CRYSTAL STRUCTURE ANALYSIS OF COPPER NITRATE

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

Donald C. Bulthaup

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ABSTRACT

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By

Donald C. Bulthaup

The lattice constants and interaxial angles of copper nitrate were determined, and the space group was limited to two possibilities using X-ray diffraction methods. The lattice constants were found to be: a = 22.2 Å, b = 4.90 Å, c = 15.4 Å, while the interaxial angle β was found to be 132° for the unit cell chosen in this monoclinic crystal. The space group was found to be either Pc or $P\frac{2}{c}$. The values for a, b, c and β agree with those found by Dornberger-Schiff and Leciejewicz,* but the space group determination does not.

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By
Donald C. Bulthaup

A THESIS

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I THEORY

A. Crystal Structure

1. Crystal Habit - Since vonLaue's work in 1912, it has been known that crystals are made up of a regular array of atoms. In the course of studying crystal structure (started long before the time of Laue) several "laws of crystallography" have been discovered and many methods devised for representing the symmetry of this structure.

The crystal habit exhibits symmetry which can be described by three "symmetry operations." These are:

a. Symmetry axes.
b. Mirror planes..
c. Centers of symmetry.

Rotating the crystal about a symmetry axis will cause it to be in a position similar to the original position after rotating through 60°, 90°, 120°, or 180° depending upon the type of axis. These axes are labeled two-fold axes if the necessary angle of rotation is $\frac{360}{2}$ or 180° (n-fold axes if the necessary angle of rotation is $\frac{360}{n}$). It can be shown that only one, two, three, four and six-fold axes are possible.

A mirror plane, as the name suggests, divides the crystal in such a way that each face, point or line on one side of the plane has a mate which appears as a mirror image on the other side.

A center of symmetry is a point within the crystal such that any line through this point intersects similar points, lines or faces on opposite sides of the crystal. Faces on opposite ends of lines through the center of symmetry must be parallel.

All crystal habit symmetry can be described by the three operations listed or combinations of these operations and the seven crystal classes* listed in Table 1 are identified in this manner. It will be noticed in this table that one combination of symmetry elements is especially common. This is the combination of a symmetry or rotation axis with a center of symmetry. The combination is commonly called an inversion axis and is given the symbol $\bar{n}$ for an n-fold axis.

TABLE 1 - CRYSTAL HABIT SYMMETRY

Crystal Class	Identifying Symmetry Elements
1. Triclinic	Center of symmetry only
2. Monoclinic	Two-fold axis (rotation or inversion) in one direction only
3. Orthorhombic	Three mutually perpendicular two-fold axes (rotation or inversion)
4. Hexagonal	Six-fold axis (rotation or inversion) along two axes
5. Trigonal	Three-fold axis in one direction only (rotation or inversion)
6. Tetragonal	Four-fold axis (rotation or inversion) one direction only
7. Cubic	Four three-fold axes

Note: Other symmetry operations exist for some classes, but the ones listed represent the highest order symmetry.

2. Bravais Lattices - Very early in the study of crystals it was hypothesised that the regularity of the crystal habit implied a regular arrangement of "building blocks" within. With this in mind, many investigators studied the possible arrangements of points in homogeneous three-dimensional lattices. In 1848 Bravais showed that there were only fourteen distinct lattice arrangements possible. (See Table 2 on Page 4.) To study these lattices it is convenient to refer the points to a coordinate system. To simplify notation the axes of this system should lie along lines of large lattice point

*Some references list only six classes by listing the trigonal system as a division of the hexagonal system.

population. This means that frequently the coordinate system chosen is not orthogonal and different coordinate systems might be chosen to describe the same crystal. The choice of coordinate system for any given crystal depends upon the structure of that crystal and is made to produce a model which is mathematically the easiest to study.

The seven crystal classes can be described microscopically in terms of angles between axes and spacing of lattice points along the axes. Table 2 lists these seven classes and the distinguishing axial angles and lattice spacing. It should be noted that by convention the spacing is labeled "a" along the x-axis, "b" along the y-axis and "c" along the z-axis. Also the interaxial angles $y \wedge z$, $z \wedge x$ and $x \wedge y$ are denoted by α, β and γ respectively.

A very useful concept in the study of microscopic crystal structure is that of the unit cell. It is defined as the smallest unit in the structure which has the physical and chemical properties of the macroscopic crystal. The crystal is formed by packing unit cells together in a three-dimensional arrangement. In all crystals a unit cell (called a primitive cell) can be chosen such that lattice points appear only at corners of regular polyhedrons and it would seem that this choice would always be the best. It is found, however, that frequently certain simplifications result if the unit cell is chosen in such a way that it is not primitive. An example of this in a two-dimensional lattice is shown in Figure 1. Note that if the cells outlined by the dashed line were chosen, a non-orthogonal coordinate system would have to be used to describe

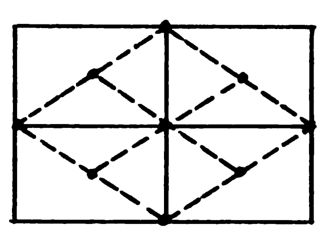


FIGURE 1 - TWO-DIMENSIONAL LATTICE

the lattice. The cells outlined by the solid line can be described with an orthogonal system but these are not primitive, in that an additional point appears at the center of each.

As mentioned before, Bravais showed in 1848 that there were only fourteen distinct three-dimensional lattices possible. These include a primitive configuration for each crystal class plus non-primitive configurations for several of the classes. These Bravais lattices are listed in Table 2.

TABLE 2 - BRAVAIS LATTICES

Symmetry	Interaxial Angles	Axial Ratios	Lattice Type
Cubic	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$	Primitive (P) Face Centered (F) Body Centered (I)
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$	Primitive (P) Body Centered (I)
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$	Primitive (P) C-Face Centered (C) Body Centered (I) Face Centered (F)
Monoclinic	$\alpha = \gamma = 90^\circ \neq \beta$	$a \neq b \neq c$	Primitive (P) C-Face Centered (C)
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$a \neq b \neq c$	Primitive (P)
Hexagonal	$\alpha = \beta = 90^\circ \ \gamma = 120^\circ$	$a = b \neq c$	Primitive (P)
Trigonal	$\alpha = \beta = \gamma \neq 90^\circ$	$a = b = c$	Primitive (P)

3. Point Groups - The crystallographic symmetry operations have already been discussed (Page 1) and it was found that crystal habit could be defined in terms of these operations. In modern crystallography, however, the study of crystal habit makes up a very small portion of the total work done. The ultimate goal is to determine the lattice structure and which atoms occupy each position. If the above symmetry operations are changed to include

inversion axes (described on Page 2) as well as rotation axes, then these operations are useful in the microscopic study of crystals. It can be shown that there are thirty-two distinct "point groups" which can be produced by applying these operations in various combinations to a single point in space. The International Tables* lists these point groups and employs the following notation:

X - X-fold rotation axis.

$\bar{X}$ - X-fold inversion axis.

$\frac{X}{m}$ - X-fold rotation axis with mirror plane normal to it.

$X2$ - X-fold rotation axis with two-fold axis (axes) normal to it.

Xm - X-fold rotation axis with mirror plane (planes) parallel to it.

$\bar{X}2$ - X-fold inversion axis with two-fold axis (axes) normal to it.

$\bar{X}m$ - X-fold inversion axis with mirror plane (planes) parallel to it.

$\frac{\bar{X}}{mm}$ - X-fold inversion axis with a mirror plane normal to it and mirror planes parallel to it.

These point groups then represent all possible ways for arranging points in space about a single point such that the group has symmetry consistent with observed crystals.

Every crystal fits into one of the thirty-two "point groups," but it is not always easy to establish which one. To aid in the determination several methods have been developed which depend

*International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1952, Vol. I, Section 3.3.

upon the physical properties of the crystal. These can be divided into two categories; (1) studies of facial development and other external features and (2) information concerning certain internal physical characteristics.

