K_{sp} – Solubility Product

In an earlier reading, you studied the concept of solubility.
In this section, you'll go from the earlier "macro" version of solubility to the "micro" version of solubility that is explained mathematically and borders on the quantitative.
By definition, the solubility product is the product of the ion concentrations in a saturated solution; it's a fixed value; and is constant at a given temperature.
It is somewhat easily explained in an equilibrium expression as follows:

$$\underline{AgCl} \Leftrightarrow Ag^{+} + Cl^{-}$$

where

$$K = \frac{[Ag^{+}][Cl^{-}]}{[\underline{AgCl}]}$$

and by rearranging,

$$K[\underline{AgCl}] = [Ag^{+}][Cl^{-}] = K_{sp}$$

where the Ksp = the solubility product constant. (Note: underlined chemical formulas indicate that the chemical is insoluble.) In spite of the constancy of actual value, you will find discrepancies in text-books. This is generally due to slight differences in methodology, barometric pressure and temperature, i.e., experimental conditions.

General Rules with K_{sp}

- **In general, if the ion product is LESS THAN the Ksp, the solution is less than saturated and there is no precipitate (ppt).**

- **If the ion product is EQUAL TO the Ksp, the solution is saturated and there is a very fine equilibrium that is constantly changing between no precipitate and a micro-precipitate. This equilibrium is so dynamic that one never observes the ppt.**

- **If the ion product is GREATER THAN the Ksp, the solution is super-saturated and there is a readily observable ppt.**

Examples of How to Write The Equilibrium Expressions for Various Insoluble Salts

$$\underline{BaSO_4} \Leftrightarrow Ba^{2+} + SO_4{}^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$$

Example 1

$$\underline{Ag_2CrO_4} \Leftrightarrow 2Ag^{+} + CrO_4{}^{2-}$$

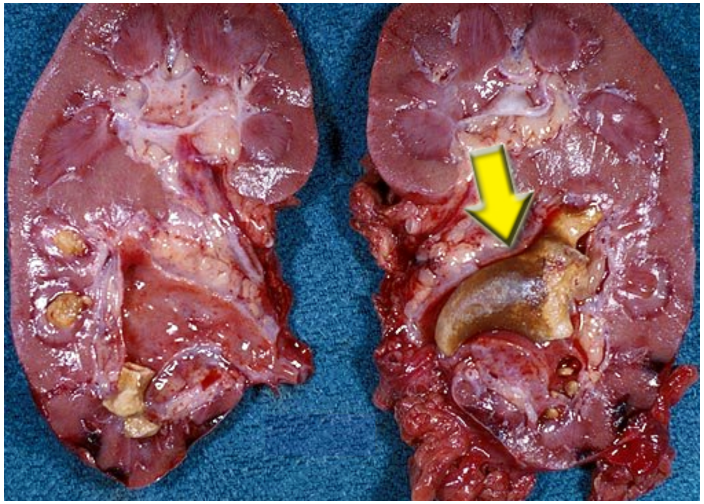
$$K_{sp} = [Ag^{+}]^2[CrO_4{}^{2-}]$$

Example 2 – Note the stoichiometric relationships in the expression.

$$\underline{MgNH_4PO_4} \Leftrightarrow Mg^{2+} + NH_4{}^{+} + PO_4{}^{3-}$$

$$K_{sp} = [Mg^{2+}][NH_4{}^{+}][PO_4{}^{3-}]$$

Example 3 – a more complex salt – “triple phosphate” – found in some urinary tract infections – precipitates so rapidly that it forms “staghorn calculi”:



These calculi are so-called because of their similarities to the head of a stag – male deer.

The Relationship between Solubility and Solubility Product

Using AgCl, again, as our example:

$$\underline{AgCl} \Leftrightarrow Ag^{+} + Cl^{-}$$

Let’s let “S” (for solubility) be the number of moles of salt ions that dissolve per liter of solution. Let’s write the Ksp expression for AgCl:

$$K_{sp} = [Ag^{+}] + [Cl^{-}]$$

Now, let’s substitute S for the ionic concentration of each ion:

$$K_{sp} = S \times S = S^{2}$$

$$and$$

$$S = \sqrt{K_{sp}} = \frac{mol}{L}$$

So, we can calculate the solubility of the salt based upon its solubility product.

Let’s try another example:

$$\underline{Fe(OH)_3} \Leftrightarrow Fe^{3+} + 3OH^-$$

and the solubility product expression is:

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

Note that the stoichiometry is conserved by cubing (raising to the third power) the hydroxide ion concentration. Now, let’s solve for the solubility based upon the molar concentration of ferric ion (I use King’s method for determining solubility, basing solubility on the metallic ion concentration, BTW):

$$K_{sp} = S\,(3S)^3 = 27S^4$$

$$and$$

$$S = \sqrt[4]{\frac{K_{sp}}{27}}$$

Now, let’s use a complex salt to demonstrate how NOT to calculate solubility by messing with the stoichiometry:

$$\underline{Bi_2S_3} \Leftrightarrow 2Bi^{3+} + 3S^{2-}$$

<table>
<tr><th>Wrong Method</th><th>Correct Method</th></tr>
<tr><td>$K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3$
$= (2S)^2 (3S)^3$
$= 98S^5$
so
$S = \sqrt[5]{\frac{K_{sp}}{98}}$</td><td>$Let\ S \equiv [Bi^{3+}],$
$then [S^{2-}] = \frac{3}{2} S$
$\therefore$
$K_{sp} = (S^2)(\frac{3}{2} S)^3 = 3.375 S^5$
$and\ S = \sqrt[5]{\frac{K_{sp}}{3.375}}$</td></tr>
<tr><td colspan="2">$\sqrt[5]{\frac{K_{sp}}{98}} \neq \sqrt[5]{\frac{K_{sp}}{3.375}}$</td></tr>
</table>

And let’s reinforce this idea with the following example:

$$\underline{Ag_2CrO_4} \Leftrightarrow 2Ag^{+} + CrO_4^{\,2-}$$

$$K_{sp} = [Ag^{+}]^2\,[CrO_4^{\,2-}]$$

Based on the stoichiometry, S ≡ [Ag+]

$$and\;[CrO_4]^{2-} = \frac{1}{2}S$$

$$\therefore$$

$$K_{sp} = (S^2)(\frac{1}{2}S)$$

$$= \frac{1}{2}S^3$$

$$and$$

$$S = \sqrt[3]{2K_{sp}}$$

Conditions That Effect Both Solubility and Solubility Product

Increased temperature increases the solubility and the K_{sp}.
The addition of an organic solvent to an aqueous solution reduces the solubility of a salt in the water.
The smaller the particle size, the greater the solubility and the K_{sp}.

In General

The higher the K_{sp}, the more soluble the salt.

The lower the K_{sp}, the less soluble the salt.

Common Ion Effect on Solubility

Let’s go back to our silver chloride example where:

$$\underline{AgCl} \Leftrightarrow Ag^{+} + Cl^{-}$$

$$and$$

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

As the silver (I) ion concentration decreases, the chloride ion concentration must increase since the product of the two is a constant (Ksp) and we can see this as the chloride ion concentration is inversely proportional to the silver (I) ion concentration:

$$\frac{K_{sp}}{[Ag^{+}]} = [Cl^{-}]$$

With silver (I) chromate:

$$[CrO_4^{\ 2-}] = \frac{K_{sp}}{[Ag^+]^2}$$

the chromate ion concentration is inversely proportional to the square of the silver (I) ion concentration.

The really cool thing about this is that we can take advantage of it in precipitating one salt from another. How do we do that?

When forming a precipitate, it is important to reduce its solubility so as to leave as little as possible in solution.

This is typically done by adding a SLIGHT EXCESS of the precipitating agent, e.g., the HCl with Group I cations.

With our AgCl example, we could visualize the reduction in silver (I) ion concentration in the following manner:

$$K_{sp} = {\scriptstyle [Ag^+]}\,\Large{[Cl^-]}$$

When forming a precipitate, it is common to add 1-2 drops in excess to facilitate precipitation.

A large excess may form a complex with the ion to be removed as an insoluble salt and actually **RESOLUBILIZE** the ion.

Solubility in the Presence of a Common Ion

There are 4 steps to determining the solubility of a salt in the presence of a common ion (usually – and we know what happens with “usually” – an anion).

1. Step 1 is to write out the balanced dissociation equation and the K_{sp} expression.
2. Step 2 is to determine how you’ll define solubility (S).
3. Step 3 is making some decisions (they’re coming, shortly).
4. Step 4 is combining equations and solving for S.

Let’s use the following as an example to walk our way through these steps:

Calculate the solubility of CaF_2 in 0.06 M NaF.

The K_{sp} for CaF_2 is $1.6*10^{-10}$ at 25°C.

Step 1-- Dissociation equation and K_{sp} expression:

$$\underline{CaF_2} \Leftrightarrow Ca^{2+} + 2F^-$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

Step 2 -- S ≡ solubility of CaF_2 in mol/L.

Step 3 – Decisions, decisions:

$$S\, mol\, CaF_2 \Leftrightarrow S\, mol\, Ca^{2+} + 2S\, mol\, F^-$$

$$where [F^-] = 0.06M + 2S$$

$$if\;\; we\, assume\, that\, 2S <<<<<< 0.06M\,,$$

$$\therefore [F^-] = 0.06M$$

Step 4 – combine and solve:

$$K_{sp} = S\,(0.06)^2$$

$$1.6 * 10^{-10} = S\,(0.06)^2$$

$$\frac{1.6 * 10^{-10}}{(0.06)^2} = S = 4.4 * 10^{-8}\ M$$

And let’s do another, albeit slightly different, example:

Some solid silver oxalate ($Ag_2Cr_2O_4$) is shaken with 0.05 M sodium oxalate ($Na_2C_2O_4$). The silver ion concentration in solution is 1.4X10^{-5} M. Calculate the K_{sp} for silver oxalate.

Combining all the steps, below:

$$\underline{Ag_2C_2O_4} \Leftrightarrow 2Ag^+ + C_2O_4{}^{2-}$$

$$K_{sp} = [Ag^+]^2[C_2O_4{}^{2-}]$$

$$[Ag^+] = 1.4*10^{-5}\ M$$

$$[C_2O_4{}^{2-}] = \frac{1}{2}(1.4*10^{-5}\ M) + 0.05M \approx 0.05\,M$$

$$K_{sp} = (1.4*10^{-5}\ M)^2\,(0.05\,M) = 9.8*10^{-12}$$

Let’s take advantage of the common ion effect to precipitate one salt preferentially over another (aka common ion effect with competition):

A solution contains 0.005 M KI and 0.05 M KCl. Silver nitrate ($AgNO_3$) is gradually added. Which precipitates first: AgI or AgCl?

