

National School on Neutron and X-ray Scattering  
October 1, 2008

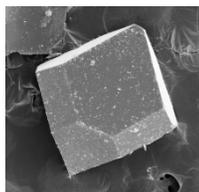
*An Introduction to*

# **Single Crystal Crystallography**

**Xiaoping Wang**

*Neutron Scattering Science Division  
Oak Ridge National Laboratory*

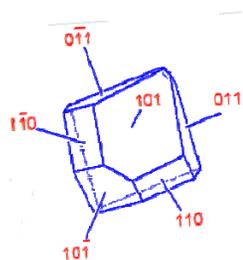
# Introduction



Single Crystal

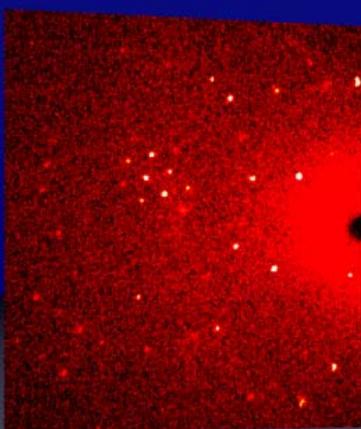
*Direct Space*

Single Crystal  
Diffraction  
Experiment



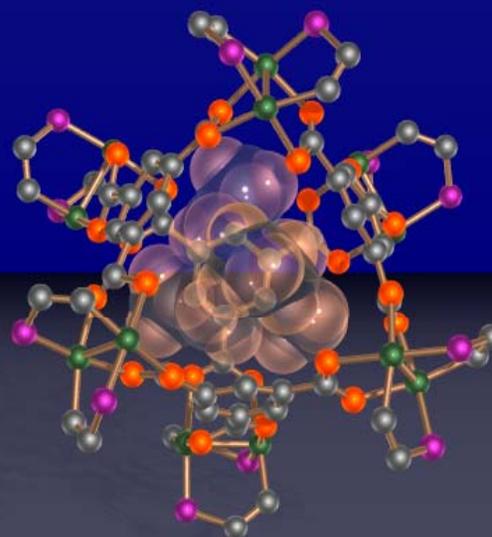
Crystal Symmetry

Diffraction Pattern



*Reciprocal Space*

**3D Molecular Structure**



# Contents

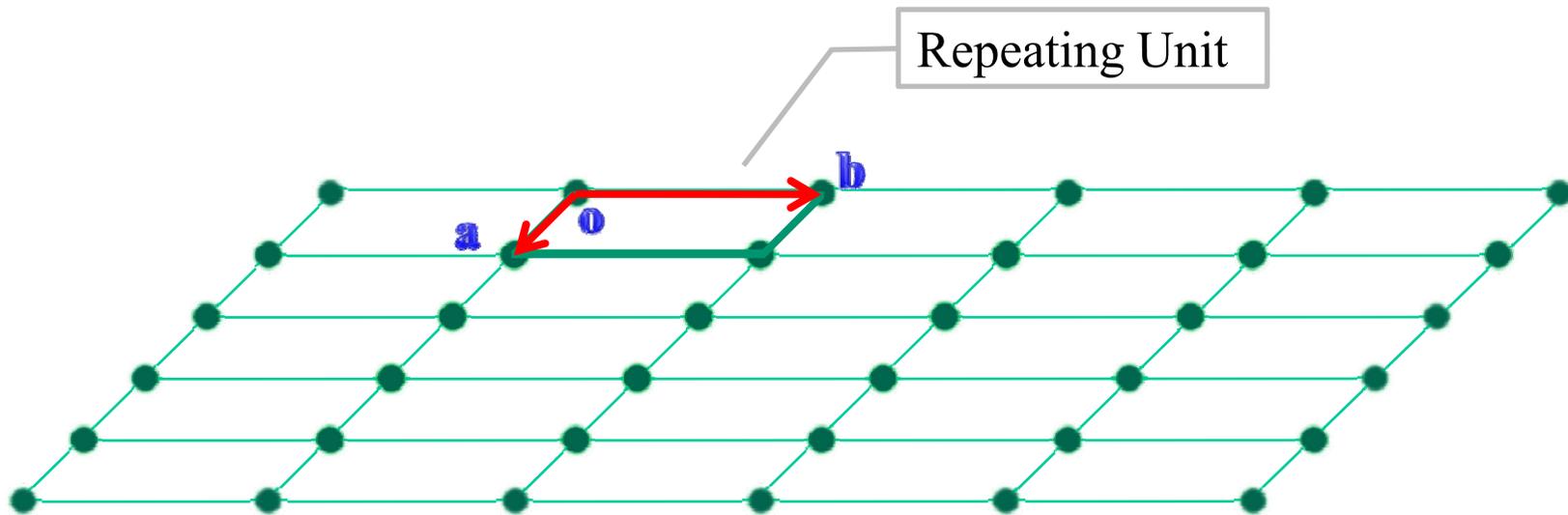
---

- Crystal Lattice
- Crystallographic Planes and Miller Indices
- Reciprocal Lattice
- Diffraction of X-rays and Neutrons
- Diffraction Conditions
- Structure Factor
- Diffraction Intensities
- Crystal Symmetry
- Structure Refinement
- Validation and Presentation of Results

# Lattice

Ordered arrangement of points in space

Periodicity  
&  
Symmetry

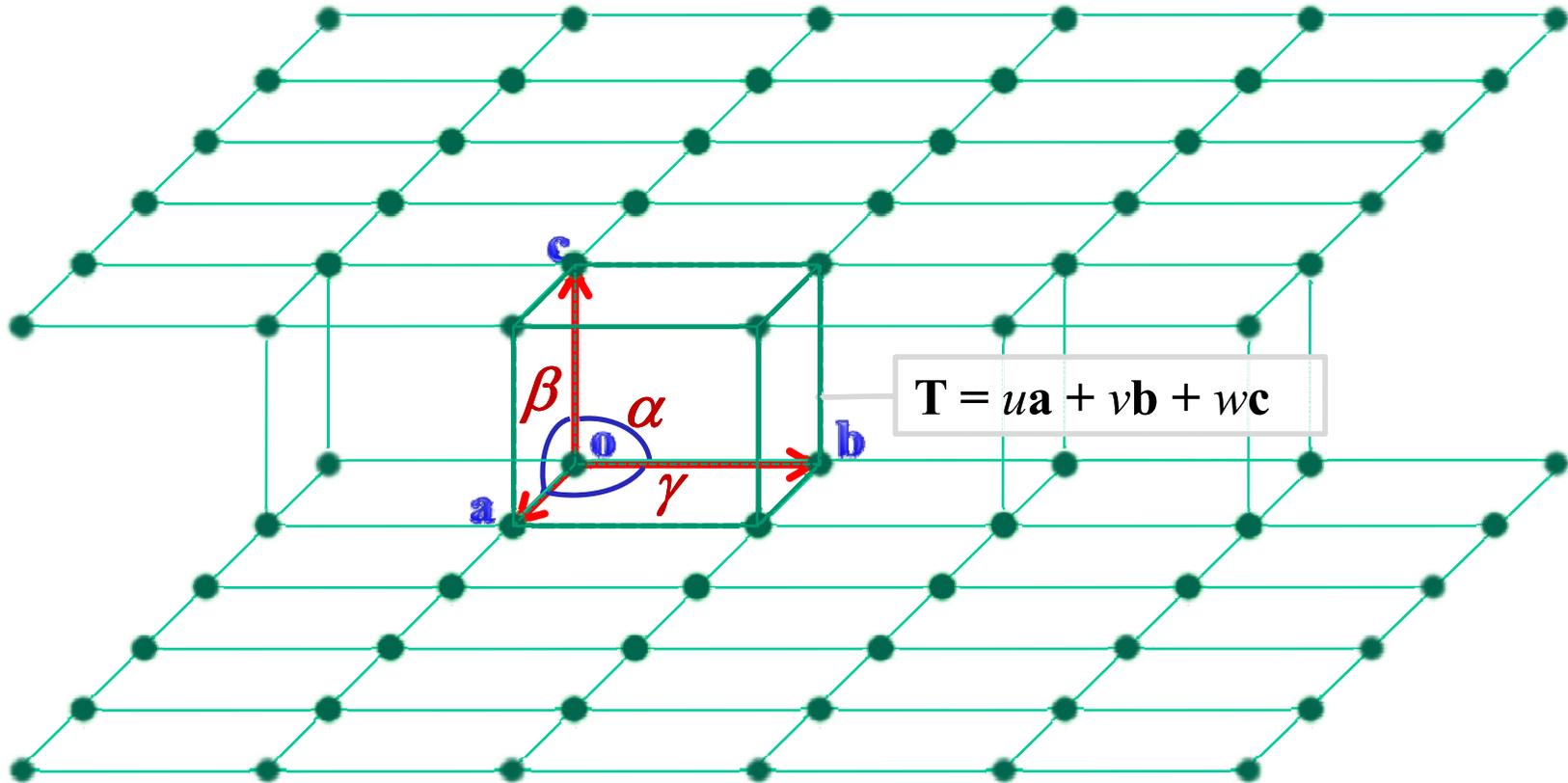


A 2-D Lattice

The environment of any one point is identical with that of all others.

# Lattice and Unit Cell

August Bravais  
(1811- 1863)

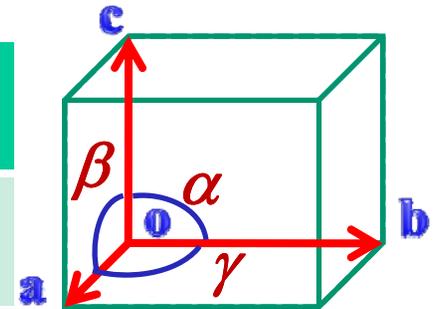


A 3-D Lattice

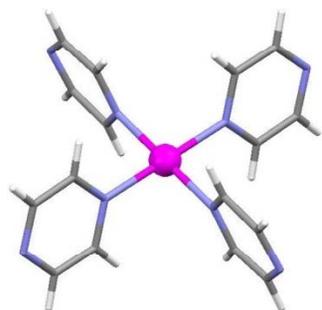
There are fourteen possible 3-D point lattices [Symmetry + Centering]

# 7 Crystal Systems and the 14 Bravais Lattices

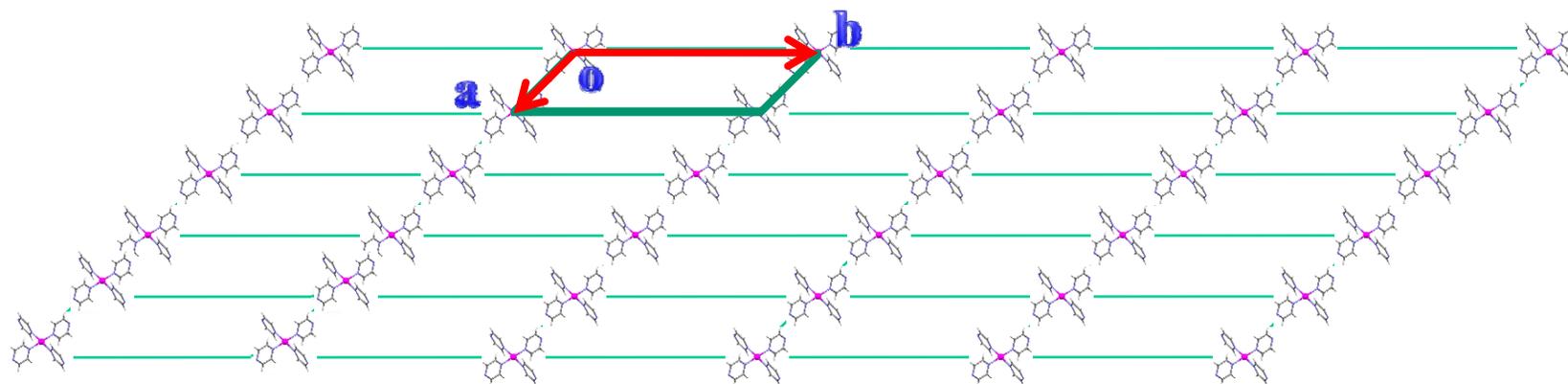
Crystal System	Lattice Symbol	Restrictions
Triclinic	$P$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	$P, C$	$a \neq b \neq c$ $\alpha = \gamma = 90, \beta \neq 90$
Orthorhombic	$P, C, I, F$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90$
Tetragonal	$P, I$	$a = b \neq c$ $\alpha = \beta = \gamma = 90$
Rhombohedral	$R$	$a = b = c$ $\alpha = \beta = \gamma < 120, \neq 90$
Hexagonal	$H$	$a = b \neq c,$ $\alpha = \beta = 90, \gamma \neq 120$
Cubic	$P, F$ (fcc), $I$ (bcc)	$a = b = c$ $\alpha = \beta = \gamma = 90$



# 2D Lattice + Motif $\rightarrow$ 2D “Crystal”

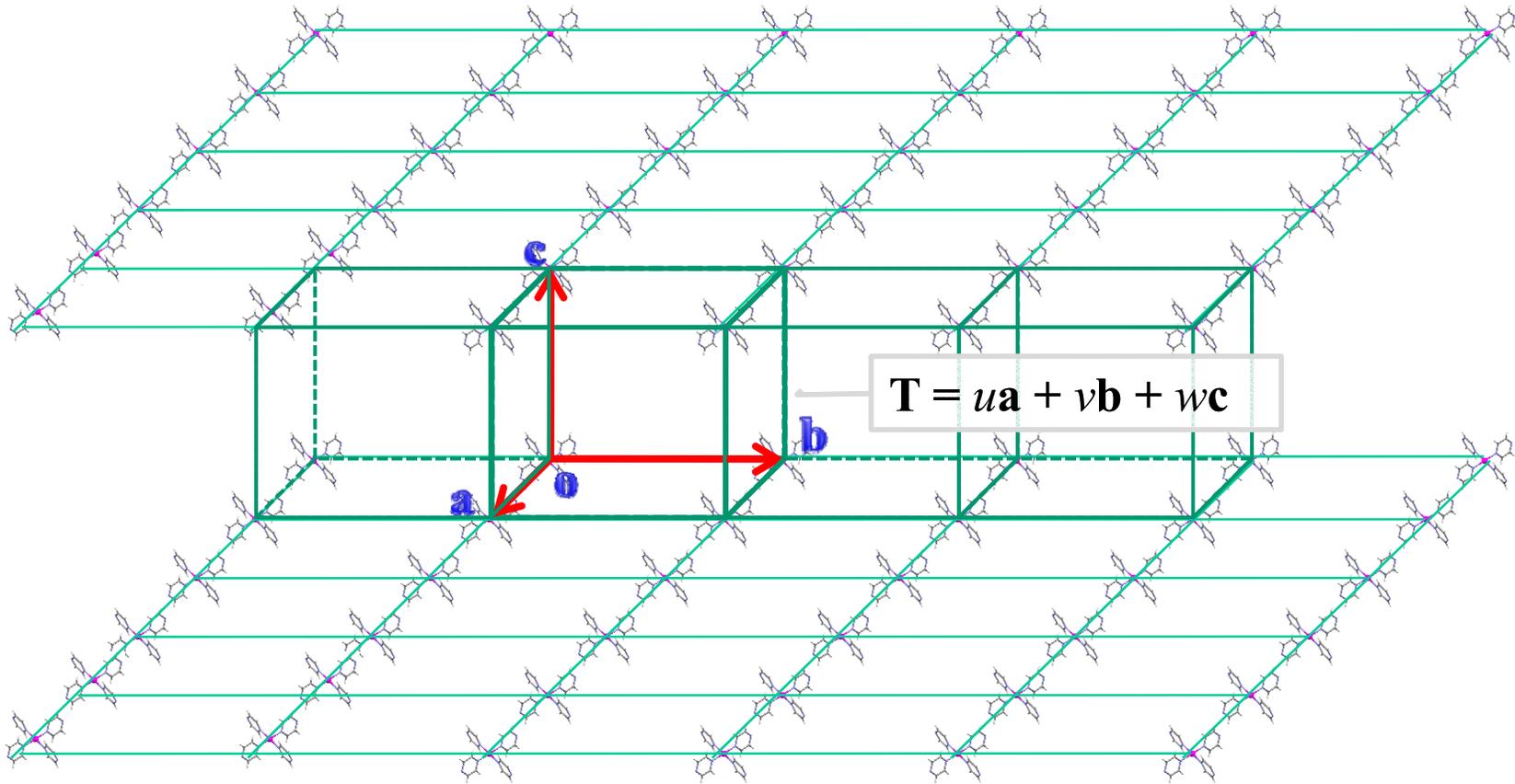


A Molecular Motif



A 2-D “Crystal”

# Lattice + Molecular Motif → Molecular Crystal



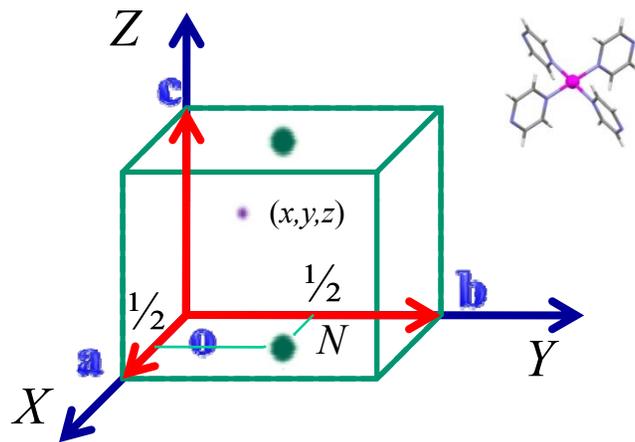
Infinite 3D periodic array

Here the molecules reside on vertices of the unit cell – *Special Positions*

# Positions of Atoms in Unit Cell

## – Fractional Coordinates

The atomic coordinates of a crystal structure are usually expressed as fractions of the  $a$ ,  $b$  and  $c$  unit cell vectors.



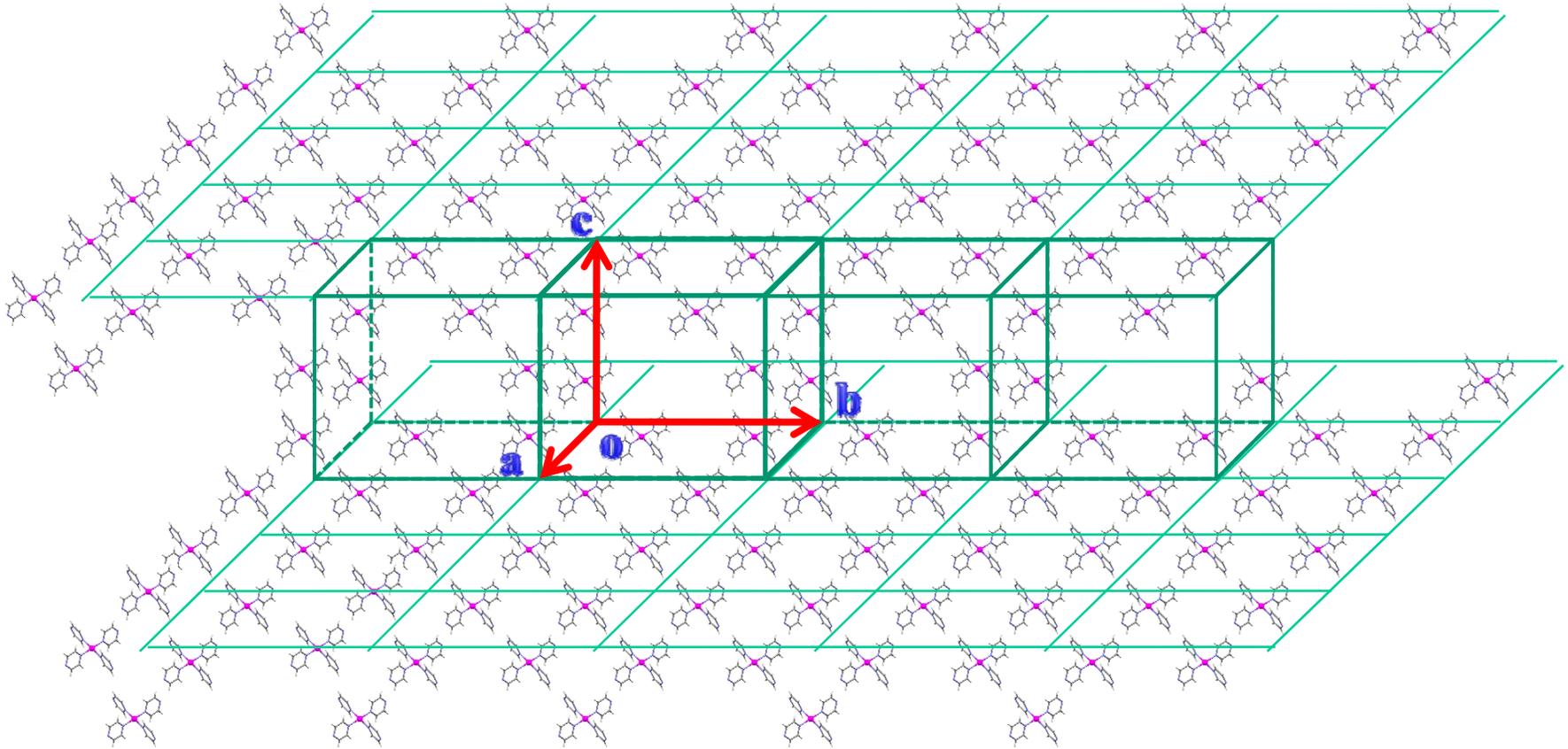
$x = X/a$  on the crystallographic  $X$  axis  
 $y = Y/b$  on the crystallographic  $Y$  axis  
 $z = Z/c$  on the crystallographic  $Z$  axis

The lengths of  $a$   $b$   $c$  define the lattice parameters  $a$ ,  $b$  and  $c$  of the unit cell.

