZ) of a grid over the unit cell, regions of high electron density can be located; these indicate the positions of the atoms (for an example, see figure 4.3). The difficulty here is that F_{hkl} must be known for all reflections. From the intensities, only $|F_{hkl}|$ can be calculated. For non-centrosymmetric structures, there are an infinity of F_{hkl}'s for each $|F_{hkl}|$. In the case of centric structures, there are only two possibilities - $\pm | F_{hkl} |$; however, even for centric structures, the determination of the unknown structure can still be very complex.

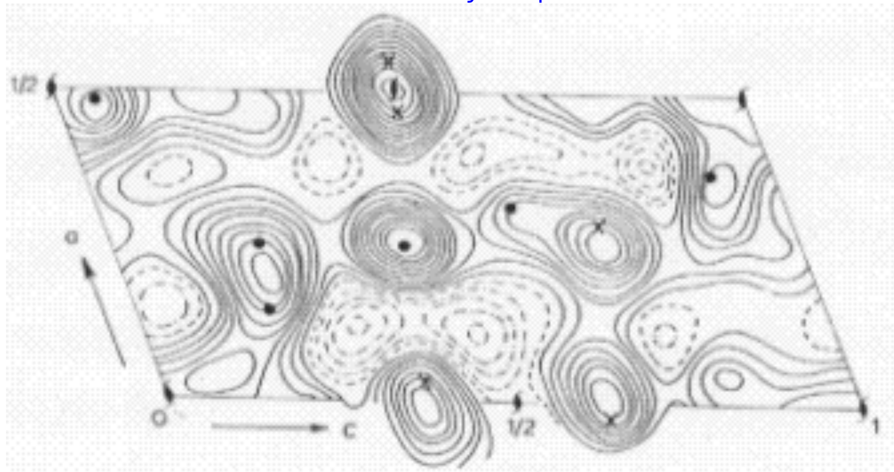


Figure 4.3. Projection of electron density for P_4S_5 for one-half the unit cell. The solid contours indicate regions of high electron density. The dashed contours are negative contours, and are artifacts of the measurement.

The net result is that it is not possible to "directly" determine an unknown crystal structure from the intensities. In the past, the procedure, after determining the space group and measuring the intensities, is to "guess" the structure, using all the atomic size, geometrical, crystal chemical, bonding, and

crystallographic information available. There are certain "direct" methods for deriving the crystal structures "directly" from the intensities; these techniques have complex mathematical foundations. Algorithms and computer programs have been developed which now can be used to determine the atom arrangements in even fairly complex crystal structures almost automatically.

Is a proposed structure model correct?

The next step in structure determination is to test a proposed structure. This is accomplished by calculating the F's for the proposed structure (F_{calc}) and comparing them to the values of $|F_{hkl}|$ obtained from the observed intensities ($|F_{obs}|$). To compare the two data sets as a whole, the quantity:

$$R = \Sigma \,|\, |F_{obs}| - |F_{calc}| \,| / \Sigma |F_{obs}|$$

is used. The structure model is satisfactory if $R < .1$, and quite good if $R < .05$. The structure model is adjusted by shifting the values for x,y,z for all the atoms until this R is a minimum. A least squares procedure is used to obtain the best R.

Summary - The procedure, in general, for the determination of crystal structures is:

1. Measure the positions and intensities of the reflections.

2. From the positions of the reflections get the lattice parameters and the space group.

3. Guess a model for the crystal structure somehow.

4. Compare the F_o values obtained from the observed intensities with the F_c values calculated for the model proposed, using R as the measure of the agreement.

5. Iterate (back to #3) if necessary. Sometimes only small shifts in the atom positions will be necessary.

Measurement of intensities:

There are several techniques which are employed for the evaluation of the intensities of x-ray reflections:

1. Peak height above background. While this type of intensity value is easy to measure, it ignores any dependence of the diffracted intensity on 2θ. Peak heights are qualitative estimates of the true intensity, and, while they are used in qualitative and sometimes quantitative analysis techniques, they are generally not useful in crystal structure analysis and other applications requiring high precision.

2. Integrated intensity - the area under the peak minus the background. The best values of the intensities are the peak areas. These can be obtained from chart recordings by integrating techniques such as square counting, etc., or through the use of a planimeter. Integrated intensities are also obtained directly during a scan by accumulating the counts over the entire peak; the background must also be counted and subtracted from such a measurement. For stored digital data, various algorithms are employed to get peak areas. Through the use of profile fitting algorithms, in which a function which closely represents the shape of the peak is calculated, it is possible to evaluate the intensities by mathematical integration.

V. THE X-RAY POWDER DIFFRACTOMETER

The instrument which is generally used nowadays for the recording of diffraction patterns for polycrystalline samples is the x-ray powder diffractometer. Manufacturers of such equipment are Philips, Siemens, Seifert, Rigaku, Scintag and Nicolet (now part of Siemens). Starting in about 1975, a number of improvements in these instrument systems have changed their character significantly and greatly expanded their capabilities. Some of the major improvements are:

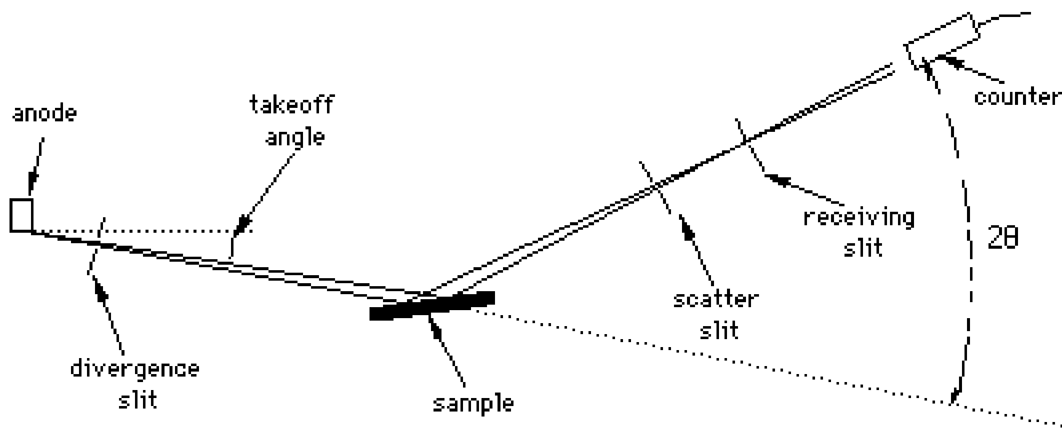
1. Redesign of x-ray tubes for higher intensities.