In theory the point group can be determined by the symmetry of facial development, and this was the only method available to early crystallographers. This method, however, is not generally good in practice because the facial development may not be clear. The facial development depends upon the lattice plane population but is subject to change by impurities in the solution during growth and so the size of a particular face may be different in different crystals of the same type.

In some cases where the development of faces is inadequate, etch figures can be used to good advantage. A non-optically active etching reagent is placed upon one face. If the trial is successful, the etching will take place at different rates in different crystal directions resulting in an etch pit which has the symmetry of one of the ten two-dimensional point groups.* From this much can be learned about the crystal symmetry. Since the etch rate in different directions is often the same, the symmetry of the etch pit must be considered as the highest possible symmetry. This must be used with other information to produce a satisfactory analysis.

In general, internal physical properties of a crystal are easier to analyze and are more satisfactory for point group analysis. The three physical properties usually studied are optical refraction, optical activity, and pyroelectric and piezoelectric effects.

If a crystal is transparent, optical refraction can be determined in several directions. Only crystals of the cubic system

*International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1952, Vol. I, Section 3.7.

are isotropic and among anisotropic crystals those in the Orthorhombic, Monoclinic and Triclinic systems are biaxial while the remainder are uniaxial.

The only characteristic which can be implied by optical activity and the piezoelectric effect is the presence or absence of a center of symmetry. Fifteen of the twenty-one non-centrosymmetric point groups are optically active and all but one exhibit the piezoelectric effect. Even though the one non-centrosymmetric group which does not exhibit the piezoelectric effect is optically active, the absence of both effects in tests does not necessarily mean the crystal is centrosymmetric because sometimes the piezoelectric effect is too weak to measure. The presence of either effect, however, does mean that the crystal is non-centrosymmetric.

In theory the presence of the pyroelectric effect means that the point group of the crystal must have a unique polar axis. In practice, however, it is found that the stresses set up in the crystal by unequal heating or cooling during the test give rise to a piezoelectric effect and so the only safe deduction is that the crystal is non-centrosymmetric.

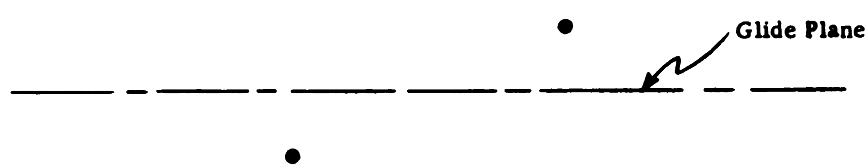
One other method is available to assist in point group determination, but this involves the symmetry of X-ray pictures and will be discussed later.

4. Space Groups - The symmetry operations discussed thus far have referred to crystal habit or lattices of indistinguishable points in space. In actual crystals the lattice positions are occupied not by indistinguishable points, but by atoms which differ from one another. This complicates the issue somewhat, and it can be seen that there will be many more than thirty-two arrangements possible. It is found that two more symmetry operations are needed to describe the additional arrangements.

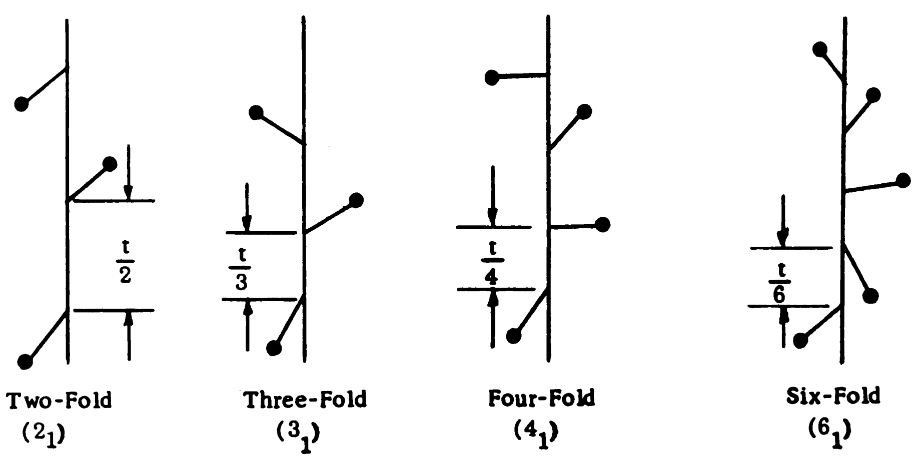
These operations are combinations of:

1. A simple rotation axis with a translation parallel to it.
2. A mirror plane with a translation parallel to it.

The first operation listed is called a screw axis, while the second is called a glide plane. Figure 2 shows equivalent points for each operation and lists the notation used for each. Note that these operations, unlike the other symmetry operations, do not bring a point back into coincidence with itself but rather bring it into coincidence with a corresponding point of a neighboring lattice position. These operations, therefore, only have meaning when applied to an extended point system.



Equivalent Points in Glide Plane Operation



SCREW AXES

(Note that each translation for an n-fold axis is $\frac{1}{n}$ of the repeat distance along the axis.)

FIGURE 2 - GLIDE PLANE AND SCREW AXES

For the complete description of atomic arrays in real crystals, some knowledge is needed of the possible "infinite" distributions of points (not all identical) in space which will bear the observed crystallographic symmetry. In 1891, Schoenflies proved that there were 230 such distributions, and these have been called the 230 space groups. The space groups can be derived by placing a point group at each point of a Bravais lattice of the same symmetry then using the appropriate symmetry operation from those introduced above (screw axis or glide plane). The symbol for each space group is a combination of the symbols representing the appropriate Bravais lattice, point group and screw axis or glide plane. A complete list of all space groups as well as the essential information about each can be found in the "International Tables for X-Ray Crystallography."

B. X-Ray Crystallography

1. Introduction - In the last section some general concepts about the structure of crystals were presented. It is found, however, that these concepts are inadequate in most cases where a complete analysis of a crystal is desired. For such a study of crystal structure one of the most useful methods available is X-ray diffraction and the purpose of this section is to outline the theory involved in this method.

2. Diffraction of X-rays - Every student of college physics has been exposed to the interference pattern formed by a double slit or a diffraction grating and knows that this pattern is formed when coherent waves reach some position either in phase or out of phase. This is somewhat analogous to the diffraction pattern formed when X-rays are allowed to strike a crystal. The major difference between the two is that in the double slit experiment the "diffracting objects" are the slits, while in diffraction by a crystal the electrons of the atoms in the lattice positions perform this function. The process involving the crystal is more difficult to analyze for two reasons:

a. It is a three-dimensional process rather than two.

b. The scattering process at the lattice positions is more difficult to describe quantitatively.

As X-radiation passes through a crystal each electron in the crystal finds itself in an oscillating field which means it experiences a periodically varying force. According to classical electromagnetic theory the acceleration which results causes the electron to emit radiation with a frequency the same as that of the varying force. This radiation is emitted with a spherical wave front, but the intensity is not the same in all directions. Viewed from an energy viewpoint, it is seen that energy is transferred from the incident radiation to the electron and then re-radiated so that the net effect is that part of the energy of the incident radiation is "scattered" by the electron. From this it would seem that the total scattering from each lattice position would be directly proportional to the number of electrons present. This is approximately true but due to the fact that at any given lattice position the electrons are separated by a short distance, there is some destructive interference in the emitted radiation.

In order to describe the interference pattern formed by a three-dimensional crystal, the scattering from each lattice position and the multiple interference at a point in space of radiation from these positions must be considered. It can be seen that this is not a simple thing to do and the calculations would be extremely cumbersome. Fortunately, a simpler alternative method involving what is known as the "Bragg Law" is available and in general use. This method is based upon the fact that the interference pattern can be accurately described by assuming that the X-ray beam is reflected from planes within the crystal drawn so that they contain many lattice points.