<table>
<tr><td colspan="2">Run the calculations side-by-side.</td></tr>
<tr><td>AgI info</td><td>AgCl info</td></tr>
<tr><td>$\underline{AgI} \Leftrightarrow Ag^{+} + I^{-}$
$K_{sp} = [Ag^{+}][I^{-}]$
$K_{sp} = 1.5 * 10^{-16}$</td><td>$\underline{AgCl} \Leftrightarrow Ag^{+} + Cl^{-}$
$K_{sp} = [Ag^{+}][Cl^{-}]$
$K_{sp} = 1.8 * 10^{-9}$</td></tr>
<tr><td colspan="2">Determine the silver ion concentration [Ag+] for precipitation of the insoluble salt product.</td></tr>
<tr><td>$\frac{K_{sp}}{I^{-}} = \frac{1.5 * 10^{-16}}{0.005} = [Ag^{+}] =$
$[Ag^{+}] = 3 * 10^{-14}\ M$</td><td>$\frac{K_{sp}}{Cl^{-}} = \frac{1.8 * 10^{-9}}{0.05} = [Ag^{+}] =$
$[Ag^{+}] = 3.6 * 10^{-8}\ M$</td></tr>
<tr><td colspan="2">AgI precipitates FIRST because of the lower silver ion concentration necessary for precipitation of the insoluble salt product.</td></tr>
</table>

Applications and Manipulations of and with K_{sp}’s

The first manipulation of these tools is to determine the pH necessary to maintain the separation of two cations when precipitated as sulfide salts.
When precipitating as sulfide salts, we use a hydrogen sulfide generator such as thioacetamide (TA). For the purposes of this discussion, we'll use hydrogen sulfide (H_2S) in the reactions . Hydrogen sulfide, BTW, is 200 times as poisonous as cyanide – this is because the sulfide ion anesthetizes the first cranial nerve (Cranial I), blocking your ability to continue smelling it and eventually causing death if no fresh air is sought.
The dissociation of hydrogen sulfide in water is as follows:

$$H_2S + 2H_2O \Leftrightarrow 2H_3O^+ + S^{2-}$$

$$and$$

$$K_d = \frac{[H_3O^+][S^{2-}]}{[H_2S]}$$

As a general rule, the concentration of hydrogen sulfide in aqueous solution is about 0.1 M.

- Another general rule requires discussion prior to jumping into an example.
- When separating 2 salts where one is as an insoluble precipitate, one must determine the concentration limit that is low enough that the presence of the ion left behind (in solution) may be neglected.
- As a general rule, that level is set at $1*10^{-5}$ M.
- This value varies with faculty member and level of chemistry, e.g., in analytical chemistry, I was taught that this level is $1*10^{-6}$ M.
- For this course, we’ll stick with the “ten to the minus fifth” rule.

Example

What is the pH necessary to maintain the separation of cadmium (II) (Cd^{2+}) and thallium (I) (Tl^{+}) when precipitated as their sulfide salts? Assume the “ten to the minus fifth” rule as a minimum remaining concentration. The solution is 0.1 M in each cation.

Solution

1. Determine the Ksp and dissociation expressions for each sulfide salt:

$$CdS \Leftrightarrow Cd^{2+} + S^{2-} \qquad K_{sp} = 2 * 10^{-28}$$

$$Tl_2S \Leftrightarrow 2Tl^{+} + S^{2-} \qquad K_{sp} = 1 * 10^{-22}$$

2. Let’s start with CdS because it has the lowest Ksp and set the concentration of the cadmium (II) ion remaining as $1*10^{-5}$ M:

$$[1*10^{-5}][S^{2-}] = 2*10^{-28}$$

$$and$$

$$[S^{2-}] = \frac{2*10^{-28}}{1*10^{-5}} = 2*10^{-23}\ M\ to\ ppt\ Cd^{2+}\ as\ a\ sulfide\ salt$$

3. Let’s do the same for the Tl_2S, remembering that this concentration is 0.1 M (from the example):

$$(0.1)^2[S^{2-}] = 1 * 10^{-22}$$

$$[S^{2-}] = \frac{1 * 10^{-22}}{0.01} = 1 * 10^{-20}\ M\ to\ precipitate\ Tl^{+}\ as\ a\ sulfide\ salt$$

4. Now, let's calculate the pH's necessary to separate these two ions, using the sulfide ion concentrations we've CALCULATED above. We'll start with the cadmium sulfide, first, rearranging the K_d expression for H_2S from above:

$$[H_3O^+]^2[S^{2-}] = (6.8*10^{-23})(0.1)$$

$$and$$

$$[H_3O^+] = \sqrt{\frac{6.8*10^{-24}}{2*10^{-23}}} = 0.583$$

$$so$$

$$pH = -\log 0.583 = 0.234$$

5. Let’s do the thallium sulfide, now, summarizing:

$$[H_3O^+] = \sqrt{\frac{6.8 * 10^{-24}}{1 * 10^{-20}}} = 0.0261$$

$$and$$

$$pH = -\log 0.0261 = 1.58$$

What this calculation tells us is that when the pH is less than 1.58, CdS precipitates.
When the pH is equal to or greater than 1.58, Tl_2S precipitates.

A variation of the sulfide precipitation is the hydroxide precipitation of cations.

Example

Is the difference between the solubilities of the hydroxide salts of iron (III) and magnesium (II) ions sufficient to permit the separation of these two cations in a solution that is 0.1 M in each cation? If possible, what hydroxide ion concentration is required to precipitate each cation?

1.Write the K_{sp} expressions and the dissociation expressions:

$$\underline{Fe(OH)_3} \Leftrightarrow Fe^{3+} + 3OH^- \qquad K_{sp} = [Fe^{3+}][OH^-]^3 = 4*10^{-38}$$

$$\underline{Mg(OH)_2} \Leftrightarrow Mg^{2+} + 2OH^- \qquad K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8*10^{-11}$$

2. Based on the 2 Ksp's, the ferric hydroxide precipitates first. Using the **"ten to the minus fifth" rule, solve for the hydroxide ion concentration necessary to ppt the ferric hydroxide:**

$$[1*10^{-5}][OH^{-}]^{3}=4*10^{-38}$$

$$[OH^{-}]=\sqrt[3]{\frac{4*10^{-38}}{1*10^{-5}}}=1.59*10^{-11}\ M$$

3. ASIDE: the pOH, then equals 10.80; therefore, the pH is 3.2; translation: this precipitates in acidic solution.

4. We still need to determine the hydroxide ion concentration to precipitate the magnesium (II) ion as an insoluble salt. Precipitation won't occur until the K_{sp} is overcome. We know that the Mg^{2+} concentration is 0.1 M, so:

$$[0.1][OH^-]^2 = 1.8 * 10^{-11}$$

$$[OH^-] = \sqrt{\frac{1.8 * 10^{-11}}{0.1}} = 1.3 * 10^{-5}\ M$$

Thus, when the hydroxide ion concentration is greater than 1.3*10-5 M, precipitation of the Mg salt will occur.

- To summarize:
- to ppt the ferric salt, the hydroxide ion concentration must be greater than $1.59*10^{-11}$ M;
- to ppt the magnesium salt, the hydroxide ion concentration must be greater than $1.3*10^{-5}$ M.

Miscellaneous K_{sp} Applications

Example 1: Will lead sulfate precipitate if 100 mL of 0.001 M lead nitrate is added to 100 mL of 0.002 M magnesium sulfate?

1. Determine the final lead (II) ion concentration:

$$[Pb^{2+}] = \frac{100\,mL * 0.001\,M}{200\,mL} = 5 * 10^{-4}\ M$$

2. Determine the final sulfate ion concentration:

$$[SO_4{}^{2-}] = \frac{100\,mL * 0.002\,M}{200\,mL} = 1 * 10^{-3}\ M$$

3. Determine the ion product:

$$[Pb^{2+}][SO_4{}^{2-}] = (5 * 10^{-4})(1 * 10^{-3}) = 5 * 10^{-7}$$

The ion product is less than the K_{sp}, so there will be no precipitation in this example.

Example 2: In a saturated solution of magnesium fluoride in water, the magnesium (II) ion concentration is 2.7*10^{-3} M. What is the K_{sp} for magnesium fluoride?

1. Write the dissociation expression and K_{sp} expression for MgF_2:

$$\underline{MgF_2} \Leftrightarrow Mg^{2+} + 2F^{-}$$

$$and$$

$$[F^{-}] = 2[Mg^{2+}]$$

$$K_{sp} = [Mg^{2+}][F^{-}]^2$$

2. Using what we wrote above, let's solve for the K_{sp}:

$$K_{sp} = [Mg^{2+}][F^-]^2$$

$$Substituting\ \ for\, [F^-] = 2[Mg^{2+}]$$

$$K_{sp} = [Mg^{2+}](2[Mg^{2+}])^2$$

$$K_{sp} = 4[Mg^{2+}]^3 = 4(2.7 * 10^{-3}\, M)^3 = 7.87 * 10^{-8}$$

Example 3: If a solution is 0.01 M in strontium (II) ions and barium (II) ions, what percent of barium (II) ions remains unprecipitated before strontium sulfate precipitates following the addition of sodium sulfate to the solution?

1. Write the dissociation and K_{sp} expressions (abbreviated, now):

$$\underline{BaSO_4} \Leftrightarrow [Ba^{2+}][SO_4^{2-}] = 1.08 * 10^{-10}$$

$$\underline{SrSO_4} \Leftrightarrow [Sr^{2+}][SO_4^{2-}] = 2.8 * 10^{-7}$$

2. Determine what the concentration of sulfate ion is that’s necessary to JUST ppt strontium sulfate:

$$(0.01M)[SO_4{}^{2-}] = 2.8 * 10^{-7}$$

$$then$$

$$[SO_4{}^{2-}] = 2.8 * 10^{-5}\ M$$

3. Substitute this value into the ionic expression for barium sulfate:

$$[Ba^{2+}](2.8*10^{-5})=1.08*10^{-10}$$

$$then$$

$$[Ba^{2+}]=3.857*10^{-6}\ M$$

This value represents how much barium (II) ion remains unprecipitated from what was originally present. Now we can calculate the percent of the barium (II) ion that remains unprecipitated:

$$\%\,Ba^{2+}\ remaining\ in\ solution\ unprecipitated$$

$$=\frac{3.857*10^{-6}\ M}{0.01M}*100=0.0386\%$$

Example 4: If ammonia follows the reaction below:

$$NH_3 + H_2O \Leftrightarrow NH_4{}^+ + OH^-$$

and the K_b or K_i (take your pick) is $1.8*10^{-5}$, calculate the hydroxide ion concentration if the solution with which you are working is 0.4 M in NH_3 and 0.3 M in $NH_4{}^+$.

$$K_i = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{[0.3]x}{[0.4]}$$

$$[OH^-] = \frac{(0.4)(1.8*10^{-5})}{(0.3)} = 2.4*10^{-5}\ M$$

Is this enough hydroxide ion to precipitate Mg2+ as magnesium hydroxide
if the magnesium (II) ion concentration is 0.01 M?

