# Crystallography:
# A foray into reciprocal space

## Chem 651B: Electron Microscopy

James R. Neilson, PhD

May 19, 2015

Central Instrument Facility Summer school

# crystallography: learning goals

- Solids are often crystalline - *the language of waves*
- Crystalline symmetry - *simplifying structures*
- Describing structures - *using the Int. Tab. Crystallography*
- Reciprocal space - *the Fourier transform of direct space*
- Reciprocal lattice - *what diffraction shows us*

---

- Kinematic scattering - *deriving intensities*

# Why do crystallography in the TEM?

**take advantage of the 'local' probe!**

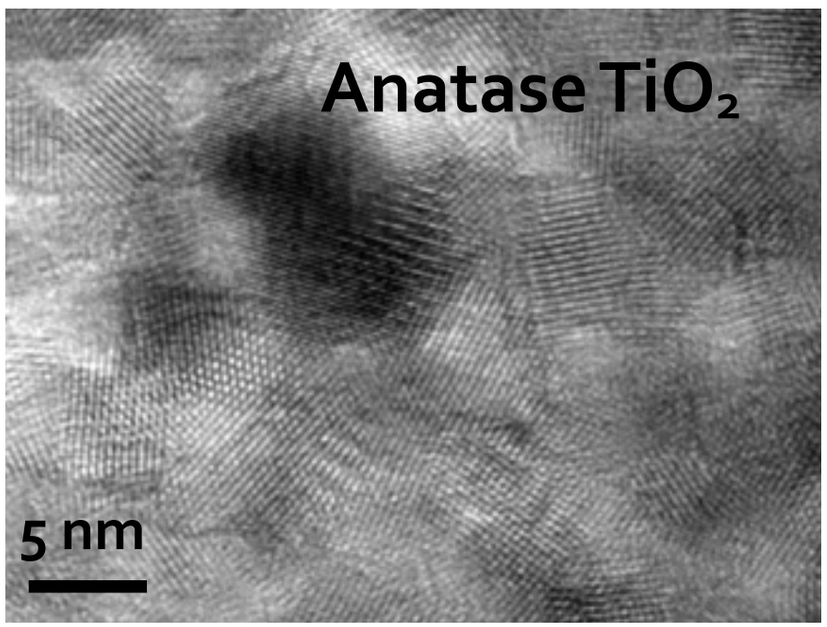
- Phase identification (lattice or point group)
- Orientation of crystals
- Finite sizes precludes macroscopic crystallography
  - *the nanostructure problem; challenges in crystal growth.*
- Supersymmetry: strong electron contrast
  - *modulated structures, charge density wave materials (e.g., $TaS_2$, $LiFeBO_3$)*
- Disorder: domains and local distortions
  - *e.g., metal-insulator transitions, ferroelectrics, superconductors*

# what are crystals?

***definition:*** **crystallinity**

The presence of three-dimensional order on the level of atomic dimensions. Crystallinity may be detected by diffraction techniques, heat-of-fusion measurements, etc. The amount of disorder within the crystalline region is not incompatible with this concept

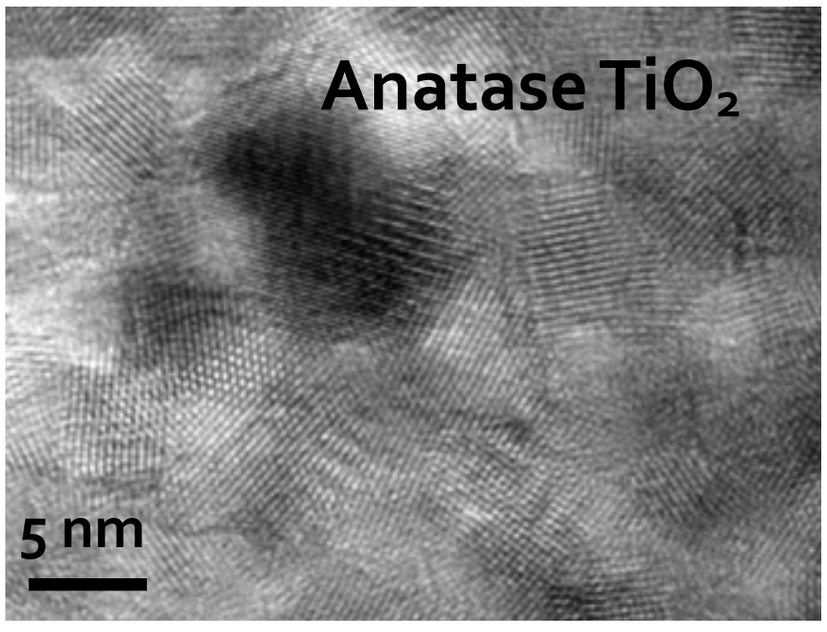
*- IUPAC Compendium of Chemical Terminology - the Gold Book (http://goldbook.iupac.org)*



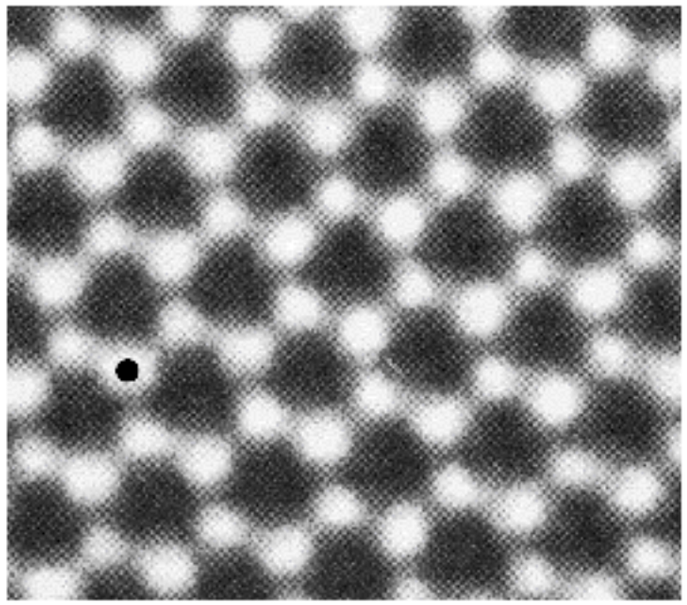

# what are crystals?

**Many condensed phases are crystals.**
We treat them as being ***infinitely periodic***.
(what's the difference between ~$10^{23}$ and $\infty$ ?)

