Lesson 3

- Look at Homework
- Review Matrix Operations
- Transformations
- Translation as symmetry
- Lattice Types

Homework Problem 2

2. Using the C5 reference coordinates (l=121, w=19, h=13.5) calculate the distance between 2 packages located at (0.33,0.16,0.45) and (0.52,0.43,0.23). Are the coordinates (0.85,0.5,1.1) valid?

calculate $\Delta(x_2-x_1)$**|a|** etc.

(.52-.33)121=22.99 (.43-.16)19=5.13 (.23-.45)13.5=-2.97

$d^2=22.99^2 + 5.13^2 + -2.97^2 =563.68$ d=23.74 ft

The coordinates are valid. However, they are not in the cargo compartment.

A value > 1 means it is behind the aircraft while < 0 is in front

Matrices

A matrix is an array of numbers. We will be concerned with two types of matrices.

First is the column matrix which is one column of three numbers. The coordinates of a point can be stored in this column.

$$\begin{vmatrix} x \\ y \\ z \end{vmatrix}$$

This is equivalent to (x,y,z)

The second type is a 3x3 matrix which can be used to store a transformation

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

Matrix Multiplication

$$\left(\begin{vmatrix} x' \\ y' \\ z' \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} x \begin{vmatrix} x \\ y \\ z \end{vmatrix}\right)$$

$x' = a_{11}x + a_{12}y + a_{13}z$

$y' = a_{21}x + a_{22}y + a_{23}z$

$z' = a_{31}x + a_{32}y + a_{33}z$

Transformations

- We can use a 3x3 matrix to represent a transformation.
- This transformation can be a symmetry transformation
- The transformation could also be a coordinate transformation
- Note that any such transformation cannot involve shifting the origin!

Transformation to Cartesian Coordinates

- Obviously there are mathematics that are more easily done in Cartesian Coordinates that are impossible to do in other coordinates
- For graphics it is easier to work in Cartesian Coordinates
- There are many transformations possible—x' along x or y' along y or z' along z.
- Want a transformation such that $T \times X_f$ *takes* fractional to Cartesisan and $T^{-1} x X_c$ goes the other way.

From Fractional to Cartesian

$$\begin{vmatrix} |a| & |b|\cos(\gamma) & |c|\cos(\beta) \\ 0.0 & |b|\sin(\gamma) & |c|(\cos(\alpha)-\cos(\beta)\cos(\gamma))/\sin(\gamma) \\ 0.0 & 0.0 & |c|*r \end{vmatrix}$$

where $r = (1-\cos^2(\alpha)-\cos^2(\beta)-\cos^2(\gamma)+2\cos(\alpha)\cos(\beta)\cos(\gamma))/\sin(\gamma)$

Translation as Symmetry

- When molecules are studied **point group** symmetry is applied.
- This implies there is only one origin and all symmetry operations pass through it.
- This restriction can be lifted in a lattice because there are many equivalent points. This is **space group** symmetry
- Therefore translation can be considered a symmetry operation.

How to apply translation

- This means x+a=x where a is some translational symmetry distance and x is along an axis of translational symmetry.
- For a three dimensional lattice there are three independent directions of translation. If the three basis vectors for the coordinate system point along these directions and have a magnitude of the translation then x+1=x

An Answer to the Question of why use non-orthogonal basis vectors

Crystals are made up of unit cells translated along their cell edges.

If the unit cell edges are used as basis vectors than x*$\mathbf{a}$+1*$\mathbf{a}$=x*$\mathbf{a}$ which is the definition of translational symmetry

If orthogonal axes are used then the transformation may not be along an axis and the math gets much more complex

Some Comments

- I always point out that this concept is the same as the Paul Simon song “One man's ceiling is another man's floor.
- It means 0.2 and 1.2 are equivalent locations simply shifted by one translation. If they are not identical locations then the translation is not defined correctly.
- It also means 0.2 and -0.8 are identical
- Be careful—the vectors (0.3,0.5,0.7) and (1.3,0.5,0.7) are different but their environments are the same!

A Hand from the Peanut Gallery

- Point group symmetry operations can be applied an infinite number of times and the result is always indistinguishable.
- After n translations we reach the end and therefore this is not infinite
- Solution 1—assume that na+x gets you exactly back to x. This is the Born-vonKarmen boundary conditions.
- Solution2 –assume n is so large that the surface can be ignored.