2. Incorporation of solid state electronics into both generator and detector systems, resulting in greater stability and reliability.

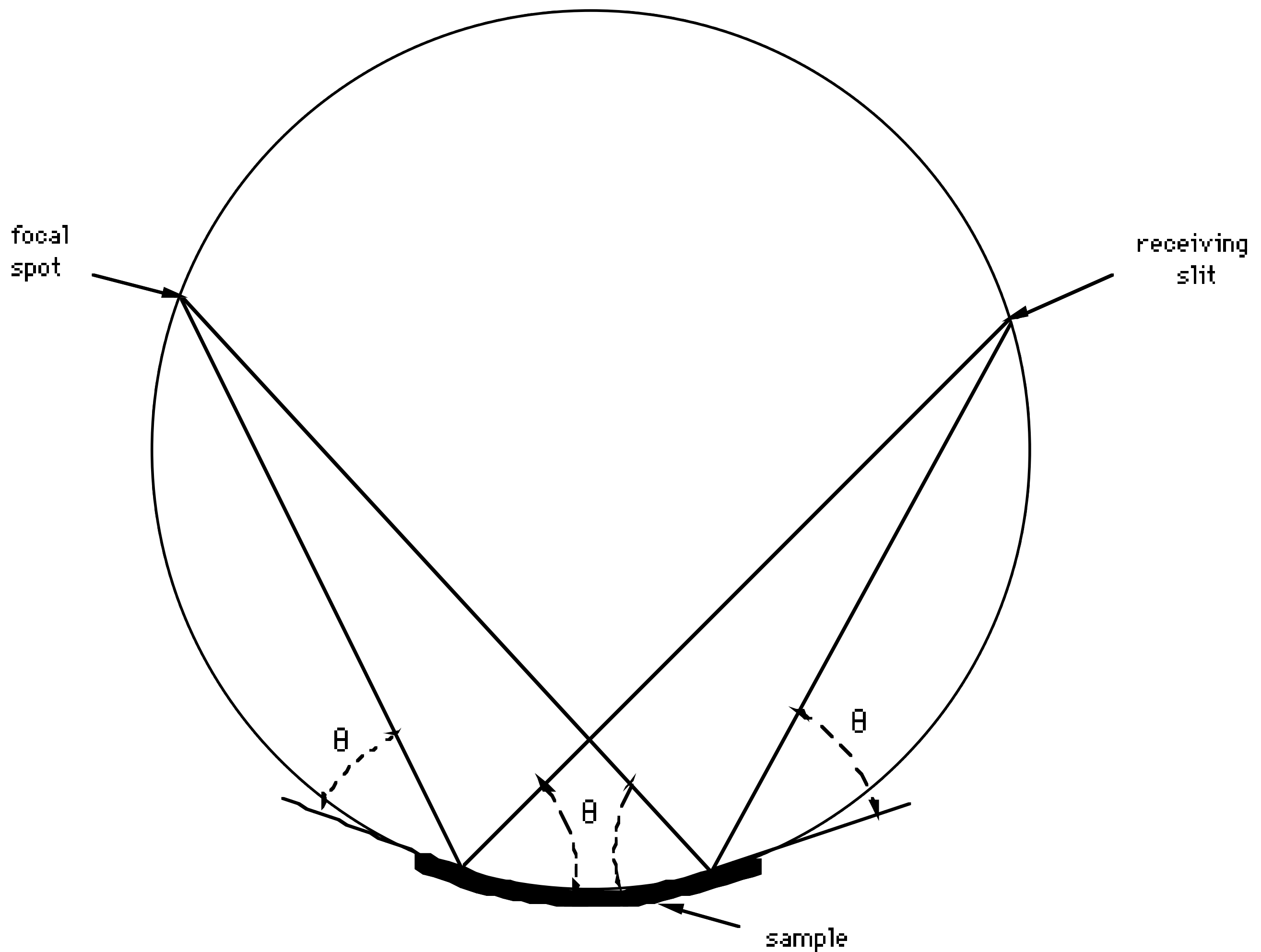
3. Incorporation of mini and microcomputers for automated operation, digital data storage, and data analysis.

However, the basic design and geometry of the diffractometer has not been changed, and can therefore be discussed in a generic way. The sample is placed at the center of the "diffractometer circle", and rotates around the center of this circle at a rate of θ°/min while the detector, monochromator, and slits assembly rotate around the same center at 2θ°/min. This maintains the Bragg condition for all possible reflections from planes which lie parallel to the surface of the sample.

Basic geometry of the powder diffractometer:



The line focus of the x-ray tube is used so that a wide beam is formed. This beam is collimated in such a way that it makes an angle (the takeoff angle) of usually 3-6° with the surface of the anode. A divergence slit is placed in the beam incident upon the sample which forms a beam that diverges, usually over an angle of 1°. This diverging beam allows the formation of a focusing geometry. If the line focus on the anode is placed on a circle (the focusing circle), along with the sample (which is curved with the same radius as the focusing circle), then a familiar theorem from geometry predicts that all the rays will be reflected from the sample at the same Bragg angle such that they focus at a point on the focusing circle, where a very narrow receiving slit is placed, at a distance from the center of the sample which is equal to the distance from the focal spot to the center of the sample.



It is difficult to use a curved sample in the diffractometer, however, because the radius of curvature is a function of Θ, and thus the flat sample compromise is made, resulting in some defocusing.

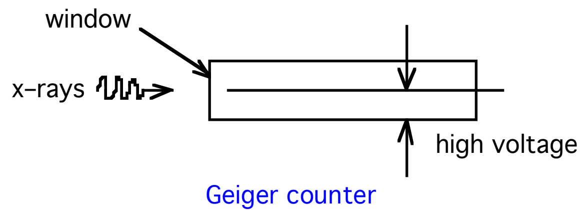
X-ray detectors:

1. Film: special film sensitive to x-rays is required. Quantitative measurement of intensities is quite difficult.

2. Fluorescent screen: ZnS doped with Cd in solid solution. Used for detecting presence of x-ray beams and alignment of instruments.