In order to use the Bragg Law described above, it is necessary to have a simple method for describing the planes within the crystal. If a three-dimensional coordinate system is placed on the lattice (origin position is arbitrary) the planes can be described in terms of the intercepts on these axes. If the plane of concern is parallel to one or two axes, then the intercept is at infinity and not at all convenient in any calculations. To eliminate this problem, Miller proposed a system whereby the plane is described by the reciprocal of the intercepts. Thus the plane parallel to the x-y plane would have the "Miller indices" (0, 0, 1).

In Figure 3 plane ABC has indices $(\frac{1}{3}, \frac{1}{2}, 1)$ or (2, 3, 6). These are equivalent indices because the labeling depends on the choice of origin which is arbitrary. By the same reasoning, the indices of plane DBE are $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ or (1, 1, 1).

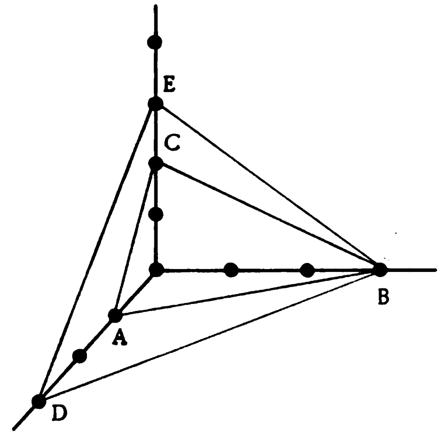


FIGURE 3 - MILLER INDICES

If the assumption of reflection from lattice planes is accepted, then the condition for constructive interference is easily derived. In Figure 4 the X-ray beam is incident from the left and "reflected" by the set of lattice planes shown. If constructive interference is to take place, the difference in path length between the beams "reflected" from adjacent planes must be equal to $n\,\lambda$. From the diagram it can be seen that $n\,\lambda = 2d \sin\theta$. This is known as the Bragg equation. A more eloquent derivation based directly upon scattering concepts can be found in many of the texts listed in the bibliography.

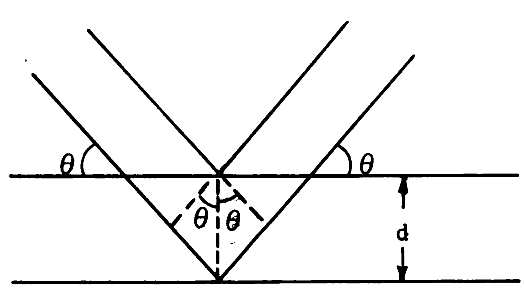


FIGURE 4 - BRAGG "REFLECTION"

In a complete crystal analysis the relative intensity of the reflection is very important, since it is from this information that the position occupied by each type of atom is determined. This project is not carried to that extent, but the conditions under which a certain reflection does not occur are important. It is from information about systematic absences of certain reflections that the space group of the crystal is determined.

As an example, consider a monoclinic, C-face centered crystal. The C-face is shown in Figure 4(a) along with planes of the form (23ℓ). Figure 5(b) shows the C-face with planes of the form (13ℓ).

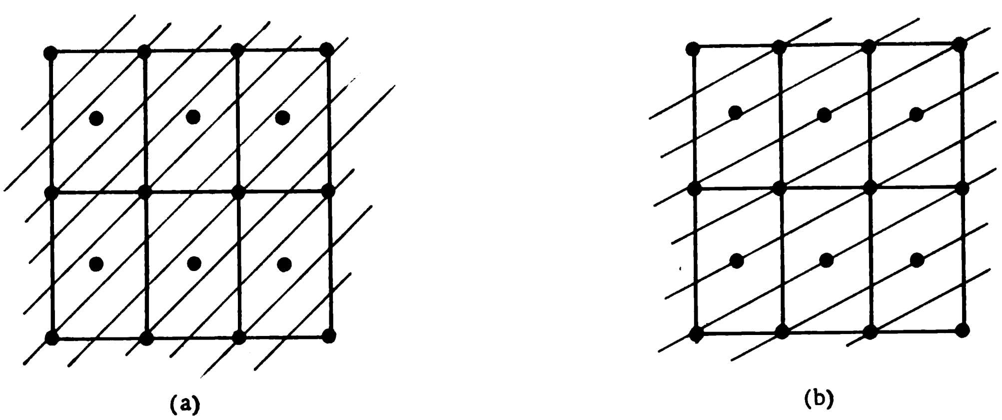


FIGURE 5 - C-FACE CENTERING EXTINCTIONS

In order for the planes (23ℓ) to produce a constructive interference for a given X-ray beam the path difference between portions of the beam reflected from consecutive planes must be equal to λ. The planes formed by the centering points are parallel to and midway between the planes (23ℓ). They also have the same scattering power (same point density), so the net result will be cancellation of these reflections. Notice that if all planes are considered, they will have the form (46ℓ). The planes of the form (13ℓ) shown in Figure 5(b) also contain the centering points, and the problem does not exist. It can be seen that both sets of planes considered which do not produce extinctions satisfy the condition $h + k = 2n$. It can be shown that this is true in general and gives a means for determining if a chosen unit cell is C-face centered. Similar arguments can be carried out for other non-primitive cells resulting in the conditions for non-extinction of general reflections for each cell as listed in Table 3.

TABLE 3 - CONDITIONS FOR POSSIBLE REFLECTION

Lattice Type	Condition for Possible Reflection
A-face centered	$k + \ell = 2n$
B-face centered	$h + \ell = 2n$
C-face centered	$h + k = 2n$
F (all faces centered)	h, k, ℓ all odd or all even
I (body centered)	$h + k + \ell = 2n$
R (rhombohedral indexed on hexagonal axes)	$-h + k + \ell = 3n$ or $h - k + \ell = 3n$
Hexagonal indexed on rhombohedral axes	$P + q + r = 3n$
P (primitive)	No restrictions

In addition to the above conditions for non-extinction of general $(hk\ell)$ reflections there are also conditions for reflections from sets of planes which have one or two of the indices zero. The list is quite long and can be found in the "International Tables for X-Ray Crystallography."

3. Geometry of X-Ray Pictures - In the analysis of crystal structure many different types of apparatus are available for use with the X-ray machine. The theory of operation varies all the way from the relatively simple Laue method to rather complex moving film methods such as those used with the Weissenburg camera. The methods involving the most complex theory are, in general, the easiest methods from which to get the necessary data. For this project the only equipment available was that necessary to take Laue pictures and simple rotation or oscillation pictures. The discussion here will be limited to those two methods.

In taking Laue pictures white X-radiation (continuous band of frequencies present) is directed on a stationary crystal. The diffraction pattern is then formed on a flat film placed either behind the crystal (transmission pattern) or in front of the crystal ("reflection" pattern). This method is the simplest and also the oldest in existence. The first diffraction pattern of a crystal formed with X-rays was the one taken by Laue in 1912 using this method.

Since the crystal and X-ray beam remain fixed, the angle θ between the beam and a given set of planes is also fixed. The Bragg equation shows that with these conditions the wavelength of radiation reflected from each set of planes is also fixed. However, closer inspection reveals that if a set of planes $(hk\ell)$ reflects a wavelength λ then the set $(2h, 2k, 2\ell)$ which is parallel to the first set will reflect radiation with wavelength $\frac{\lambda}{2}$. These reflections will be in the same direction, and so it can be seen that one spot on the film could be contributed by several distinct wavelengths.

One characteristic feature of Laue photographs is that the spots all fall on a series of conic sections which pass through the central position on the film. The reason for this can be seen if reflection from a set of planes with a common line of intersection (called a zone axis) is considered. Figure 6 illustrates this condition. It would appear that since a real crystal contains an extremely large number of planes about any zone axis, the conic section would contain a very large number of spots and perhaps be almost a solid line. Closer inspection, however, reveals that each set of planes about the axis has a definite spacing which will reflect only a certain wavelength, so that since <u>all</u> wavelengths of radiation are not present, some planes will not reflect.