Vector presentation of a *general position*  $\mathbf{r} = (\mathbf{a} \ \mathbf{b} \ \mathbf{c}) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$

An atom  $N$  with fractional coordinates 0.5, 0.5, 0 would lie at the center of  $ab$  plane ( $1/2, 1/2, 0$ ), also called  $C$ -center position.

# 3D-Lattice + Molecular Motif $\rightarrow$ Molecular Crystal



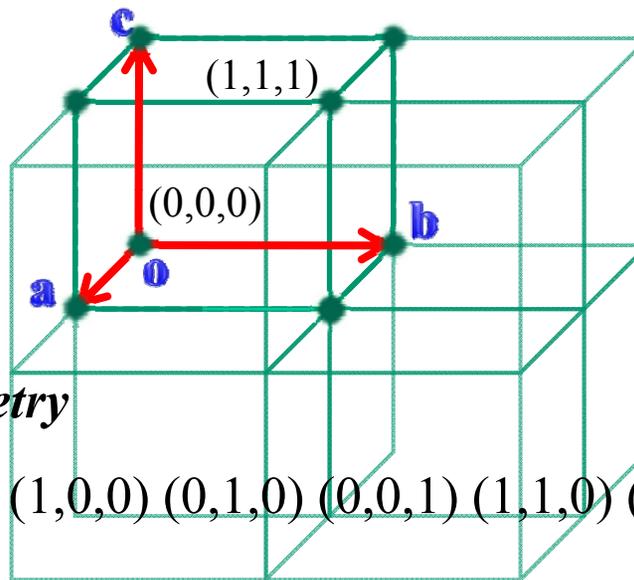
The molecules reside on general positions  $(x\ y\ z)$

# Equivalent Positions

Lattice points are related to each other by symmetry.

*Example* - A primitive cell contains only one lattice point.

$$\mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$



$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

$(x, y, z)$  General position

||

$(u+x, v+y, w+z)$

## *Translational symmetry*

Lattice points  $(0,0,0)$   $(1,0,0)$   $(0,1,0)$   $(0,0,1)$   $(1,1,0)$   $(1,0,1)$   $(0,1,1)$   $(1,1,1)$  are all equivalent.

Each of the vertices is shared by eight adjacent unit cells

## *Space group symmetry* ( 230 space groups)

*Symmetry and Space Group Tutorial,*

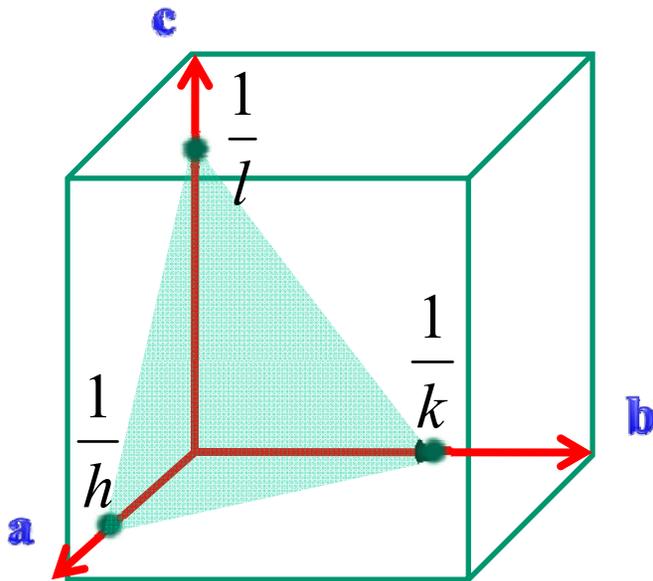
Jerry P. Jasinski and Bruce M. Foxman, Brandeis Univ. 2007

<http://people.brandeis.edu/~foxman1/teaching/indexpr.html>

# Crystallographic Planes and Miller Indices

Miller indices ( $hkl$ ), defined by *three lattice points*, are used to identify planes of atoms within a crystal structure.

The ( $hkl$ ) plane intercepts  $a/h$ ,  $b/k$ ,  $c/l$  on crystallographic axes  $X$ ,  $Y$ ,  $Z$ , where  $h$ ,  $k$ ,  $l$  are relatively prime integers.



Intercepts

$$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$$

Fractional intercepts

$$\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$$

Reciprocals of the fractional intercepts

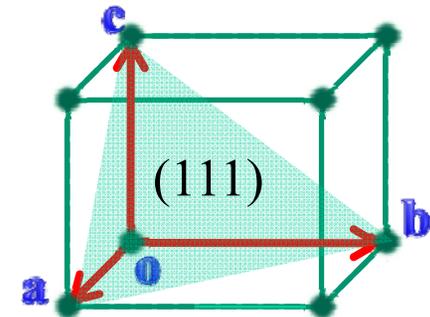
$$h, k, l$$

Miller Indices  
(*prime integers*)

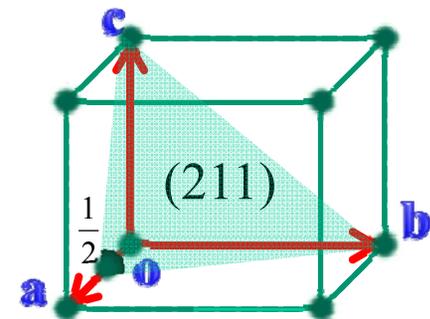
$$h, k, l$$

# Examples of Crystallographic Planes

1. A plane intersects the three crystallographic axes at  $(1\ 0\ 0)$ ,  $(0\ 1\ 0)$  and  $(0\ 0\ 1)$  has the miller indices  $(111)$
2. The plane intercepts the  $x$ -axis at  $a/2$ , the  $y$ -axis at  $b/1$  and the  $z$ -axis at  $c/1$ .



Fractional intercepts	$\frac{1}{2}, 1, 1$
Reciprocals of the fractional intercepts	$2, 1, 1$
Miller Indices ( <i>prime integers</i> )	$(211)$



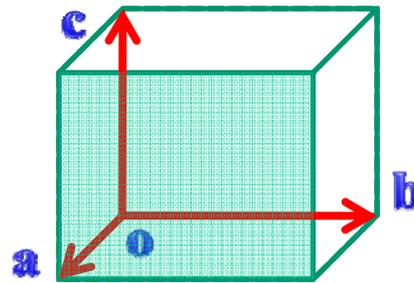
*Reciprocals of these intercepts are the corresponding miller indices*

# Examples of Crystallographic Planes

## 3. Lattice planes parallel to unit cell axes

$(hkl)$   
*a set of parallel planes*

$\{hkl\}$   
*a set of all symmetry-equivalent planes*



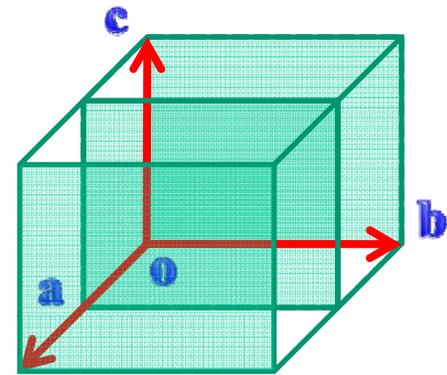
(100)

$1a, \infty b, \infty c$

$1, \infty, \infty$

$1, \frac{1}{\infty}, \frac{1}{\infty}$

(100)



(100)

$2a, \infty b, \infty c$

$2, \infty, \infty$

$\frac{1}{2}, \frac{1}{\infty}, \frac{1}{\infty}$

(100)

Intercepts :

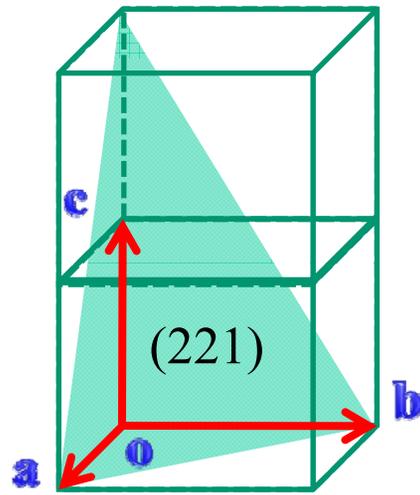
Fractional intercepts :

Reciprocals of the fractional intercepts

Miller Indices  
*(prime integers)*

# Examples of Crystallographic Planes

4.



Intercepts

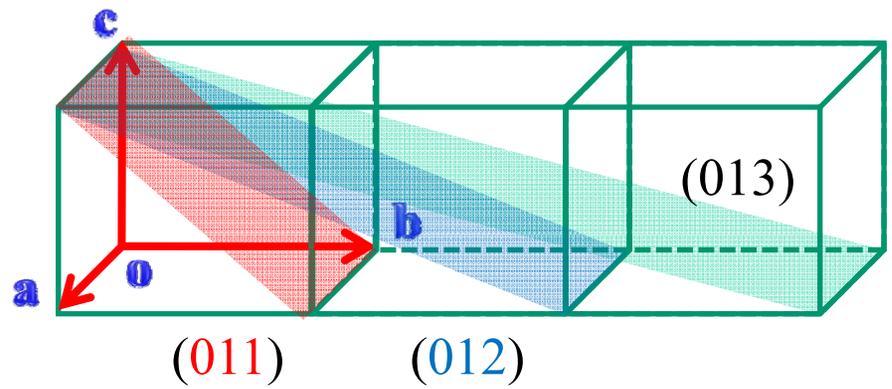
'Fractional' intercepts

Reciprocals of the fractional intercepts

Miller Indices  
(*prime integers*)

	A	B
Intercepts	$1a, 1b, 2c$	$\infty a, 3b, 1c$
'Fractional' intercepts	$1, 1, 2$	$0, 3, 1$
Reciprocals of the fractional intercepts	$1, 1, \frac{1}{2}$	$0, \frac{1}{3}, 1$
Miller Indices ( <i>prime integers</i> )	$(2\ 2\ 1)$	$(0\ 1\ 3)$

5.



(011) (012) (013)

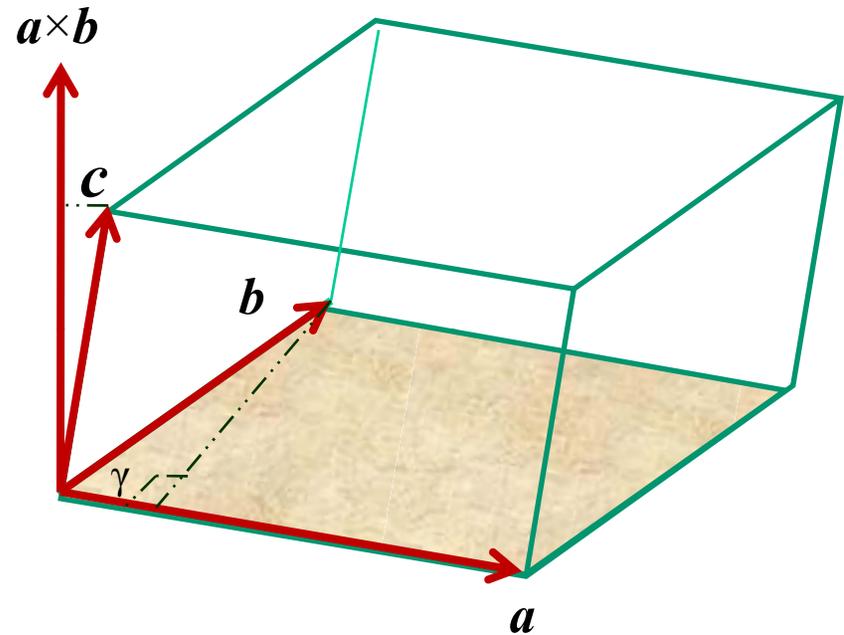
# Unit Cell Volume

The vector product of  $\mathbf{a}$  and  $\mathbf{b}$  is  $\perp$  to both  $\mathbf{a}$  and  $\mathbf{b}$ , and

$$|\mathbf{a} \times \mathbf{b}| = ab \sin \gamma$$

which equals the area of  $ab$  plane.

The scalar triple product of  $(\mathbf{a} \times \mathbf{b})$  and  $\mathbf{c}$  equals the area times height of the parallelepiped, *i.e.* the volume of the cell.



$$V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$$

$$V = (\mathbf{b} \times \mathbf{c}) \cdot \mathbf{a} = (\mathbf{c} \times \mathbf{a}) \cdot \mathbf{b} = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c} = \begin{vmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ba \cos \gamma & b^2 & bc \cos \alpha \\ ca \cos \beta & cb \cos \alpha & c^2 \end{vmatrix}^{\frac{1}{2}}$$

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}}$$

# The Reciprocal Lattice

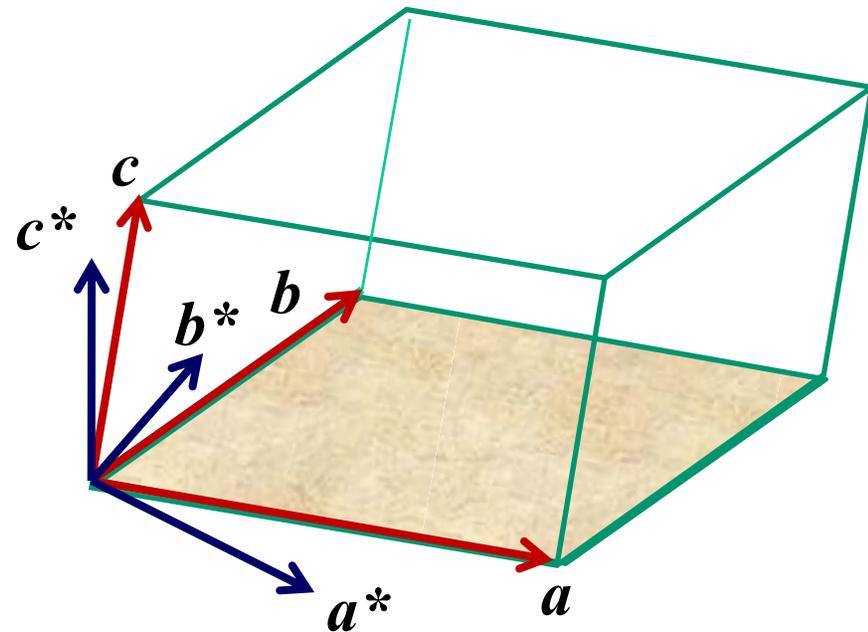
The translations of direct lattice by the two conditions:

$$\left\{ \begin{array}{l} \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = 0 \\ \mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \end{array} \right.$$

$$\mathbf{a}^* \perp (bc) \text{ plane}$$

$$\mathbf{b}^* \perp (ca) \text{ plane}$$

$$\mathbf{c}^* \perp (ab) \text{ plane}$$



# The Reciprocal Lattice – Unit Cell Parameters

Reciprocal lattice parameters  $a^*$   $b^*$  and  $c^*$ .

$\mathbf{a}^*$  is normal to the  $(bc)$  plane, let  $\mathbf{a}^* = p(\mathbf{b} \times \mathbf{c})$ , where  $p$  is a constant.

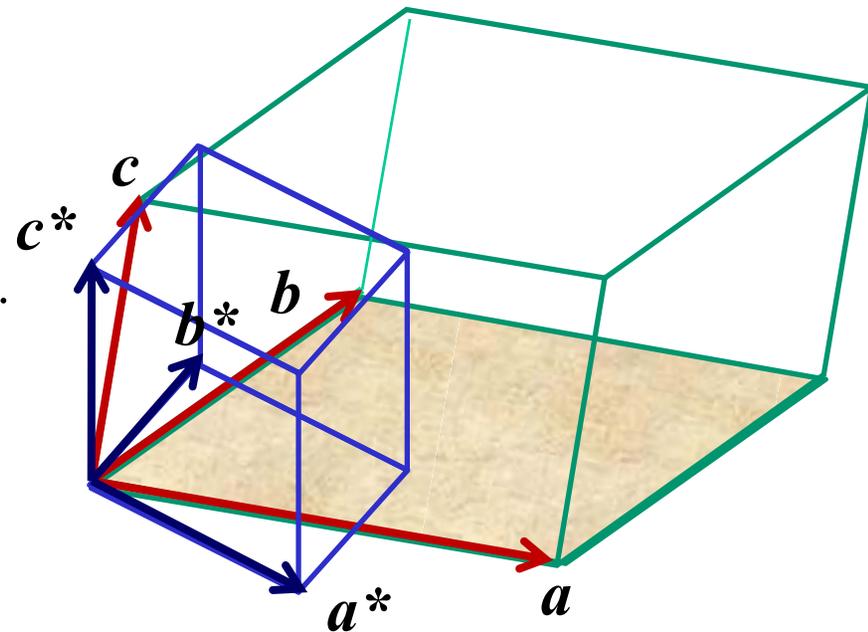
Multiply both sides by  $\mathbf{a}$ :

$$\mathbf{a}^* \cdot \mathbf{a} = p(\mathbf{b} \times \mathbf{c}) \cdot \mathbf{a} = pV,$$

where  $V$  is the volume of the unit cell.

$$1 = pV \quad \Rightarrow \quad p = 1/V$$

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}$$



Similarly,

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}$$

$$\mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V}$$

# Reciprocal Vector

## – Direction to $(hkl)$ Plane

Reciprocal vector  $\mathbf{r}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

### *Properties of reciprocal vector*

(a)  $\mathbf{r}^*$  is normal to the family of lattice planes  $(hkl)$ .

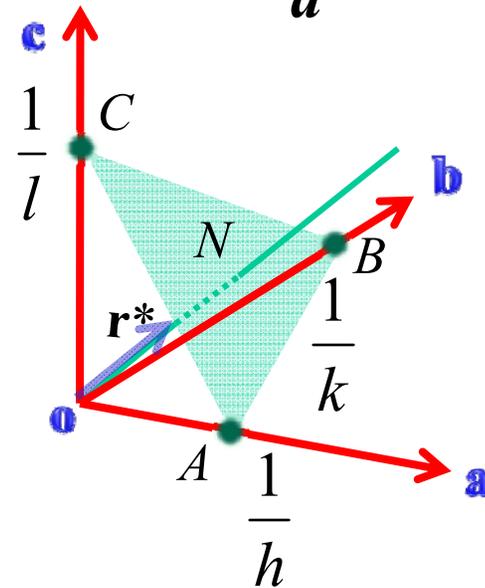
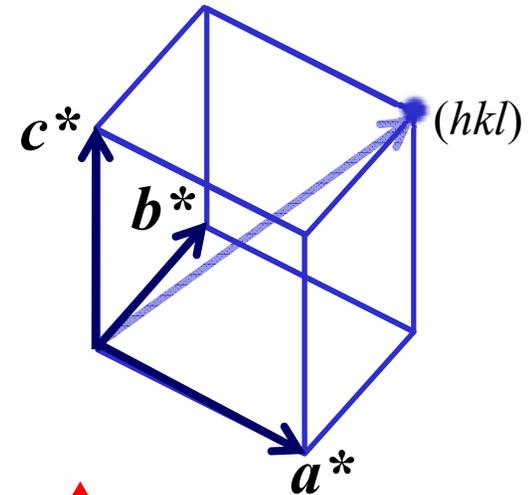
Vectors

$$\begin{aligned} AO &= \mathbf{a}/h & BA &= \mathbf{b}/k - \mathbf{a}/h \\ BO &= \mathbf{b}/k & CA &= \mathbf{c}/l - \mathbf{a}/h \\ CO &= \mathbf{c}/l & CB &= \mathbf{c}/l - \mathbf{b}/k \end{aligned}$$

$$\begin{aligned} \mathbf{r}^* \cdot BA &= (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (\mathbf{b}/k - \mathbf{a}/h) \\ &= -1 + 1 + 0 = 0 \end{aligned}$$

$$\mathbf{r}^* \cdot CA = \mathbf{r}^* \cdot CB = 0$$

Since  $\mathbf{r}^*$  is perpendicular to two lines in the  $(hkl)$  plane, it is normal to the plane.