1. Write the dissociation and Ksp expressions:

$$\underline{Mg(OH)_2} \Leftrightarrow Mg^{2+} + 2OH^-$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.1 * 10^{-11}$$

2. Solve for the minimal concentration of hydroxide ion necessary to just make the Ksp:

$$[OH^-] = \sqrt{\frac{K_{sp}}{Mg^{2+}}} = \sqrt{\frac{1.1 * 10^{-11}}{0.01}} = 3.32 * 10^{-5}\ M$$

3. Determine the difference between the two calculations:

$$\frac{[What\ you\ have]-[What\ you\ need]}{[What\ you\ need]}*100=\%\ Long\ or\ Short$$

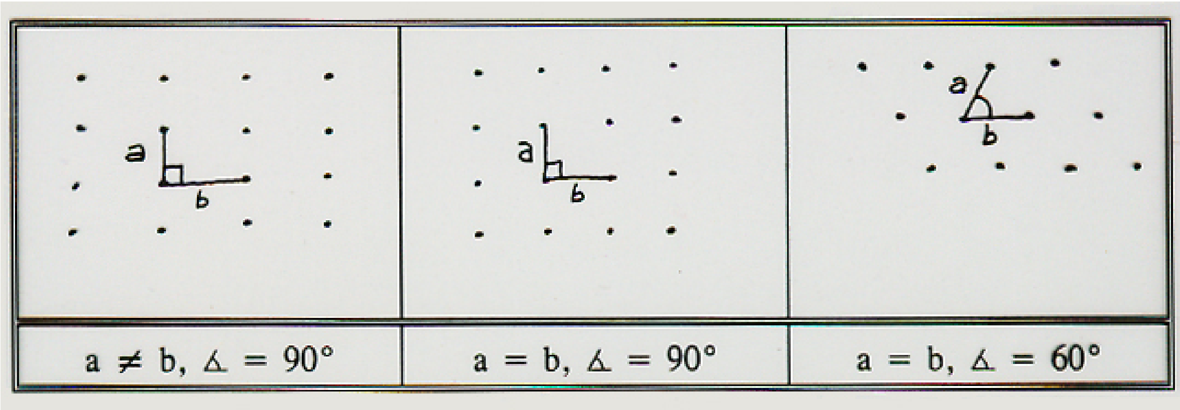
$$\frac{2.4*10^{-5}\ M-3.32*10^{-5}\ M}{3.32*10^{-5}\ M}*100=-27.7\%$$

So, there is not enough hydroxide ion in your solution of ammonia to ppt the magnesium (II) ion as an insoluble salt – almost 28% short of the necessary concentration.

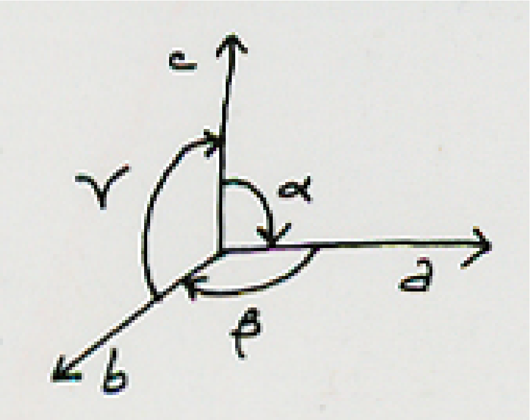
The Solid State and X-Ray Crystallography

- Solids have a definite, fixed shape and volume
- The atoms in a solid occupy fixed positions in a crystal lattice

Crystal Lattices

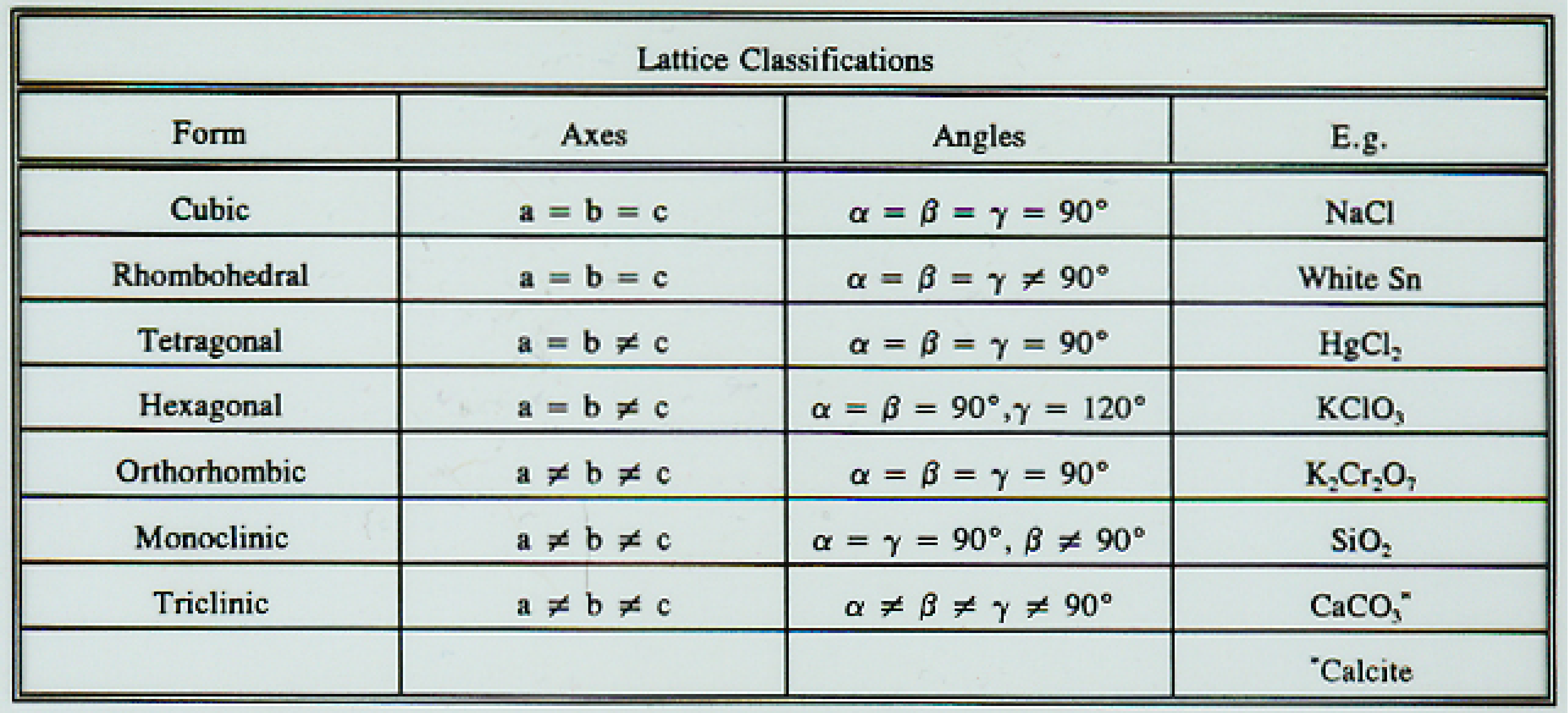


a ≠ b, ∡ = 90° | a = b, ∡ = 90° | a = b, ∡ = 60°



- A lattice is a highly ordered structure in which the atoms are arranged periodically in 3-D
- The kinetic energy of these atoms is manifested by atomic/ionic vibrations in these fixed positions
- Left, above = 2-D; Right, above = 3-D

Lattice Classifications



Lattice Classifications

Form	Axes	Angles	E.g.
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$	NaCl
Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90°$	White Sn
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90°$	$HgCl_2$
Hexagonal	a = b ≠ c	$\alpha = \beta = 90°, \gamma = 120°$	$KClO_3$
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	$K_2Cr_2O_7$
Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°, \beta \neq 90°$	SiO_2
Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90°$	$CaCO_3$*
			*Calcite

Graphic examples follow X-Ray Diffraction discussion

- Different compounds which crystallize in the same structure are called ISOMORPHOUS
- Examples
  - NaF, KCl, CaS all have the same crystalline structure as NaCl
  - $SrCl_2$, ZrO_2 and CdF_2 all have the same crystalline structure as CaF_2

- Compounds that have 2 or more crystalline structures due to different conditions undergo POLYMORPHISM
- Examples
  - Low temperature $CaCO_3$ is rhombohedral and called calcite
  - High temperature $CaCO_3$ is orthorhombic and called aragnonite
- Crystalline structure of the lattice is determined by X-Ray Diffraction

Diffraction

- “break into pieces”
- Isolation of individual wavelengths by “splitting” the electromagnetic energy into various individual wavelengths

Why Use X-Rays?

- X-rays typically have wavelengths around 0.1 nm.
- The spaces between the planes in solid crystals are about 0.1 nm.
- Hence, x-rays fit “perfectly”.

How Does X-Ray Diffraction Work?

- The MOST INTENSE SCATTERING is our focus
- Arithmetically:

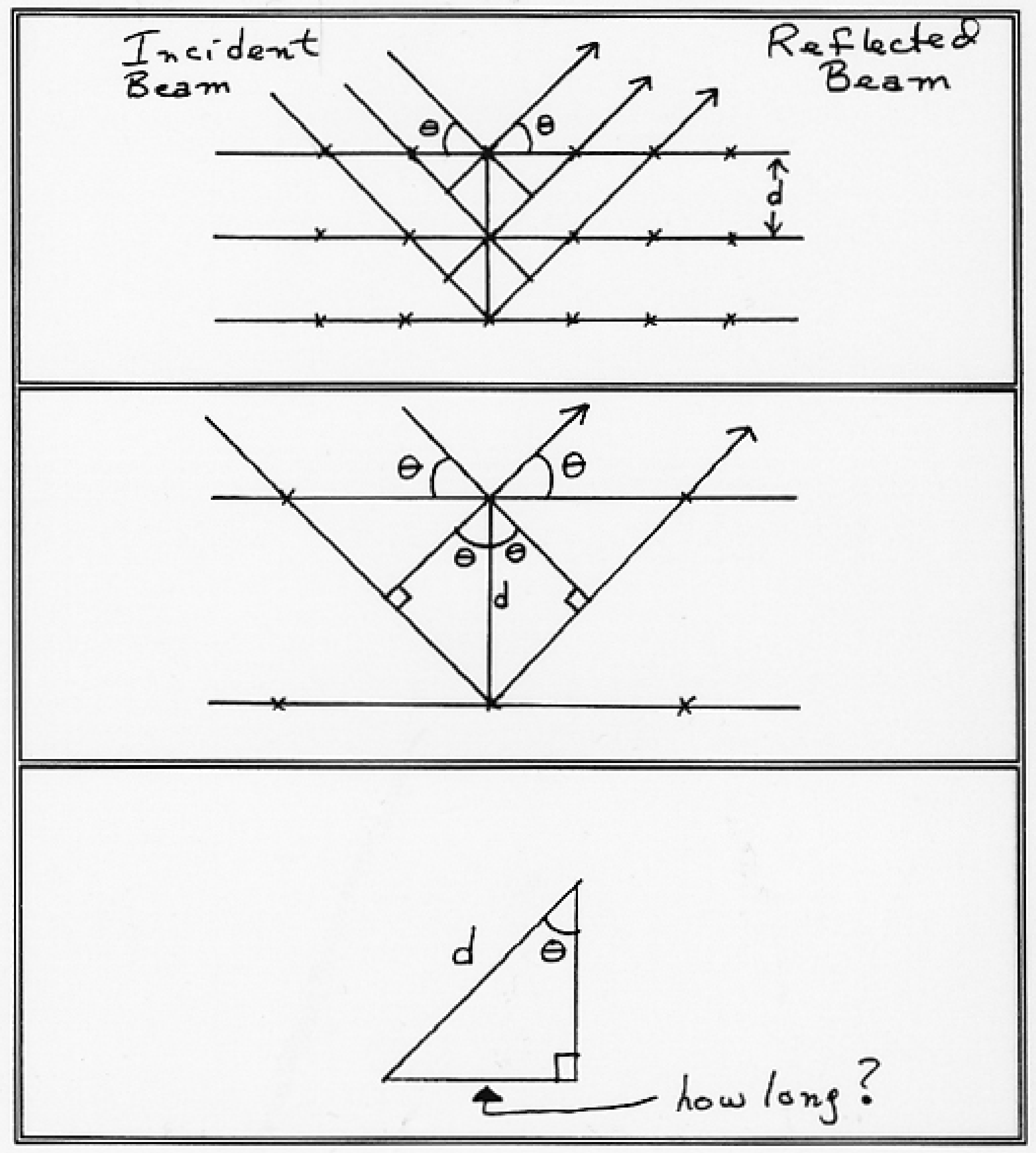
$$n \lambda = 2 d \sin \theta$$

- When “n” =1, the most intense scattering is observed:

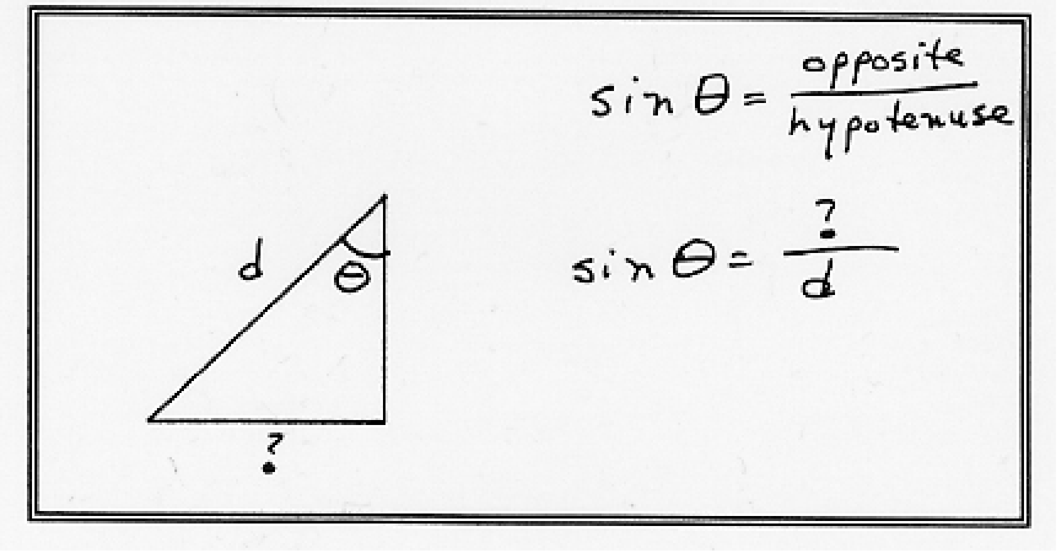
$$\lambda = 2 d \sin \theta$$

- Where λ = x-ray wavelength; d = distance between lattice planes (“reflectors”) and θ = the angle of incidence and reflection of x-rays

- Where λ = x-ray wavelength;
- d = distance between lattice planes (“reflectors”) and
- θ = the angle of incidence and reflection of x-rays



Review: sin



$$\sin\Theta = \frac{x}{d}$$

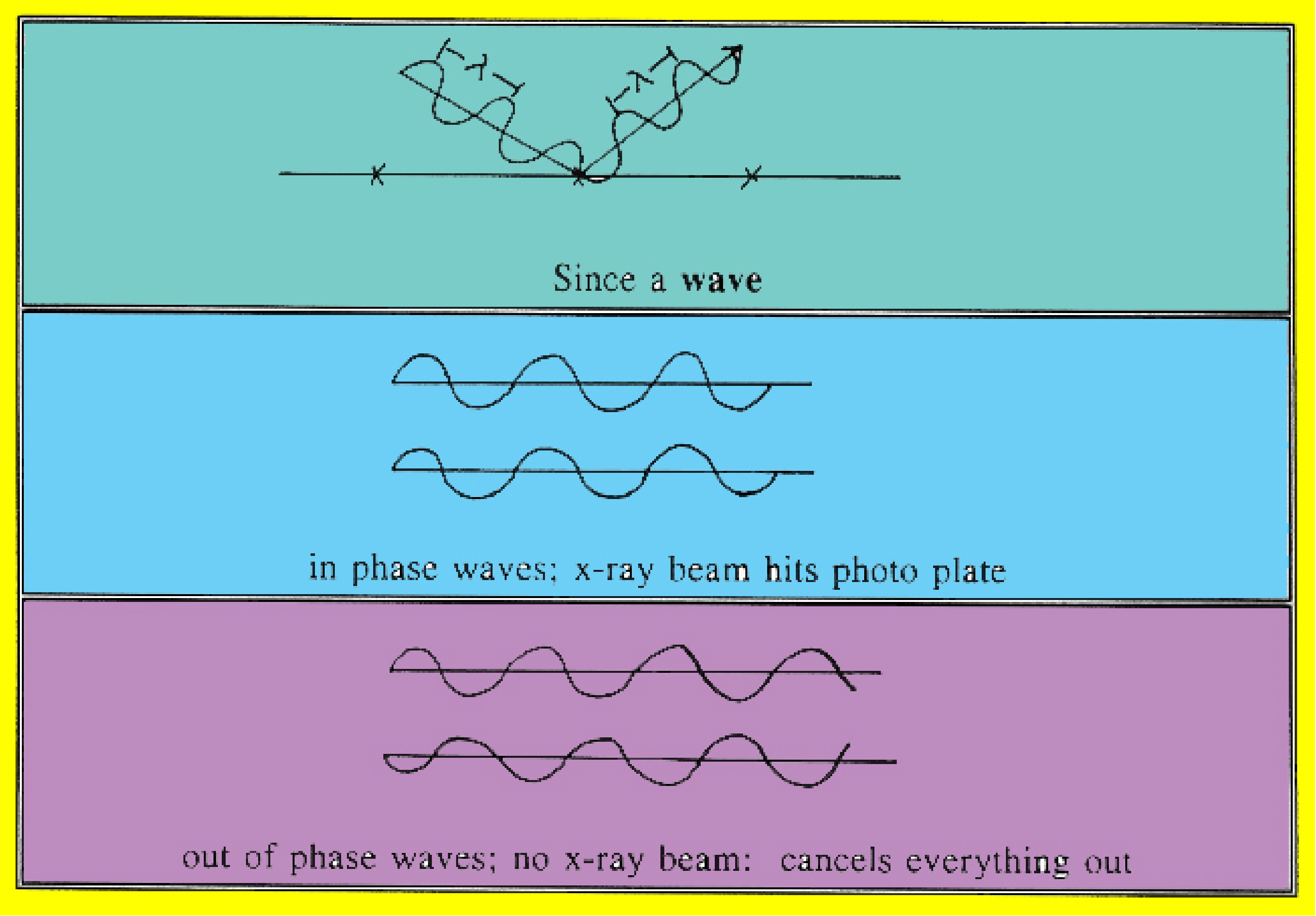
hence

$$d\sin\Theta = x$$

$$\therefore\ \textit{beam 2 travels } 2d\sin\Theta \textit{ farther than beam } 1$$