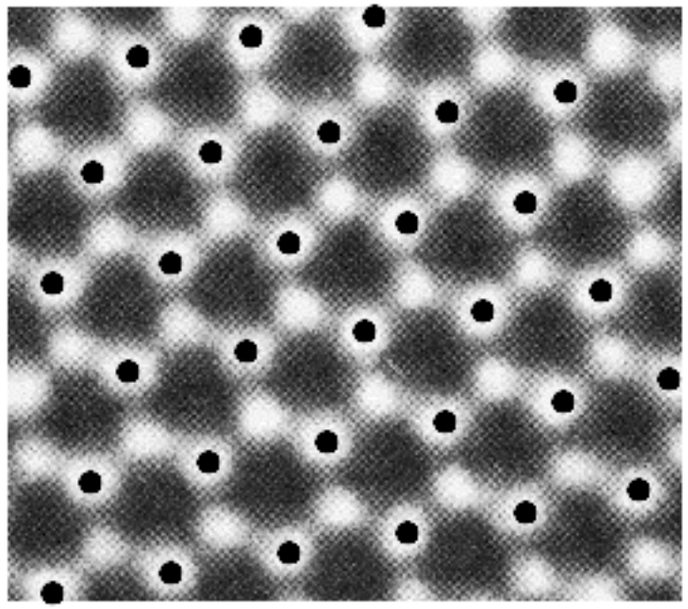
**Why? Consider the packing of spheres (*i.e.*, oranges at the fruit stand).**
The most dense packing for spheres (T. Hales; Kepler conjecture).
This hexagonal/cubic close packing: $\pi/(3\sqrt{2}) \sim 74\%$ (derive this for fun)