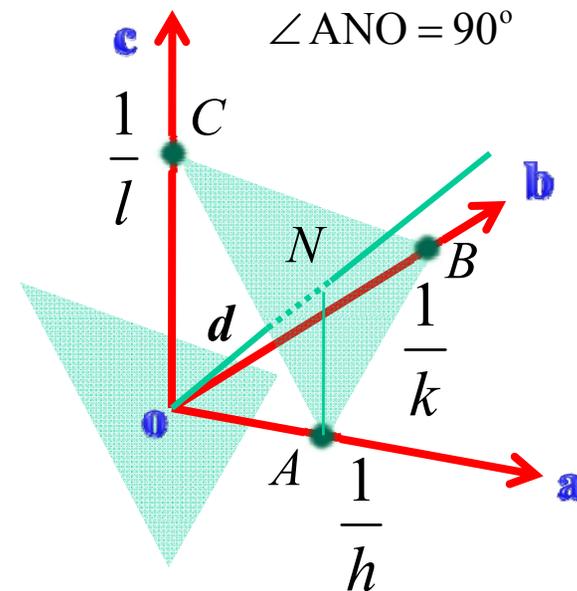
$$|\mathbf{r}^*| = ?$$

# Reciprocal Vector – Relation to $d$ -Spacing

$$(b) \quad r^* = \frac{1}{d}$$

The distance between two successive lattice planes in the  $(hkl)$  family equals the projection of the vector  $\mathbf{a}/h$  on the direction of the plane normal, which has the same direction as  $\mathbf{r}^*$ .

$$\begin{aligned} d &= \frac{\mathbf{a}}{h} \cdot \frac{\mathbf{r}^*}{r^*} \\ &= \frac{\mathbf{a}}{h} \cdot \frac{(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)}{r^*} \\ &= \frac{\cancel{\mathbf{a}}}{\cancel{h}} \cdot \frac{\cancel{h}\mathbf{a}^*}{r^*} + 0 + 0 \\ d &= \frac{1}{r^*} \quad \text{or} \quad r^* = \frac{1}{d} = d^* \end{aligned}$$



# Relation of Direct and Reciprocal Space Vectors

---

Vector presentation of a lattice position

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

where  $(x \ y \ z)$  are *fractional coordinates* in direct space

(c) *The product relation.* The scalar product of  $\mathbf{r}^* \cdot \mathbf{r} = hx + ky + lz$

$$\begin{aligned}\mathbf{r}^* \cdot \mathbf{r} &= (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) \\ &= (hx\mathbf{a}^* \cdot \mathbf{a} + 0 + 0) + (0 + ky\mathbf{b}^* \cdot \mathbf{b} + 0) + (0 + 0 + lz\mathbf{c}^* \cdot \mathbf{c}) \\ &= hx + ky + lz\end{aligned}$$

In structure factor calculation, the dot product  $\mathbf{r}^* \cdot \mathbf{r}$  can be replaced with  $\mathbf{h} \cdot \mathbf{x}$

$$\mathbf{h} \cdot \mathbf{x} = hx + ky + lz$$

# X-ray and Neutron Scattering

Diffraction arises from the interaction of matter with waves of X-rays and neutrons.

Consider the wave as a function of position  $x$  along its direction of propagation at time  $t$ . At any point on the  $x$ -axis:

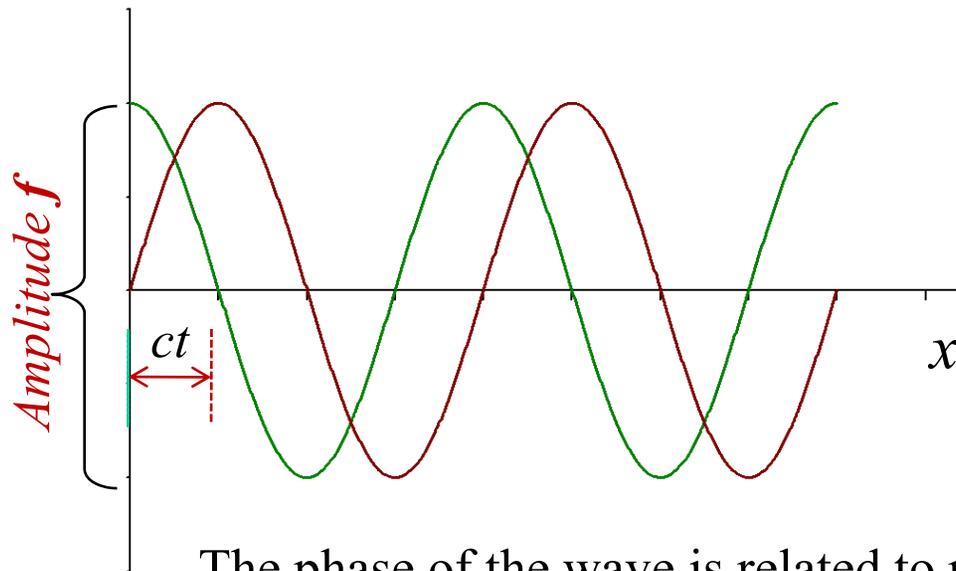
$$\mathbf{E}(t) = f \cos\left(\frac{2\pi}{\lambda}(x - ct)\right)$$

Where  $f$  is the amplitude,  $c$  is the velocity of the wave and  $\lambda$  is the wave length.

The frequency  $\nu = \frac{c}{\lambda}$

The phase of the wave is related to path length  $x$  by  $\phi = \frac{2\pi}{\lambda}x$ , and

$$\mathbf{E}(t) = f \cos(\phi - 2\pi\nu t)$$

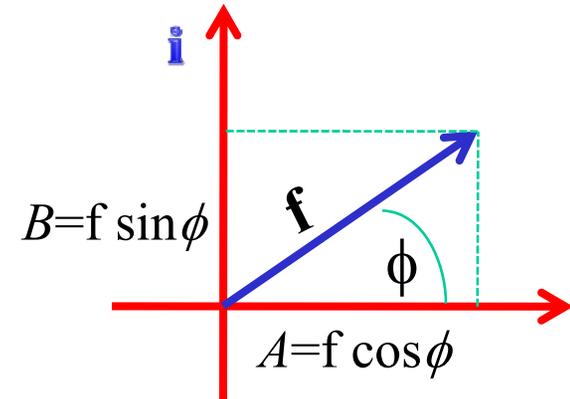


# Wave Vector in Complex Form

*Euler's theorem*

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

$$\begin{aligned} \mathbf{E}(t) &= f \cos(\phi - 2\pi\nu t) \\ &= \underbrace{f \cos \phi}_{\text{amplitude of cosine part}} \cos(-2\pi\nu t) + \underbrace{f \sin \phi}_{\text{amplitude of sine part}} \sin(-2\pi\nu t) \end{aligned}$$



This can also be written in complex form:

$$\mathbf{E}(t) = fe^{i(2\pi\nu t - \phi)} = \boxed{fe^{i\phi} \cdot e^{-i2\pi\nu t}}$$

$$fe^{i\phi} = f \cos \phi + if \sin \phi$$

$$fe^{i\phi} = A + iB$$

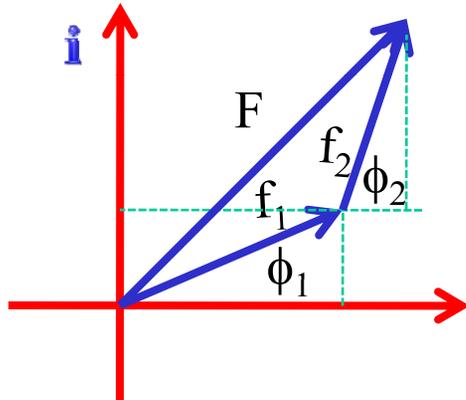
The quantity  $fe^{i\phi}$  involves both the amplitude and the phase angle,  $\phi$ , is known as the atomic form factor

$$\mathbf{f} = fe^{i\phi}$$

# Combination of Wave Vectors

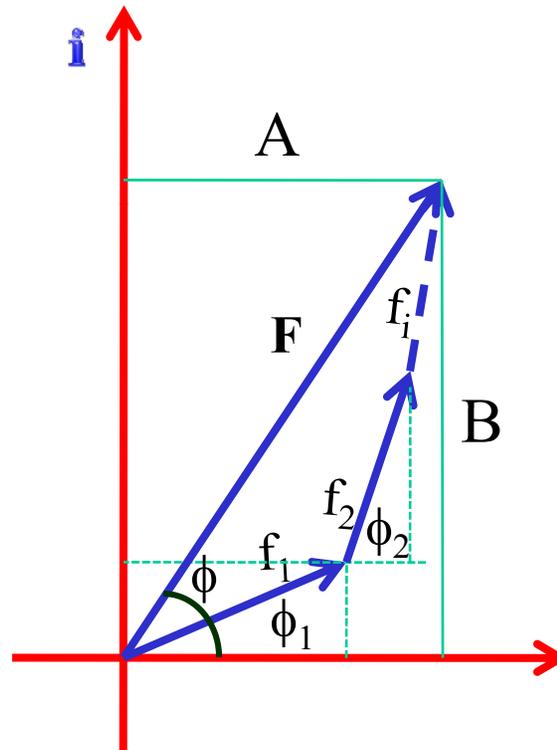
$$\mathbf{f}_1 = f_1 \cos \phi_1 + \mathbf{i} f_1 \sin \phi_1$$

$$\mathbf{f}_2 = f_2 \cos \phi_2 + \mathbf{i} f_2 \sin \phi_2$$



$$\mathbf{f}_1 = f_1 e^{i\phi_1} \quad \mathbf{f}_2 = f_2 e^{i\phi_2}$$

$$\mathbf{F} = f_1 e^{i\phi_1} + f_2 e^{i\phi_2}$$



$$\mathbf{F} = |F| e^{i\phi}$$

$$|F|^2 = (A^2 + B^2)$$

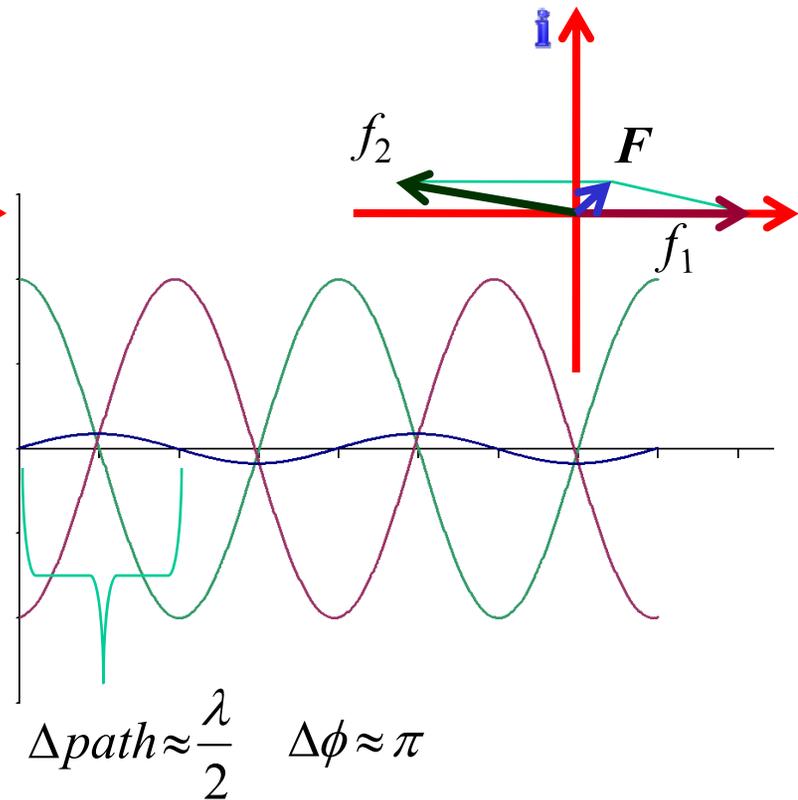
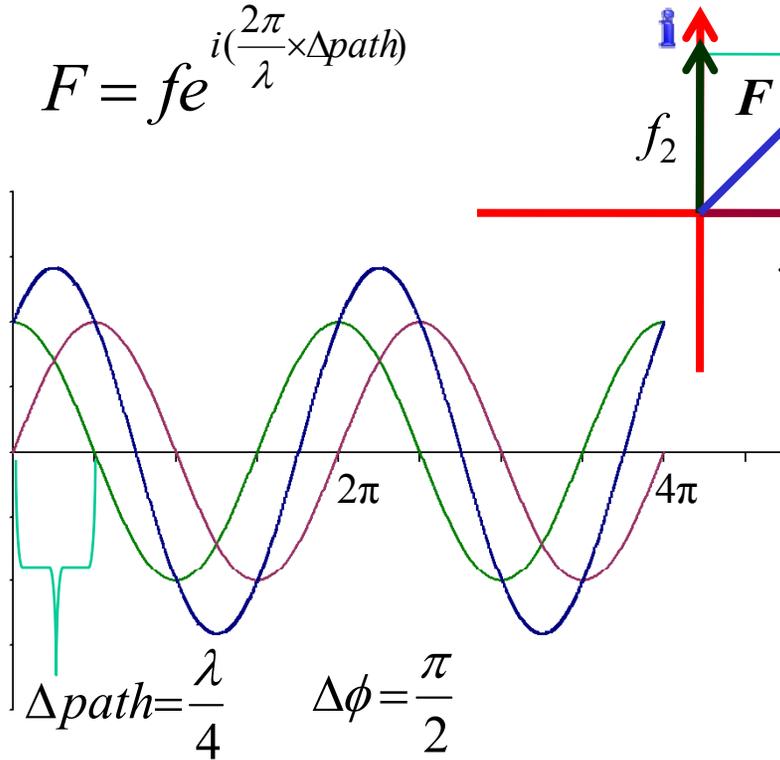
$$A = \sum_{j=1}^N f_j \cos \phi_j$$

$$B = \sum_{j=1}^N f_j \sin \phi_j$$

$$\tan \phi = \frac{B}{A}$$

# Interference of Two Plane Waves

$$F = fe^{i\left(\frac{2\pi}{\lambda} \times \Delta path\right)}$$



For maximum positive interference,

$$\Delta \phi = \frac{2\pi}{\lambda} \times \Delta path = 2\pi \times n \quad \longrightarrow \quad \Delta path = n\lambda$$

# The Bragg's Equation

*Reflection condition from a series of equally spaced planes*

The path difference between lattice planes  $(AO + OC) = n\lambda$

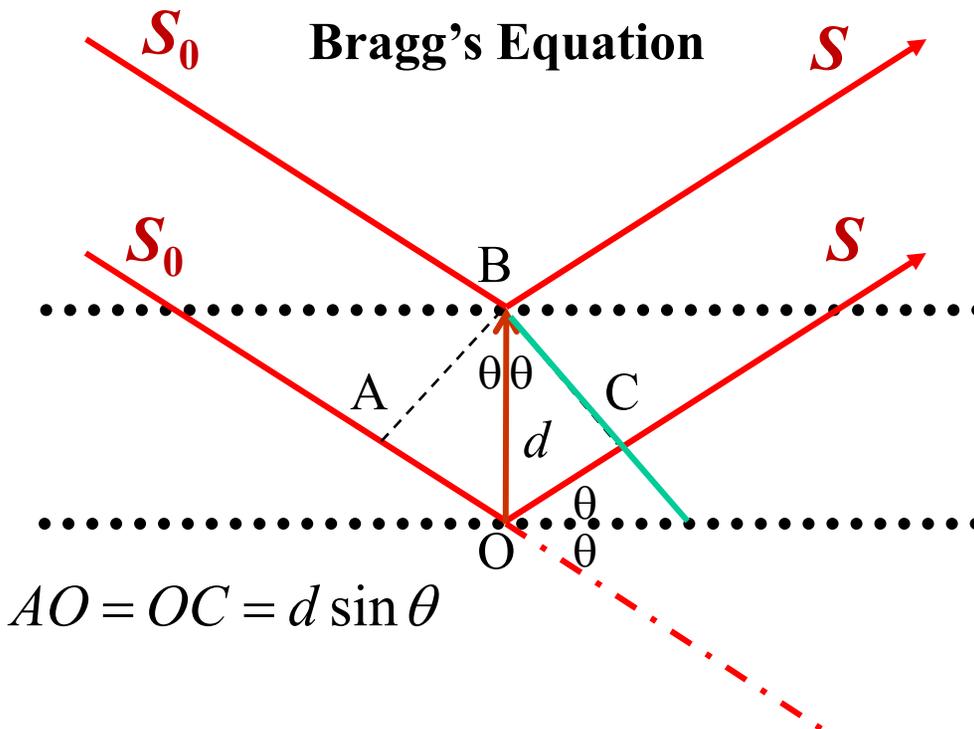
$$AO + OC = 2 OB \sin \theta = n\lambda$$

For family of  $(nh \ nk \ nl)$  planes,

$$d_{nhnknl} = \frac{d_{hkl}}{n}$$

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

$$2d_{hkl} \sin(\theta) = \lambda$$



Note: In practice we need only consider the  $n = 1$  values, since higher orders of  $n$  for the  $(hkl)$  planes correspond to  $(nh \ nk \ nl)$  planes with  $n = 1$ .