3. Counters:

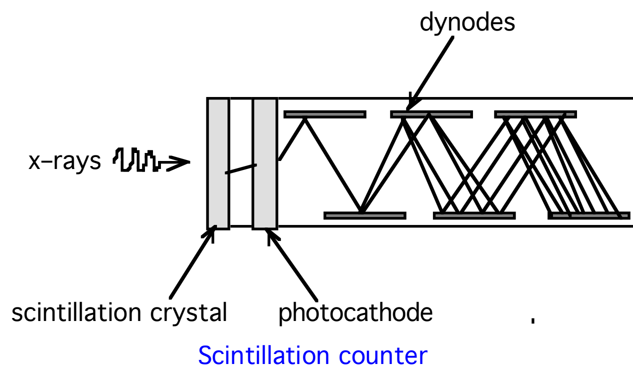
Geiger: obsolete, used in early instruments. It is useful, however, to understand how the Geiger counter operates. A central wire in the counter is maintained at a high voltage (500-1500 V) with respect to its case. When an x-ray photon enters the counter through a window, it ionizes the gas in the counter and causes a discharge to take place across this voltage. The pulse produced by this discharge is sent to the counting circuitry.



Geiger counter

Proportional: very similar to the Geiger counter except that the height of the pulse produced in this counter is proportional to the energy of the incoming x-ray photon. Pulse height analysis can then be carried out on the counter signals; pulses corresponding to x-ray photons which have the wrong energies can be rejected by the counting circuitry.

Scintillation: most common; consists of a scintillator crystal which gives off a burst of light wherever an x-ray photon hits. Light photons hit a photosensitive material which gives off electrons and this electron signal is amplified by a series of photomultiplier devices.



Scintillation counter

Solid state detector: relatively new, has a very high energy resolution, plus a very low noise level. The counter has its own energy window and no β filter or monochromator is required. It is also possible to do energy dispersive analyses when this detector is used; thus, x-ray fluorescence analysis is possible with this type of counter. These counters are quite expensive, and must be operated at low temperatures. They must be operated in liquid nitrogen temperatures, and most operators prefer to quite the counters at this temperature range at the time. Recently, counters cooled by thermoelectric cooling devices have become available.

Position sensing detectors: also relatively new. These counters are similar to a proportional counter; the location of the position in space (usually along a line) of where an incident photon hits can be determined by electronically determining the time required for the pulse to exit the counter. Two dimensional position sensing detectors are also available.

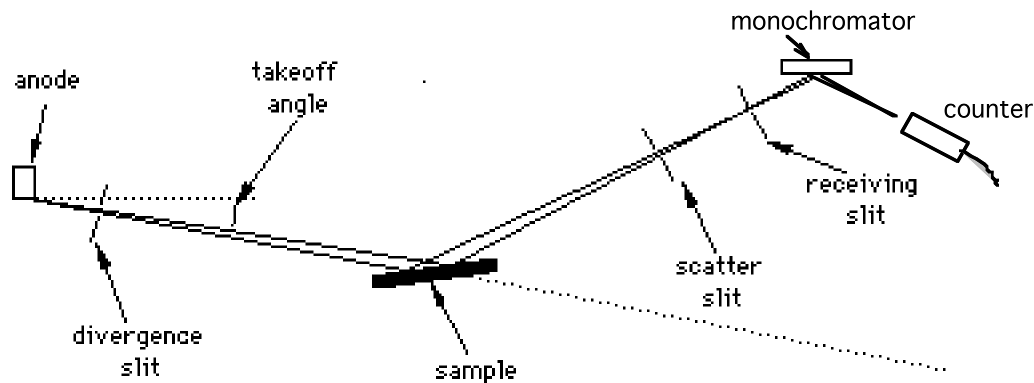
Solid state image intensifiers: relatively new, act like a 2-D detector. Used for real time x-ray diffraction "photography".

4. Hands: Disadvantage - too slow (7-10 days); advantages - detection is permanent, and can be quite dramatic in character.

The x-ray diffractometer, of course, uses counters as x-ray detectors.

<u>Monochromators.</u>
The use of a monochromator, usually placed on the diffracted beam side of the sample just before the counter, results in the removal of white radiation from the x-ray tube, fluorescent radiation from the sample, and the β component of the characteristic radiation (if not set to specifically detect that wavelength). The monochromator consists of a single crystal, usually pyrolytic graphite because of its very

high diffracting power, oriented so that Bragg reflection occurs from a desired set of planes in the crystal. For graphite, this set of planes is the (002) set. Bragg's law is used to calculate the correct angular setting for the desired wavelength (d_{hkl} is fixed). The intensity of the diffracted beams from the sample is reduced to about $\frac{1}{2}$.



Summary-ways to clean up the radiation.

1. Use a β filter
2. Use a monochromator
3. Use a solid state counter
4. Employ pulse height discrimination

The two most common configurations for x-ray diffractometers are 1) a monochromator and a scintillation counter, used with pulse height analysis, and 2) a solid state detector used with pulse height analysis.

For camera instruments, essentially the only choice is to use a β filter.

Modern x-ray diffractometers:

X-ray diffractometers have been improved considerably over the last 10 years or so. The reasons for this are:

1. the development of tubes of greater intensity or brilliance
2. x-ray tubes have been designed which have smaller focal spots
3. much better counters and counting electronics are now available
4. better instrument design
5. more stable electronics for x-ray generators
6. the advent of small computers

The role of the computer and automation:

1. Control of the diffractometer: the computer performs the scan, according to the operating conditions preset by the user. The usual mode for scanning is the step-scan, where the diffractometer moves to a certain angle, stops and counts the incoming radiation for a specified time, and then stores that number in a file, before moving to the next angle and repeating. Count times are usually varied over the range 0.1-10 sec, and step sizes are typically 0.01-0.05° 2θ. Longer count times give more precise data since the standard deviation in the number N of counts measured is $\sqrt{N}$.

The Scintag diffractometer is capable of a scan mode called the fast scan, in which the diffractometer does not step scan but moves continuously, and the electronics records the number of counts accumulated over successive time intervals as preset by the user.

2. Data analysis: what the computer can do with the data is limited only by what software is available on the instrument. The following are common.

a. Processing of raw data - removal of background, smoothing, α_2 stripping, peak finding, calculating intensities.

b. Applications - search/match, quantitative analysis, lattice constant calculations, machine indexing, graphics, including comparison of patterns. Many other types of programs are available on commercial instruments.