# translational symmetry: the periodic lattice



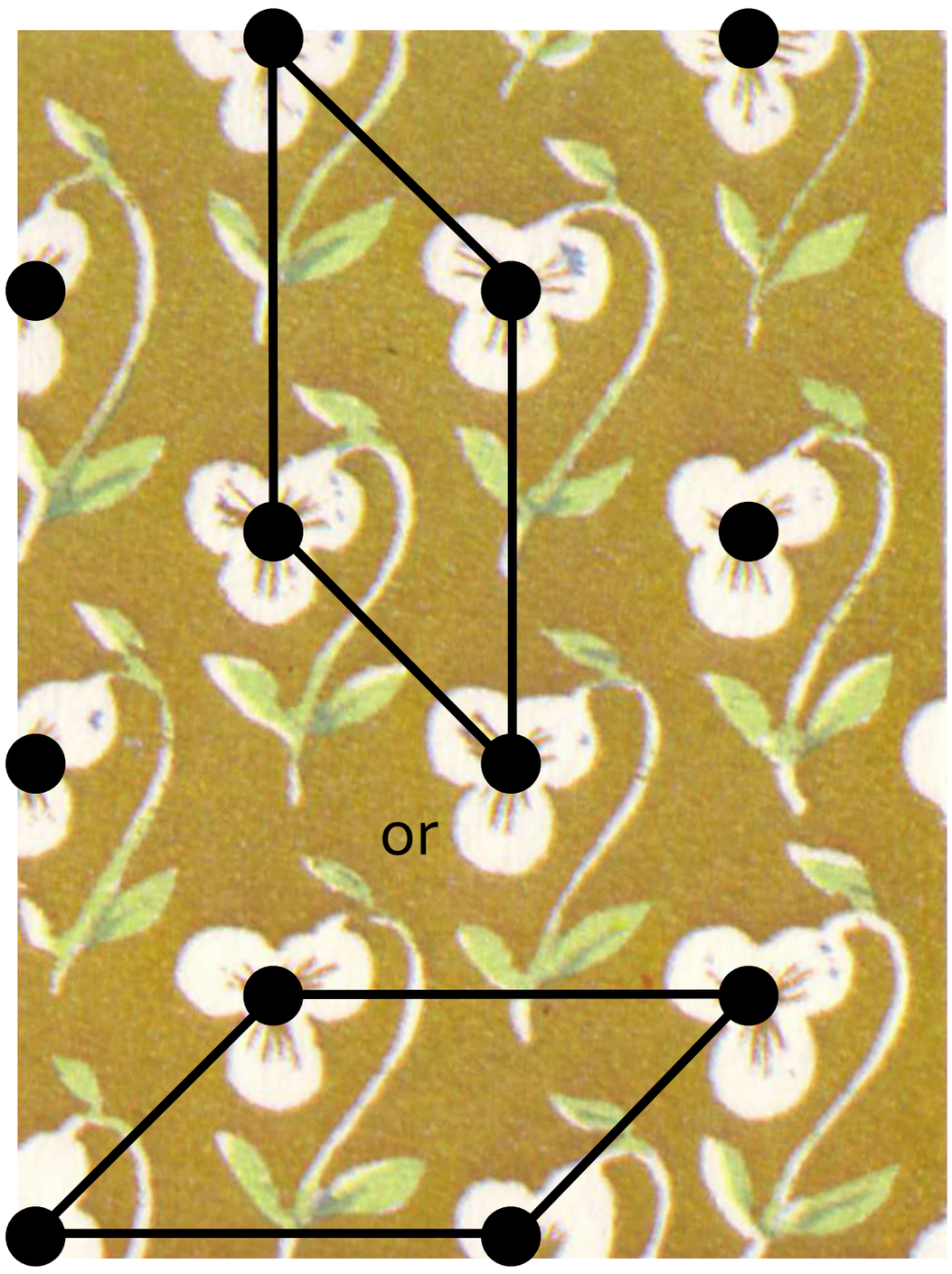
a lattice point



the periodic lattice

http://www.doitpoms.ac.uk/tlplib/crystallography3/lattice.php

# identify the lattice points

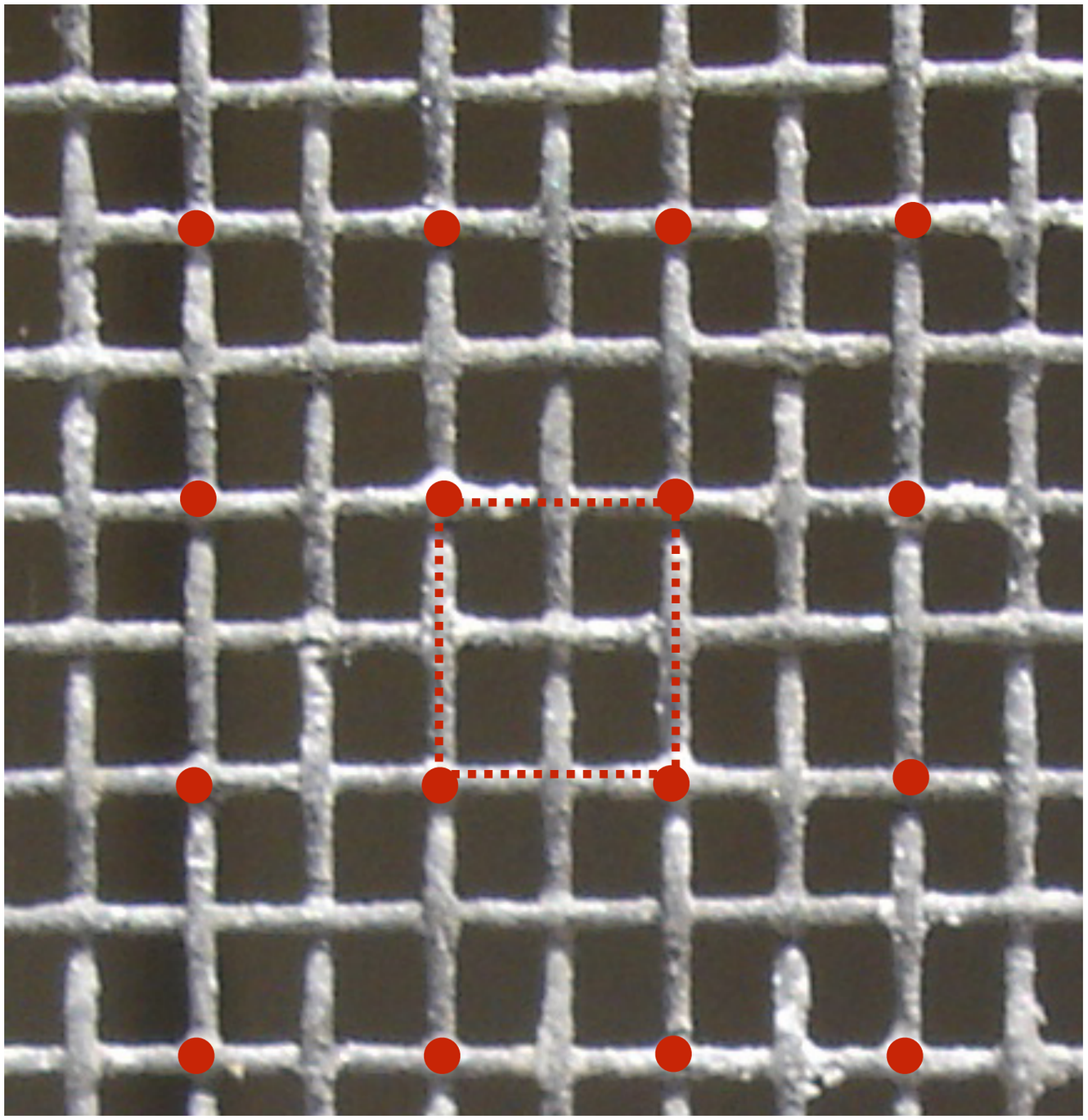



http://en.wikipedia.org/wiki/Wallpaper_group

*p1*

Medieval Wall paper

# identify the lattice points

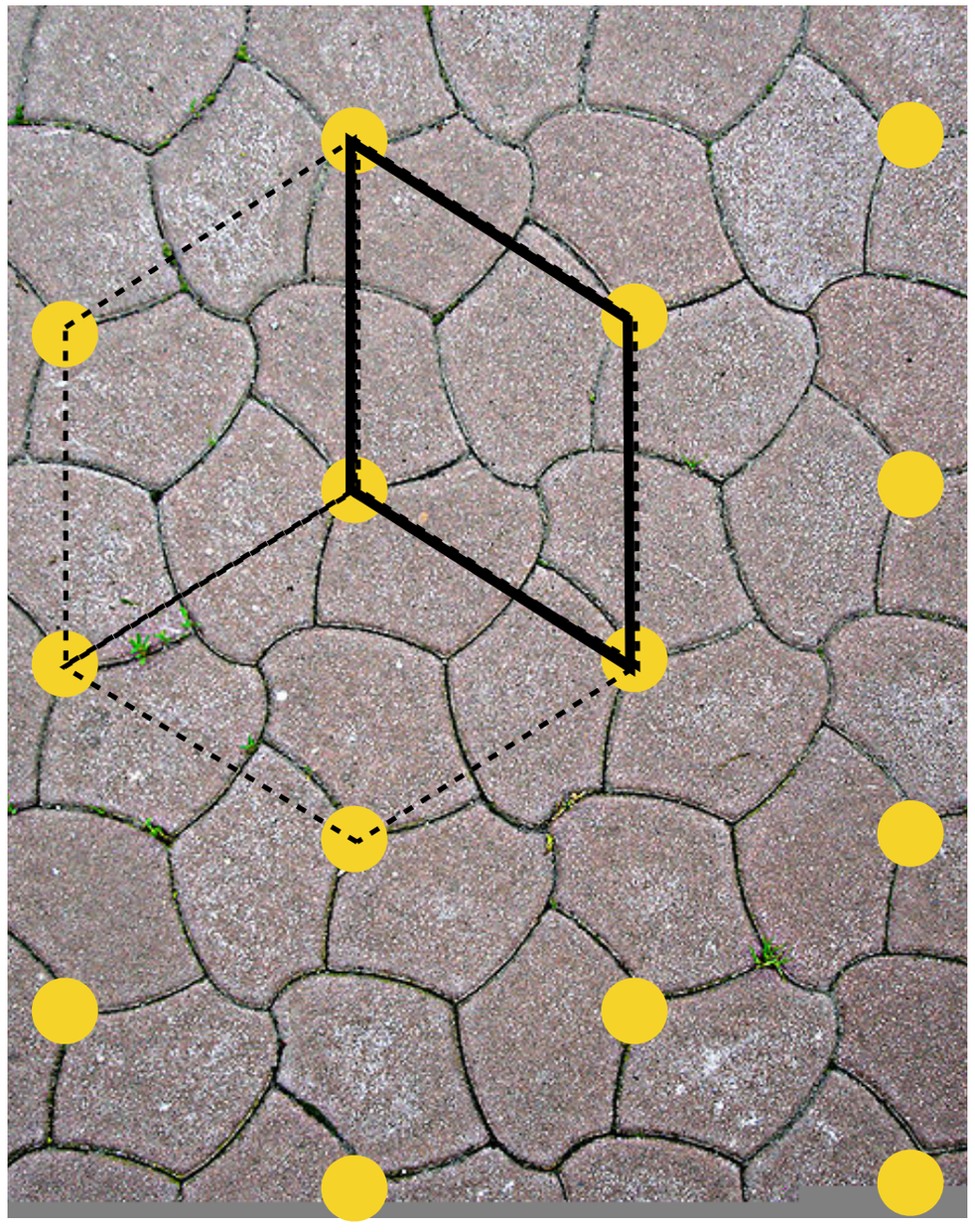