# Laue Conditions for Diffraction

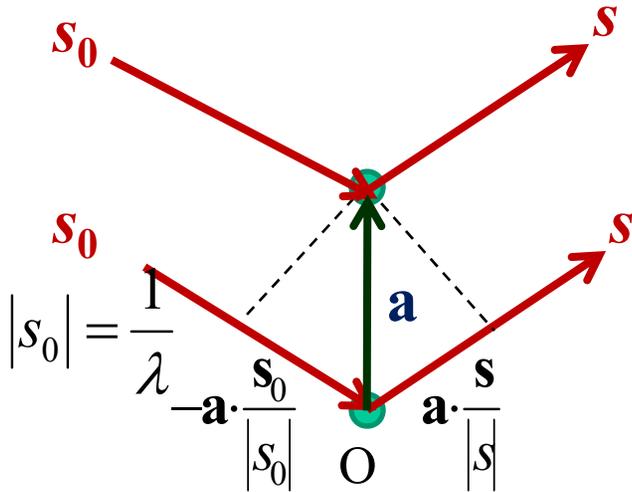
## Scattering condition from lattice points

For wave vectors  $\mathbf{s}_0$  and  $\mathbf{s}$  each with a magnitude of  $|\mathbf{s}_0| = |\mathbf{s}| = \frac{1}{\lambda}$

Path difference for the lattice points on  $\mathbf{a}$

$$-\mathbf{a} \cdot \frac{\mathbf{s}_0}{|\mathbf{s}_0|} + \mathbf{a} \cdot \frac{\mathbf{s}}{|\mathbf{s}|} = \lambda \mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) = h\lambda \quad \text{or}$$

$$\mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) = h$$



In three dimensions  $\Rightarrow$

$$\left. \begin{aligned} \mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) &= h \\ \mathbf{b} \cdot (\mathbf{s} - \mathbf{s}_0) &= k \\ \mathbf{c} \cdot (\mathbf{s} - \mathbf{s}_0) &= l \end{aligned} \right\} \text{Laue Equation}$$

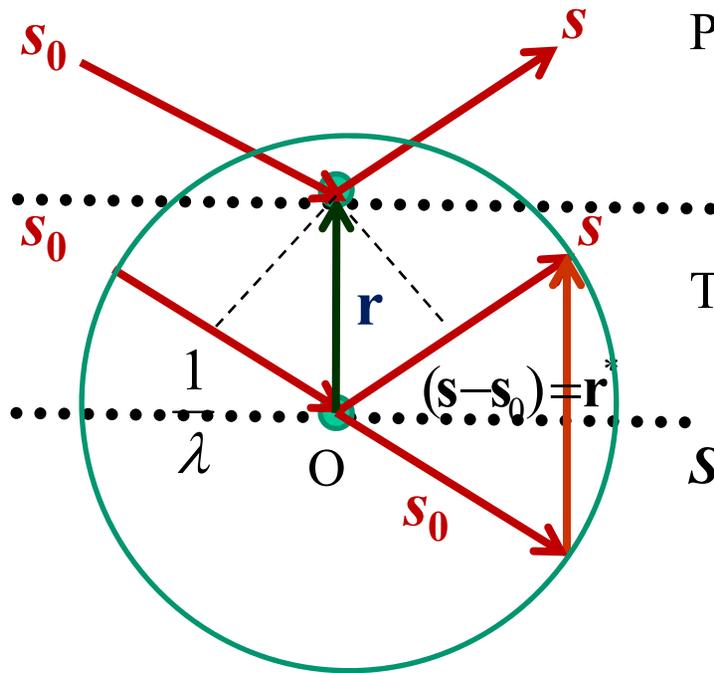
# Diffraction of an Atom – Scattering Factor

Apply the Laue condition to an atom with fractional coordinates  $(x,y,z)$ ,

$$\left. \begin{aligned} x \mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) &= xh \\ y \mathbf{b} \cdot (\mathbf{s} - \mathbf{s}_0) &= yk \\ z \mathbf{c} \cdot (\mathbf{s} - \mathbf{s}_0) &= yl \end{aligned} \right\}$$

$$\begin{aligned} (\mathbf{xa} + \mathbf{yb} + \mathbf{zc}) \cdot (\mathbf{s} - \mathbf{s}_0) &= (xh + yk + zl) \\ \parallel \\ \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0) &= (xh + yk + zl) \\ \therefore \mathbf{r} \cdot \mathbf{r}^* &= (xh + yk + zl) \end{aligned}$$

$$(\mathbf{s} - \mathbf{s}_0) = \mathbf{r}^*$$



Path difference of lattice point  $\mathbf{r}$  from origin

$$\mathbf{r} \cdot \left( \frac{\mathbf{s}}{|\mathbf{s}|} - \frac{\mathbf{s}_0}{|\mathbf{s}_0|} \right) = \lambda \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0) = \lambda \mathbf{r} \cdot \mathbf{r}^*$$

The phase of point  $\mathbf{r}$  :  $\phi = \frac{2\pi}{\lambda} \times \lambda \mathbf{r} \cdot \mathbf{r}^* = 2\pi \mathbf{r} \cdot \mathbf{r}^*$   
 $= 2\pi(hx + ky + lz)$

**Scattering Factor**

$$f(hkl) = f e^{i\phi} = f e^{2\pi i(hx + ky + lz)}$$

# Ewald Sphere

Geometrical description of the conditions for diffraction.

The path difference between the scattering waves from two lattice points B and O can be related by a sphere of radius  $1/\lambda$

$$|\mathbf{r}^*| = |\mathbf{s} - \mathbf{s}_0| = \frac{2}{\lambda} \sin \theta$$

Conditions for diffraction [Bragg's equation]:

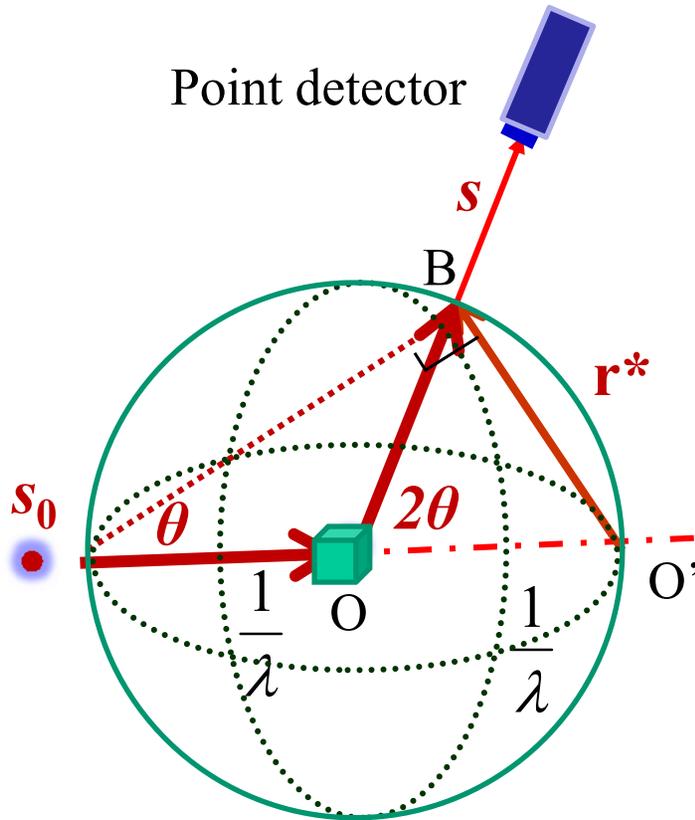
$$2d_{hkl} \sin \theta = \lambda$$

The modulus of  $\mathbf{r}^*$

$$|\mathbf{r}^*| = \frac{1}{d_{hkl}} = \frac{2}{\lambda} \sin \theta$$

Minimum  $d$  space or highest resolution =  $\lambda/2$

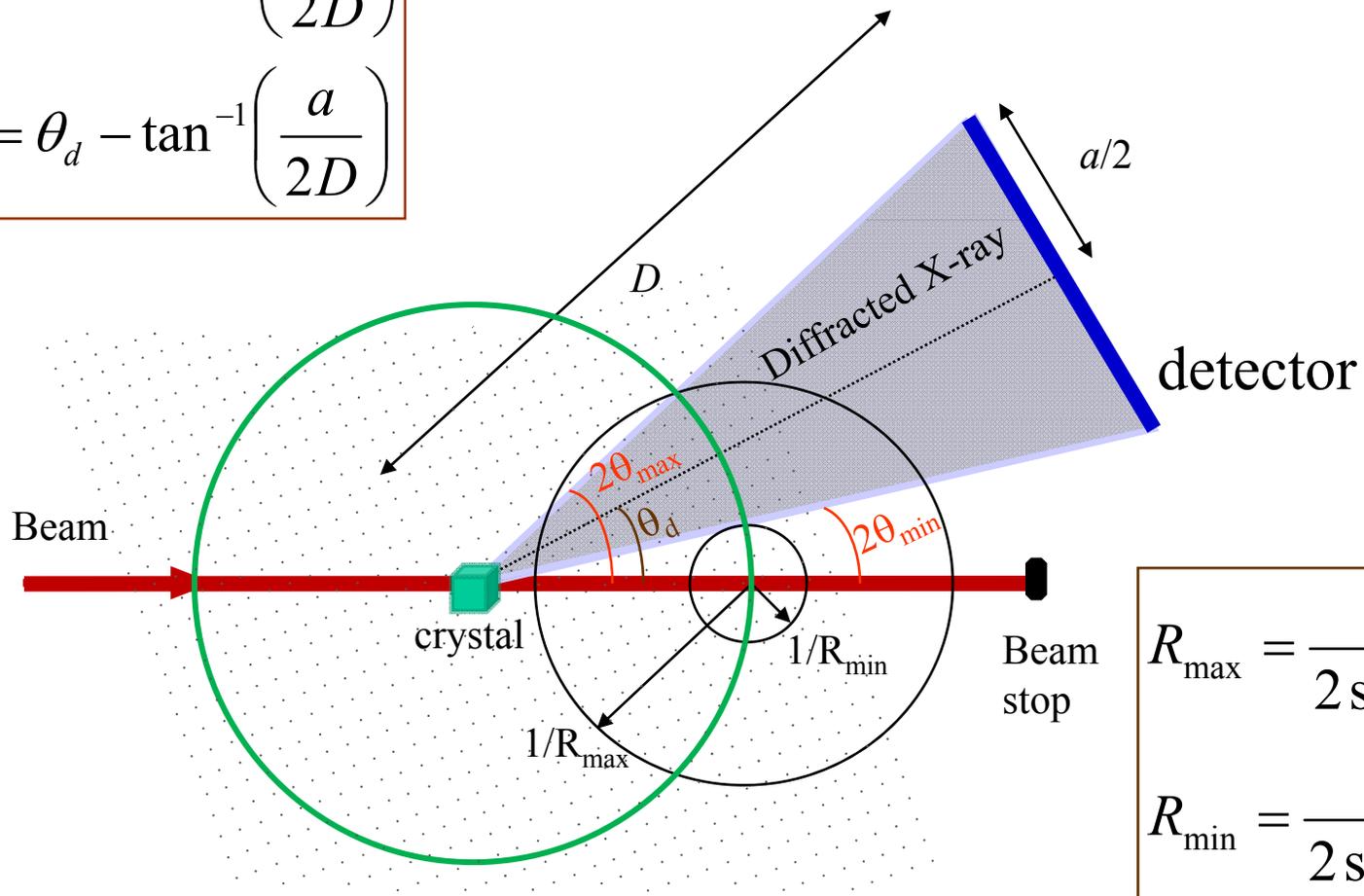
Ewald sphere is also called the *limiting sphere*.



# Data Collection with an Area Detector

$$2\theta_{\max} = \theta_d + \tan^{-1}\left(\frac{a}{2D}\right)$$

$$2\theta_{\min} = \theta_d - \tan^{-1}\left(\frac{a}{2D}\right)$$



$$R_{\max} = \frac{\lambda}{2 \sin \theta_{\max}}$$

$$R_{\min} = \frac{\lambda}{2 \sin \theta_{\min}}$$

$R_{\max}$  Resolution at maximum  $2\theta$

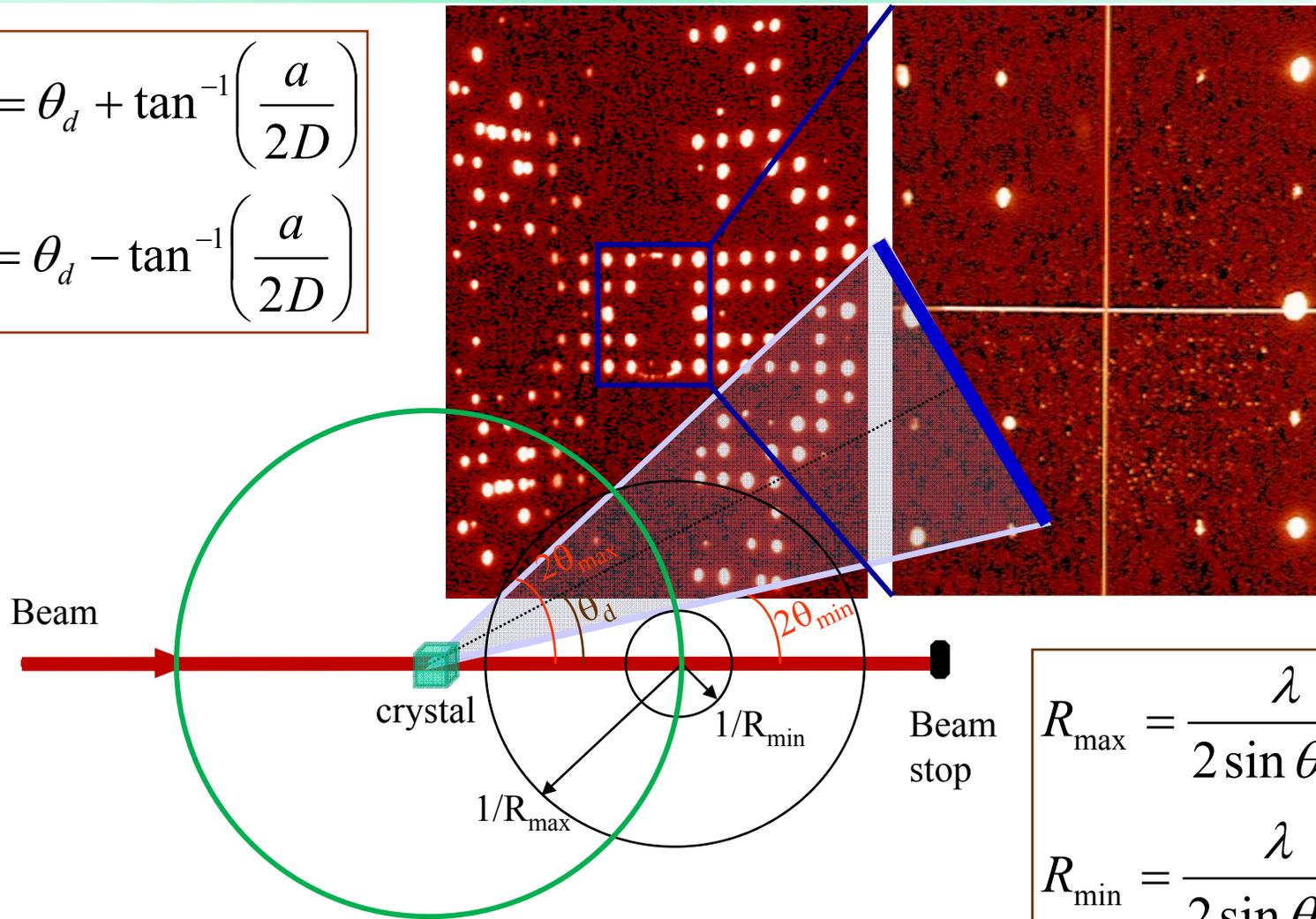
# Detector Coverage

$D = 60 \text{ mm}$

$D = 210 \text{ mm}$

$$2\theta_{\max} = \theta_d + \tan^{-1}\left(\frac{a}{2D}\right)$$

$$2\theta_{\min} = \theta_d - \tan^{-1}\left(\frac{a}{2D}\right)$$



$$R_{\max} = \frac{\lambda}{2 \sin \theta_{\max}}$$

$$R_{\min} = \frac{\lambda}{2 \sin \theta_{\min}}$$

$R_{\max}$  Resolution at maximum  $2\theta$

# Resolution

---

The minimum plane spacing ( $d$ ) given by Bragg's law for a particular set of diffraction intensities.

*Higher* resolution means

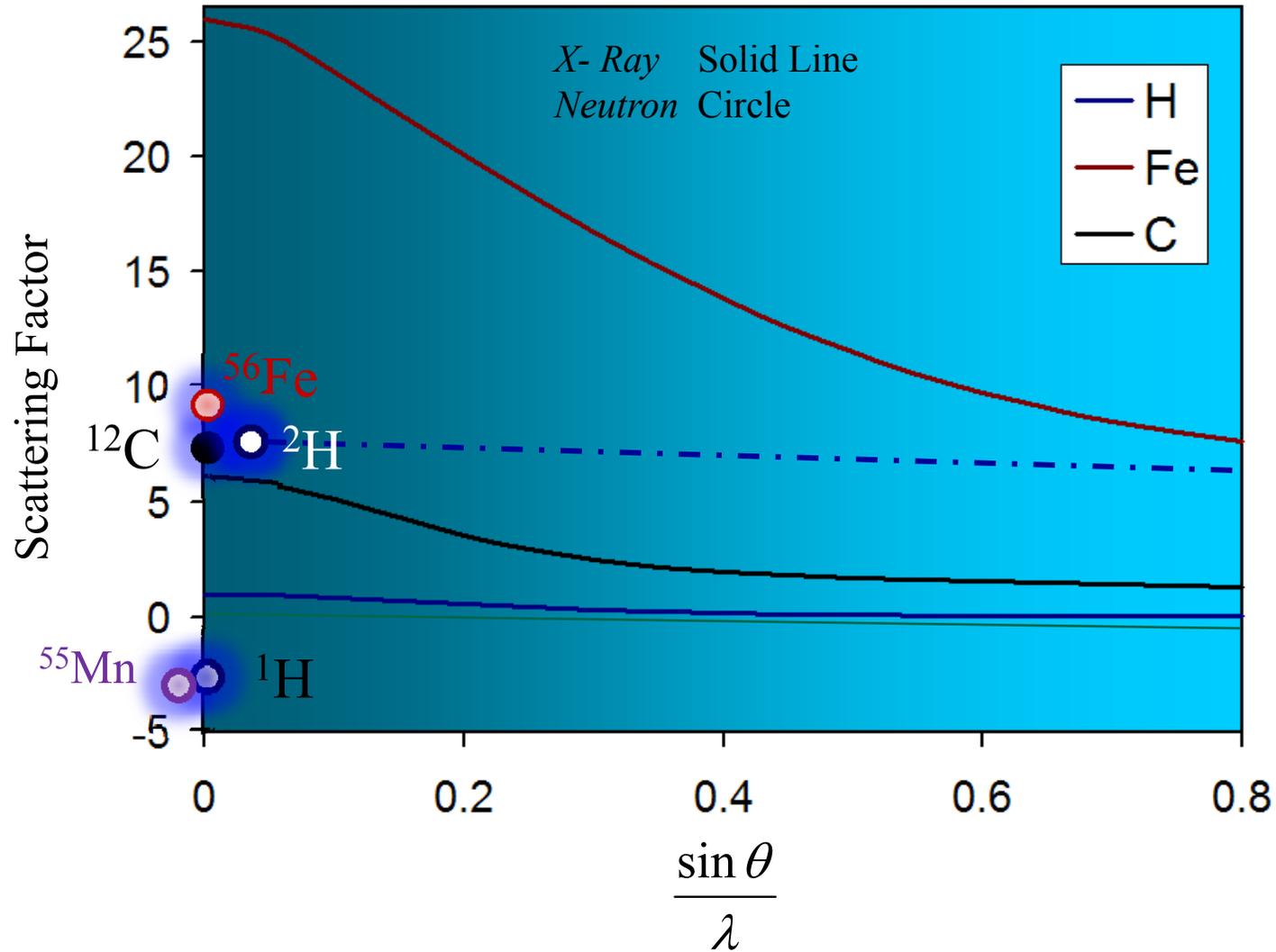
- *smaller*  $d$ -spacing
- *better* the ability to resolving neighbouring features in an electron density map.

*Example:* Resolution for a crystal that diffracts to maximum  $2\theta = 50^\circ$  from Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ )

$$R_{\max} = \frac{\lambda}{2 \sin \theta_{\max}} = \frac{0.7107 \text{ \AA}}{2 \times \sin 25^\circ} = 0.84 \text{ \AA}$$

The resolution improves with an increase in the maximum value of  $\sin\theta/\lambda$  ( $\text{\AA}^{-1}$ ).