REMEMBER: d = *distance between reflecting planes*

λ

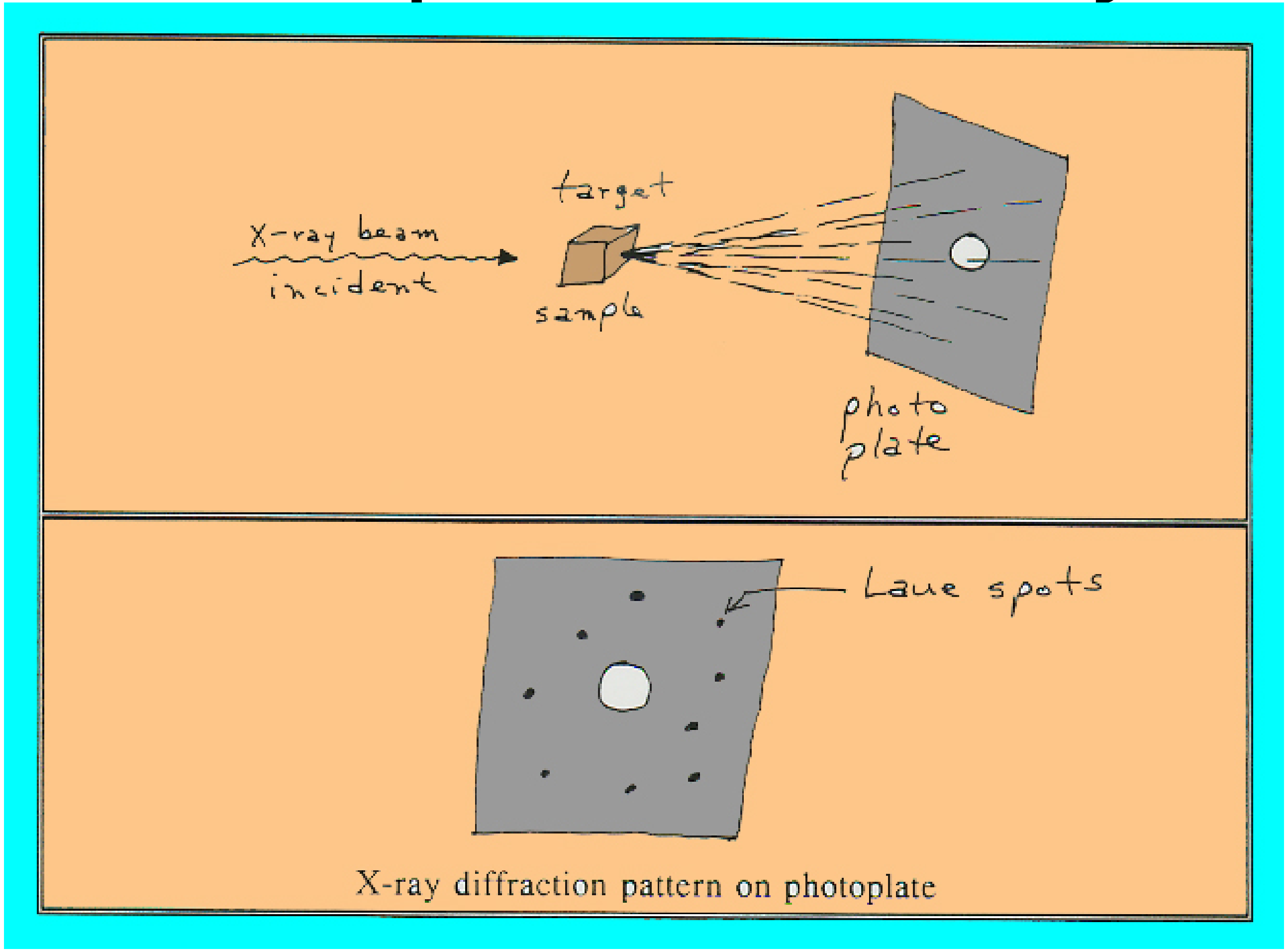


Since a **wave**

in phase waves; x-ray beam hits photo plate

out of phase waves; no x-ray beam: cancels everything out

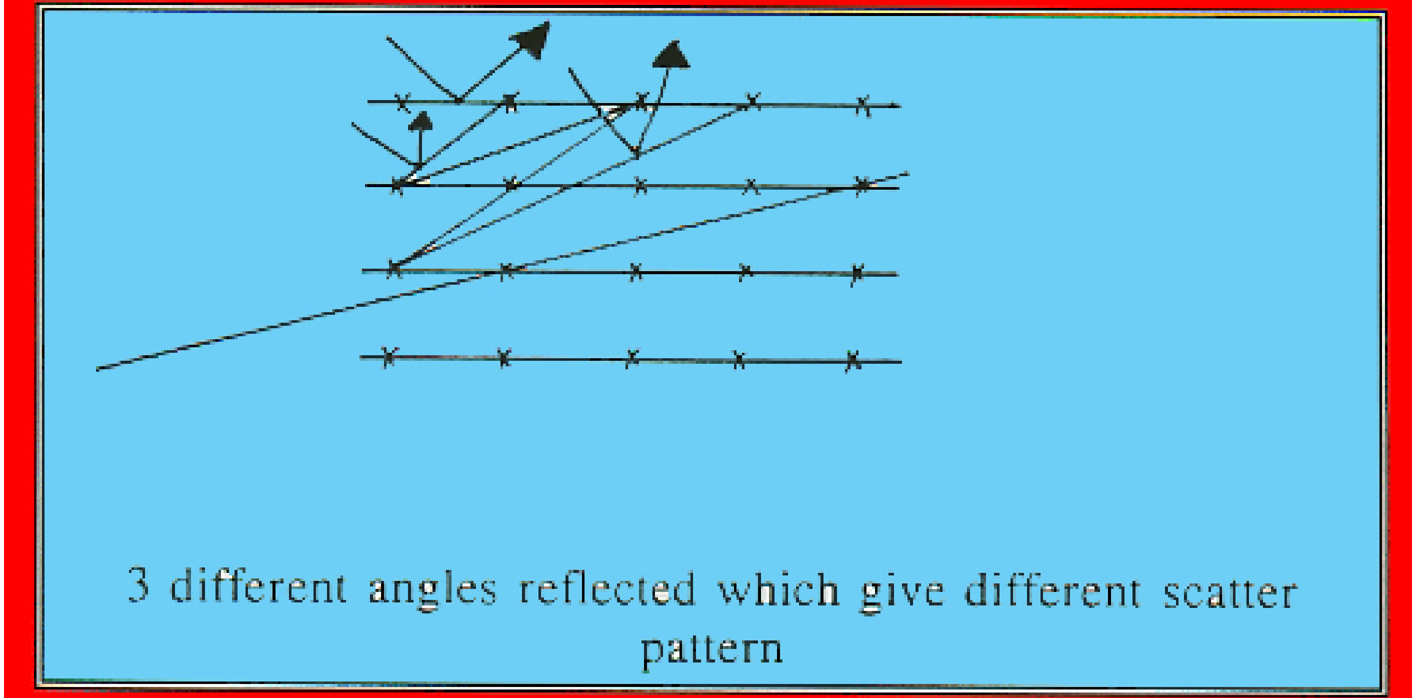
Photoplate? History.



X-ray diffraction pattern on photoplate

Different crystalline lattices give different x-ray diffraction patterns

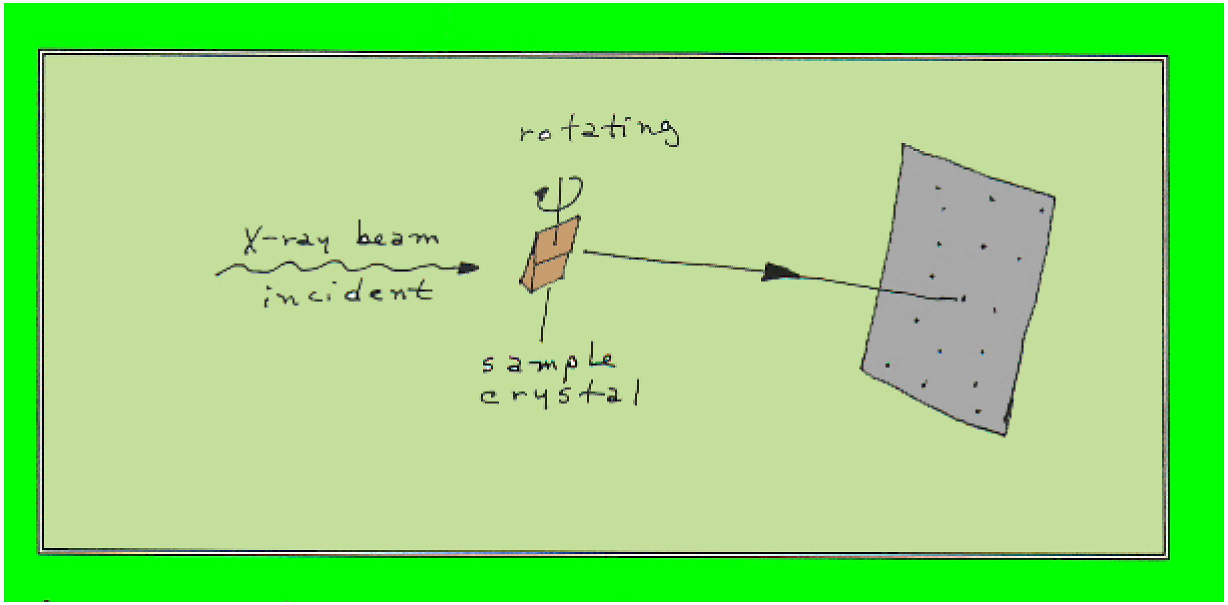
- Different patterns are because different planes cause different diffraction.



3 different angles reflected which give different scatter pattern

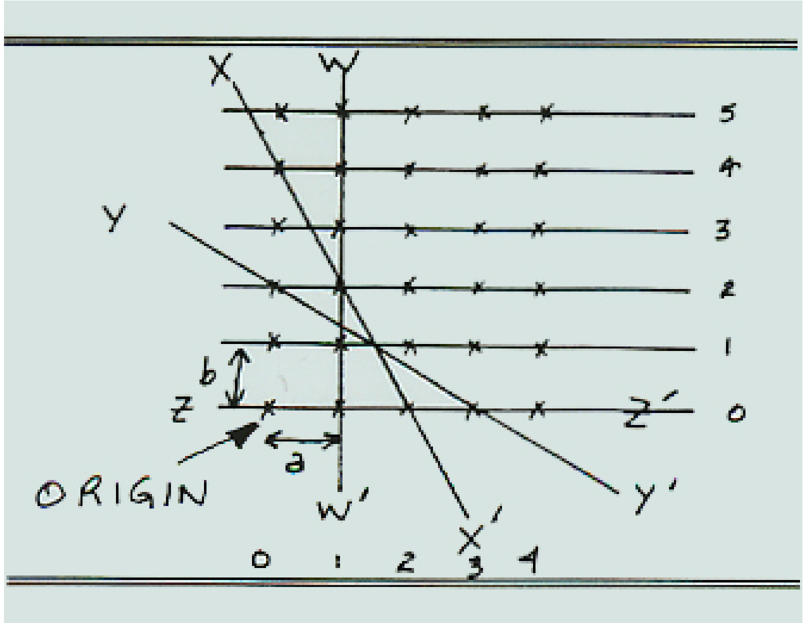
X-Ray Diffraction

- Gives data “ONLY” when target sample is rotated to specific angles from the incident x-ray beam.
- This allows for the determination of the “monochromatic” x-ray wavelength for each Laue spot:



The Laue spots are formed as the crystalline plane sets are brought to the required angles.

- In crystallography, it is convenient to describe a given crystal by way of a set of planes
- Let’s examine a 2-D lattice with different planes of different orientations:



PLANE	Intercepts at AXES		
	AXIS a	AXIS b	AXIS c
ZZ’	∞* a	1 b	∞* c
YY’	3 a	2 b	∞* c
XX’	2 a	4 b	∞* c
WW’	1 a	∞* b	∞* c
			* parallel to axis

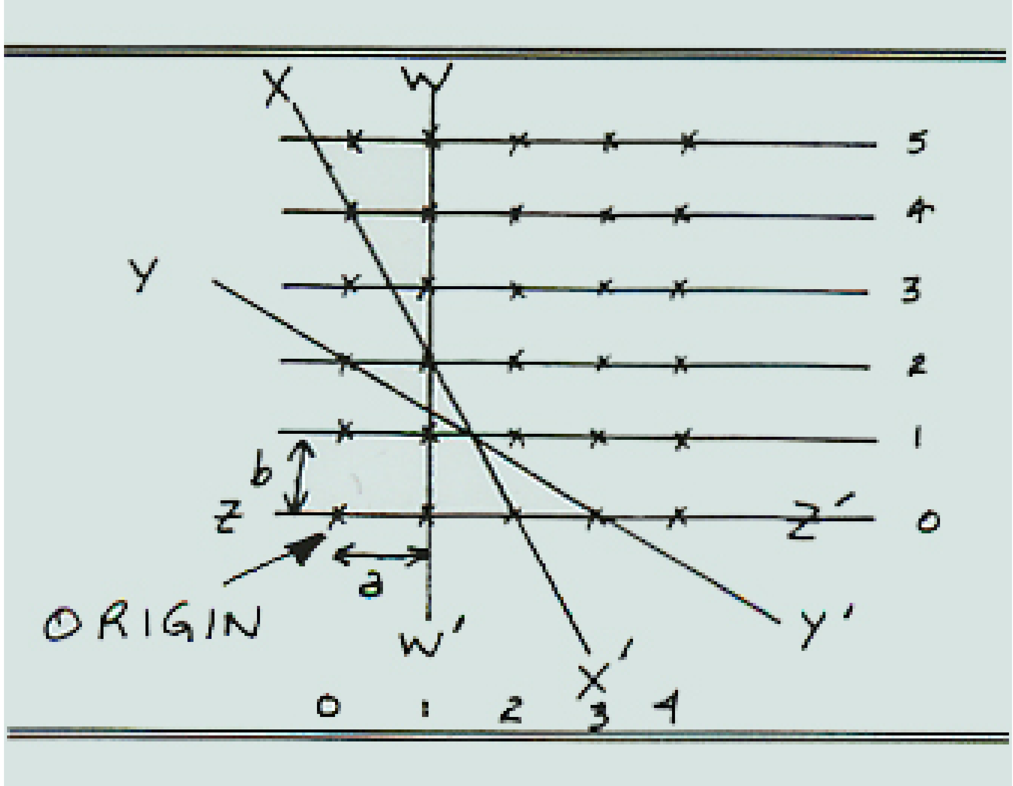
- The intercepts are used to determine 3 numbers called Miller Indices of the PLANE, i.e., its “address” in the crystalline structure.