http://en.wikipedia.org/wiki/Wallpaper_group

*p4g*
Fly screen

# the unit cell

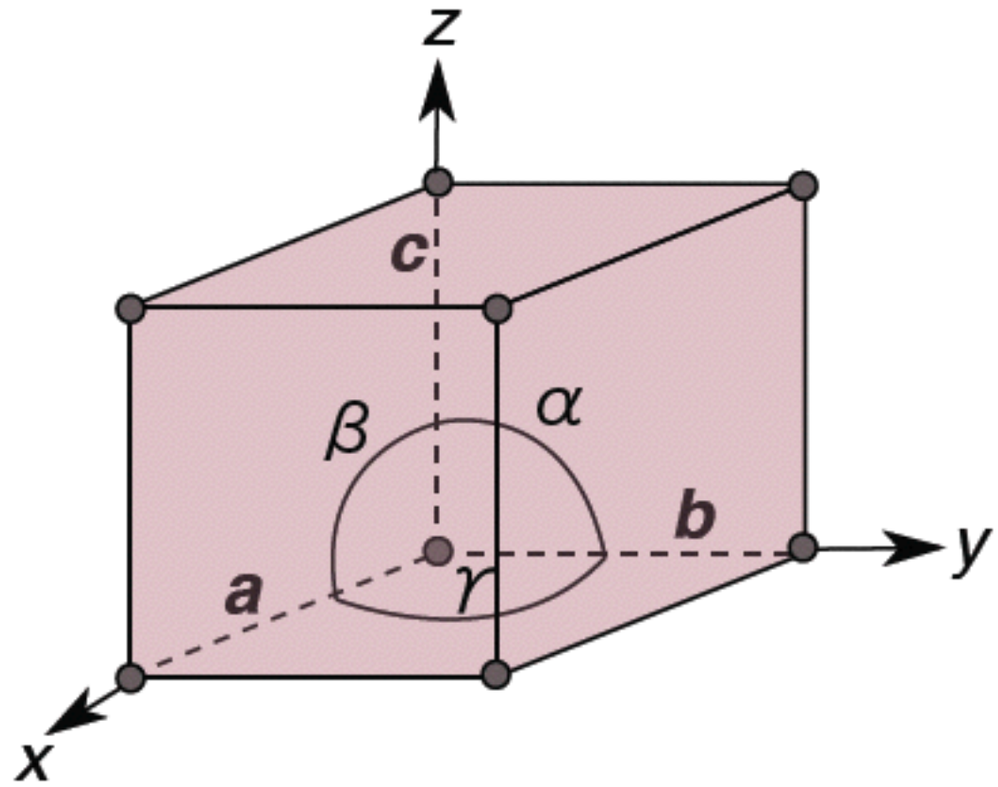
- this is the object that tiles space
  - must tile completely, without gaps
  - the contents of the cell just also perfectly repeat
  - take the smallest repeating unit with the least # of parameters
- in 2D: parallelogram
- in 3D: parallelepiped