# X-Ray and Neutron Scattering Amplitude



# Micro-Crystal and Charge Density Setups at APS

## ChemMatCARS-15ID-B

APEXII detector  $2\theta$  range  
~ 25 to -110 deg

- Readout (8x8 binning) ~ 1 s  
(uncorrelated)

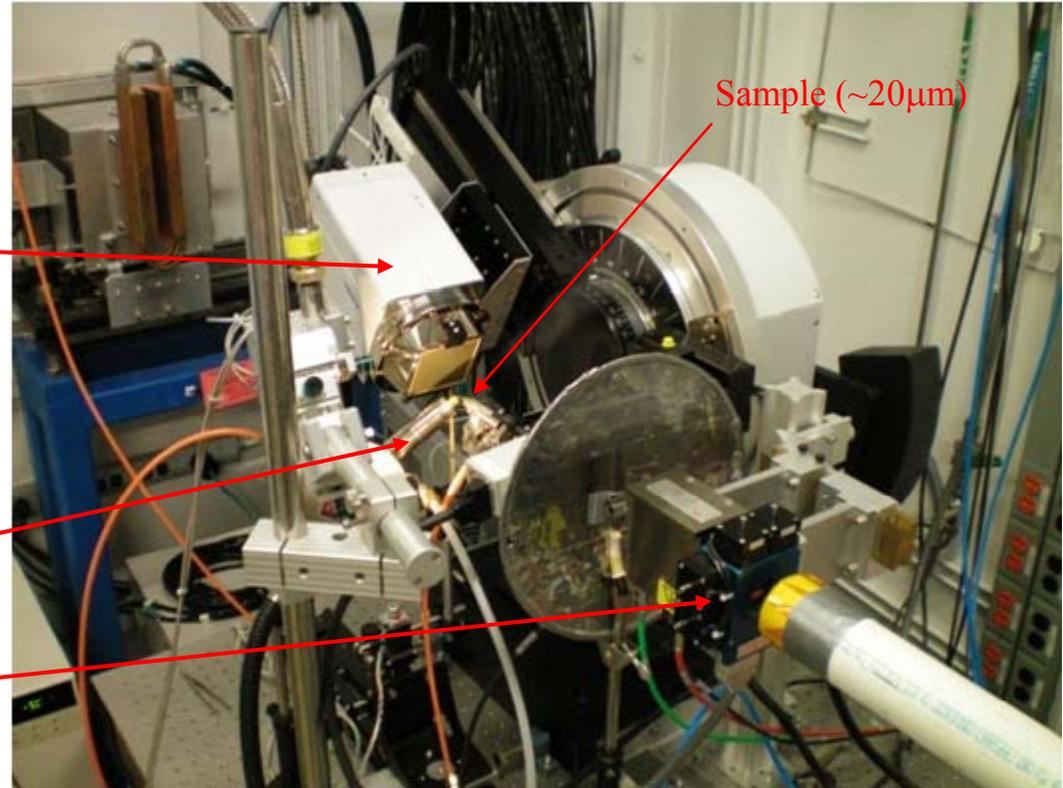
- Readout (4x4 binning) ~ 1.5 s  
(uncorrelated)

LHe cryostat  $T = 15-70$  K

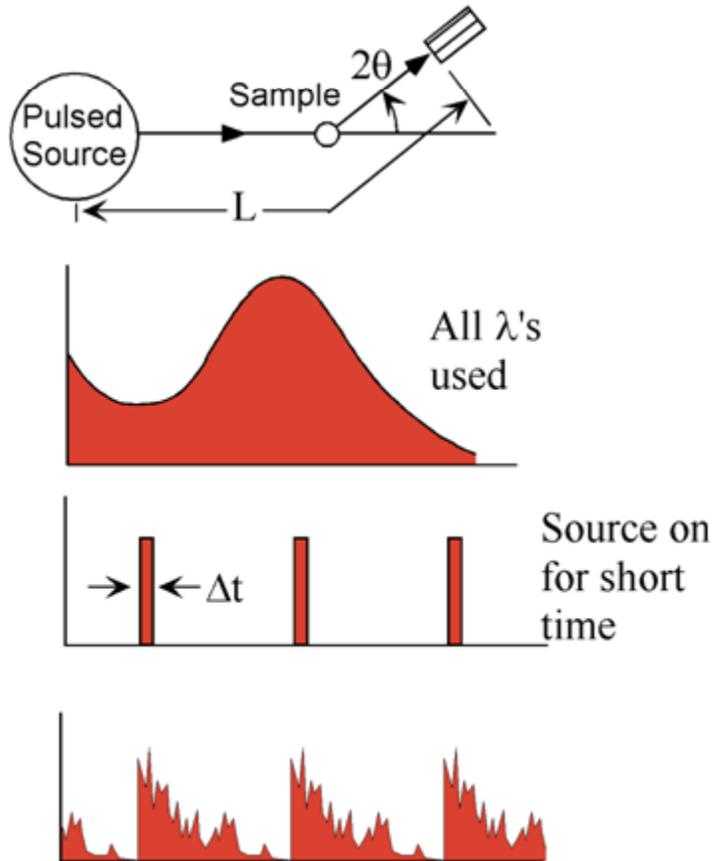
Beam size 80 to 500  $\mu\text{m}$

Energy range ~6 to 32 KeV

Highest spatial resolution  $2.1 \text{ \AA}^{-1}$  (0.24  $\text{\AA}$ )



# TOF Neutron Scattering



$$\lambda = \frac{h}{mv} = \frac{h}{m} \cdot \frac{t}{L}$$

where  $h$  is the Planck constant,  $m$  and  $v$  are the mass and velocity of neutron,  $L$  is the neutron flight path length and  $t$  is the time of flight.

Thermal neutrons ( $\lambda = 1.8 \text{ \AA}$ ) travel at the speed of  $2200 \text{ m/s}$ .

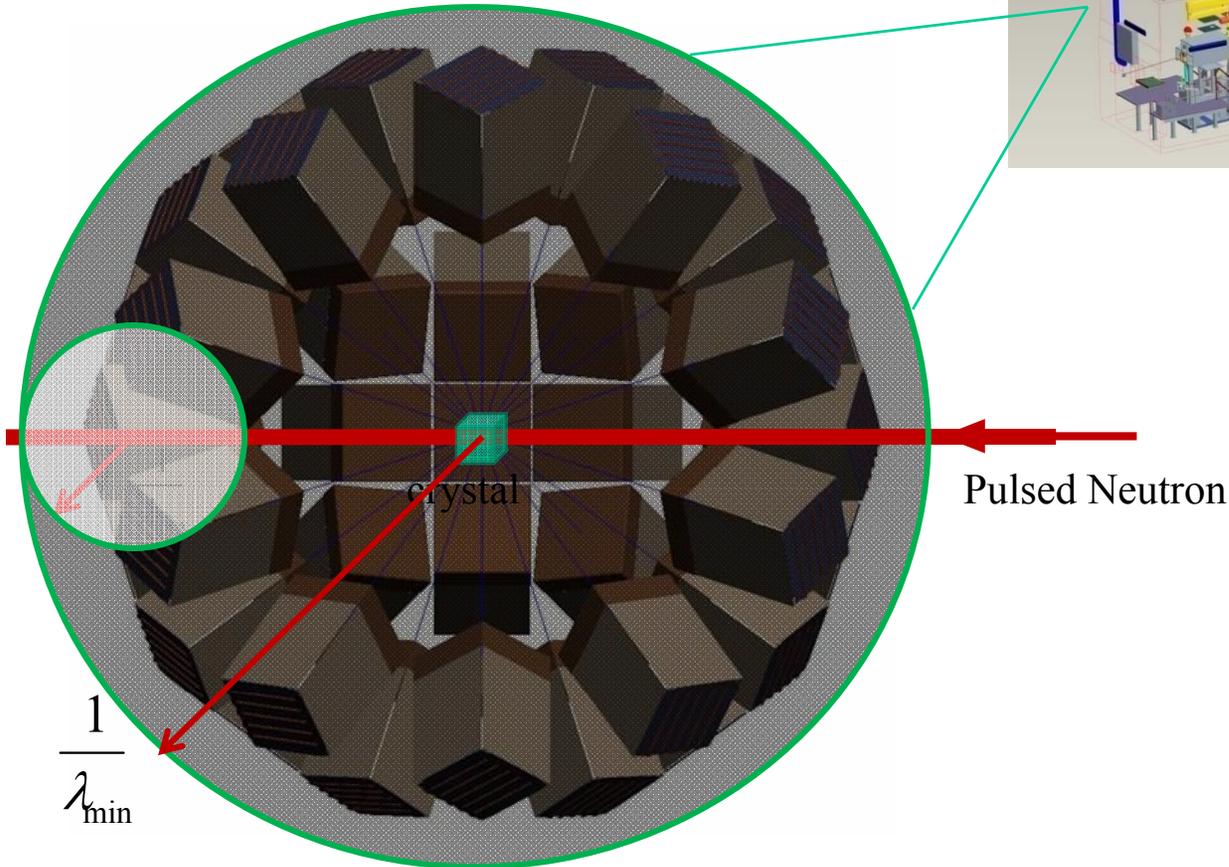
SNS electronics can determine both the *time* and position of each of the pulsed *neutron* from diffraction at the detector position.

# TOPAZ Single Crystal Diffractometer at SNS

Neutron time of flight Laue technique

3-D Reciprocal space mapping ( $x, y, \lambda$ )

Optimized for high throughput on samples with unit cell sizes  $\sim 50 \text{ \AA}$



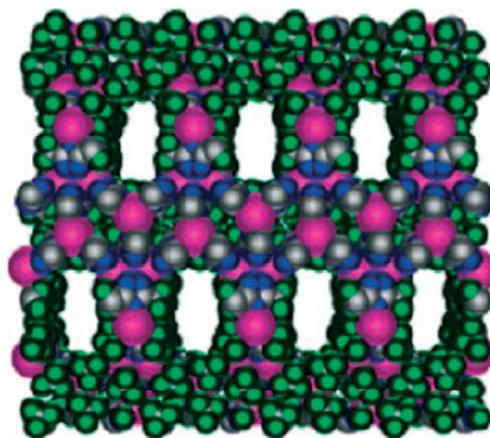
Detector pixel size	$6.2 \times 10^{-6} \text{ sr}$ (1 mm)
Detector angles	0–180°
Wavelength bandwidth	3.35 Å
Frame 1	0.5–3.85 Å
Resolution	0.1%
Sample size	$0.001 \text{ mm}^3 < S < 1 \text{ mm}^3$

## Highlights

### Metal–Organic Frameworks

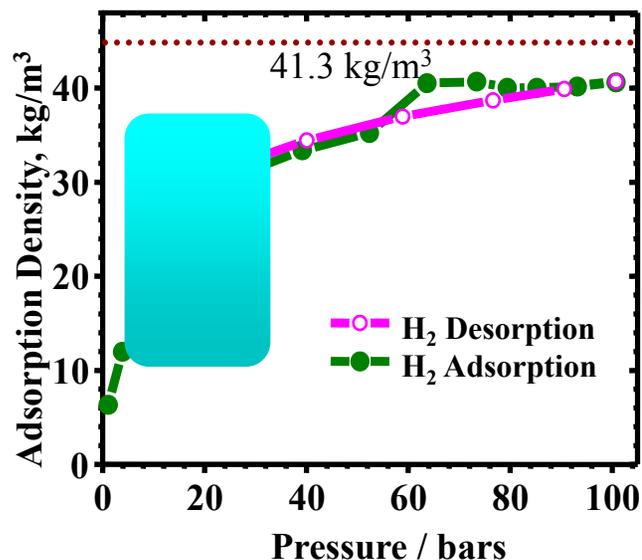
R. A. Fischer,\* C. Wöll\* — ■■■■—■■■■

Functionalized Coordination Space in  
Metal Organic Frameworks



● Ag ● C ● N ● F

Two significant advances in the development of metal–organic frameworks (MOFs) are perfluoro MOFs (see structure) with an outstanding volumetric gas uptake and hysteretic sorption of dihydrogen, and the modular synthesis of functional MOFs using a two-component framework, in which one component is an integral component of the framework and the other can be exchanged after formation of the matrix.



*J. Am. Chem. Soc.*, **129** (50), 15454–15455, 2007. 10.1021/ja0775265 S0002-7863(07)07526-9

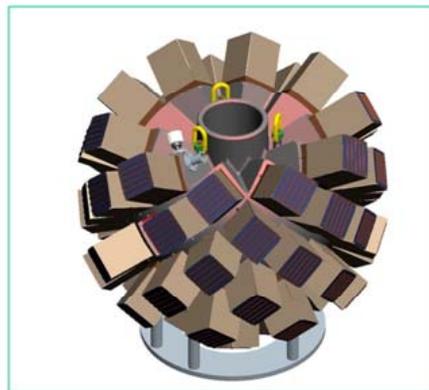
Web Release Date: November 23, 2007

Copyright © 2007 American Chemical Society

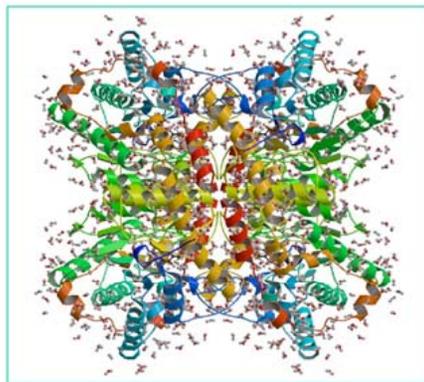
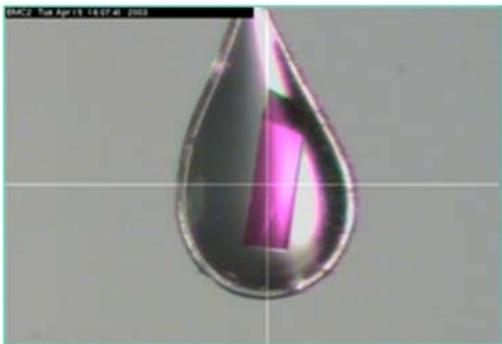
### Fluorous Metal–Organic Frameworks for High-Density Gas Adsorption

Chi Yang, Xiaoping Wang, and Mohammad A. Omary\*

# Macromolecular Neutron Diffractometer (MaNDi)



- Large solid angle detector coverage
- Reduced crystal size requirement  $\sim 0.1 \text{ mm}^3$  and below
- Reduced data collection time (1 day to 1 Week)
- Increased resolution  $1.5\text{-}2.0 \text{ \AA} (D_{\min})$
- Larger unit cell repeats  $50\text{-}300 \text{ \AA}$



**Chemistry, Structural  
Biology and Enzymology**

(Online 2012)

## Structure Factor $F(hkl)$

---

For a lattice point with coordinate  $(x_j, y_j, z_j)$ , the phase difference relative to the origin is

$$\begin{aligned}\phi_j &= 2\pi \mathbf{r}^* \cdot \mathbf{r}_j = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}) \\ &= 2\pi(hx_j + ky_j + lz_j)\end{aligned}$$

$$f_j(hkl) = f_j e^{i\phi_j} = f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

The **atomic structure factor**  $f_j(hkl)$  represents the wave resulted from diffraction of atom  $j$ .

For  $N$  atoms in the unit cell

$$F(hkl) = \sum_j^N f_j(hkl) = \sum_j^N f_j e^{i\phi_j} = \sum_j^N f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

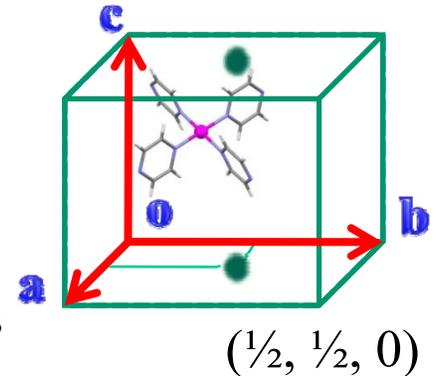
# The Effect of Lattice Centering on $F(hkl)$

*Example* C-face centered lattice

For each point  $(x,y,z)$  there must be another at  $(\frac{1}{2}+x, \frac{1}{2}+y, z)$ .

$$F(hkl) = \sum_j^{N/2} f_j \left[ \exp\{2\pi i(hx_j + ky_j + lz_j)\} + \exp\{2\pi i(hx_j + ky_j + lz_j + \frac{1}{2}h + \frac{1}{2}k)\} \right]$$

$$= \sum_j^{N/2} f_j \left[ \exp\{2\pi i(hx_j + ky_j + lz_j)\} \left( 1 + \exp\left\{2\pi i \frac{h+k}{2}\right\} \right) \right]$$



The last factor  $\left( 1 + \exp\left\{2\pi i \frac{h+k}{2}\right\} \right)$  can only have two values

**Reflection Conditions**

$$= 2 \quad \text{for } h + k = 2n \quad F(hkl) = \sum_j^{N/2} 2f_j \left[ \exp\{2\pi i(hx_j + ky_j + lz_j)\} \right]$$

$$= 0 \quad \text{for } h + k = 2n + 1 \quad F(hkl) = 0 \quad \text{Systematic absences}$$

The systematic absences allow lattice centering glide planes and screws axes to be detected.

# Reflection Conditions for Centered Lattices

Reflection Condition	Centering Type	Symbol
None	Primitive	$P$
$h + k = 2n$	<i>C-face centered</i>	$C$
$k + l = 2n$	<i>A-face centered</i>	$A$
$h + k + l = 2n$	<i>B-face centered</i>	$B$
$h + k + l = 2n$	<i>Body centered</i>	$I$
$h + k, h + l$ and $k + l = 2n$ or: $h, k, l$ all odd or all even (‘unmixed’)	All-face centered	$F$

# Diffraction Intensity

Intensity data

$$I_{observed}(hkl) \propto F(hkl) \cdot F(hkl)^* \\ = |F(hkl)| e^{i\phi} \cdot |F(hkl)| e^{-i\phi} = |F(hkl)|^2$$

$$I_{observed}(hkl) = KC(hkl) |F_0(hkl)|^2$$

where  $K$  is a scale factor,  $C(hkl)$  are corrections: Lorentz, polarization(X-ray), and absorption corrections.

*In practice*, the observed intensity data are processed and corrected for  $C(hkl)$  and then exported to programs for structure solution and refinement.

$$I_o(hkl) = K \sum f_i^2 \exp\left(-2B \frac{\sin^2 \theta}{\lambda^2}\right)$$

Correction for thermal motion.  $B$  is the atomic displacement parameter.

$$B = 8\pi^2 U (\text{\AA}^2)$$

$U$  is the square mean shift of the atom from equilibrium position.

The phase is **not** an observable quantity  
Information on phase  $\phi$  is lost.

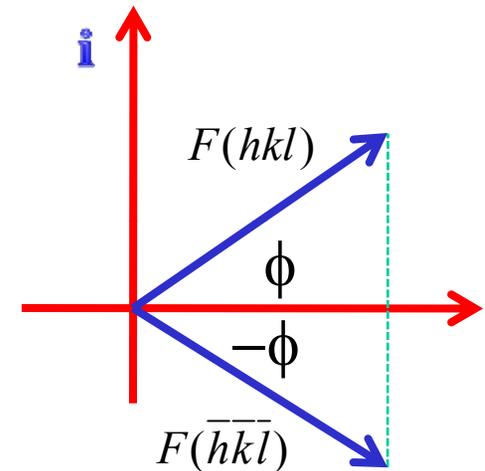
# Friedel's Law

$$F(hkl) = \sum_i f_i \{ \cos[2\pi(hx_i + ky_i + lz_i)] + i \sin[2\pi(hx_i + ky_i + lz_i)] \}$$

$$\begin{aligned} F(\bar{h}\bar{k}\bar{l}) &= \sum_i f_i \{ \cos[-2\pi(hx_i + ky_i + lz_i)] + i \sin[-2\pi(hx_i + ky_i + lz_i)] \} \\ &= \sum_i f_i \{ \cos[2\pi(hx_i + ky_i + lz_i)] - i \sin[2\pi(hx_i + ky_i + lz_i)] \} \end{aligned}$$



$$I \propto |F(hkl)|^2 = F(hkl)F^*(hkl) = |F(\bar{h}\bar{k}\bar{l})|^2$$



The diffraction by itself introduce a(n) (*apparent*) center of symmetry.

$$|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})| \quad \phi(hkl) = -\phi(\bar{h}\bar{k}\bar{l})$$

# Anomalous Scattering

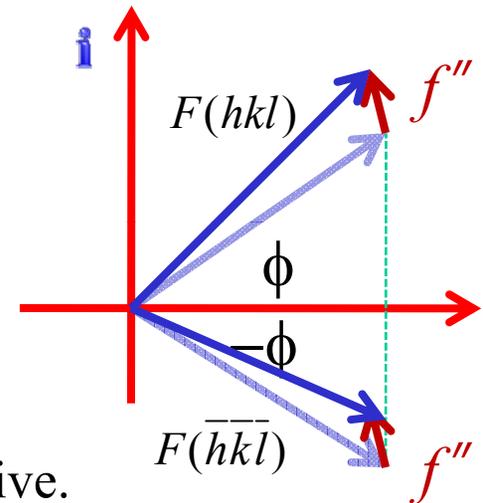
Anomalous scattering resulted from absorption and re-emission of X-rays.