Another feature of Laue photographs which is very important is the symmetry of spots which occurs when the X-ray beam is directed along a crystalline axis. The symmetry of the pattern on

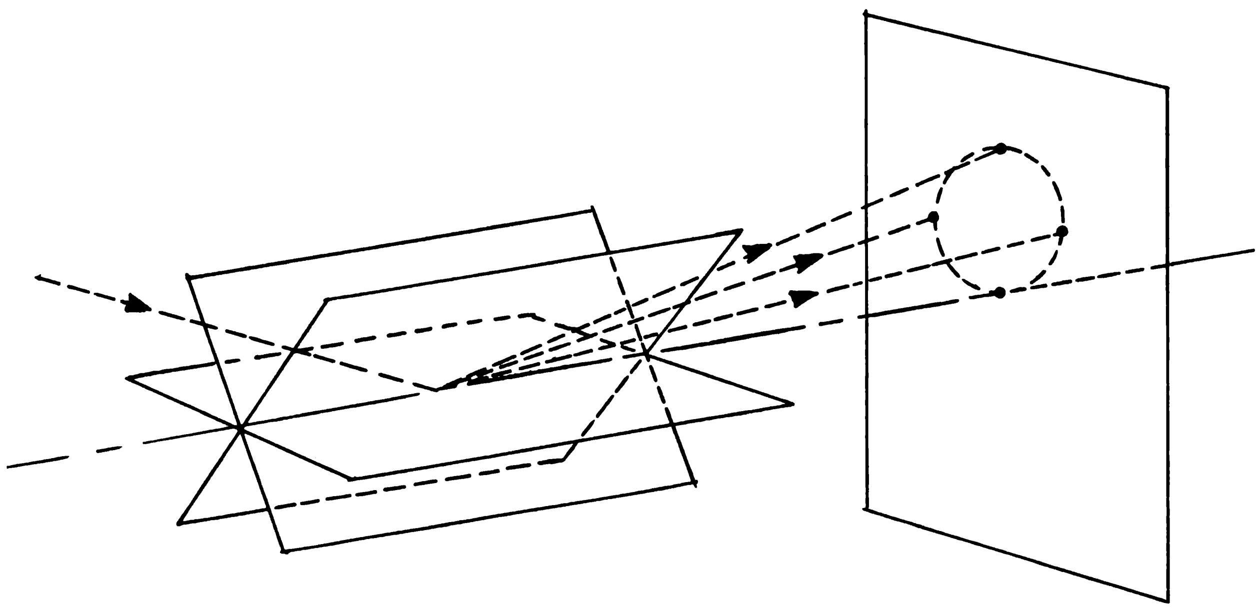


FIGURE 6 - LAUE PHOTOGRAPH GEOMETRY

the film is quite sensitive to changes in crystal position and therefore provides a suitable method for aligning the crystal on the X-ray machine.

Although the Laue pictures are useful for certain things, the information obtainable is very limited and other methods are necessary for a complete crystal analysis.

The oscillation photograph is generally considered the fundamental type of single crystal photograph. All more elaborate methods for examining crystals are merely extensions of this basic method. An oscillation picture is produced by allowing essentially monochromatic X-radiation to fall on a crystal which is rotating about an axis perpendicular to the X-ray beam. The film is usually situated on a cylinder whose axis is the rotation axis of the crystal. As the crystal rotates, many reflecting planes are brought into the proper position thus producing a spot on the film.

The most noticeable feature of oscillation photographs taken on cylindrical film is the arrangement of spots on parallel, horizontal lines. The reason for this occurrance can be seen by considering the scattering of X-rays by points along a straight line. All points along the line scatter X-rays in all directions but the radiation from neighboring points will interfere destructively except for "preferred" directions as illustrated in Figure 7. From the figure it is apparent that for each value of n there is a fixed angle which the scattered beam makes with the line of points. There is no condition on the azimuthal direction so from a single line of points the scattered radiation which does not interfere destructively must fall along lateral surfaces of cones which have the line of points as axes. If two or more non-parallel lines of points are present, the constructive interference can take place only in directions where the cones associated with each line of points intersect.

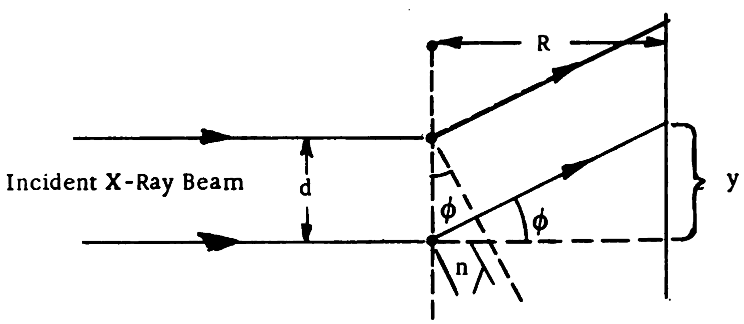


FIGURE 7 - X-RAY SCATTERING
BY A LINE OF POINTS

With a crystal properly oriented on an oscillation goniometer one of the crystalline axes and hence a row of lattice points is the oscillation axis. With this arrangement, all radiation interfering constructively falls along the cones associated with the axis of rotation. Since these cones intersect a circumscribing cylinder in circles, the observed pattern of spots is formed. It can also be seen from Figure 7 that by measuring the distance between these "layer lines" (y) and knowing the wavelength of the radiation, the repeat distance along the axis can be found.

$$d = \frac{n\lambda}{\sin \tan^{-1} \frac{y}{R}}$$

In studying crystals, much information is best conveyed by referring to a direct crystal lattice. Some information, however, is not easily conveyed by this method and it is found convenient to introduce the concept of the reciprocal lattice. This lattice consists of a three-dimensional array of points each of which represents a family of planes in the direct lattice. The reciprocal point lies on the normal to the set of planes it represents and its distance from the origin is inversely proportional to the spacing of the planes. This concept is primarily used in X-ray studies of crystals and it is found useful to let the constant of proportionality be equal to the wavelength of radiation used.

The fact that the points in reciprocal space form a regular three-dimensional lattice is not immediately obvious and requires proof. Any set of planes $(hk\ell)$ in the direct lattice can be represented in vector notation if unit vectors $\hat{a}, \hat{b}, \hat{c}$, are defined along the three axial directions. Since the intercepts of the planes on these axes are $\frac{1}{h}, \frac{1}{k}, \frac{1}{\ell}$, the plane is represented by the vectors $\frac{\hat{a}}{h}, \frac{\hat{b}}{k}, \frac{\hat{c}}{\ell}$. If $\vec{d}_{hk\ell}$ is the vector representing the normal drawn from the origin to the plane $(hk\ell)$, and $\vec{d}^{*}_{hk\ell}$ is the vector representing the position of the reciprocal point, then by the definitions of reciprocal vector and reciprocal point $\vec{d}_{hk\ell} \cdot \vec{d}^{*}_{hk\ell} = 1$. Figure 8 illustrates these vectors. From the figure it can also be seen that

$$\vec{d}_{hk\ell} \cdot \frac{\hat{a}}{n} = d_{hk\ell}\left(\hat{n} \cdot \frac{\hat{a}}{n}\right) = (d_{hk\ell})^2 \qquad (1)$$

where $\hat{n}$ is the unit normal to the planes $(hk\ell)$ and $d_{hk\ell}$ is the distance between them. Since $\vec{d}_{hk\ell}$ and $\vec{d}^{\,*}_{hk\ell}$ are colinear

$$d_{hk\ell} = \frac{1}{d^{*}_{hk\ell}} \tag{2}$$

and so $$d_{hk\ell} \cdot \frac{\hat{a}}{n} = \frac{1}{(d^{*}_{hk\ell})^2} \tag{3}$$