http://en.wikipedia.org/wiki/Wallpaper_group

# the geometry of the unit cell

- lattice parameters: ***a***,***b***,**c** (use the right-hand rule)
  - angles:
    - *α :* angle between ***b*** and ***c***
    - *β*: angle between ***a*** and ***c***
    - *γ*: angle between ***a*** and ***b***

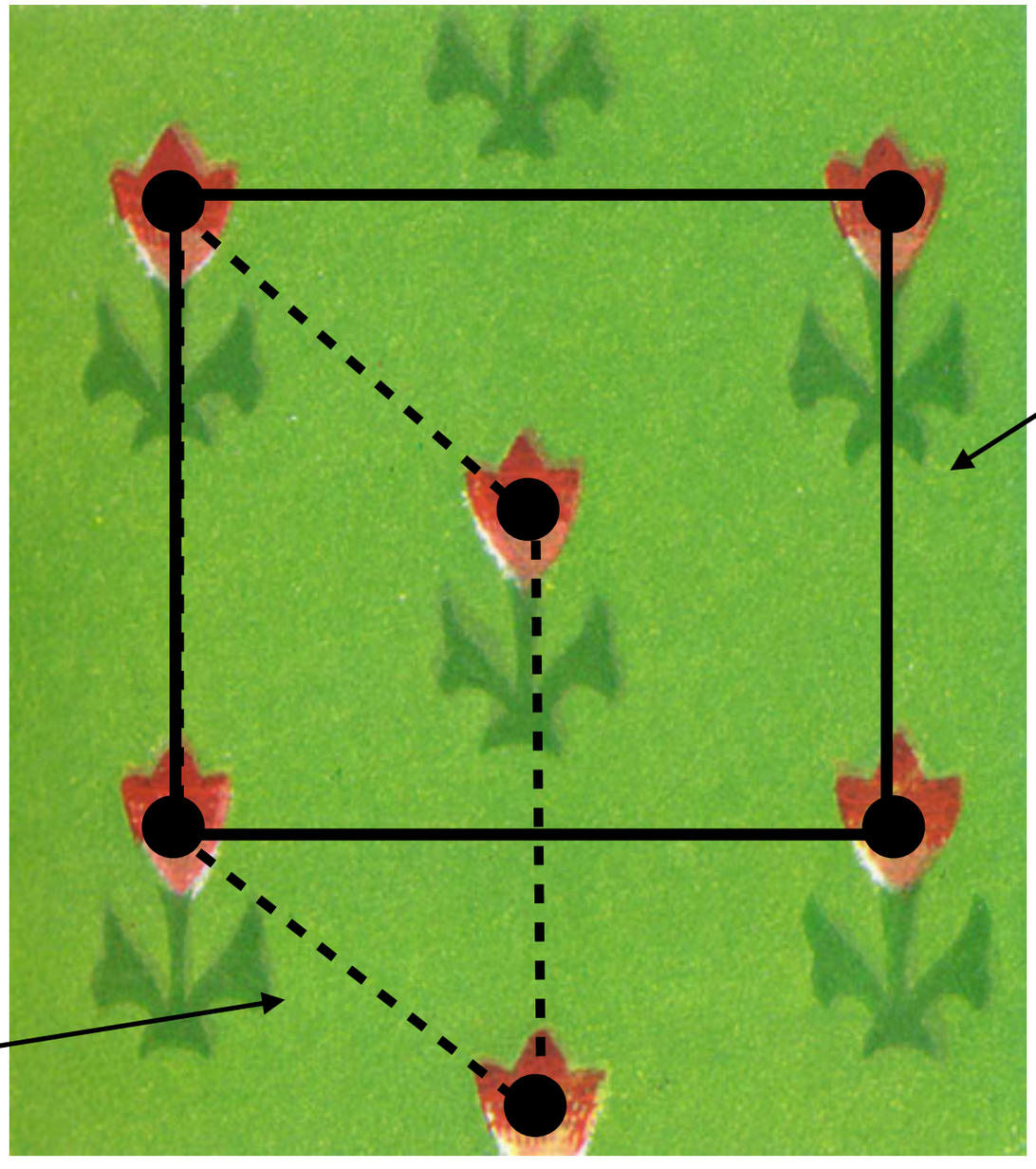



- Lattice vectors:
  - ***t*** = u***a*** + v***b*** + w***c***
  - For shorthand, ***t*** = [u v w]
  - for negative values, we write: $\mathbf{t} = [\bar{u}vw]$ (pronounced, "*u-bar*")

http://www.doitpoms.ac.uk/tlplib/crystallography3/parameters.php

# primitive *vs*. centered unit cells

pick the smallest cell that requires you to describe the least number of features



**centered cell (2 edges)**

primitive cell (2 edges + 1 angle)