Unit Cell

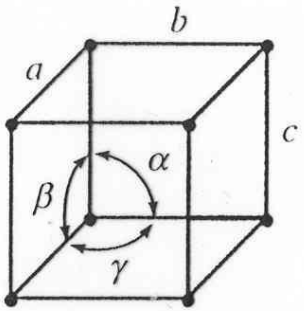
- A unit cell is a volume formed by three vectors that are the basis for the translational symmetry.
- A primitive unit cell contains the smallest volume that can be such defined.
- A cell is centered if there are one or more pure translations that translate to identical positions within the same unit cell

The Unit Cell

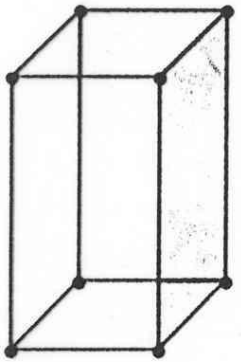
The unit cell is the smallest repeating unit of the lattice that belongs to the highest crystal system.

Cell Centering is used to move up the hierarchy.

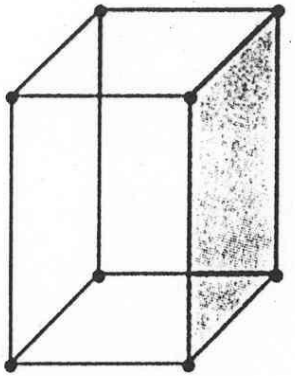
Crystal Systems



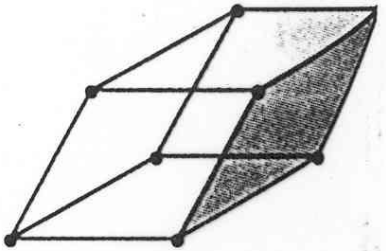
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$



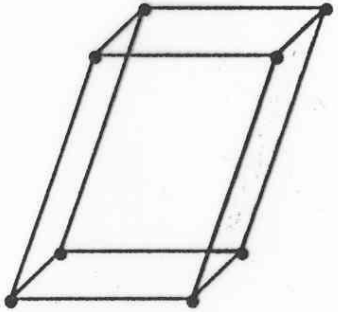
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



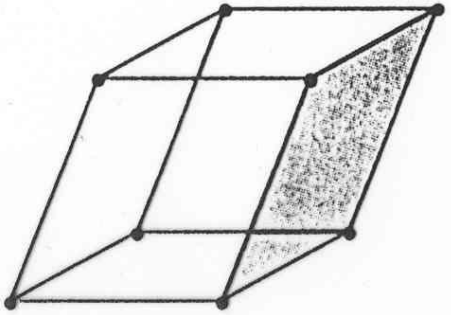
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



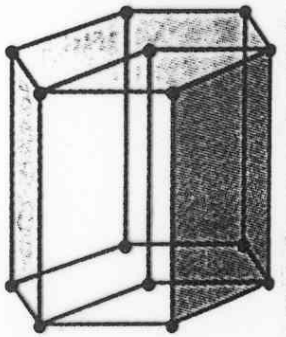
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