Also because of the colinearity

$$\hat{n} d_{hk\ell} = \frac{\hat{n}}{d^{*}_{hk\ell}} = \frac{\hat{n} d^{*}_{hk\ell}}{(d^{*}_{hk\ell})^2} \tag{4}$$

so that $$\vec{d}_{hk\ell} = \frac{\vec{d}^{\,*}_{hk\ell}}{(d^{*}_{hk\ell})^2} \tag{5}$$

now by substituting (5) in (3)

$$\frac{\vec{d}^{\,*}_{hk\ell}}{(d^{*}_{hk\ell})^2} \cdot \frac{\hat{a}}{n} = \frac{1}{(d^{*}_{hk\ell})^2} \tag{6}$$

$$\left.\begin{aligned} &\text{and} && \vec{d}^{\,*}_{hk\ell} \cdot \hat{a} = h \\ &\text{similarly} && \vec{d}^{\,*}_{hk\ell} \cdot \hat{b} = k \\ &\text{and} && \vec{d}^{\,*}_{hk\ell} \cdot \hat{c} = \ell \end{aligned}\right\} \tag{7}$$

Again from the definition of reciprocal vector

$$\hat{a} \cdot \hat{a}^* = 1 \ , \ \hat{a} \cdot \hat{b}^* = 0$$

so that equations (7) are satisfied only if

$$\vec{d}^{\,*}_{hk\ell} = h\hat{a}^* + k\hat{b}^* + \ell\hat{c}^*$$

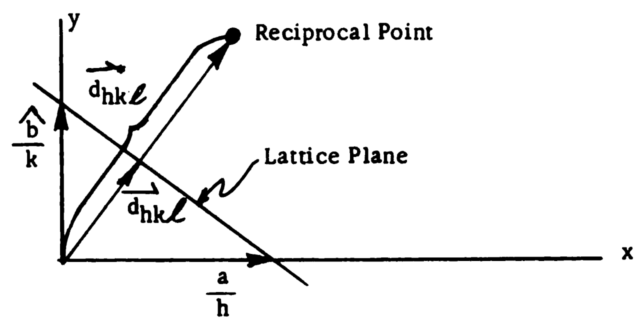


FIGURE 8 - VECTOR RELATIONSHIPS IN THE FORMATION OF A RECIPROCAL LATTICE

From this it can be seen that for every set of planes $(hk\ell)$in the direct lattice there is a reciprocal point with coordinates $h\hat{a}^*$, $k\hat{b}^*$ and $\ell\hat{c}^*$ in a lattice defined by the three unit vectors. Also since h, k, and ℓ are integers, it can be seen that the reciprocal lattice consists of regularly spaced points.

It should be noted that when the axes of the direct lattice are orthogonal then the axes of the reciprocal lattice are colinear with them. If the direct lattice axes are not at right angles, as with the x and z axes of the monoclinic cell, then the reciprocal lattice axes are not colinear with them as illustrated in Figure 9.

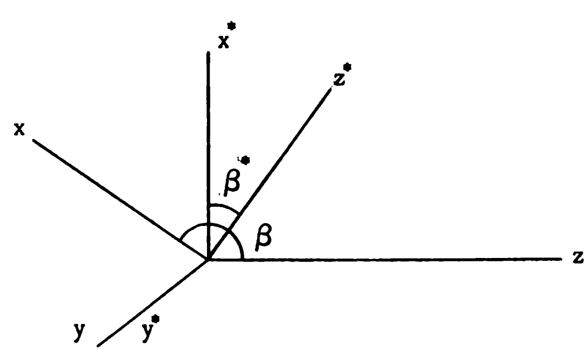


FIGURE 9 - DIRECT AND RECIPROCAL LATTICE AXES FOR A MONOCLINIC CRYSTAL

One of the principal reasons for introducing the reciprocal lattice is that it simplifies the otherwise complicated process of indexing the spots on the X-ray photographs. To understand this process as applied to oscillation pictures it is necessary to discuss the geometry of diffraction pattern formation using the reciprocal lattice. The basis for this discussion is the concept of the reflecting sphere which was first introduced in 1921 by Ewald. In Figure 10 a cross section of a reflecting sphere is shown along with one set of direct lattice planes and some reciprocal lattice points. The sphere is drawn with a radius $R = \frac{k}{\lambda}$ where k is the reciprocal constant. Since k is usually chosen to be equal to λ, the radius is a unitless 1. P is the reciprocal point for the set of planes drawn.

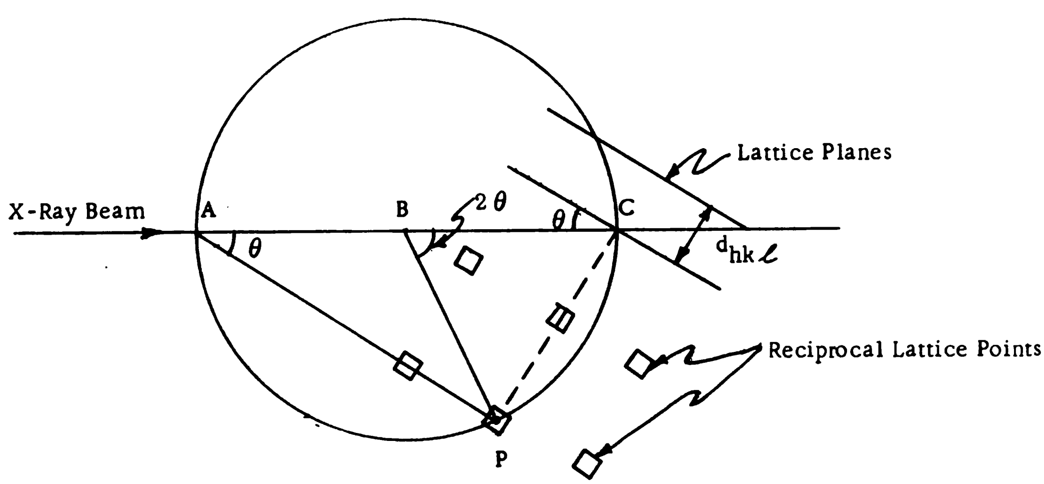


FIGURE 10 - THE REFLECTING SPHERE

In the diagram it is apparent that angle APC is 90° and $\angle CBP = 2(\angle BAP)$. Since the line PC is perpendicular to both the lattice planes and line AP, the angle BAP = θ. The reflected X-ray beam, then, has a direction the same as the line BP. If this reflection occurs then Bragg's equation must be satisfied

and $$\lambda = 2d \sin \theta$$

$$\sin \theta = \frac{\lambda}{2d}$$

From the diagram

$$\sin \theta = \frac{CP}{CA}$$

but CA = 2 by construction and by the definition of reciprocal lattice

$$CP = \frac{k}{d} = \frac{\lambda}{d}$$

so $$\sin \theta = \frac{\lambda}{2d}$$

From this it is seen that whenever a reciprocal lattice point falls on the reflecting sphere, the corresponding set of lattice planes is in a position to reflect. If an oscillation picture is being taken, the process can be thought of as the rotation of a reciprocal lattice so that many different lattice points in turn pass through the reflecting sphere thus indicating a reflection from a set of lattice planes.

In the course of studying a crystal by X-ray methods it is necessary to know which spot on the film was caused by which set of crystalline planes. The concepts of the reflecting sphere and reciprocal lattice discussed above are helpful in this determination. Figure 11 shows the reflection geometry and the coordinates which can be measured. The oscillation axis is, of course, on the axis of the cylindrical film but the radius of the reflecting sphere is so small compared with the radius of the film that its center can also be considered as lying on the axis. In the diagram, the point P is a reciprocal lattice point on the reflecting sphere while Q is the spot produced on the cylindrical film by the corresponding reflection.

ξ and ζ are two of the cylindrical coordinates of the point P. It can be seen that since P is required to be on the reflecting sphere (which has a known radius), the coordinates of the spot on the film will be sufficient to determine ξ and ζ for the lattice point producing it and also which lattice point if the orientation of the crystal is known. If the picture is being made by rotating the crystal through 360° it is not usually possible to determine which lattice point was in position because in fact more than one point may produce a spot in the same location. For this reason most oscillations are made by limiting the motion of the crystal to 10° to 15° and the orientation of the crystal is carefully noted.