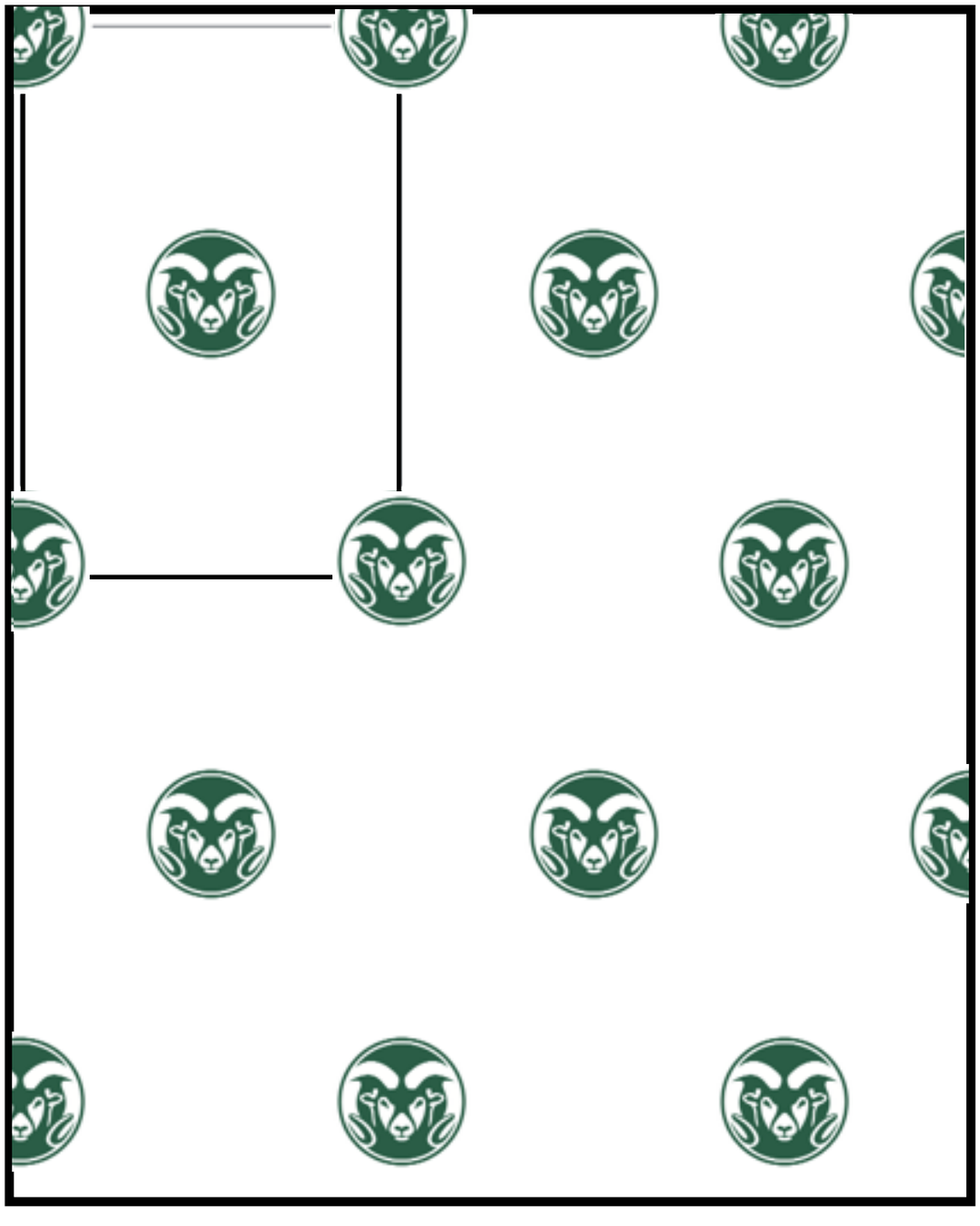
http://en.wikipedia.org/wiki/Wallpaper_group

*cm*

Persian Tapestry

# building a crystal structure

- crystal system
- identify the lattice type (centering)
  - insert motifs into the unit cell
  - coordinates expressed as fractions of the lattice parameters
- tile with abandon

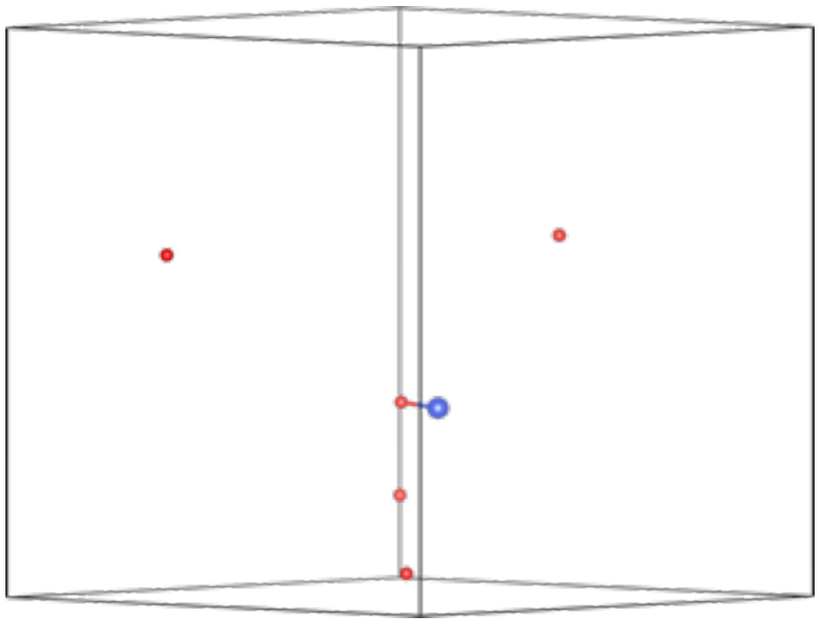


# symmetry in the solid state

Why? Simplification of crystal structures

***Consider the zeolite, "Faujasite" ($SiO_2$):***

640 atoms tile space infinitely, yet only 5 symmetry-independent atoms.