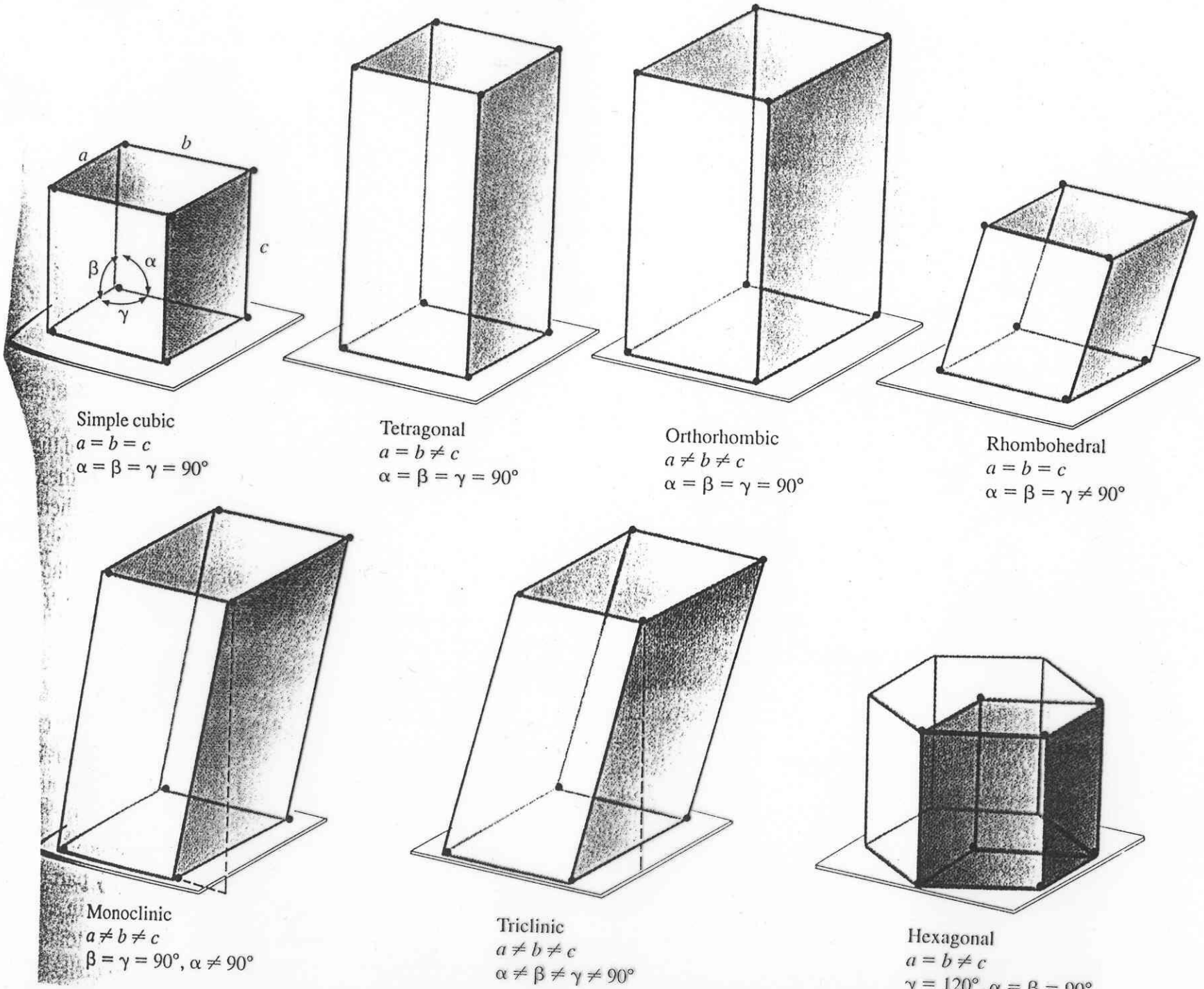
Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$



Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

Monoclinic
$a \neq b \neq c$
$\beta = \gamma = 90°, \alpha \neq 90°$

Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Hexagonal
$a = b \neq c$
$\gamma = 120°, \alpha = \beta = 90°$

TABLE 17–1 CONVENTIONAL UNIT CELLS, THEIR SYMMETRIES AND SYMBOLS

Crystallographic System and Point Groups	Axial and Angular Relationships[1]	Characteristic Symmetry	Number of Bravais Lattices in System
Triclinic 1, $\bar{1}$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	1-fold (identity or inversion)[7] symmetry only	1
Monoclinic 2, m, 2 m[8]	1st setting $a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	2-fold axis (rotation or inversion) in one direction only, this being taken as the z-axis in the 1st setting and as the y-axis in the 2nd setting	2
	2nd setting $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$		
Orthorhombic 222, $mm2$, mmm	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	2-fold axes (rotation or inversion) in three mutually perpendicular directions.	4
Tetragonal 4, $\bar{4}$, 4 m;[8] 422, $4mm$, $\bar{4}2m$, $4/mmm$[8]	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	4-fold axis (rotation or inversion) along the z-axis.	2
Trigonal and Hexagonal 3, $\bar{3}$; 32, $3m$, $\bar{3}m$; 6, $\bar{6}/m$; 622, $6mm$, $\bar{6}m2$	(Rhombohedral axes) $a = b = c$ $\alpha = \beta = \gamma < 120° \neq 90°$	3-fold axis (rotation or inversion) along the body diagonal using rhombohedral axes, or . . .	1
	(Hexagonal axes) $a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	along the z-direction using hexagonal axes.	1
Cubic 23, $m3$; 432, $\bar{4}3m$, $m3m$	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Four 3-fold axes, each inclined at 54° 44′ to the crystallographic axes.	3

[1] The sign $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.