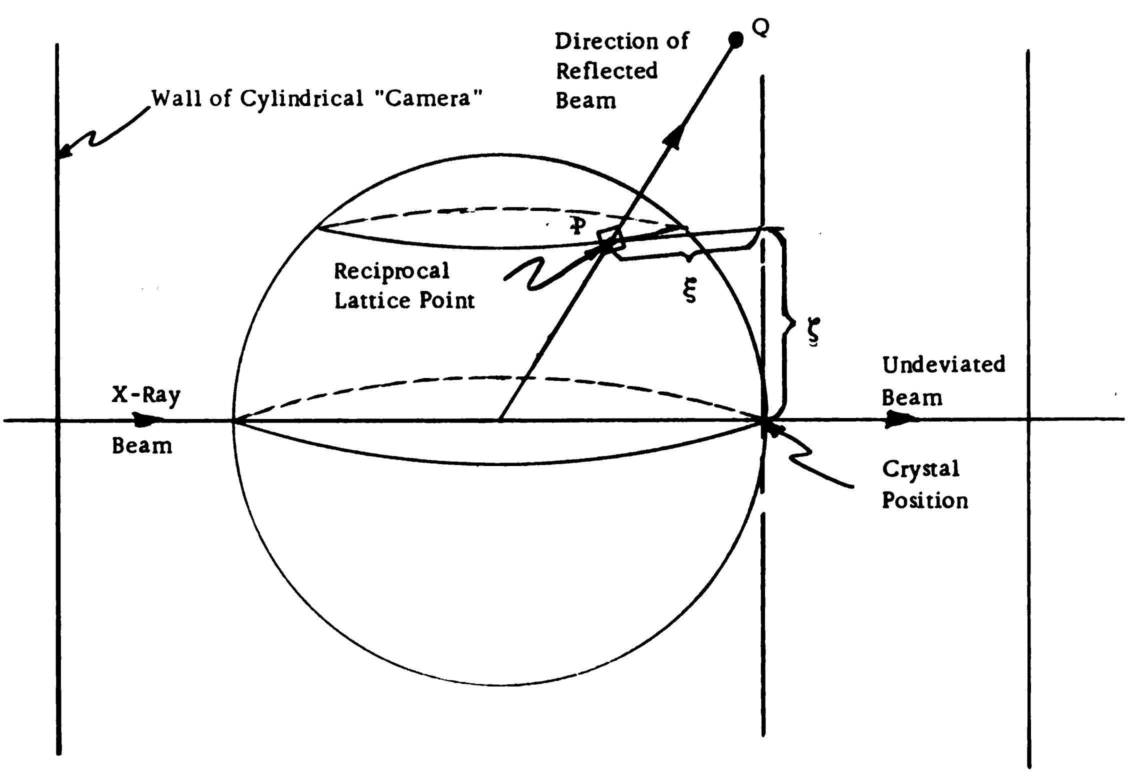


FIGURE 11 - OSCILLATION PICTURE GEOMETRY

The spots on any given layer line are produced as the reciprocal lattice points in a plane normal to the rotation axis cross the reflecting sphere. The intersection of the plane and sphere is a circle, called the reflecting circle, which can be used to index the spots on any given layer line. It should be noticed that for layer lines other than the zero line the reflecting circle has a radius smaller than that of the reflecting sphere and does not pass through the axis of rotation (the origin of the reciprocal lattice plane).

II EXPERIMENTAL PROCEDURE

A. Introduction

This research was undertaken in order to obtain the following information about copper nitrate:

1. The lattice constants.
2. The interaxial angles.
3. The space group.

The crystal class had previously been established as monoclinic by morphological studies. Before work along these lines could be started, however, a method had to be found for keeping the crystal from deliquescing. The humidity in the laboratory was very high (70-75% at times), and it was found that the crystal would not last long enough for even one Laue picture.

Several methods were tried for isolating the crystal without making it inaccesible for X-ray pictures. First, the crystal was dried in a desiccator then while inside a sealed glove box was sprayed with a plastic coating. When mounted on the X-ray machine, the crystal again deliquesced leaving a plastic shell. The process was repeated several times with great care, yet the result was the same.

The second attempt involved sealing the crystal in ordinary scotch tape. This may have worked, except that the necessary visual alignment on the X-ray machine could not be accomplished.

The third method tried was to seal the crystal in a glass tube which had been drawn out so that the walls were very thin. There were two drawbacks to this method. The glass absorbed too much radiation (Lindemann glass was not available) and the tube did not offer enough mobility for alignment about all axes.

The method which was finally used involved mounting the crystal in modeling clay then inverting half of a clear gelatin capsule over it. The capsule did not produce an interference pattern, and was thin enough to not absorb a significant amount of radiation. Also, the crystal was clearly visible for alignment and was accessible for reorientation at any time. It was found that by placing the goneometer assembly in a desiccator every night, the crystal remained dry.

B. Determination of Lattice Constants and Interaxial Angles

The crystal was first mounted so that its long dimension was vertical. By viewing the faces through a microscope attachment, the crystal could be aligned so that the X-ray beam would be parallel to a face. A series of Laue pictures was taken to complete the alignment. As was mentioned in Part I of this report, the Laue picture is highly symmetrical when the X-ray beam is parallel to a crystalline axis. It was found that the position could be detected by this method to within one-quarter degree.

After taking many Laue pictures as described above, the presence of axes in the horizontal plane was established as indicated in Figure 12.

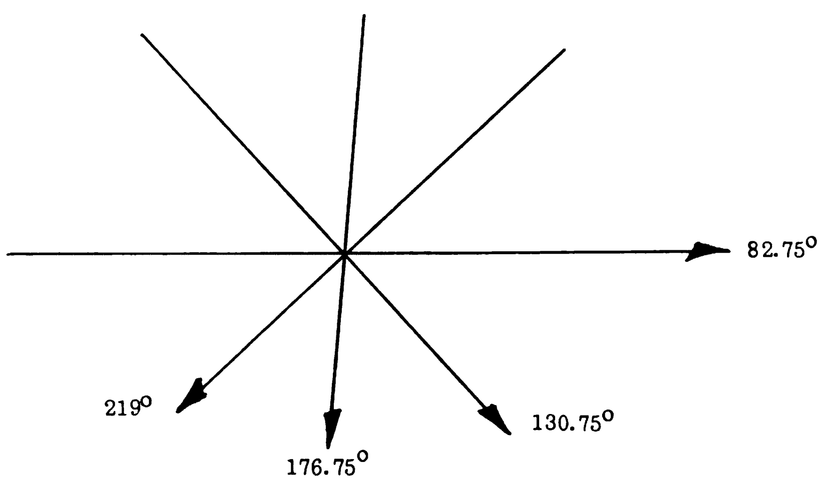


FIGURE 12 - AXIAL DIRECTIONS IN ONE PLANE

Since no two axes were 90° apart, it was concluded that the vertical axis was the y-axis of the crystal. Since the crystal was aligned with this axis vertical, a rotation picture was taken to determine the lattice spacing along y. This was found to be 4.90 Å. (See Appendix I.)

Now that one axial direction had been established there remained to select the directions from those shown in Figure 12 which would be called x and z axes. To accomplish this the crystal was set so that the X-ray beam would be parallel to the axis marked 176.75^{o} in Figure 12 then turned <u>about this axis</u> until the y-axis was horizontal and the direction marked 82.74^{o} was up. More Laue pictures were then taken to perfect alignment and the crystal was tipped 4^{o} so the axis marked 82.75^{o} would be vertical. A rotation picture showed good layer line formation which indicated good alignment of the crystal. A similar method was followed for each of the other axes and a lattice constant was computed for each as follows:

1. Axis at 82.75^{o} - 15.4 Å.
2. Axis at 130.75^{o} - 22.2 Å.
3. Axis at 219.75^{o} - 16.7 Å.

Figure 13 shows the lattice point positions for the points in the x - z plane. From this diagram it is seen that there are several possible choices for unit cells. One choice gives a cell with a = 22.2 Å, b = 4.90 Å, c = 15.4 Å and $\beta = 132^{o}$ while the other choice gives a cell with a = 16.7 Å, b = 4.90 Å, c = 15.4 Å and $\beta = 94^{o}$.