Sample preparation:

The reliability and precision of the data from a powder diffractometer are very sensitive to the method used for the preparation of the diffractometer sample.

The biggest problem encountered in the preparation of samples for x-ray diffractometer studies is that of avoiding preferred orientation. Preferred orientation is the condition in which the grains in the polycrystalline sample are not randomly oriented. A set of crystallographic planes and/or crystallographic direction in the grains are aligned along some particular physical direction(s) in a sample which exhibits preferred orientation. A powdered sample can be easily oriented by the pressing or smoothing of the powder into the sample holder cavity. When the sample cannot be powdered and it is necessary to use to use a bulk sample, preferred orientation is frequently a significant problem since it can be produced by plastic deformation or a casting process.

Preferred orientation in x-ray diffractometer samples presents difficulties in the determination of the correct intensities. The reason for this is that **the only planes that contribute to a reflection are those oriented parallel to the surface of the sample**. Thus, in a sample containing a very large number of particles or grains which are randomly oriented, the probability of **all** (hkl) planes being so oriented is the same. Thus, the measured intensities are all on the same basis. However, in a sample which exhibits preferred orientation, this probability is not the same, and the resulting measured reflection intensities will be incorrect, with respect to those from a randomly oriented sample. Intensities for samples with preferred orientation can be employed if the extent of the preferred orientation is reproducible from sample to sample, but they cannot be usefully compared with those from randomly oriented samples.

If the particles in a diffractometer sample are all perfect spheres, it would be essentially impossible to attain any state of preferred orientation during the preparation of a diffractometer sample. Preferred orientation occurs in samples made up of grains which have a shape other than a sphere. An extreme example is that of "powdered" mica. Finely ground mica particles, when placed in a diffractometer sample holder, will all align so that the flakes are parallel to the surface of the sample. Thus, only one reflection, and its higher orders, can be observed.

Spherically shaped powder particles are difficult to pack into the diffractometer sample holder cavity...they tend to flow out easily.

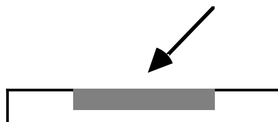
Erroneous intensity values cause problems in, for example, search/match procedures. Another example is in the quantitative analysis. Consider the case where it is desired to determine the relative amounts the two phases in rutile-anatase (both TiO_2) mixtures. The intensities of, say, the rutile reflections change depending upon how much rutile is present in the sample. Incorrect intensity values, then, obviously yield the wrong analysis.

<u>Specimen Preparation Techniques:</u>

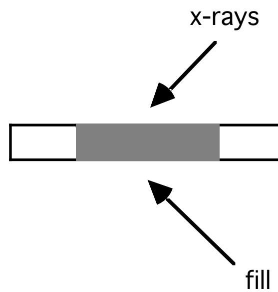
1. Massive sample - may have to cut to size. Probable difficulties with preferred orientation.

2. Slide preparation - powder is sprinkled onto glass slide and adhered thereto using, commonly, alcohol, water, acetone, etc. Problems are a) preferred orientation, b) sample surface may be sufficiently off the diffractometer axis to cause small shifts in the peak positions, c) intensities may be low due to the small amount of sample, and d) the glass gives a broad scattering maximum around 20-30°.

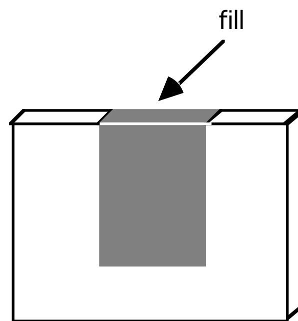
3. Cavity fill - front-filled. Sample surface on axis OK and lots of sample, but possible preferred orientation problems from smoothing the surface of the sample.



4. Backload - filled from the side that will not be exposed to the x-rays. Probability of preferred orientation problems is drastically reduced.



5. Side drift - the sample is drifted into the cavity between two removable plates through an opening in the side of the sample holder. This is the standard NIST technique, used to hopefully eliminate all problems with preferred orientation.



6. Two other techniques which really do effectively deal with the problem of preferred orientation are spray drying, a method in which the sample powder and a binder are blown into a large bin through a special nozzle, and the filter method, a rapid, inexpensive method in which the sample powder is made into a smoke and gently sucked into a special filter which becomes the sample holder.

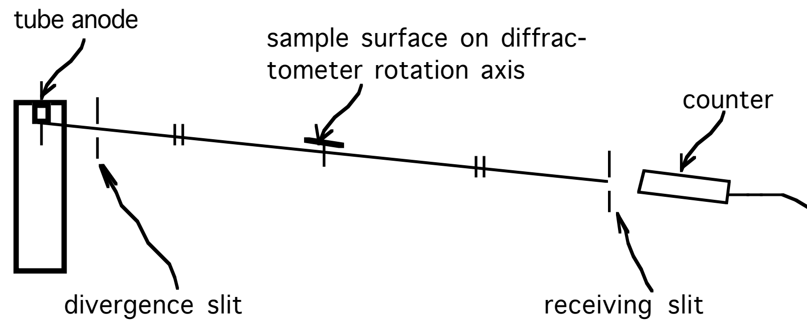
7. A less expensive version of the spray-drying technique is one in which the finely ground powder is sprayed with a polymer mist, such as one of the clear spray acrylics. The polymer droplets are spherical in shape, and the powder particles attach themselves to these spherical droplets.

8. Some types of diffractometer samples must be made very thin. This is particularly true in the case of materials whose absorption coefficients are very low, where the considerable penetration of the incident beam into a thick sample makes the sample appear to be off the diffractometer axis, and reflections are shifted to lower 2θ values. The solution is to make a very thin sample by sprinkling the powder onto a plate (method 2 above). The diffracted beams will be relatively weak. Any scattering from the supporting plate will degrade the quality of the x-ray diffraction pattern. This can be avoided by using what is known as a zero background sample holder, which is a plate-like piece of a single crystal (frequently quartz) whose surface is ground so that it is not parallel to any crystal planes which can reflect the x-radiation used. Of course, there can be a problem with preferred orientation with this type of sample.