[2] When referring to lattices alone, it is conventional to call the side-centered orthorhombic lattice C. In the space groups of the point group $mm2$, the "z-axis unique" convention requires that the side-centered lattice shall sometimes be called C, and sometimes A (or B).

[3] The tetragonal lattices P and I may also be described as C and F, but only if the **a** and **b** vectors chosen are not the shortest ones perpendicular to **c**.

[4] The R-lattice is here described on rhombohedral axes, but it may also be referred to hexagonal axes. Where it is necessary to distinguish these, the symbols R_{obv} or R_{rev} are used for the description on rhombohedral axes and R_{hex} for that on hexagonal axes.

Drago, Physical Methods in Chemistry, 1977

The presence of rotation or reflection symmetry in a crystal structure, relating molecules or parts of molecules to each other, imposes restrictions on the geometry of the lattice and unit cell. For example, four-fold rotation symmetry in a two-dimensional lattice requires a square unit cell with two equal sides and a 90° angle, while reflection symmetry gives a 90° angle but still allows the two unit cell sides to be of different length (Fig. 1.8).

Table 1.1 Crystal systems

Crystal system	Essential symmetry	Restrictions on unit cell
Triclinic	none	none
Monoclinic	one two-fold rotation and/or mirror	$\alpha = \gamma = 90°$
Orthorhombic	three two-fold rotations and/or mirrors	$\alpha = \beta = \gamma = 90°$
Tetragonal	one four-fold rotation	$a = b$; $\alpha = \beta = \gamma = 90°$
Rhombohedral	one three-fold rotation	$a = b = c$; $\alpha = \beta = \gamma (\neq 90°)$
Hexagonal	one six-fold rotation	$a = b$; $\alpha = \beta = 90°$; $\gamma = 120°$
Cubic	four three-fold rotation axes	$a = b = c$; $\alpha = \beta = \gamma = 90°$

Clegg, Crystal Structure Determination, 1998

	Minimum point group symmetry of a crystal in this system	Diffraction symmetry (Laue symmetry)
1. Triclinic	None.	$\bar{1}$
2. Monoclinic	Two-fold axis parallel to **b**.	$2/m$
3. Orthorhombic	Three mutually perpendicular two-fold axes.	mmm
4. Tetragonal	Four-fold axis parallel to **c**.	$4/m$ or $4/mmm$
5. Trigonal/ rhombohedral	Three-fold axis parallel to (**a** + **b** + **c**).	$\bar{3}$ or $\bar{3}m$
6. Hexagonal	Six-fold axis parallel to **c**.	$6/m$ or $6/mmm$
7. Cubic	Three-fold axes along the cube diagonals.	$m3$ or $m3m$