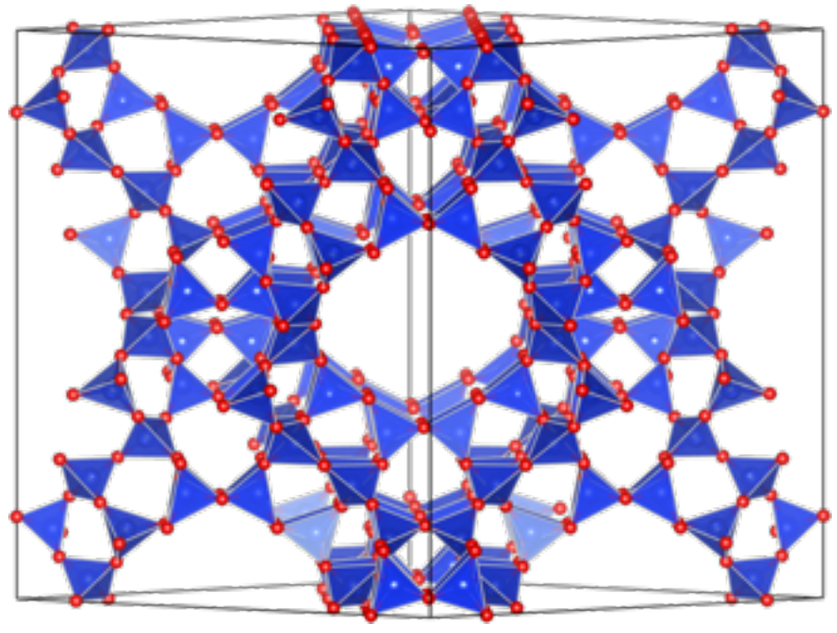


symmetry independent atoms
(5 atoms)

***symmetry operations***

$$\longrightarrow$$

$$Fd\bar{3}m$$



full unit cell
(640 atoms)

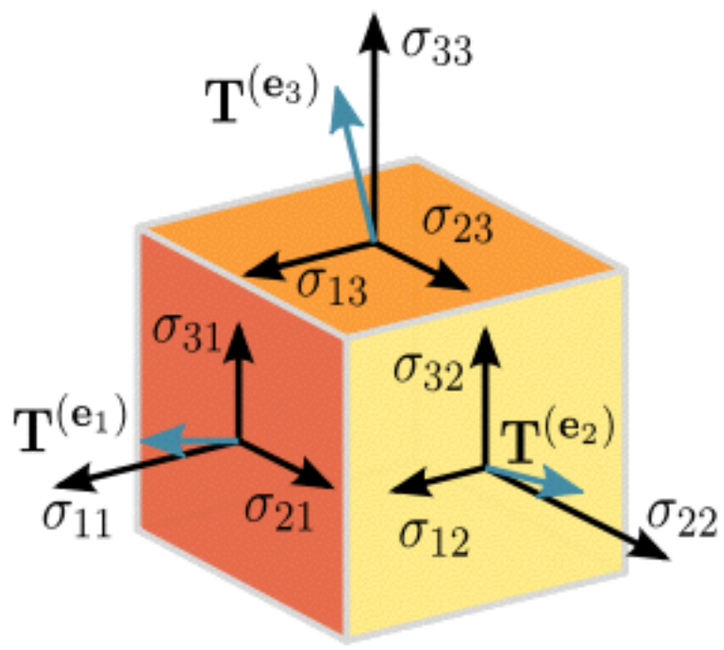
# symmetry in the solid state

Why? Simplification of crystal ~~structures~~ **properties**

Example: the Cauchy stress tensor (2nd order)

No symmetry:

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}$$




Tetragonal symmetry:

$$\sigma = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} = \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

# symmetry operations

- **32 point groups**
  - operations:
    - identity, rotations, mirrors, inversions, improper rotations
      - finite # of combinations (32)
- **in 3D, we also have translation operations**
  - introduces centering, screw axes and glide planes
  - centering: face centering (*F*), body centering (*I*), ***c***-centering (*C*)
- **230 space groups (three-dimensional crystals belong to a closed group)**

*I = Innenzentriert*

# incompatible operations

- **Only 2,3,4, and 6-fold rotation axes allowed in 3D.**

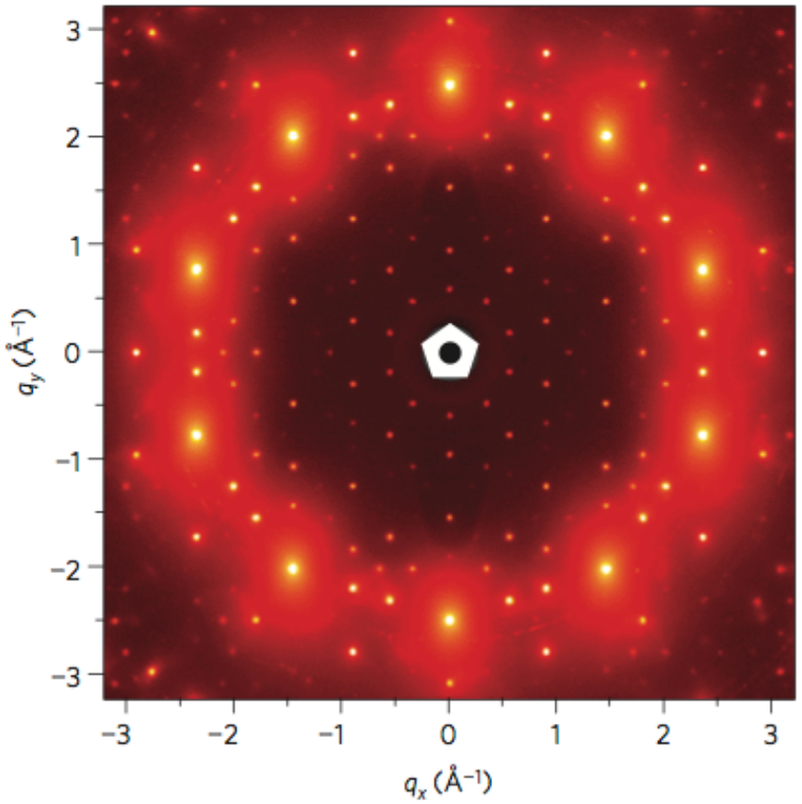
- Yet, 5-fold rotation axes are observed in diffraction patterns!