How Do This?

1. Start with the intercepts for ZZ’
    1. ∞ a, 1 b, ∞ c
2. Take the reciprocals
    1. 1/∞ a, 1/1 b, 1/∞ c
3. Lose the letters
    1. 1/∞, 1/1, 1/∞
4. Clear the fractions by lowest common denominators: 1 in this case:
    1. 0, 1, 0
5. Lose the commas:
    1. 010
6. The indices (*hkl*) give the orientation of the plane in the crystalline lattice via its 3 internal axes

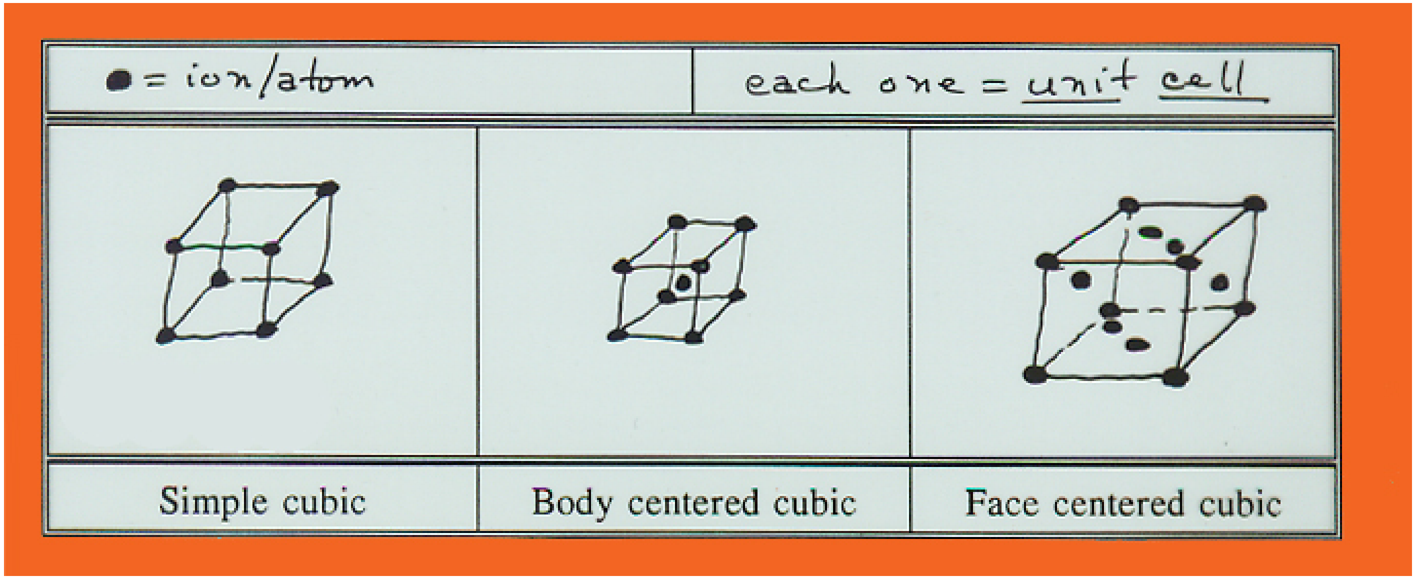
For The Remaining 3 Sets of Data:

PLANE	Intercepts	Reciprocal	Lose Letters	*hkl*
YY’	3a 2b ∞c	1/3a 1/2b 1/∞c	1/3 1/2 1/∞	230***(6)**
XX’	1a 2b ∞c	1/1a 1/2b 1/∞c	1/1 1/2 1/∞	210
WW’	1a ∞b ∞c	1/1a 1/∞b 1/∞c	1/1 1/∞ 1/∞	100



How Use with Lattices?

There are 14 Bravais Lattices and Rules for Using Them.

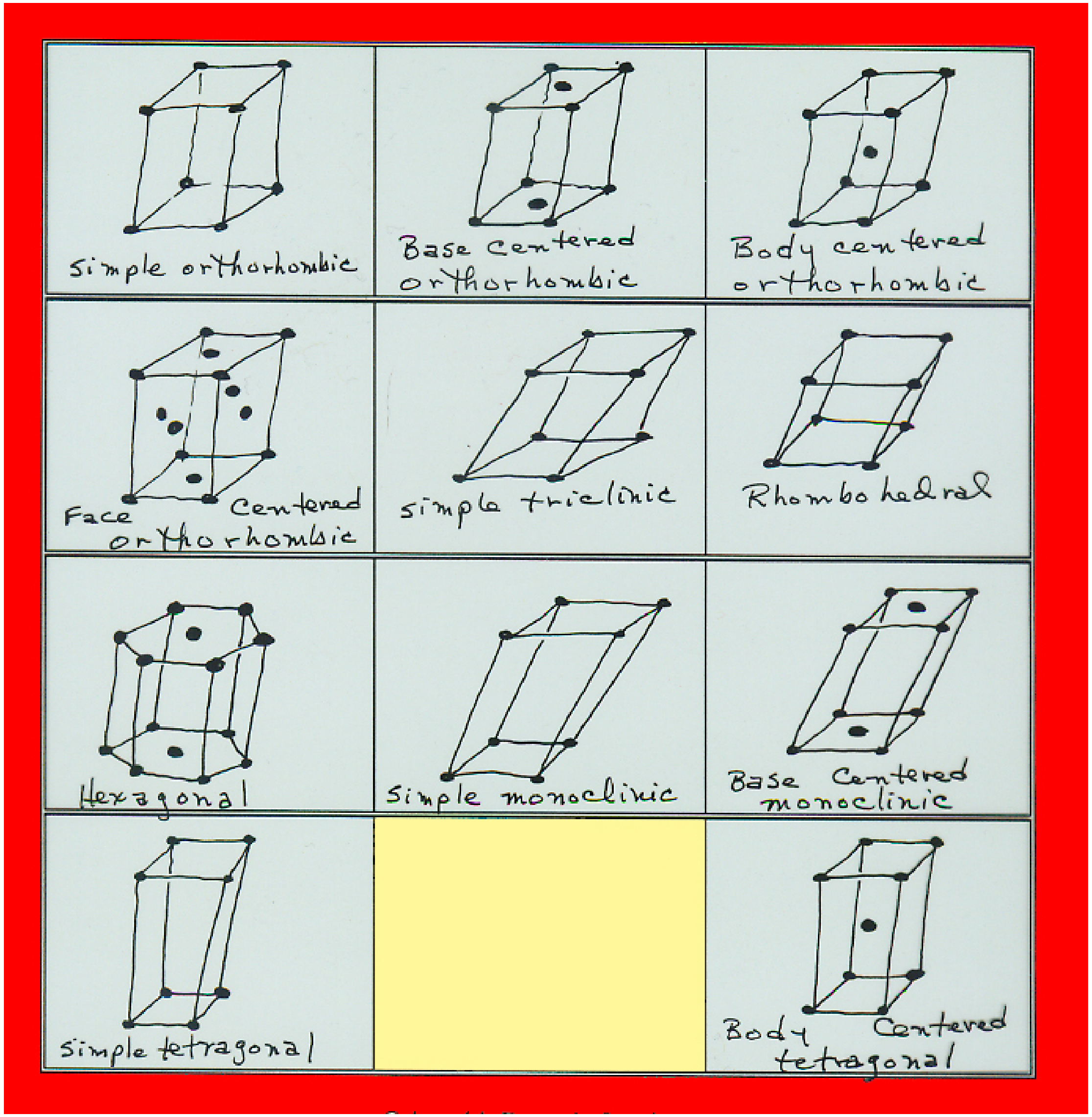


Three Examples, above.

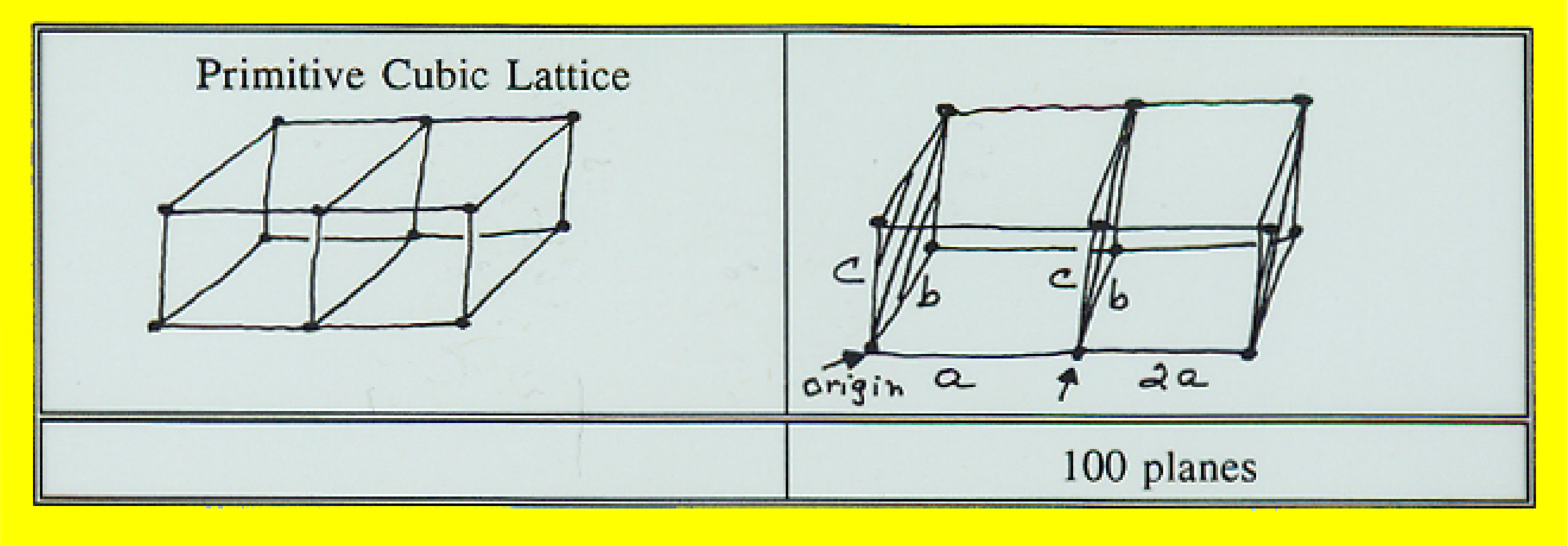
Rules for Counting Atoms in Unit Cells:

1. Corner atoms are shared with 8 unit cells, therefore, each corner is worth 1/8 of an atom at each corner UNLESS in hexagon, then = 1/6
2. Edge atoms are shared with 4 unit cells, therefore, each edge = ¼ of an atom at each edge
3. Face-centered atoms are shared with 2 unit cells, therefore, each face = ½ of each atom at each face
4. Body centered atoms are shared with 1 unit cell, therefore each body = 1 full portion of each atom in “body”

The Other 11 Bravais Lattices

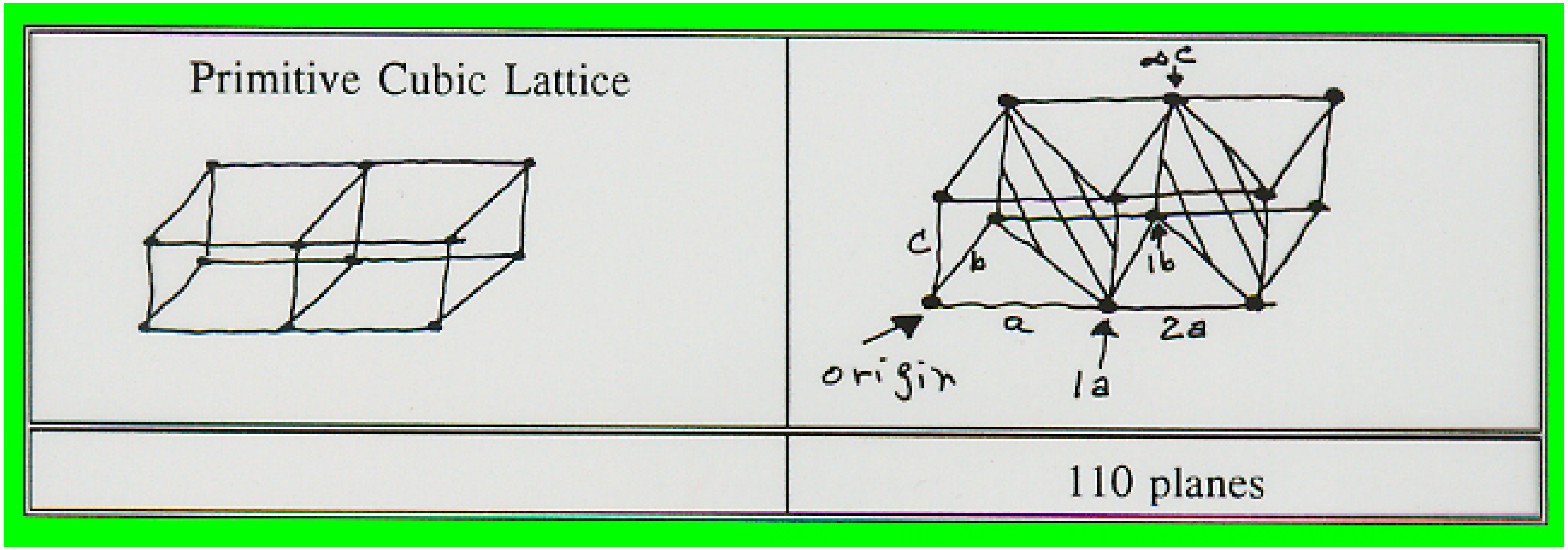


Miller Indices May be Used with 3-D Crystal Lattices



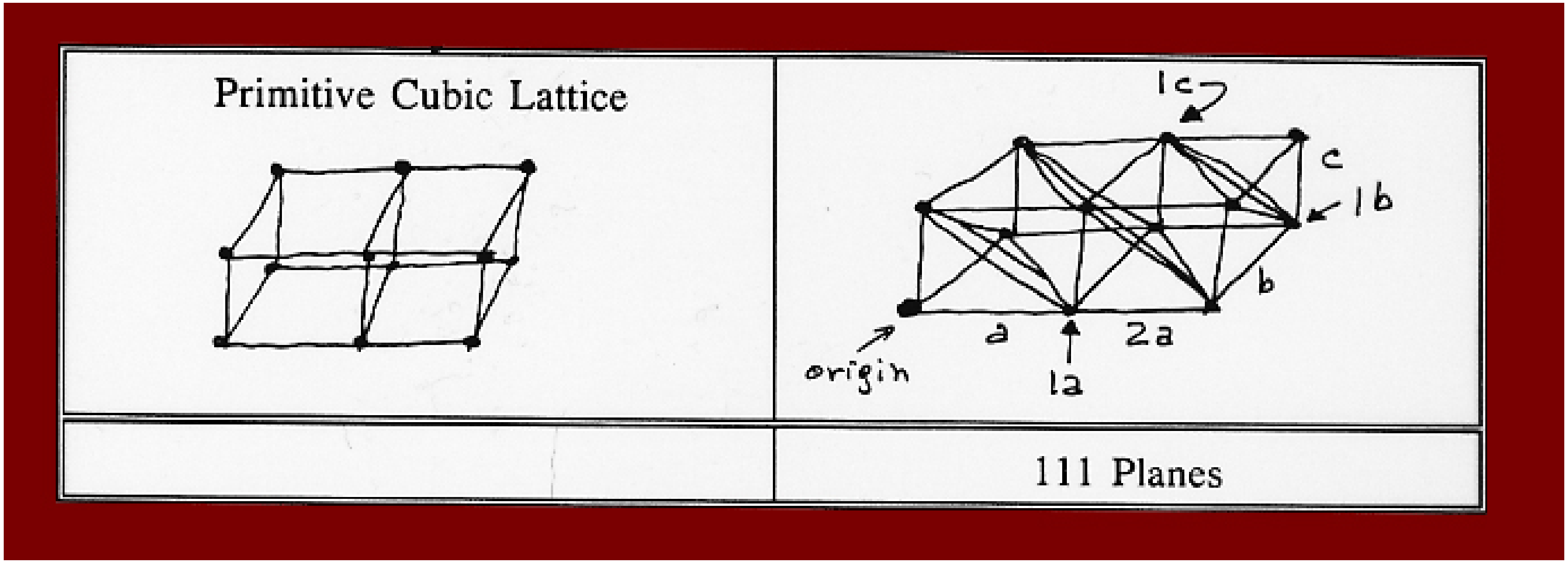
Intercepts	Reciprocal	Lose Letters	hkl
1a ∞b ∞c	1/1a 1/∞b 1/∞c	1/1 1/∞ 1/∞	100