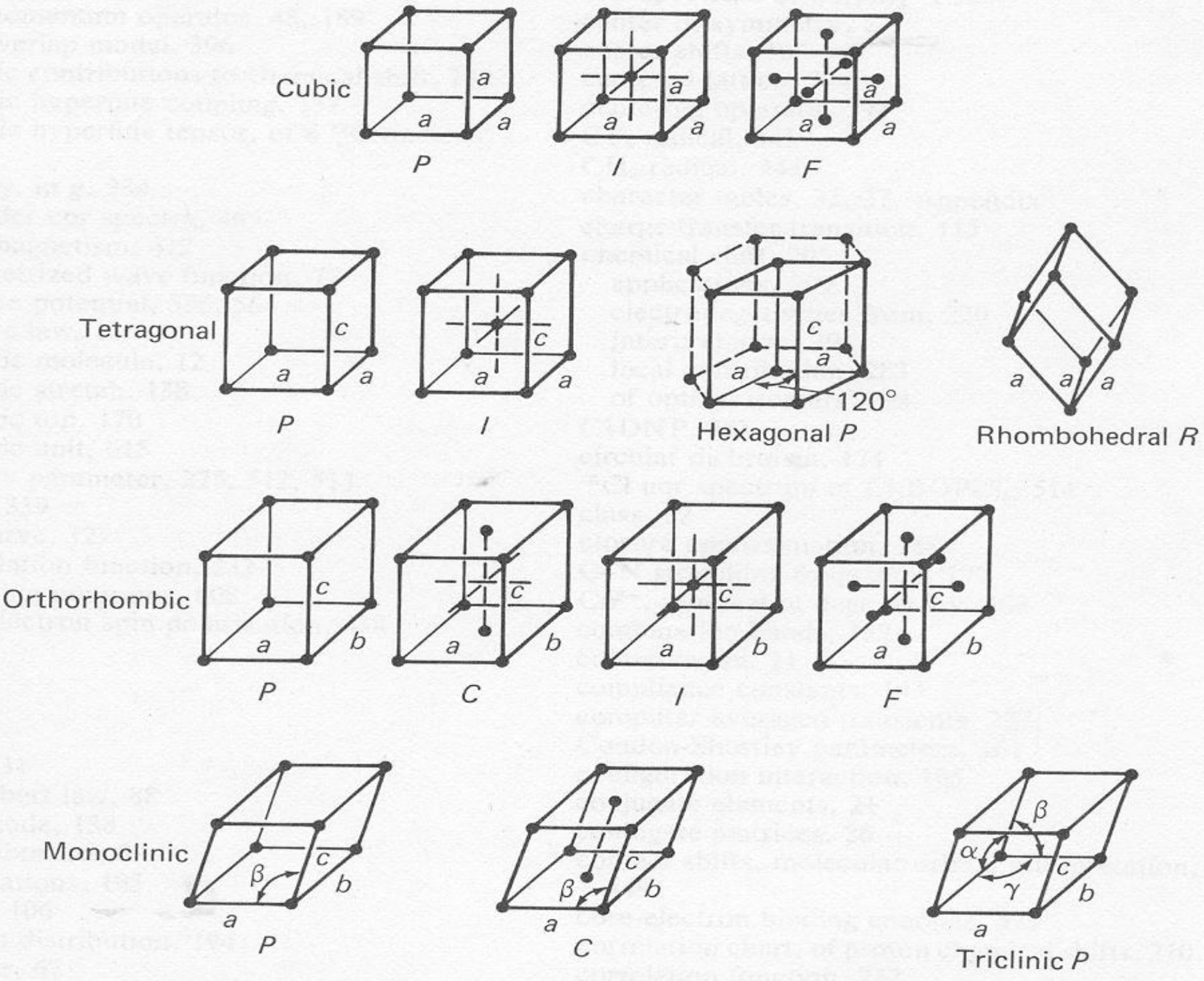
Glusker and Trueblood, Crystal Structure Analysis, 1985

Crystal Systems

- Defining each of the 7 system
- Providing an Algorithm for System Determination

There must be a heirarchy of crystal systems

Some are more symmetrical than others


Cubic
a
P
I
F
Tetragonal
c
120°
Hexagonal P
Rhombohedral R
Orthorhombic
b
C
Monoclinic
β
Triclinic P
α
γ

Homework Problem 3

The azide ion can exist in two tautomers. One has a neutral N_2 bonded by a triple bond and a single bonded N^- single bonded to it. The other has the form $N{=}{=}N^+{=}{=}N^-$.

A nickel azide crystallizes in a monoclinic space group with cell parameters a=13.691 b=19.211 c=12.582Å α=90.000 β=98.13 γ=90.000.

The nickel and three nitrogens (starting with the one bonded to the nickel) have coordinates:
Ni1 -0.25629 0.42630 0.21902
N1 -0.10880 0.43340 0.22220
N2 -0.05860 0.39790 0.24420
N3 0.01270 0.35510 0.27080

Using the non-orthogonal coordinates calculate the N1-N2 distance and the N2-N3 distance and the N1-N2-N3 angle. Which form is the azide ion in

Calculate the orthogonal transformation matrix and use it to calculate the Cartesian coordinate of Ni, N1 and N2. Calculate the Ni-N1 distance and the Ni-N1-N2 angle.