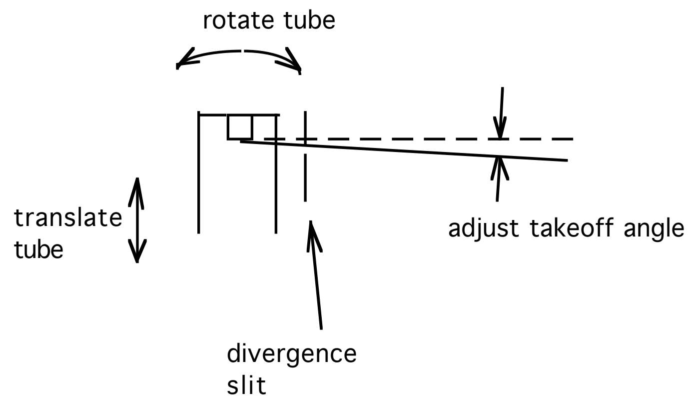
Principles of diffractometer alignment:

The second major thing which determines the quality of the x-ray diffraction data is the state of the alignment of the diffractometer. While the specific procedures for the alignment of a powder diffractometer vary from manufacturer to manufacturer, the following geometrical adjustments are common to all of them.

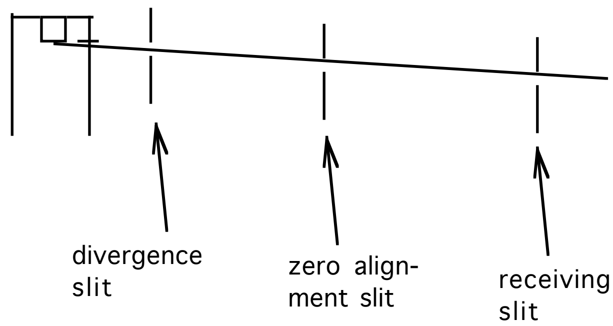
1. Make the distance from the focal spot on the anode to the diffractometer rotation axis equal to the distance from the rotation axis to the receiving slit.



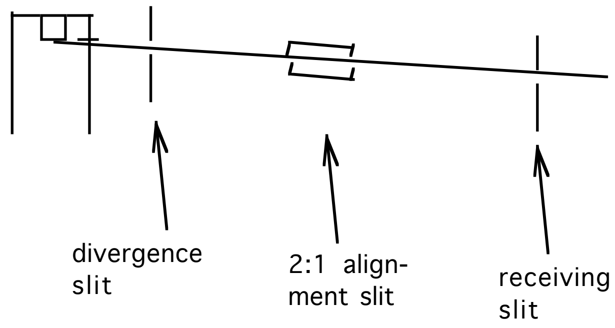
2. Position tube with respect to diffractometer system.



3. Set 0° 2θ



4. Adjust 2:1 setting



VI. APPLICATIONS OF X-RAY DIFFRACTION ANALYSIS

The applications of x-ray diffraction methods are very numerous. A few of the more common types of applications are listed below.

1. Materials analysis, qualitative and quantitative.
2. Studies of phase diagrams
    - A. Phase boundaries
    - B. Solid solutions
    - C. Phase transitions
3. Studies of chemical reactions and identification of reaction products.
4. Thermal vibration measurements.
5. Studies of order-disorder reactions.
6. Measurement of thermal expansion coefficients.
7. Compressibilities (from high pressure measurements).
8. Studies of imperfections (e.g., compare x-ray densities with densities measured by ordinary techniques).
9. The measurement of particle or crystallite sizes.
10. The determination of grain sizes.
11. The measurement of residual stresses.
12. Crystallinity.
13. Preferred orientation in polycrystalline bodies.
14. Crystal alignment.
15. Crystal perfection.
16. Solid state reactions (e.g., Guinier-Preston zones).
17. Crystal structure studies.
18. The determination of interatomic distances.
19. Many more.

Some of these applications are discussed below.

1. Qualitative analysis - x-ray diffraction analysis here gives specifically the phases present. This is particularly useful because ordinary techniques for chemical analysis do not give this type of information. For example, if several polymorphic forms of a substance are present, chemical analysis techniques cannot differentiate between them. The same is true if a particular element, for which the analysis is being carried out, is contained in more than one phase in the sample.

An x-ray diffraction pattern is a fingerprint of a substance. There is a fingerprint database - the Powder Diffraction File (PDF) (a product of the International Centre for Diffraction Data, formerly the Joint Committee for Powder Diffraction Standards (JCPDS), Swarthmore, PA), and search manuals for locating specific entries in the PDF. There are at present about 55,000 entries in the PDF. The file data have been published in book form, on cards, microfiche, magnetic tape, diskettes, and CD-ROM. The most popular medium for the database, at present, is the CD-ROM. The format and information for each of the entries is illustrated below.

21-1152 JCPDS-ICDD Copyright 1988 QM= *

$MgAl_2 O_4$

Magnesium Aluminum Oxide Spinel, syn

Rad: CuKa1 Lambda: 1.5405 Filter: Mono. d-sp:
Cutoff: Int: Diffractometer I/Icor: 1.70
Ref: Nat. Bur. Stand. (U.S.) Monogr. 25, (1971)

Sys: Cubic S.G.: Fd3m (227)
a: 8.0831 b: c: A: C:
A: B: C: Z: 8 mp:
Ref: Ibid.

Dx: 3.58 Dm: SS/FOM: F(29)=58.2(.0151,33)

---

ea: nwB: 1.718 ey: Sign: 2V:
Ref: Ibid.

Color: Colorless
Pattern at 25 C. The sample was furnished by H.R. Shell of the Bureau of Mines, College Park, Maryland, USA. He used a carbon electrode furnace and removed an excess of MgO with hot HCl after crushing. Spinel group, spinel subgroup.
Silver used as internal standard. PSC: cF56.

Strong lines: 2.44/X 2.02/7 1.43/6 1.56/5 2.86/4 4.66/4 0.82/2 1.05/1

---

29 reflections in pattern. Page 1 of 1. Radiation= 1.54050

d (Å)	Int.	h k l	d (Å)	Int.	h k l
4.66	35	1 1 1	1.0524	12	7 3 1
2.858	40	2 2 0	1.0104	8	8 0 0
2.437	100	3 1 1	0.9527	2	6 6 0
2.335	4	2 2 2	0.9334	8	7 5 1
2.020	65	4 0 0	0.9274	2	6 6 2
1.650	10	4 2 2	0.9038	6	8 4 0
1.5554	45	5 1 1	0.8872	2	9 1 1
1.4289	55	4 4 0	0.8820	<2	8 4 2
1.3662	4	5 3 1	0.8616	<2	6 6 4
1.2780	4	6 2 0	0.8474	8	9 3 1

1.2330	8	5 3 3	0.8249	18	8 4 4
1.2187	2	6 2 2	0.8123	<2	7 7 1
1.1666	6	4 4 4	0.7927	2	0 2 0
1.1320	2	5 5 1	0.7814	12	9 5 1
1.0802	6	6 4 2			

Note that the intensities given are peak heights above background.