The form factor of an anomalously scattering atom is wavelength dependent

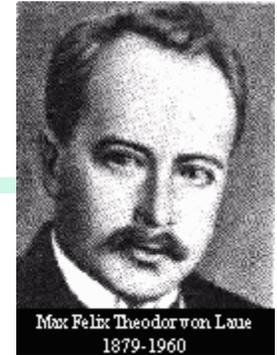
$$F(\lambda) = f^0 + f'(\lambda) + if''(\lambda)$$

Friedel's Law is broken whenever there is anomalous scattering because the imaginary term  $f''$  is always positive.

$$|F(hkl)| \neq |F(\bar{h}\bar{k}\bar{l})|$$



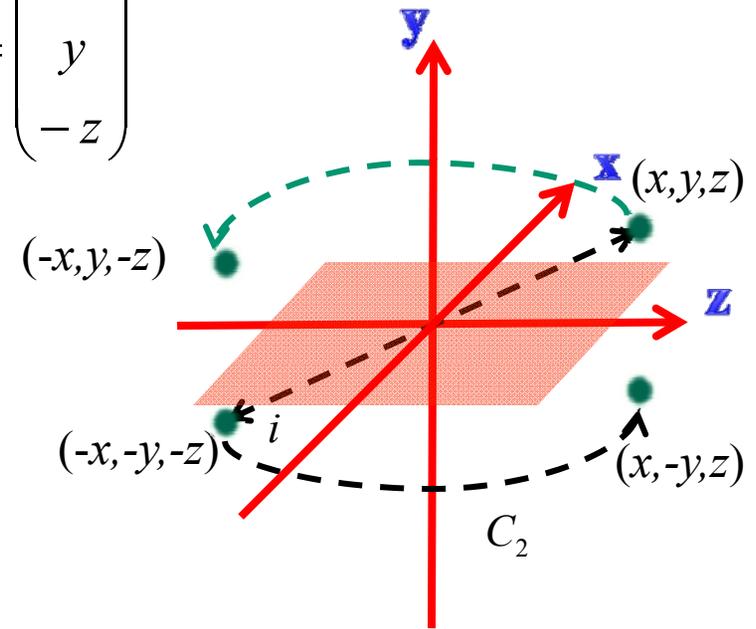
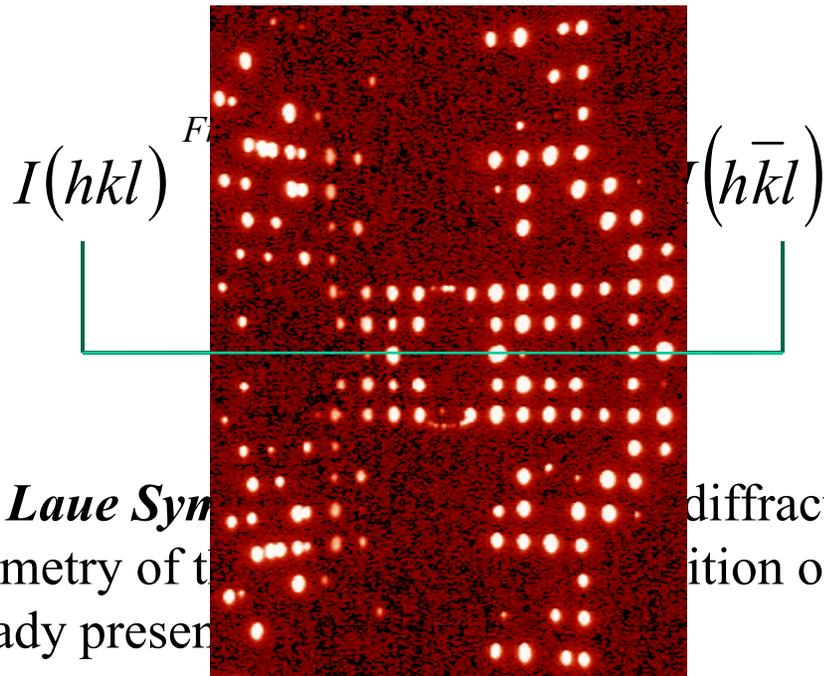
# Laue Symmetry



Describe the relationships between symmetry equivalent reflections.

Monoclinic  
Space Group  $P2$

$$C_2 \rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ -z \end{pmatrix}$$



The *Laue Symmetry* of the diffraction pattern is the point-group symmetry of the crystal (if not already present).

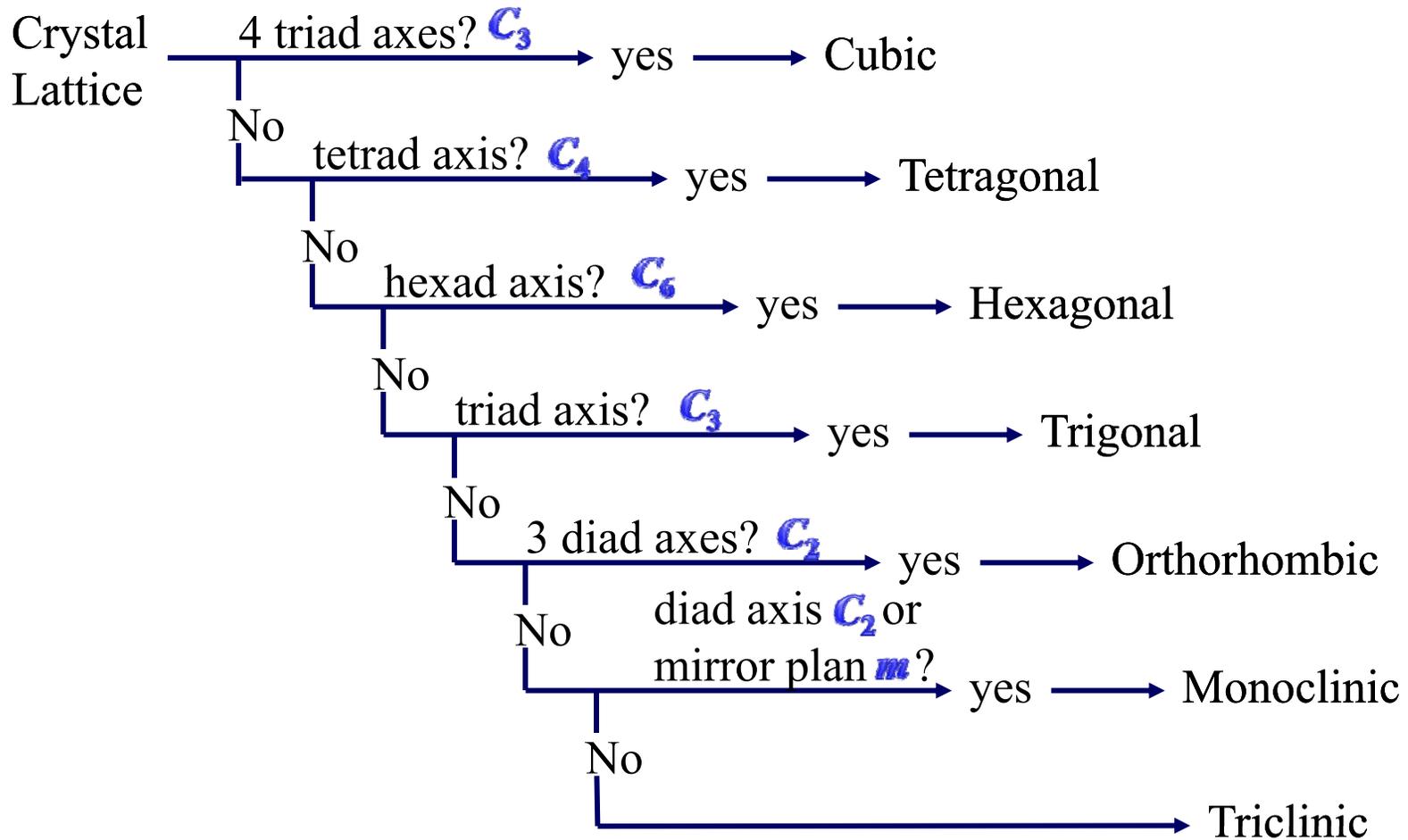
The Laue symmetry of the diffraction pattern is the point-group symmetry of the crystal (if not already present).

# Point Groups and Laue Classes

Crystal Systems	Point Groups		Laue Classes	Lattice Point Groups
	Non-centrosymmetric	Centrosymmetric		
Triclinic	1		$\bar{1}$	$\bar{1}$
Monoclinic	2	<i>m</i>	2/ <i>m</i>	2/ <i>m</i>
Orthorhombic	222	<i>mm</i> 2	<i>mmm</i>	<i>mmm</i>
Tetragonal	4	$\bar{4}$	4/ <i>m</i>	4/ <i>m</i>
	422	4 <i>mm</i> , $\bar{4}$ 2 <i>m</i>	4/ <i>mmm</i>	4/ <i>mmm</i>
Trigonal	3		$\bar{3}$	$\bar{3}$ <i>m</i>
	32	3 <i>m</i>	$\bar{3}$ <i>m</i>	$\bar{3}$ <i>m</i>
Hexagonal	6	$\bar{6}$	6/ <i>m</i>	6/ <i>mmm</i>
	622	6 <i>mm</i> , $\bar{6}$ 2 <i>m</i>	6/ <i>mmm</i>	6/ <i>mmm</i>
Cubic	23		<i>m</i> $\bar{3}$	<i>m</i> $\bar{3}$ <i>m</i>
	432	$\bar{4}$ 3 <i>m</i>	<i>m</i> $\bar{3}$ <i>m</i>	<i>m</i> $\bar{3}$ <i>m</i>

[Overview of 32 point groups](#)

# Classification of crystal lattices



# Unique Data – Asymmetric Unit

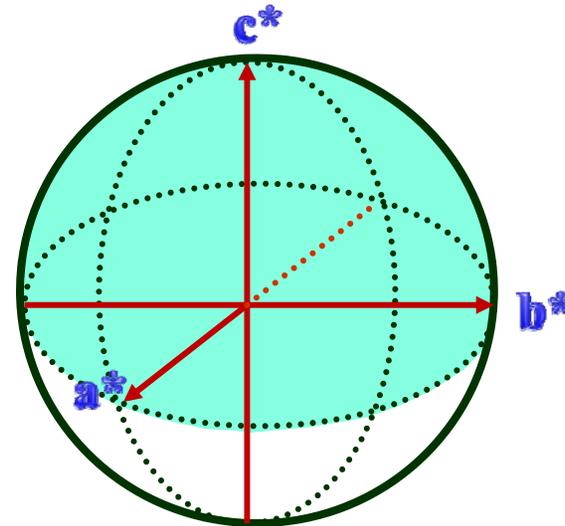
## Triclinic

$$I(hkl) \stackrel{\text{Friedel's Law}}{=} I(\bar{h}\bar{k}\bar{l})$$

$$I(\bar{h}kl) = I(h\bar{k}\bar{l})$$

$$I(h\bar{k}l) = I(\bar{h}kl)$$

$$I(hk\bar{l}) = I(\bar{h}k\bar{l})$$



- Half of the points in within the limiting sphere represent independent observations.

- *Laue Symmetry*

$$\bar{1}$$

$$h \quad 0 \rightarrow \infty$$

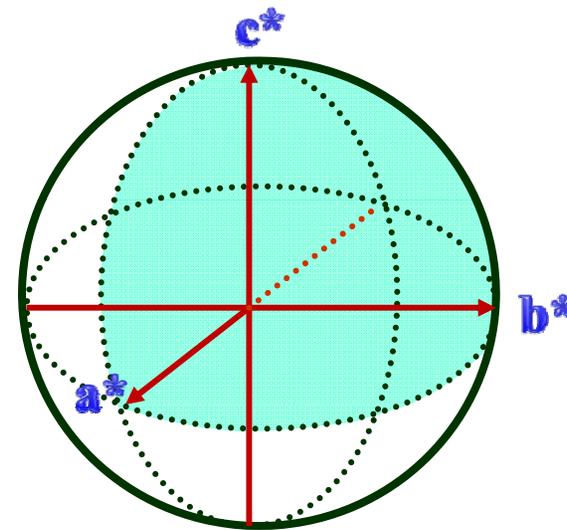
$$k \quad -\infty \rightarrow \infty$$

$$l \quad -\infty \rightarrow \infty$$

# Unique Data – Asymmetric Unit

Monoclinic

$$\begin{aligned}
 I(hkl) & \stackrel{\text{Friedel's Law}}{=} I(\bar{h}\bar{k}\bar{l}) \stackrel{C_2}{=} I(h\bar{k}\bar{l}) \\
 I(\bar{h}kl) & = I(h\bar{k}\bar{l}) = I(\bar{h}\bar{k}\bar{l}) = I(hk\bar{l}) \\
 I(hkl) & \neq I(\bar{h}kl)
 \end{aligned}$$



- *Laue Symmetry*

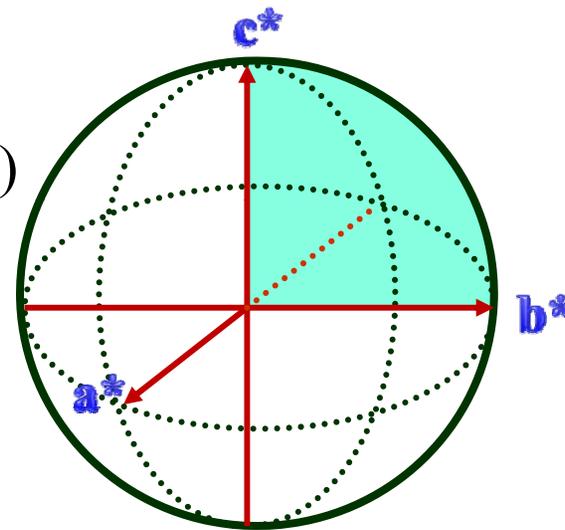
$$2/m$$

$$\begin{aligned}
 h & -\infty \rightarrow \infty \\
 k & 0 \rightarrow \infty \\
 l & 0 \rightarrow \infty
 \end{aligned}$$

# Unique Data – Asymmetric Unit

Orthorhombic

$$\begin{aligned}
 I(hkl) &= I(\bar{h}kl) = I(h\bar{k}l) = I(hk\bar{l}) \\
 &= I(\bar{h}\bar{k}\bar{l}) = I(h\bar{k}\bar{l}) = I(\bar{h}k\bar{l}) = I(\bar{h}k\bar{l})
 \end{aligned}$$