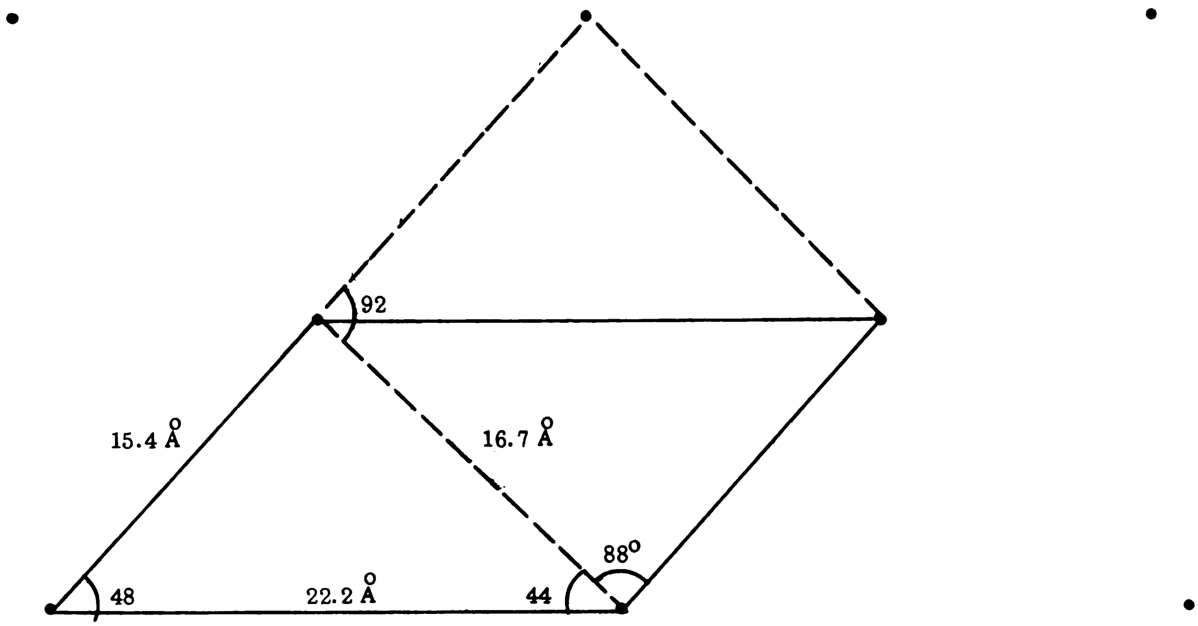


FIGURE 13 - LATTICE POINTS IN X-Z PLANE

The first choice was selected and the analysis of the space group was based upon this cell.

C. Determining the Space Group

As was indicated in Part I, the space group for a crystal can be determined by analyzing the systematic absences in X-ray reflections. In order to do this the spots on the film must be indexed and catalogued. Ten oscillation pictures were taken about the z axis and these were indexed.

The indexing is a geometrical process based upon the concepts of the reciprocal lattice and the reflecting sphere which were previously discussed. As can be seen from Figure 11 (Page 23), it is necessary to determine the value of ξ and ζ for each spot from measurements made on the film. To facilitate this, a Bernal chart was used. This chart is drawn for a "camera" of a particular radius and consists of a mesh of lines labeled with values of ξ and ζ. By placing the film on the chart, a set of values for each spot can be obtained directly.

Again referring to Figure 11 it can be seen that a crystal oscillation of 10° between known limits is comparable to oscillating the reflecting sphere about the oscillation axis through the same angle over a known region of the lattice. The spots expected on the film, then, are those corresponding to lattice points crossed by the surface of the sphere. In practice the layer lines are analyzed separately and so the important consideration is for lattice points on a particular lattice plane which were crossed by a reflecting circle. This circle, of course, is the intersection of the sphere and the lattice plane.

The next step in the indexing process was to draw, to scale, the reciprocal lattice plane normal to the oscillation axis. This is shown in part in Figure 14. (Reciprocal lattice dimensions are calculated in Appendix II.) Note that marked on this diagram are angles which refer to the position of the crystal. It had been previously noted from known axial directions in the crystal that an oscillation from 0° to 10° would be as indicated on this diagram.

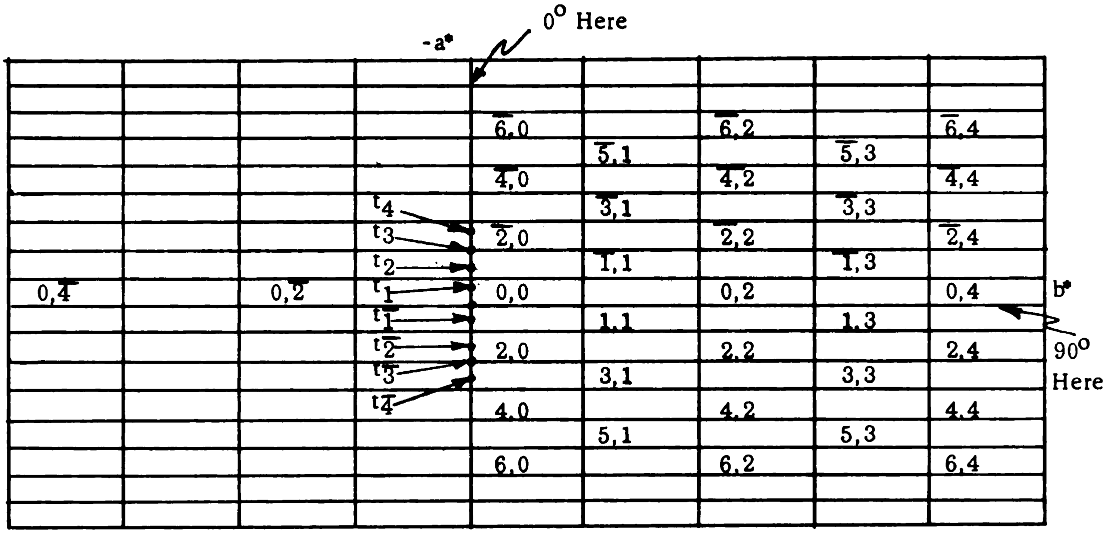


FIGURE 14 - X^* - Z^* PLANE OF RECIPROCAL LATTICE

The points labeled t_1, t_2, etc., in Figure 14 represent the origin of the reciprocal plane for different layer lines. Since the z-axis is not perpendicular to the x-axis, the z^* reciprocal axis is not normal to the x^* - z^* plane. Because of this, if the same drawing is to be used for each layer line a new origin must be computed. These computations are also in Appendix II.

The next step, as might be expected, was to draw reflecting circles for each layer line as shown in Figure 15. As is indicated in Figure 11, the radius of the circle depends on the layer line but the distance from the origin of the lattice plane to the center of the circle is a constant. Two circles are drawn as shown to indicate a 10° oscillation. With this diagram placed on the diagram of the reciprocal lattice in the proper position, all points falling within the lunes could have produced spots.

The final step in indexing consisted in marking arcs on the reflecting circles for each layer line of each oscillation picture. Each arc corresponded to an observed reflection and had a radius equal to ξ for that spot. This diagram is now placed in the proper position on the reciprocal lattice, and as can be seen from Figure 11, each arc will intersect a point of the reciprocal lattice within the lunes. This point has the same indices as the planes which produced the reflection. Table 4 is a compilation of all reflections observed. The indices are arranged in a regular order to facilitate the location of systematic absences of reflections.