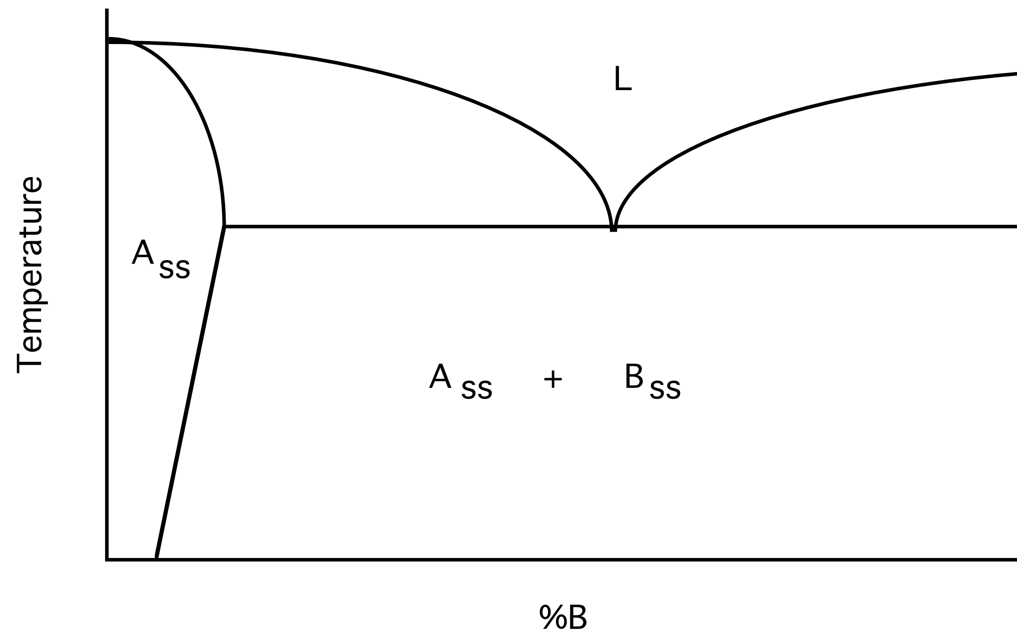
The manuals accompanying the database consist of an alphabetical listing, a formula listing, and Hanawalt and Fink search manuals. The Hanawalt technique uses the d's for the three most intense reflections as a basis for the search. The Hanawalt search manual lists the d's for the three most intense reflections for every substance in the database; this list is searched systematically until a match with the three observed values is found. The entry for the substance corresponding to the match is then checked (cards, microfiche, CD-ROM, or other) to make sure that the observed and PDF d's and I's agree well for all of the reflections. In the Fink search technique, instead of the three most intense reflections, the d's in the search manual are listed in order of decreasing d value, starting from one of the four most intense reflections. Both search techniques are variously useful in making an identification for a particular pattern.

In searching the file for the purpose of locating a pattern which matches that of an unknown pattern, the d's and I's of the most intense reflections are used. It is essential to be very systematic in a manual search. Computer searching techniques are available, but, in general, the result of a computer search is a list of a relatively large number of possibilities for the identification, unless specific chemical information is given. It is still up to the diffractionist to decide which compound or compounds are present.

When an analysis of an unknown pattern is begun, the rank of the observed intensities is first noted. In the Hanawalt method, then, the section of the search manual which lists the d for the most intense reflection is located. An attempt is next made to match the d for the next most intense reflection with one of the d's listed in the second column in this section. Finally, when the d for third most intense reflection is found in the third column in this section, the keying is completed. In the case where there are two or more phases in the sample, a match may not be found for the d's for the first and second most intense reflections; a match for the d's for the first and third most intense reflections should be sought. Following this, the first and the fourth most reflections, etc., should be tried. If these attempts fail, the first and third reflections with the fourth, etc., should be tried.

2. Phase diagram studies - x-ray diffraction patterns can be used to locate single and multiple phase fields, and to determine the limits of solubility in phases (even as a function of temperature, if high temperature diffraction studies are carried out) and to determine the crystal structures of new phases found. In a single phase field, the lattice parameters vary, while in a multiple phase field, the lattice parameters of the phases present do not change. Two techniques are used to determine the limit of solubility of a solid solution phase: the lattice parameter variation method, and the disappearing phase method, in which the intensities of selected reflections are measured as a function of composition (the phase boundary location is that where the intensities extrapolate to zero).

Suppose we have a simple eutectic phase diagram with limited terminal solid solubility as shown below.

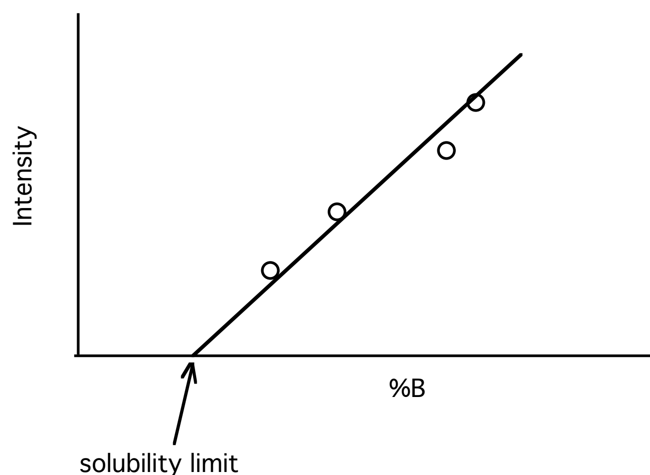


In the region A_{ss}, an x-ray diffraction pattern will exhibit peaks for only the phase A_{ss} The lattice parameter(s) for A_{ss} derived from this pattern change with composition, generally because of the difference in atomic radii. This variation may have either a positive or negative slope, depending upon the relative atom sizes and the type of solid solution, and it is frequently linear or close to linear in nature.