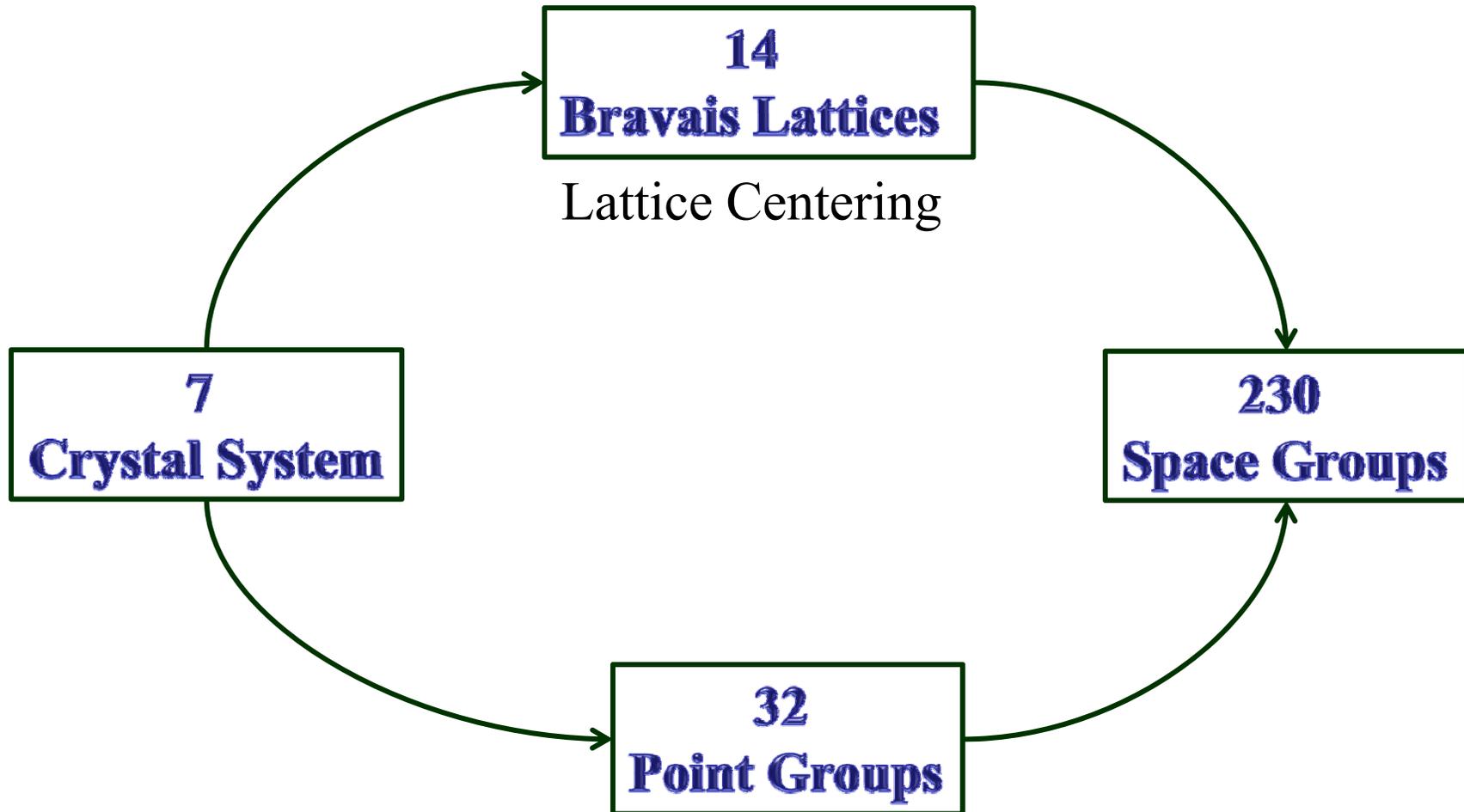
- *Laue Symmetry*

$mmm$

$h$	$0 \rightarrow \infty$
$k$	$0 \rightarrow \infty$
$l$	$0 \rightarrow \infty$

# Crystal Symmetry and Space Groups

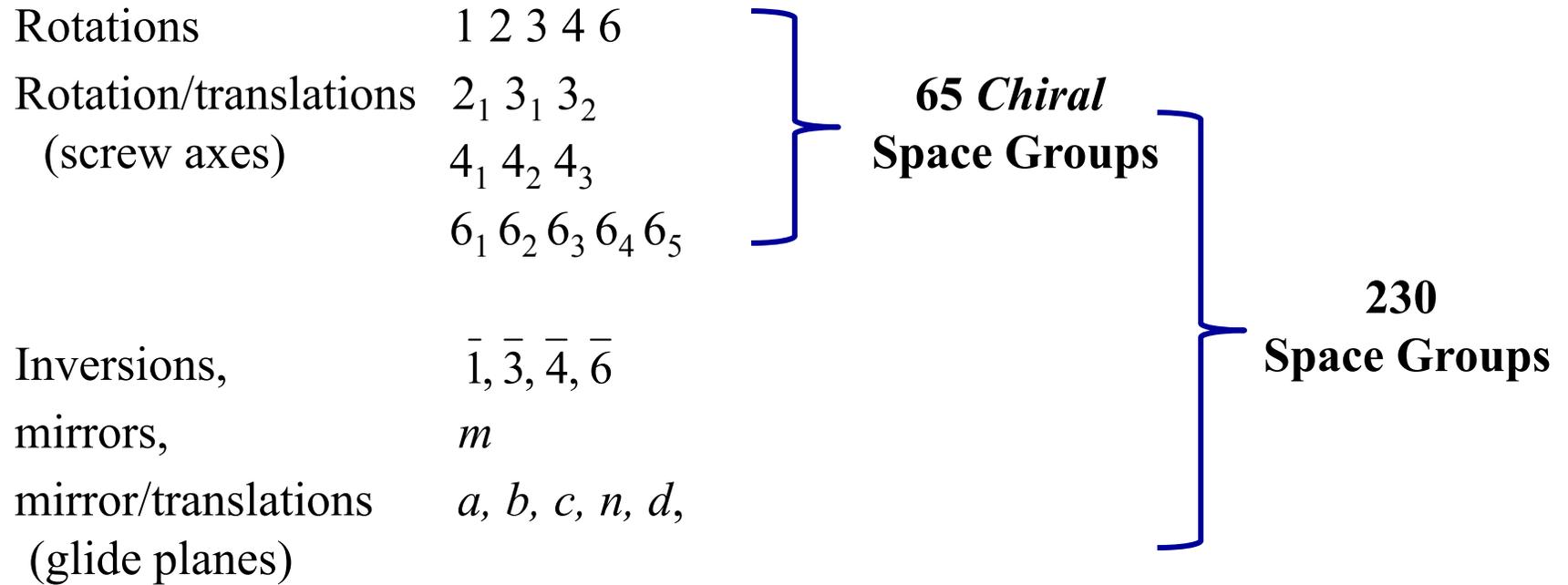
---



Symmetry of the Primitive Unit Cell

# Symmetry Operations

---



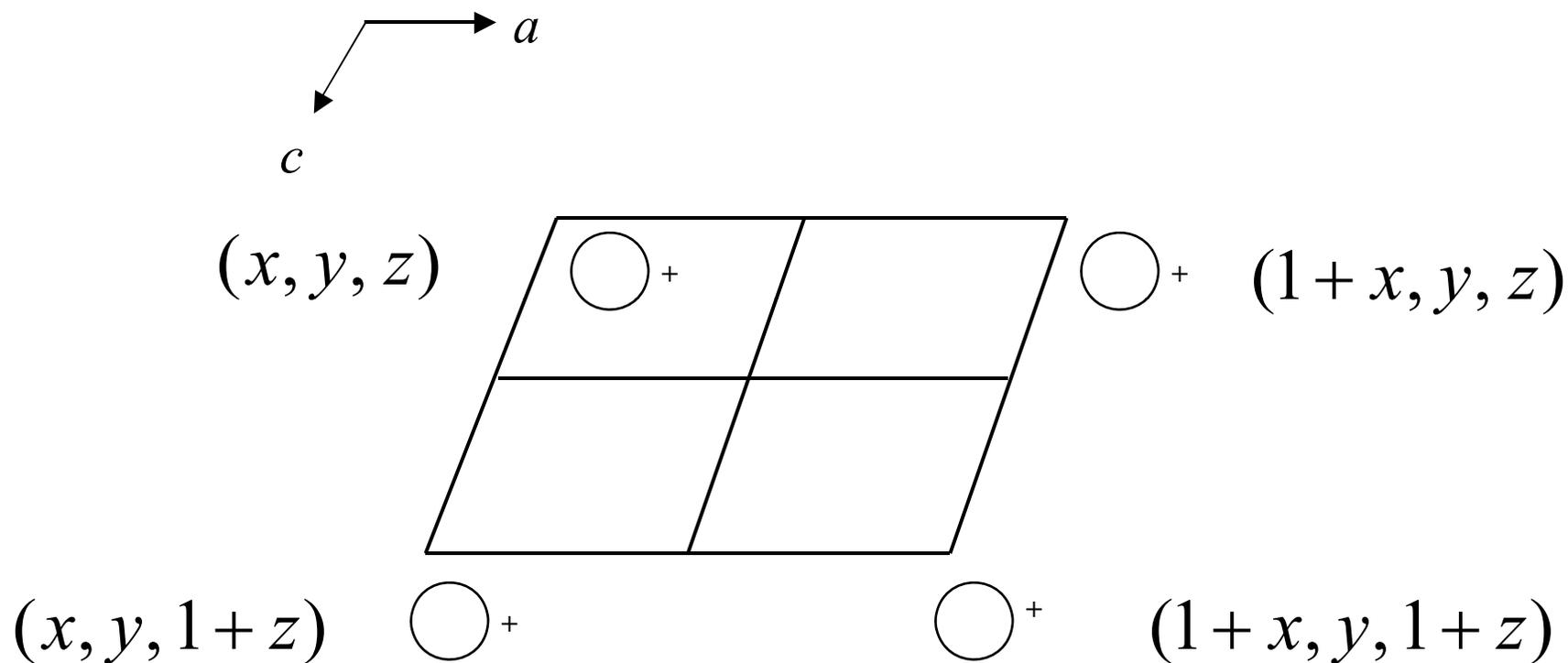
# Symbol for Symmetry Elements

Symmetry axis or symmetry point	Graphical symbol*	Symmetry axis or symmetry point	Graphical symbol*
Identity	None 1	Centre of symmetry, inversion centre: '1 bar' } Reflection point, mirror point (one dimension) }	$\circ \bar{1}$
Twofold rotation axis } Twofold rotation point (two dimensions) }	 2	Inversion axis: '3 bar' } Inversion axis: '4 bar' } Inversion axis: '6 bar' }	$\blacktriangle \bar{3}$ $\blacklozenge \bar{4}$ $\blacktriangle \bar{6} \equiv 3/m$
Twofold screw axis: '2 sub 1'	 2 <sub>1</sub>	Twofold rotation axis with centre of symmetry	 2/m ( $\bar{1}$ )
Threefold rotation axis } Threefold rotation point (two dimensions) }	$\blacktriangle 3$	Twofold screw axis with centre of symmetry	 2 <sub>1</sub> /m ( $\bar{1}$ )
Threefold screw axis: '3 sub 1'	 3 <sub>1</sub>	Fourfold rotation axis with centre of symmetry	$\blacklozenge 4/m$
Threefold screw axis: '3 sub 2'	 3 <sub>2</sub>	'4 sub 2' screw axis with centre of symmetry	 4 <sub>2</sub> /m
Fourfold rotation axis } Fourfold rotation point (two dimensions) }	$\blacklozenge 4$ 	Sixfold rotation axis with centre of symmetry	$\blacklozenge 6/m$
Fourfold screw axis: '4 sub 1'	 4 <sub>1</sub> 	'6 sub 3' screw axis with centre of symmetry	 6 <sub>3</sub> /m
Fourfold screw axis: '4 sub 2'	 4 <sub>2</sub> 		
Fourfold screw axis: '4 sub 3'	 4 <sub>3</sub> 		
Sixfold rotation axis } Sixfold rotation point (two dimensions) }	$\blacklozenge 6$		
Sixfold screw axis: '6 sub 1'	 6 <sub>1</sub>		
Sixfold screw axis: '6 sub 2'	 6 <sub>2</sub>		
Sixfold screw axis: '6 sub 3'	 6 <sub>3</sub>		
Sixfold screw axis: '6 sub 4'	 6 <sub>4</sub>		
Sixfold screw axis: '6 sub 5'	 6 <sub>5</sub>		

*International Tables for Crystallography,  
Volume A, Table 1.4.5, p. 9 (2002)*

# Space Group $P1$

$P1$  No.1



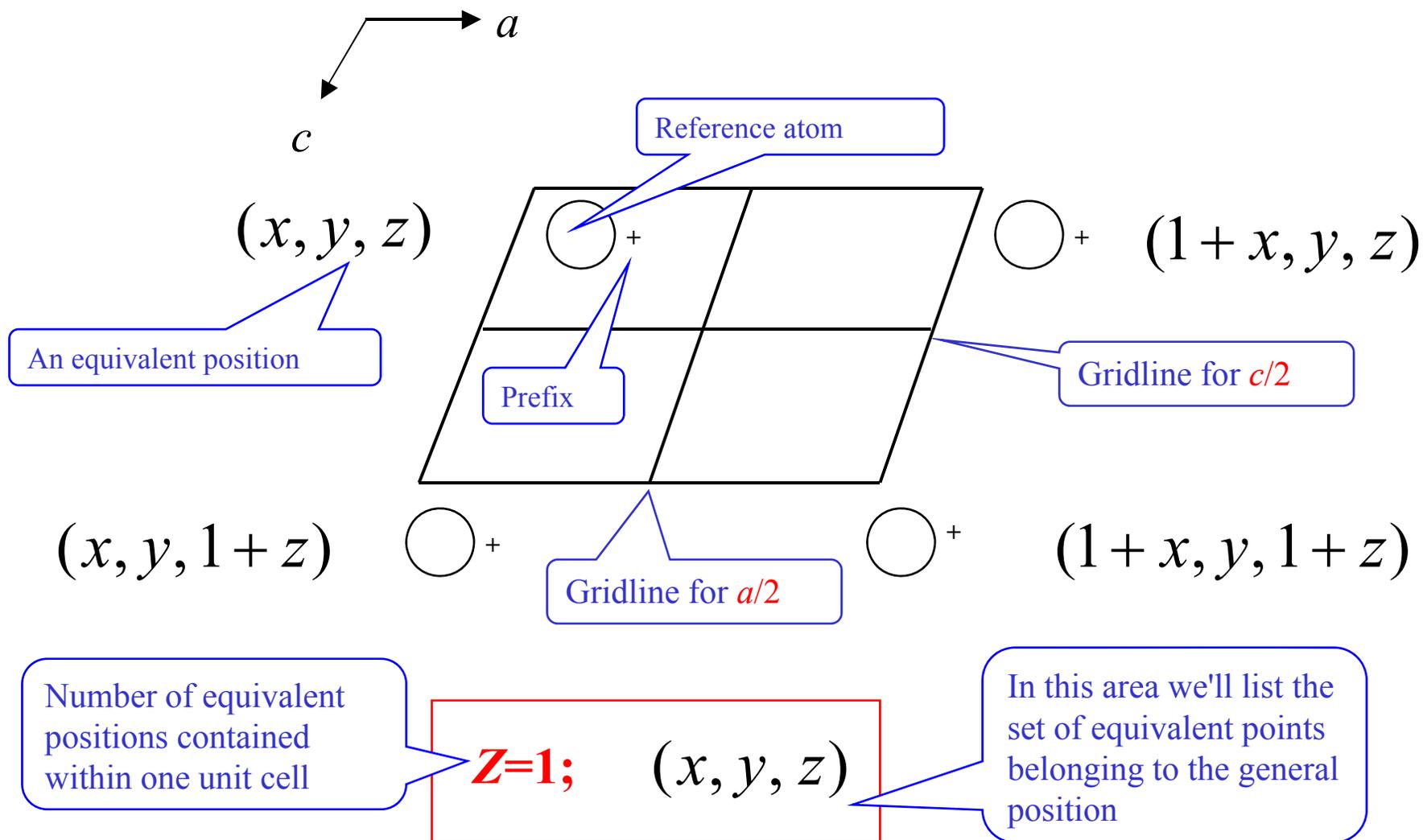
**$Z=1$** ;  $(x, y, z)$

*Enantiomorphous*

*Non-centrosymmetric*

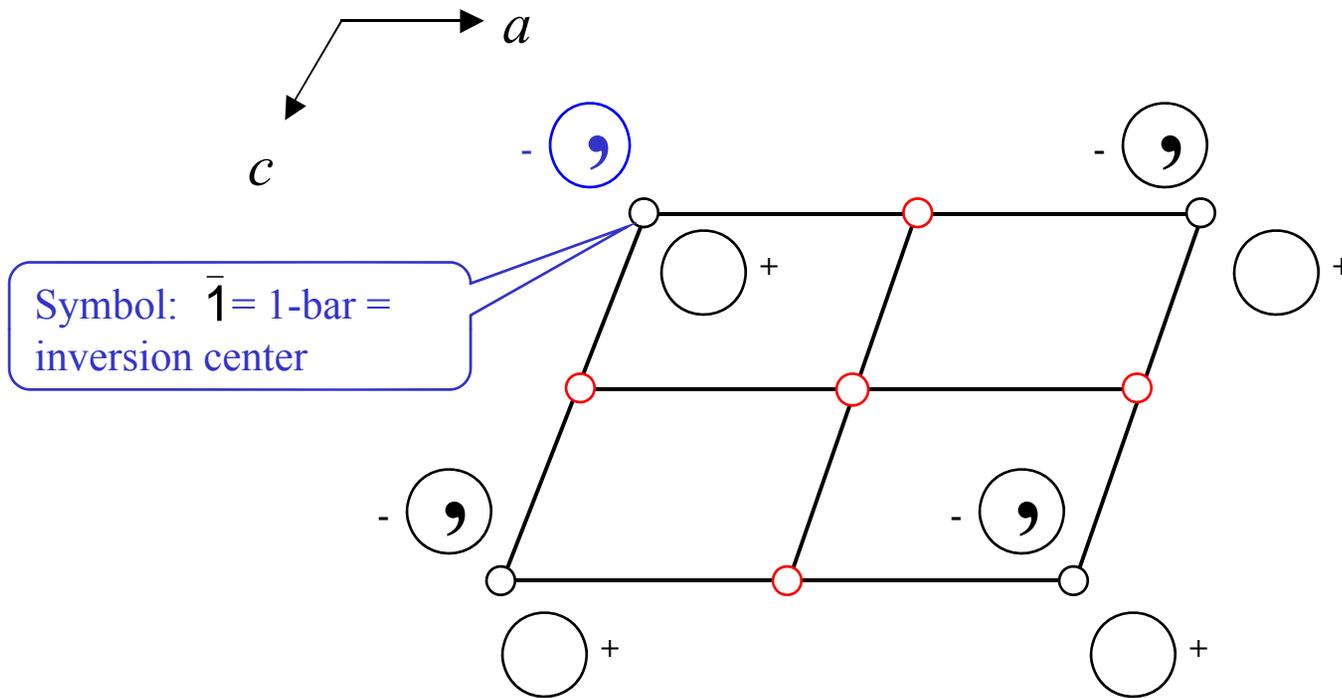
# Space Group *P* 1

# *P*1 No.1



# Space Group $P\bar{1}$

$P\bar{1}$  No.2



*Non-enantiomorphous*

$$Z=2; \quad (x, y, z) \quad (\bar{x}, \bar{y}, \bar{z})$$

# Space Group $P\bar{1}$

CONTINUED

No. 2

$P\bar{1}$

**Generators selected** (1);  $t(1,0,0)$ ;  $t(0,1,0)$ ;  $t(0,0,1)$ ; (2)

**Positions**

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates

Reflection conditions

General:

no conditions

Special: no extra conditions

2  $i$  1 (1)  $x,y,z$  (2)  $\bar{x},\bar{y},\bar{z}$

1  $h$   $\bar{1}$   $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

1  $g$   $\bar{1}$   $0,\frac{1}{2},\frac{1}{2}$

1  $f$   $\bar{1}$   $\frac{1}{2},0,\frac{1}{2}$

1  $e$   $\bar{1}$   $\frac{1}{2},\frac{1}{2},0$

1  $d$   $\bar{1}$   $\frac{1}{2},0,0$

1  $c$   $\bar{1}$   $0,\frac{1}{2},0$

1  $b$   $\bar{1}$   $0,0,\frac{1}{2}$

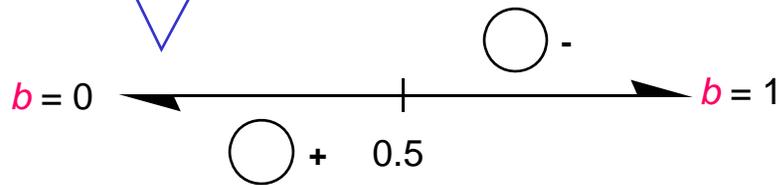
1  $a$   $\bar{1}$   $0,0,0$

ITA  $p115$

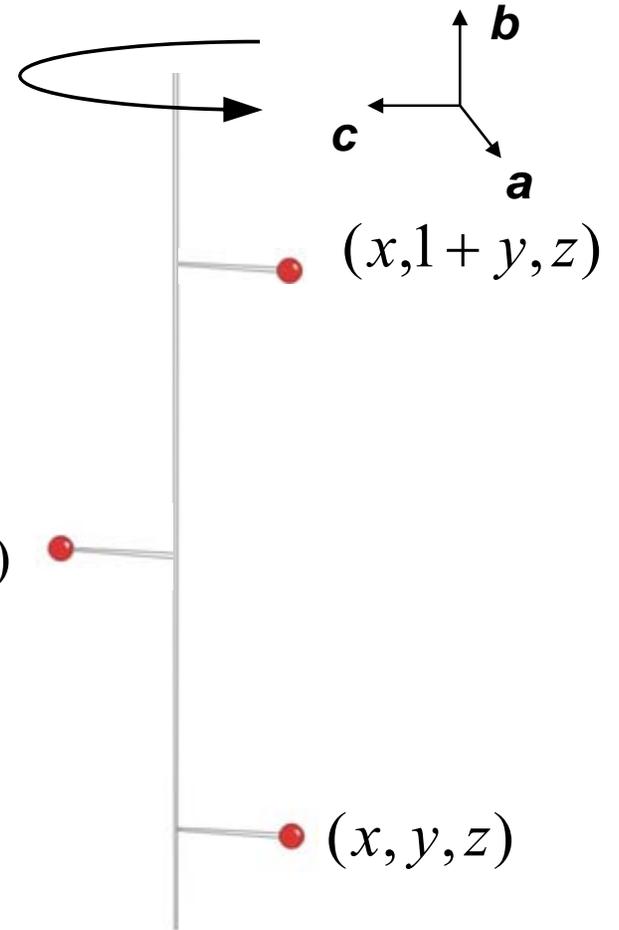
# 2<sub>1</sub> Screw Axis

2<sub>1</sub> is a 180° (two-fold) rotation followed by a translation of 1/2 of the lattice vector. This operation would take a point from (x,y,z) to (-x, 1/2+y, -z) for a 2<sub>1</sub> screw axis along b.

Symbol: 2<sub>1</sub> || page  
is a half-arrow



In the diagram on the following page, the 2<sub>1</sub> axis is perpendicular to the plane of the screen, we'll use the symbol 2<sub>1</sub> (a half-circle with a vertical line through it).



2<sub>1</sub> Screw Axis along **b**



# Space Group $P2_1$

---

CONTINUED

No. 4

$P2_1$

**Generators selected** (1);  $t(1,0,0)$ ;  $t(0,1,0)$ ;  $t(0,0,1)$ ; (2)

## Positions

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates

Reflection conditions

General:

2  $a$  1

(1)  $x, y, z$

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

$0k0 : k = 2n$

# Space Groups Determination

Table 3.1.4.1. Reflection conditions, diffraction symbols and possible space groups

TRICLINIC, Laue class  $\bar{1}$

Reflection conditions	Extinction symbol	Point group	
		1	$\bar{1}$
None	$P-$	$P1(1)$	$P\bar{1}(2)$

Unit Cell Symmetry and Dimensions

Intensity Statistics

Systematic Absences

Space Group Symmetry

MONOCLINIC, Laue class  $2/m$

Unique axis $b$			Extinction symbol	Laue class $1\ 2/m\ 1$		
Reflection conditions				Point group		
$hkl$ $Ok\ l\ hk0$	$hOl$ $h00\ 00l$	$0k0$		2	$m$	$2/m$
		$k$	$P1-1$ $P12_11$ $P1a1$	$P121(3)$ $P12_11(4)$	$P1m1(6)$ $P1a1(7)$	$P1\ 2/m\ 1(10)$ $P1\ 2_1/m\ 1(11)$ $P1\ 2/a\ 1(13)$ $P1\ 2_1/a\ 1(14)$
	$h$ $h$ $l$ $l$ $h+l$ $h+l$	$k$ $k$ $k$ $k$ $k$ $k$	$P1c1$ $P1\ 2_1/c\ 1$ $P1n1$ $P1\ 2_1/n\ 1$		$P1c1(7)$ $P1n1(7)$	$P1\ 2/c\ 1(13)$ $P1\ 2_1/c\ 1(14)$ $P1\ 2/n\ 1(13)$ $P1\ 2_1/n\ 1(14)$
$h+k$	$h$	$k$	$C1-1$	$C121(5)$	$C1m1(8)$	$C1\ 2/m\ 1(12)$
$h+k$	$h, l$	$k$	$C1c1$		$C1c1(9)$	$C1\ 2/c\ 1(15)$
$k+l$	$l$	$k$	$A1-1$	$A121(5)$	$A1m1(8)$	$A1\ 2/m\ 1(12)$
$k+l$	$h, l$	$k$	$A1n1$		$A1n1(9)$	$A1\ 2/n\ 1(15)$
$h+k+l$	$h+l$	$k$	$I1-1$	$I121(5)$	$I1m1(8)$	$I1\ 2/m\ 1(12)$
$h+k+l$	$h, l$	$k$	$I1a1$		$I1a1(9)$	$I1\ 2/a\ 1(15)$

# Intensity Statistics – Wilson Plot

Estimation of temperature factor  $B$

$$I_o(hkl) = K \sum f_i^2 \exp\left(-2B \frac{\sin^2 \theta}{\lambda^2}\right)$$

$$\frac{I_o(hkl)}{\sum f_i^2} = K \exp\left(-2B \frac{\sin^2 \theta}{\lambda^2}\right)$$

$$Y = \ln\left[\frac{I_o(hkl)}{\sum f_i^2}\right] = \ln K - 2B \frac{\sin^2 \theta}{\lambda^2}$$

X

Linear lot of  $\ln\left[\frac{I_o(hkl)}{\sum f_i^2}\right]$  versus  $\frac{\sin^2 \theta}{\lambda^2}$   $\rightarrow$   $\left\{ \begin{array}{l} \text{Intercept} = \ln K \\ \text{Slope} = -2B \end{array} \right.$

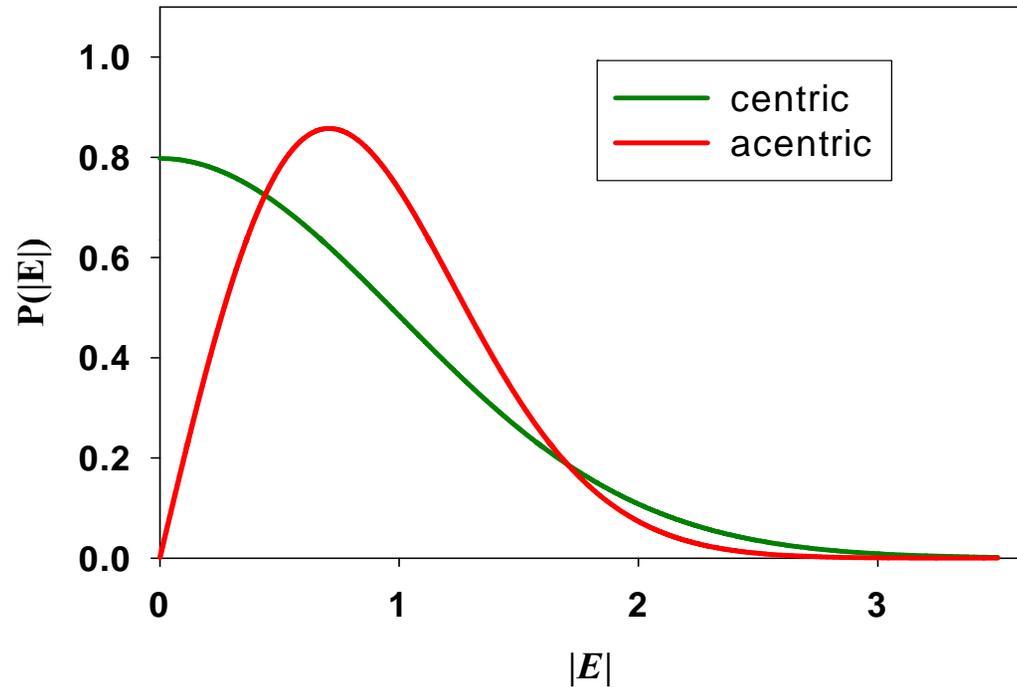
Arai, S. Chatake, T. Suzuki, N. Mizunob, H. and Niimura, N. *Acta Cryst.* (2004). D60, 1032.  
WILSON, A. J. C. *Nature (London)*, (1942). 150, 151.