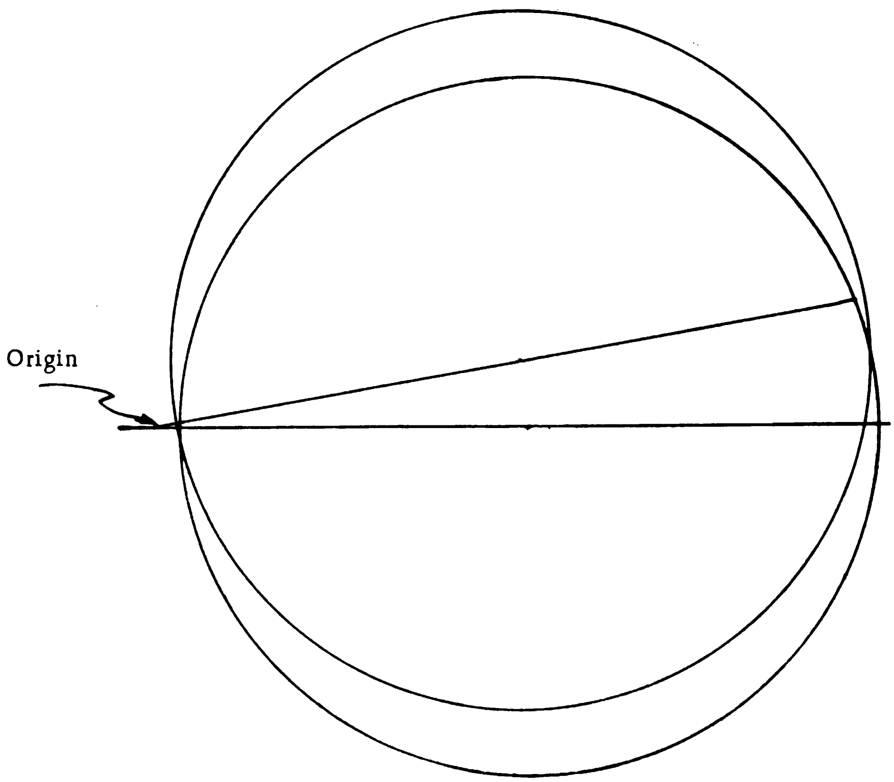


FIGURE 15 - REFLECTING CIRCLES FOR FOURTH LAYER

TABLE 4 - OSCILLATION PICTURE DATA

					4,0,0				8,0,0			11,0,0									
		110		310		5,1,0			810	910		11,1,0		13,1,0		15,1,0	16,1,0		18,1,0		
hk0	020				420				820				12,2,0						18,2,0		
		130		330						930		11,3,0		13,3,0	14,3,0	15,3,0					
	040		240		440		640		840		10,4,0	11,4,0	12,4,0		14,4,0	15,4,0					
			211					711		911		11,1,1							18,1,1	19,1,1	
hk1	021	121		321	421		621		821	921							16,2,1				
		131				531		731				11,3,1		13,3,1				17,3,1			
			241		441		641		841	941	10,4,1	11,4,1	12,4,1	13,4,1	14,4,1						
						502	602				10,0,2		12,0,2				16,0,2	17,0,2	18,0,2		
	012	112		312	412				812	912	10,1,2	11,1,2		13,1,2	14,1,2	15,1,2		17,1,2		19,1,2	
hk2	022	122		322				722	822	922	10,2,2		12,2,2	13,2,2			16,2,2	17,2,2	18,2,2		20,2,2
		132		332		532		732				11,3,2		13,3,2		15,3,2		17,3,2			
		142	242		442			742	842		10,4,2		12,4,2		14,4,2						
	013		213		413											15,1,3			18,1,3		
hk3			223	323		523							12,2,3				16,2,3				
	033		233		433					933		11,3,3		13,3,3							
	043	143			443		643	743	843	943	10,4,3		12,4,3								
											10,0,4				14,0,4		16,0,4				
		114			414	514		714	814	914		11,1,4	12,1,4	13,1,4	14,1,4	15,1,4		17,1,4		19,1,4	
hk4		124	224		424	524				924	10,2,4			13,2,4	14,2,4				18,2,4		
		134	234	334	434		634			934		11,3,4		13,3,4		15,3,4					
	044	144	244	344	444	544	644	744	844	944	10,4,4		12,4,4								

Note: A triangle in the corner of a block indicates that the indices were observed more than once.

III CONCLUSIONS

As stated previously, the unit cell chosen has the dimensions

$a = 22.2\ \mathring{A}$

$b = 4.90\ \mathring{A}$

$c = 15.4\ \mathring{A}$

$\beta = 132^{o}$

This is an agreement with the findings of Dornberger-Schiff and Leciejewicz.*

Examination of the data in Table 4 shows that there are no systematic absences for the general reflections $(hk\ell)$ but reflections of the type (h, o, ℓ) only occur when $\ell = 2n$. There are no other special absences which indicates that there are no screw axes.

The above observations would indicate that the cell chosen is primitive and has a glide plane normal to the y-axis with a glide component of $\frac{c}{2}$. This is not in agreement with Dornberger-Schiff and Leciejewicz because they indicated a space group of Cc or $C\frac{c}{2}$ while the above information leads to the conclusion that the space group is Pc or $P\frac{2}{c}$.

Several things need be considered in analyzing the accuracy of the results. One is the fact that the spots (especially high θ spots) on the oscillation pictures were split. According to Buerger** this indicates a flaw in the crystal known as lineage structure. This type of flaw usually causes some reflections to be very weak; perhaps to the extent they would not be observed. It is doubtful that this flaw caused an error in the determination but it rendered the films practically useless for density measurements and a more complete analysis.

*Acta Crystallographic, 11,825 (1958).

**Buerger - Crystal Structure Analysis, John Wiley & Sons, 1960.

The fact that one flaw occurred in the crystal raises the question of another possible flaw called twinning. If this occurred (there is no real reason for assuming it did) then there would be a tendency for spots to appear on the film which the symmetry of the crystal would indicate should not be there. The author believes this to be highly unlikely and that the space group is either Pc or $P\frac{2}{c}$.

APPENDIX I

CALCULATION OF LATTICE CONSTANTS

λ for K_{α_1} is 1.5374 Å

1. For a - spacing

$y = 0.346$ cm

$R = 5$ cm

$$t = \frac{n\lambda}{\sin \tan^{-1} \frac{yn}{R}} = \frac{1 \times 1.5374\ \text{Å}}{\sin \tan^{-1} \frac{0.346\ \text{cm}}{5\ \text{cm}}}$$

$$t = 22.2\ \text{Å}$$

2. For b - spacing

$y = 1.65$ cm

$R = 5$ cm

$$t = \frac{1.5374\ \text{Å}}{\sin \tan^{-1} \frac{1.65\ \text{cm}}{5\ \text{cm}}} = 4.90\ \text{Å}$$

3. For c - spacing

$y = 0.487$ cm

$R = 5$ cm

$$t = \frac{1.5374\ \text{Å}}{\sin \tan^{-1} \frac{0.487\ \text{cm}}{5\ \text{cm}}} = 15.4\ \text{Å}$$

APPENDIX II

CALCULATION OF RECIPROCAL LATTICE QUANTITIES

$$a^* = \frac{\lambda}{a} = \frac{1.5374}{22.2} = 0.069$$

$$b^* = \frac{\lambda}{b} = \frac{1.5374}{4.90} = 0.313$$

$$c^* = \frac{\lambda}{c} = \frac{1.5374}{15.4} = 0.099$$

Radii of Reflecting Circles

First Layer Line: $R = \sqrt{1 - \zeta^2}$

$R_1 = \sqrt{1 - 0.00941} = 0.995$

Second Layer Line: $R_2 = \sqrt{1 - 0.0376} = 0.982$

Third Layer Line: $R_3 = \sqrt{1 - 0.0846} = 0.957$

Fourth Layer Line: $R_4 = \sqrt{1 - 0.151} = 0.920$

Displacement of Origin of Reciprocal Lattice for Higher Layer Lines

For $n = 1$ $t_1 = C^* \text{ Cos } 48$

$t_1 = 0.099 \times 0.6691 = 0.0667$

For $n = 2$ $t_2 = 0.133$

For $n = 3$ $t_3 = 0.200$

For $n = 4$ $t_4 = 0.267$

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