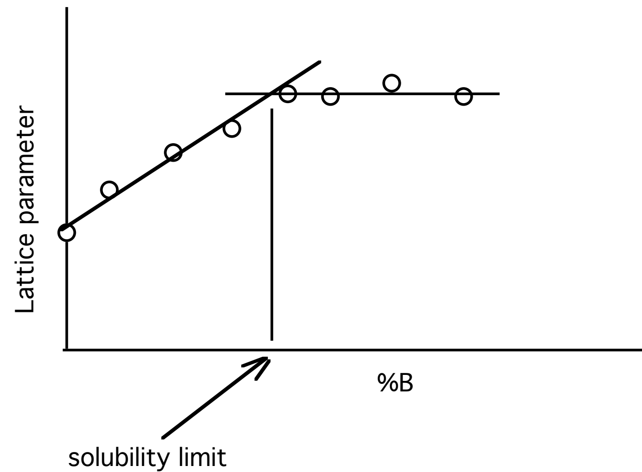
In the region A_{ss} + B_{ss}, an x-ray diffraction pattern will exhibit peaks for both the phase A_{ss} and B_{ss}. However, here, the lattice parameter(s) for A_{ss} and B_{ss} are constant, but the intensities of the reflections change. For example, the intensities for the reflections for the phase A_{ss} increase linearly with %A since the amount of the phase A_{ss} has to increase.

Thus, to determine the position of a phase boundary at a particular temperature, two procedures can be followed.

1) The intensities of the peaks of one of the phases will decrease to zero when the solubility limit of the other phase is reached. If the intensities of one of the reflections is measured at various compositions in the two phase region, these intensity values can be thus be plotted to find the solubility limit. This is the disappearing phase method.

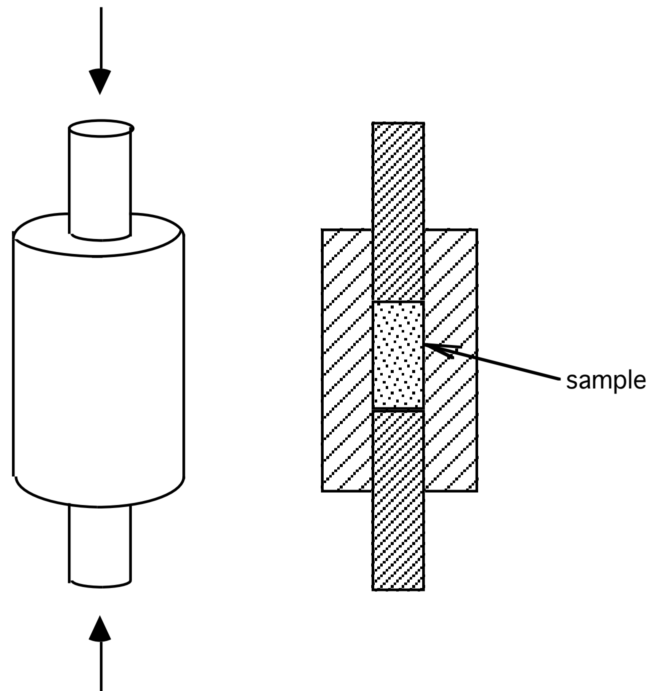


2) The lattice parameters for both phases vary in the solid solution regions and are constant in the two-phase region $A_{ss} + B_{ss}$. If one of the lattice parameters for one of the phases is measured at various compositions in both the solid solution and two-phase regions, then these values can plotted so that the break in the plot corresponds to the solubility limit. This is the lattice parameter variation method. Precise values of the lattice parameters should be calculated from the diffraction data for solvus determinations.



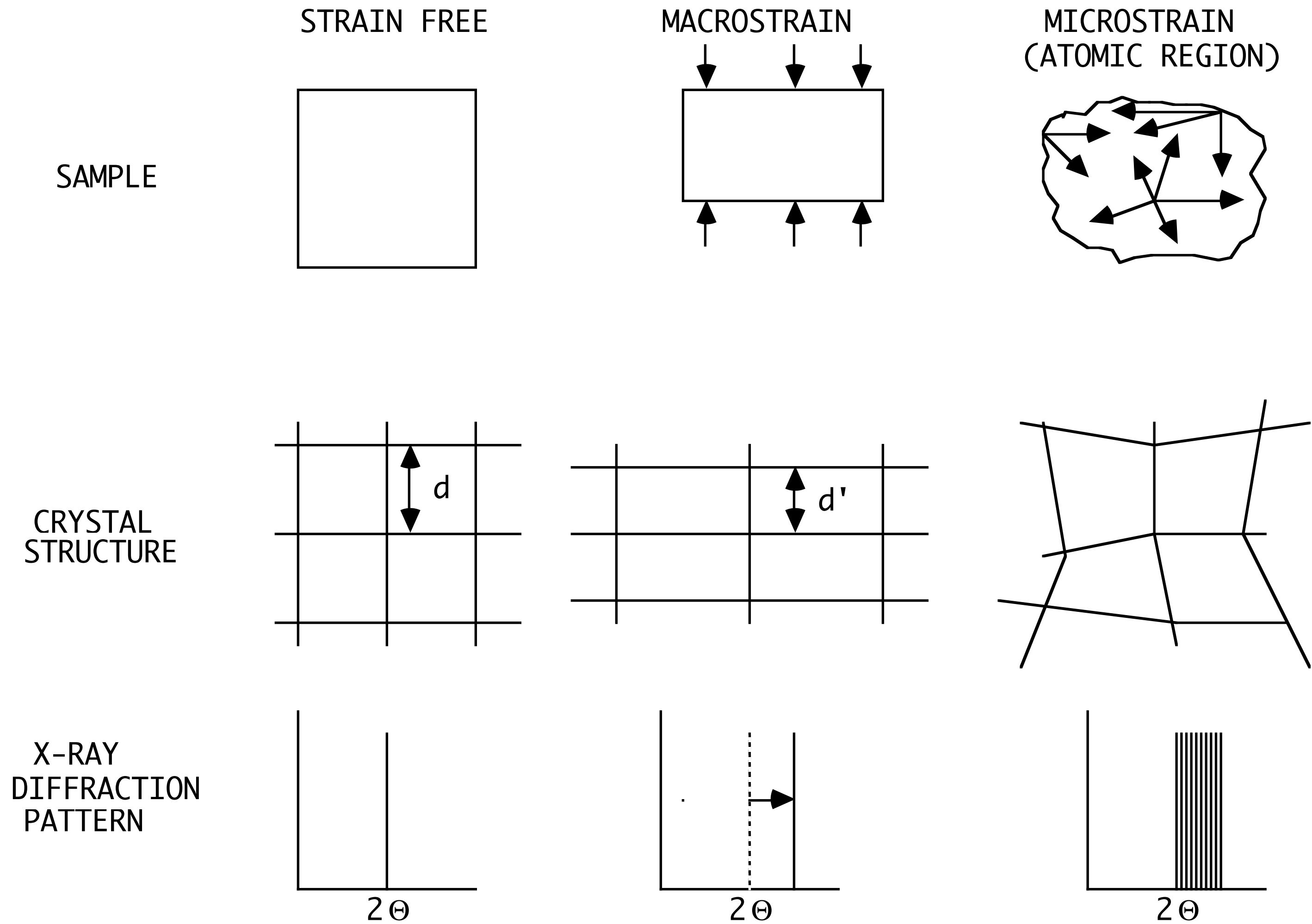
3. Thermal expansion - requires measurements over a range of temperature. Cohen's method is generally used to obtain precise parameters. The x-ray diffraction method has the advantage of yielding the crystallographic anisotropy in expansion from one set of measurements. On the other hand, obtaining highly precise high temperature x-ray diffraction data demands considerable experimental technique. Also, an interesting anomaly presents itself here. To obtain highly precise data, high angle reflections should be used; however, it is these high angle reflections that are most affected by the temperature effect, such that they tend to disappear as the temperature is increased.