Example 2



Intercepts	Reciprocal	Lose Letters	hkl
1a 1b ∞c	1/1a 1/1b 1/∞c	1/1 1/1 1/∞	110

Example 3



Intercepts	Reciprocal	Lose Letters	hkl
1a 1b 1c	1/1a 1/1b 1/1c	1/1 1/1 1/1	111

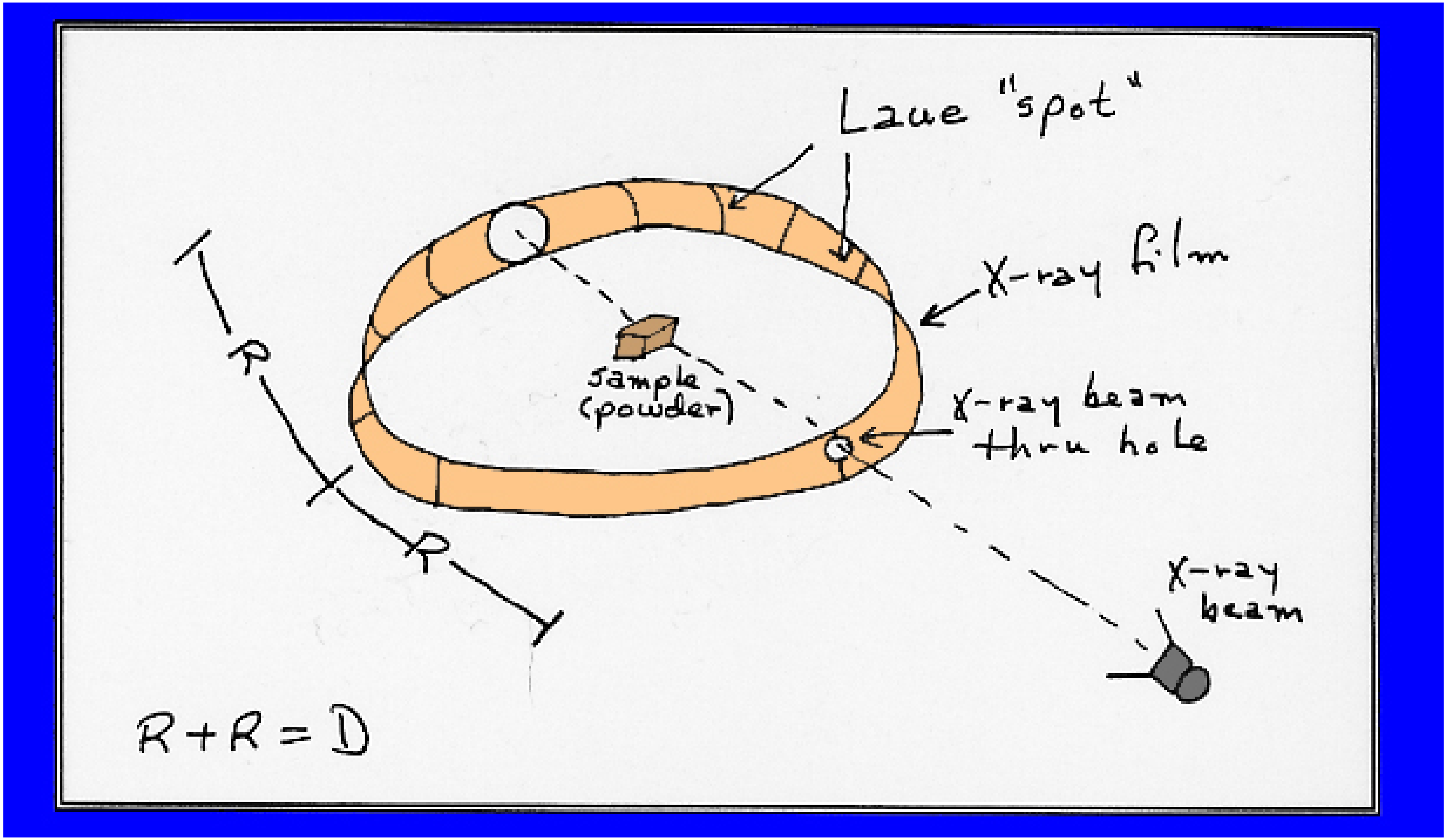
- Interestingly enough,

$$h^2 + k^2 + l^2 = \mathrm{N}$$

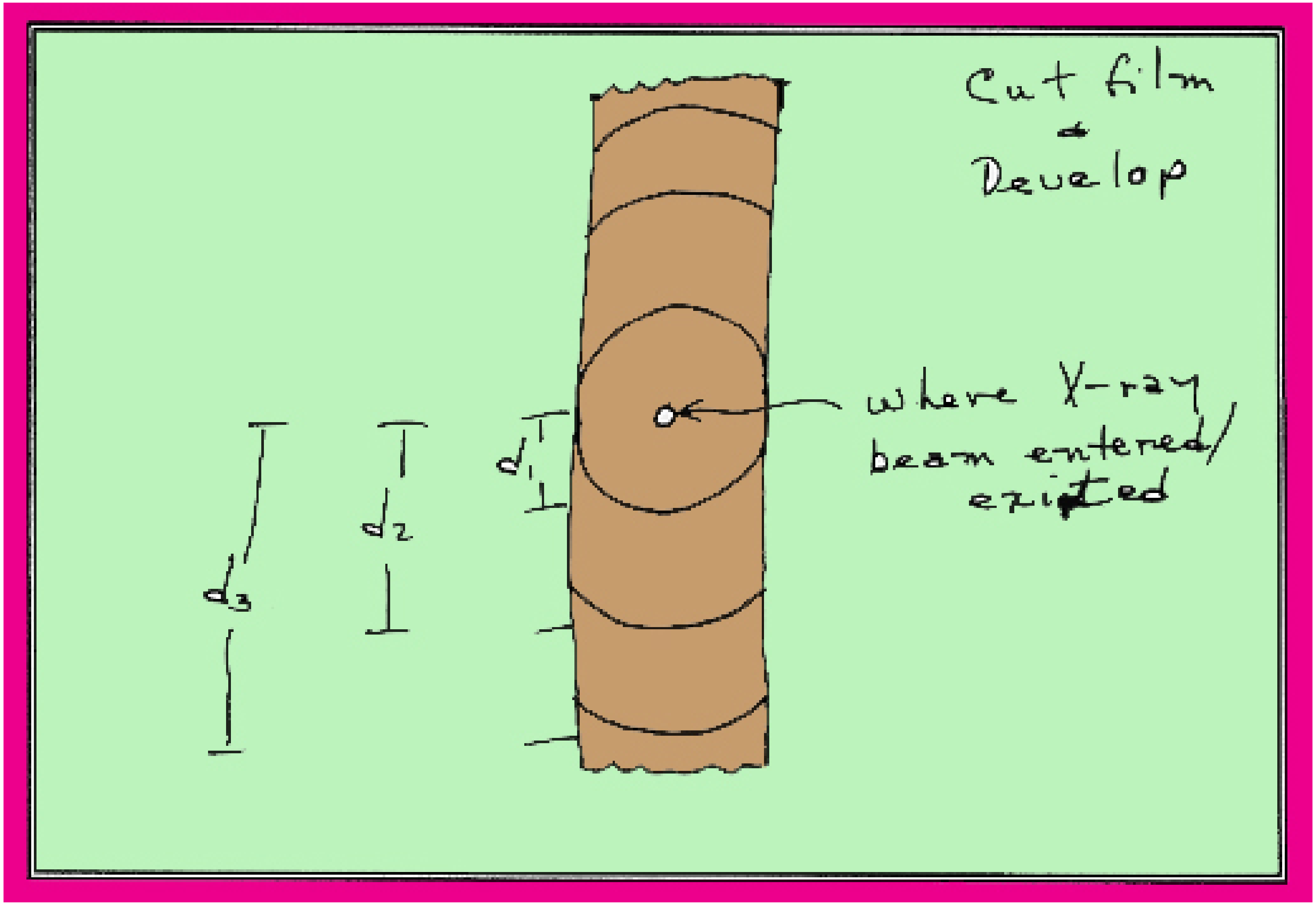
- N may be found in a table of values for various lattices

Primitive Cubic Lattice	
hkl	N
100	1
110	2
111	3
200	4
210	5
211	6

How Get “N”??? Experimentally!



How Get "N"??? Experimentally! #2



How Get “N”??? Experimentally! #3

Record the distances, e.g.,

$d_1 = 1$ (Relative Distance)

$d_2 = 3$

$d_3 = 5$

And calculate θ

How Calculate θ?

- x = relative distance from data
- R = radius of circle of film about the sample; generally a determined constant

$$\theta = \frac{x}{2R} = \frac{x}{D}$$

NEXT!

1. Compute $\sin^2\theta$ and compare $\sin^2\theta$ for each point
2. Find largest common factor between all of the values for $\sin^2\theta$ and divide every $\sin^2\theta$ by this value
3. Round each value to the nearest whole integer (providing it's not too great for error)
4. This value is "N"
5. "N" may be matched in a table and the lattice type determined

Value of N

Good Match of “N”	Bad Match of “N”/Bad Sample
All allowed N for a lattice are in list of derived N values	N values that are not allowed = incorrect lattice OR =impurity in the sample

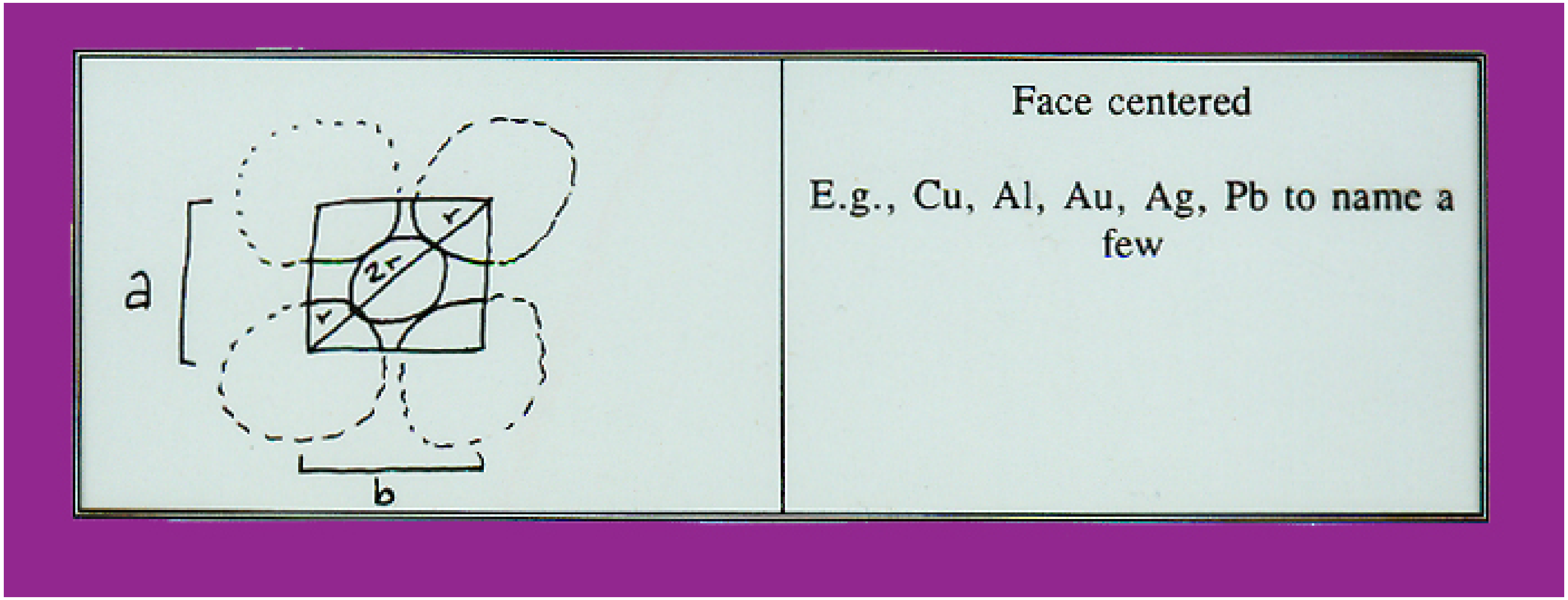
Can use N, then, to calculate for “a”, where “a” = the edge length of a single cell:

$$\sin^2\theta = \left(\frac{\lambda^2 N}{4a^2}\right)$$

$$where$$

$$a = \sqrt{\left(\frac{\lambda^2 N}{4\sin^2\theta}\right)}$$

How Do We See “a”?



Face centered

E.g., Cu, Al, Au, Ag, Pb to name a few

Pythagoras Revisited

$$a^2 + b^2 = c^2$$

$$where\ \ a = a, b = a,\ and\ c = 4r\ \ (r = atomic\, radius)$$

$$if\ \ we\ know\ "a",\ can\ solve\ \ for\ atomic\ or\ ionic\ radius\ of\ \ subs\tan ce:$$

$$a^2 + a^2 = (4r)^2$$

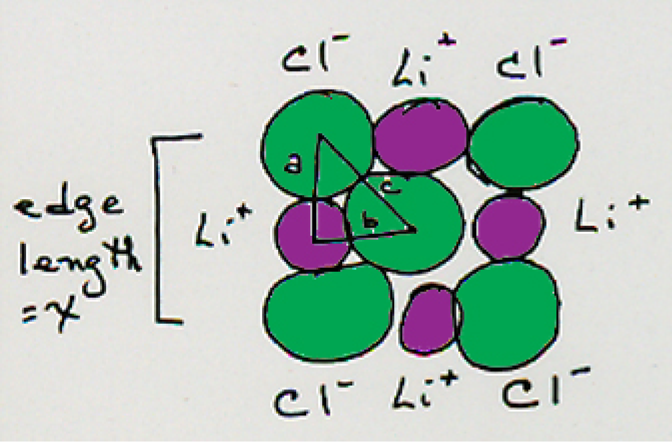
$$2a^2 = 4^2 * r^2$$

$$r = \sqrt{\frac{2a^2}{4^2}} = \left(\frac{a}{4}\right)\sqrt{2}$$

$$or,\ r = 0.354a$$

- Knowing the edge length of a unit cell, we may then calculate the ionic radii.

- E.g., Calculate the ionic radius for Li^+ if LiCl (face centered) edge length = 0.514 nm; assume anion-anion contact.



$$a = \frac{x}{2} = \frac{0.514}{2} = 0.257\ nm\ (Li^{+} \rightarrow Cl^{-})$$

$$b = \frac{x}{2} = \frac{0.514}{2} = 0.257\ nm\ (Li^{+} \rightarrow Cl^{-})$$

$$How\ get\ Cl^{-} \rightarrow Cl^{-}???$$

$$c^{2} = a^{2} + b^{2}$$

$$c = \sqrt{(a^{2} + b^{2})} = \sqrt{(0.257)^{2} + (0.257)^{2}}$$

$$c = 0.363\ nm = ionic\ DIAMETER\ (Cl^{-} \rightarrow Cl^{-})$$

$$ionic\ radius\ of\ Cl^{-} = \frac{0.363}{2} = 0.182\ nm$$

If center to center between Li^+ and Cl^- is 0.257 nm, can calculate the Li^+ ionic radius:

$$Li^+ \rightarrow Cl^- = 0.257\ nm$$

$$Cl^-\ radius = 0.182$$

$$\therefore$$

$$0.257\ nm - 0.182\ nm = 0.075\ nm = Li^+\ radius$$