# Intensity Statistics - $E$ Value

Normalized structure factors

$$|E_h| = \frac{|F_h|}{\sqrt{\langle |F|^2 \rangle}}$$

Plot of the probability distribution of  $|E|$



$\langle  E^2 - 1  \rangle$	Centrosymmetric	Non-centrosymmetric
	0.968	0.736

# Structure Solution - Fourier Synthesis

Scattering density (electron or neutron)

**Missing phase information**

$$\rho(X, Y, Z) = \frac{1}{V} \sum_{\mathbf{H}} \mathbf{F}_{\mathbf{H}} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j)$$
$$= \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l |F(hkl)| e^{i\phi(hkl)} e^{-i2\pi(hX+kY+lZ)}$$

electron or neutron  
density

structure factor

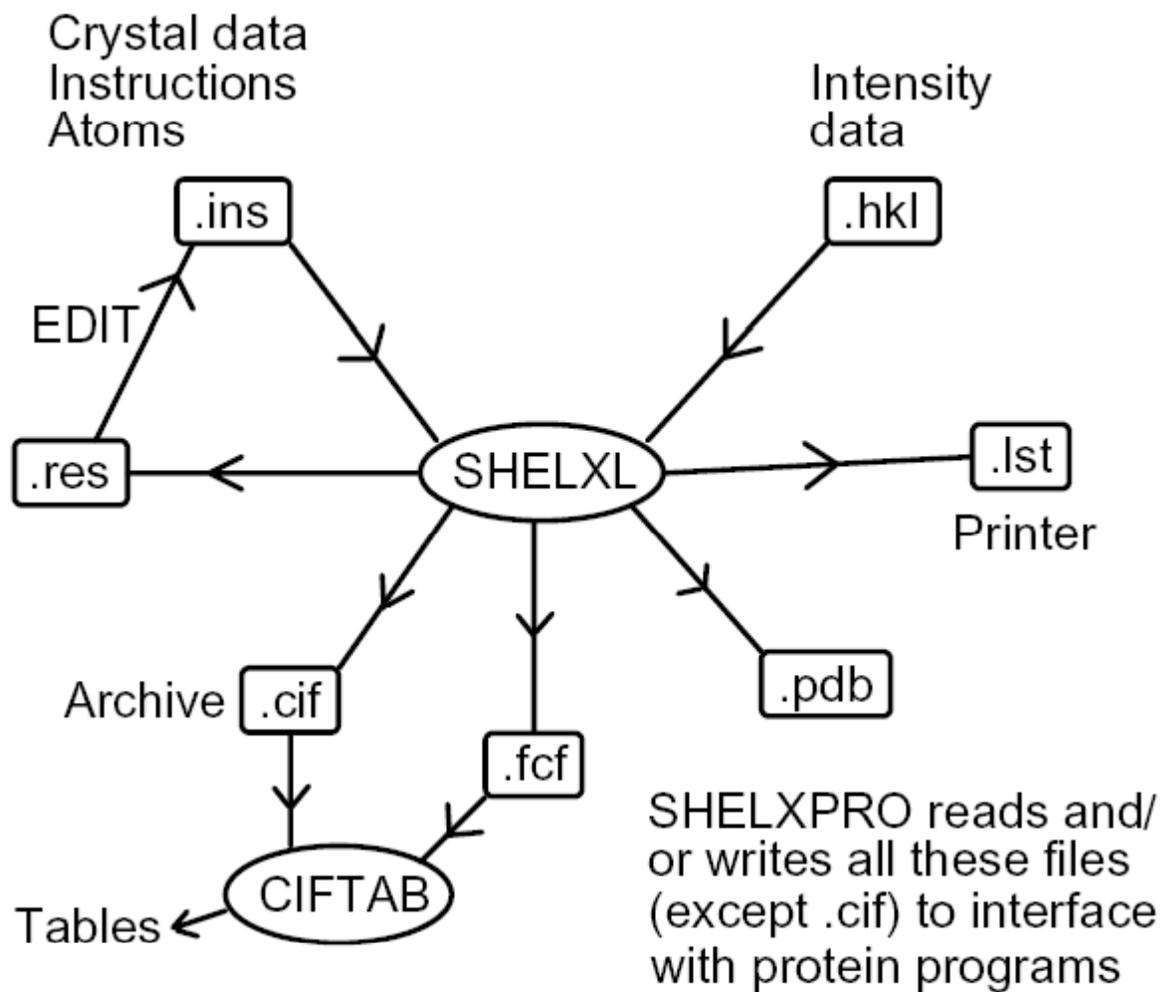
$X, Y, Z$  – points in unit cell

Fourier synthesis will give the *scattering density*, and hence the crystal structure

## ***The Phase Problem***

Need the full wave equations  $|F(hkl)|e^{i\phi}$  for each reflection to do the reverse Fourier transform.

# Structure Analysis



# Structure Refinement

SHELXL always refines against  $F^2$  [measured intensities  $I_o$ ]

## *Merge of reflection data*

$$R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$$

$$R_{\text{sigma}} = \sum [\sigma(F_o^2)] / \sum [F_o^2]$$

*Agreement between  
symmetry equivalent reflections*

Quality of the  
diffraction data

## *R-indices and weight*

$$wR2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{\frac{1}{2}}$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$$

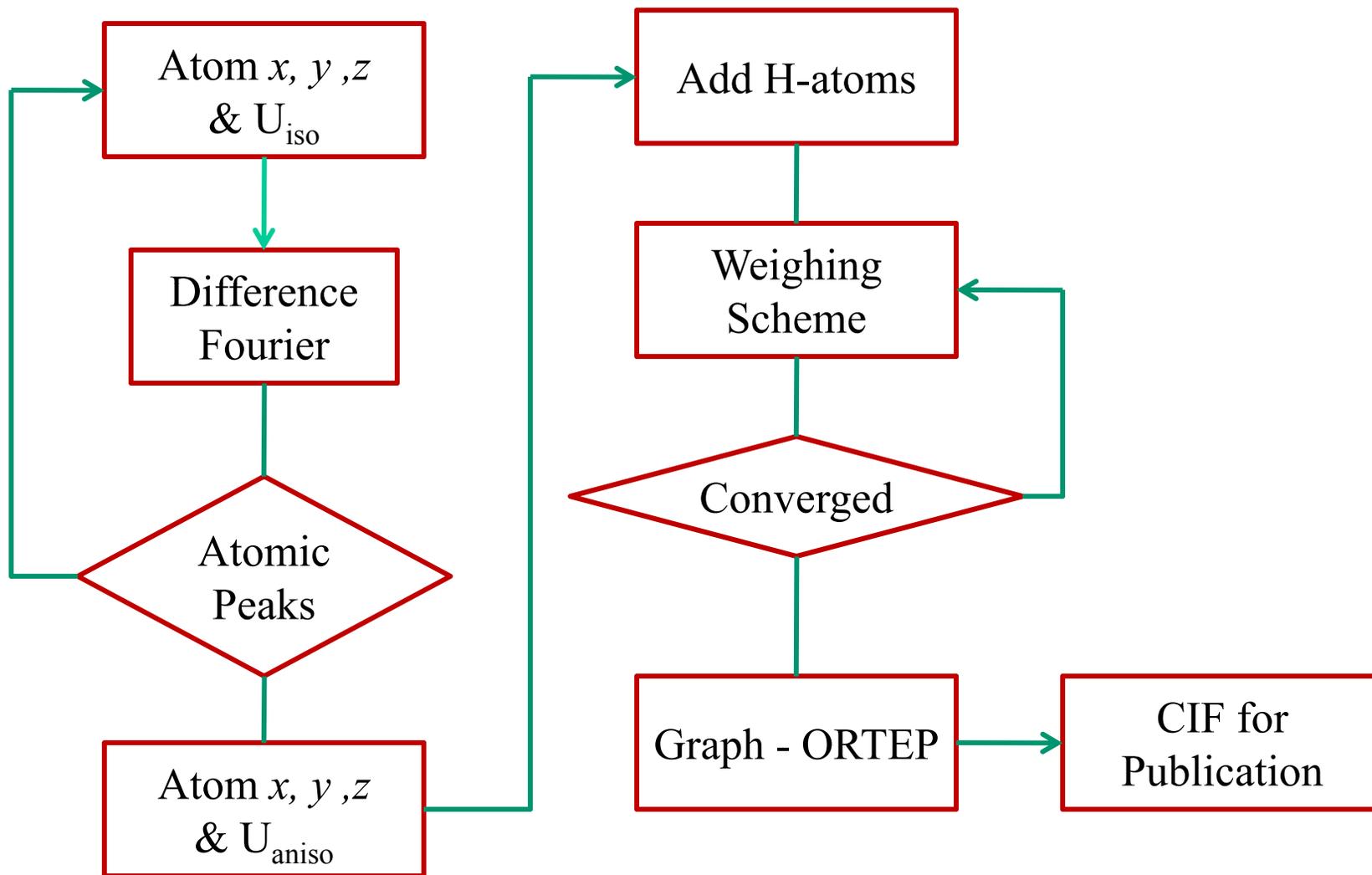
where  $P$  is  $[ 2F_c^2 + \text{Max}(F_o^2, 0) ] / 3$

$$GooF = S = \left\{ \sum (w(F_o^2 - F_c^2)^2) / (n - p) \right\}^{\frac{1}{2}}$$

where  $n$  is the number of reflections and  $p$   
is the total number of parameters

Quality of the  
structure model

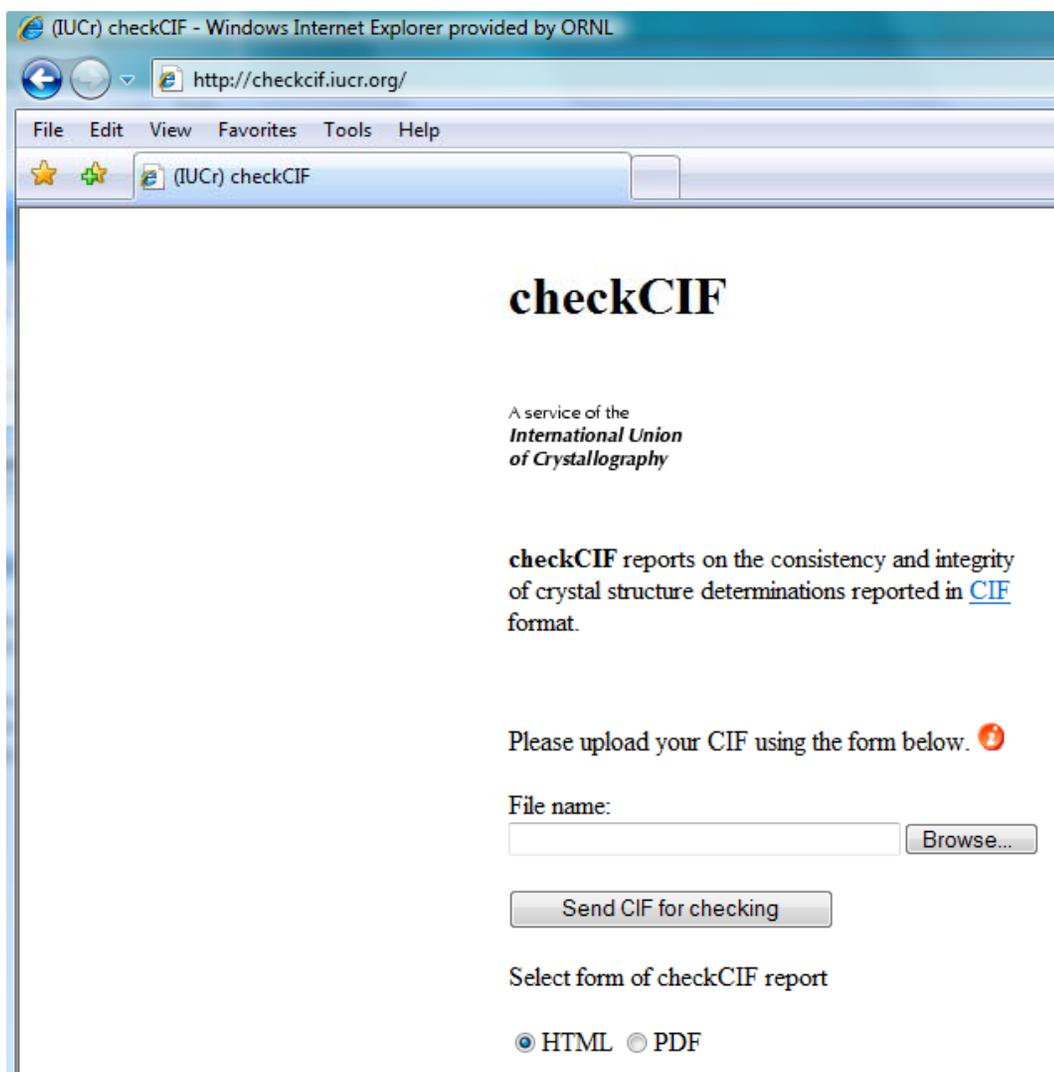
# Refinement Procedure



# Structure Validation

checkCIF Program

http://checkcif.iucr.org



# Problem Address by checkCIF

---

Data completeness and resolution

Missing or inadequate absorption correction

Missed higher space group symmetry

Absolute structure

Indications of a poor structure

*Solvent accessible voids in the structure*

*Population/occupancy parameters*

*Displacement parameters*

***Treatment of H atoms***

*etc.*

## refine\_ls\_hydrogen\_treatment

---

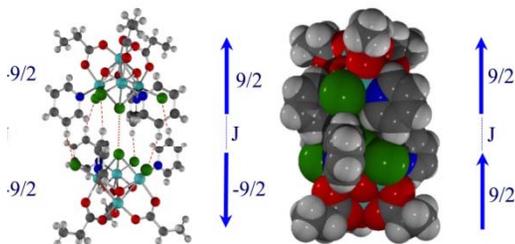
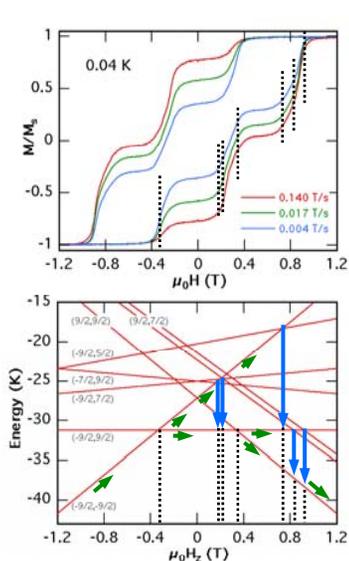
Treatment of hydrogen atoms in the least-squares refinement.

refall	<i>refined all H-atom parameters</i>
refxyz	<i>refined H-atom coordinates only</i>
refU	<i>refined H-atom U's only</i>
noref	<i>no refinement of H-atom parameters</i>
constr	<i>H-atom parameters constrained</i>
mixed	<i>some constrained, some independent</i>
undef	<i>H-atom parameters not defined</i>

# Science at TOPAZ

## Single Molecule Magnets:

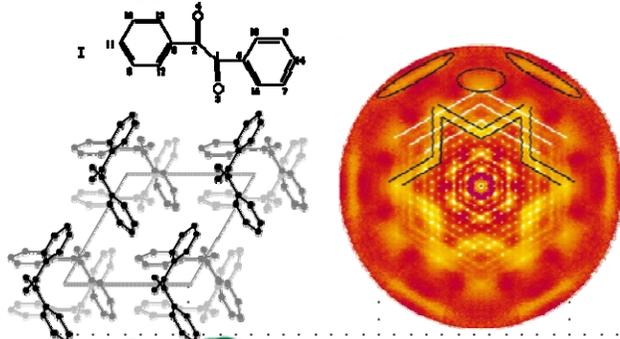
Supramolecular Dimers of Mn4  $[[\text{Mn}_4\text{Pr}]_2 \cdot \text{MeCN} (\text{NA}_3)]$ : Example of exchange-biased Quantum Tunnelling of Magnetization



Wernsdorfer, Christou, et al. *Nature* 2002, 416, 406

## Diffuse Scattering:

Structure modulations in Benzil exhibit diffuse scattering patterns



Welberry et al., *J. Appl. Cryst.*, 2003

OAK RIDGE NATIONAL LABORATORY  
Single crystal diffractometer, TOPAZ

## Yb<sub>14</sub>MnSb<sub>11</sub>

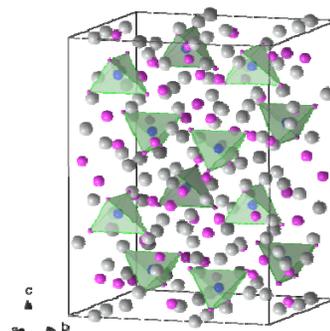
Ferromagnet regarded as a rare example of an underscreened Kondo lattice. (T<sub>C</sub> = 53 K)

Tetragonal with space group *I4<sub>1</sub>/acd*

1 Mn atom

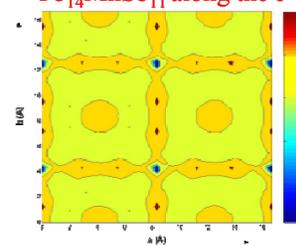
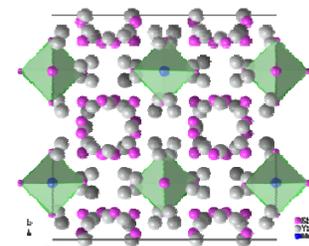
4 inequivalent Sb atoms

Sb (2) involved in Mn-Sb tetrahedra



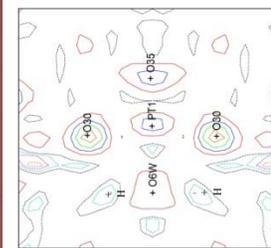
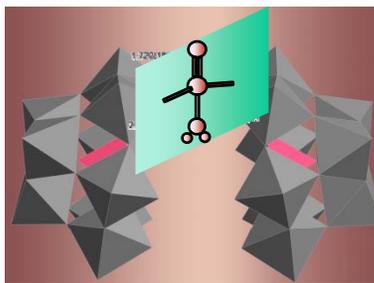
→ maximum entropy magnetization density reconstruction reveals the presence of a magnetic moment on the Sb site with opposite sign with respect to the Mn moment

Projection of the spin density in Yb<sub>14</sub>MnSb<sub>11</sub> along the c-axis.



Garlea, et al. *ACNS 2005, Phensant Run, IL*.

Terminal hydrogen or water on the Pt in the Late-Transition Metal-Oxo Complex,  $\text{O}=\text{Pt}(\text{H}_2\text{O})\text{L}_2$ ,  $\text{L} = [\text{PW}_9\text{O}_{34}]^{9-}$



Interesting catalyst

→ Large unit cell [29x32x38]

→ High H content

→ Disordered lattice water



# Acknowledgement

---

Arthur J. Schultz

Yu-Sheng Chen

Argonne National Laboratory

Christina Hoffmann

Bryan C. Chakoumakos

Oak Ridge National Laboratory