4. Compressibilities - lattice parameters as a function of pressure. Need precise parameters here also. Special high pressure equipment is required here. For example, one of the first high pressure cameras employed a beryllium (low absorption) sample holder similar to that shown in the figure below. Again, the experimental difficulties are considerable.



5. Residual stresses - residual elastic strains which are homogeneous result in shifts of positions of reflections due to changes in lattice parameters in response to some type of applied stress. Non homogeneous strains broaden the x-ray reflection peaks. An analysis of the shapes of the peaks results in the calculation of a microstrain distribution function.

Since there can be no residual stresses normal to a free surface, the measurement of residual stress cannot be made in an unmodified conventional diffractometer, where only the planes parallel to the surface of the sample are diffracting. Instead, the measurement is made with the sample inclined to the incident beam at an angle other than θ, and the residual stress parallel to the surface of the sample is calculated from the shift in the position of a particular high angle reflection. A difficulty here is that this non-θ inclination to the incident beam in part destroys the focusing condition of the conventional diffractometer; the reflections are distorted and broadened.



6. Crystallite size - very small crystallite size is another cause of peak broadening. To avoid size broadening, crystallite size should be $>10^{-5}$ cm. To avoid other problems, crystallite size should be $<10^{-3}$ cm.

On the other hand, peak broadening can be used to determine crystallite size. There are a number of methods for this type of determination, but the simplest is perhaps the Scherrer method. In the Scherrer method, the broadening, B_{size},of the diffraction peak due to the small crystallite size is determined. Then

$$\text{size} = \frac{0.9\,\lambda}{B_{size}\cos\theta}$$

The factor os 0.9 is a geometrical correction factor; it varies with the diffraction geometry used.

For any technique in which the peak broadening is measured, the instrumental broadening must be removed. This instrumental broadening comes from finite slit widths in the diffractometer, spectral broadening, sample transparency, geometrical defocusing, etc. For an excellent discussion of these sources of broadening, see Klug and Alexander.

To determine the instrumental broadening, peaks from a standard sample which exhibit no broadening other than that due to the instrument are measured. It is convenient to use a standard which is the same material as the sample being studied, if possible. In the Scherrer method, the instrumental broadening correction is made thus

$$B^2_{size} = B^2_{sample} - B^2_{std}$$

The determination of crystallite sizes is complicated by the presence of strain broadening as discussed above. The strain broadening and the size broadening must be separated. The so-called Warren-Averbach technique, a mathematically procedure, is generally used for this. See Warren: X-ray Diffraction.

7. Quantitative analysis - for diffractometers, the integrated intensity of a reflection, measured by the area under a peak, minus background, is

$$I = I_o \cdot \text{constant} \cdot 1/v^2 \cdot p \cdot LP \cdot e^{-2M} \cdot 1/2\mu^* \cdot |F|^2$$

where v = unit cell volume, p = multiplicity - the number of individual planes in a family of planes, L = the Lorentz factor - accounts for the increase in the breadth of the peaks as a function of 2θ, P = the polarization factor - accounts for intensity changes as a function of 2θ for various states of polarization of the incident x-ray beam, e^{-2M} is the temperature factor, with $M = 8\pi^2 \mu^2 (\sin \theta/\lambda)2$, where μ^2 is the mean square amplitude of vibration of the atoms, in a direction perpendicular to the reflecting planes, and μ^* is the linear absorption coefficient.

There are several techniques used in quantitative analysis by x-ray diffraction. One, for a binary mixture, is to compare the intensity I_α of a reflection for phase α in the mixture to be analyzed with that for the pure material. A curve of this ratio, calculated from the mass absorption coefficients, is plotted versus composition; this curve is used for the analysis. Alternatively, the curve can be constructed from the ratios of intensities measured on samples of known compositions.

8. % crystallinity - obtained from the measurement of the intensity of the very broad peaks representing scattering from the amorphous material in the sample compared to the intensity from the crystalline portion of the material.

Other sources of radiation useful for diffraction studies

Other sources of radiation frequently used for diffraction studies are

synchrotron radiation
neutrons
electrons

Synchrotron radiation is really an x-ray beam produced by the deceleration of electrons or positrons traveling in a storage ring.

Some advantages of synchrotron radiation are

Stable radiation source
Extreme brilliance
Broad bandwidth - tunable wavelengths
Beam divergence is about 10^{-5} °
Highly monochromatic
Dynamic, real-time measurements ($\sim$ millisec)

Neutrons and electrons are particles which exhibit wavelike characteristics. Bragg's law works just fine to describe the diffraction patterns using these radiations.

For neutron diffraction, the following are required

A nuclear reactor or pulsed neutron source with a neutron flux of at least 10^{12} neutrons/cm^2/sec
Relatively larger samples

Since the neutrons are scattered by the nucleus, there are several advantages of using neutron diffraction

The neutron scattering factors are very different from those for x-rays
Scattering from magnetic atoms can be observed