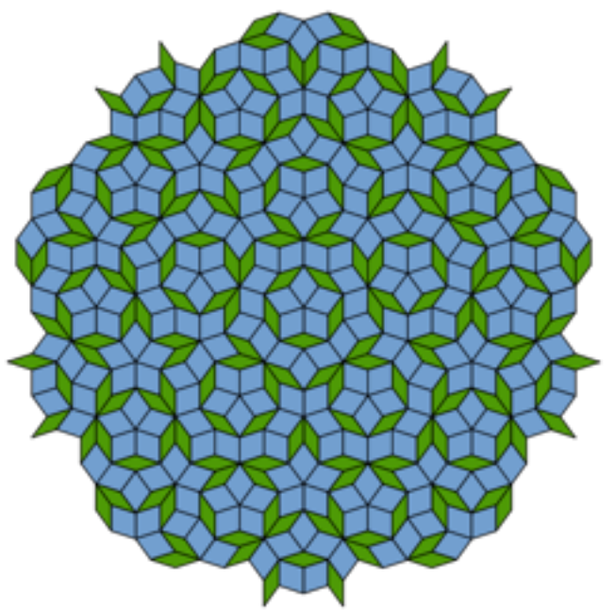
  - **quasicrystals**

  - short range order; no long range *translational* order (in 3D). Akin to a Penrose tiling

  - possess perfect periodicity in higher dimensions (4- to 6D!!)

    - incommensurate, superspace crystallography required



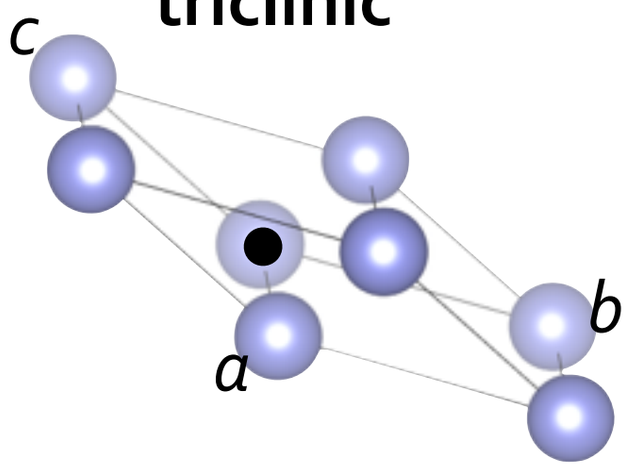



Takakura, Hiroyuki, et al. "Atomic structure of the binary icosahedral Yb–Cd quasicrystal." *Nature Materials* 6(1) 58-63 (2006).

# 7 unique crystal systems

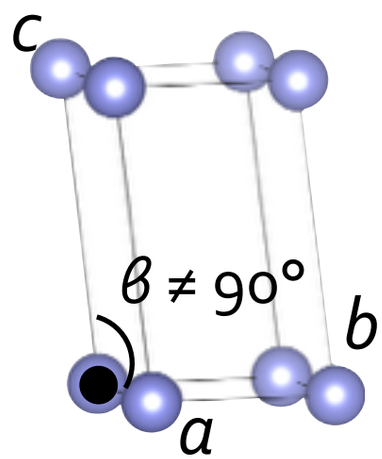
These are the possible parallelepipeds that tile space

**triclinic**



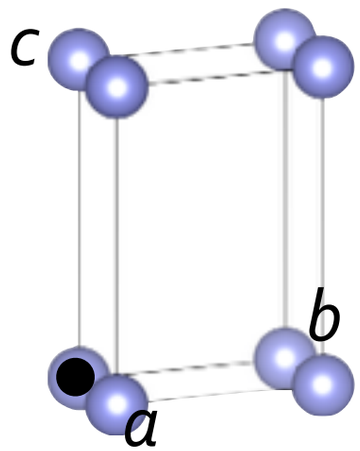

$[\alpha \neq \beta \neq \gamma] \neq 90°$

**monoclinic**



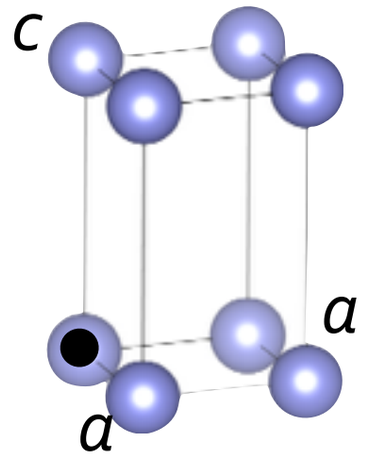

$\alpha = \gamma = 90°$

**orthorhombic**



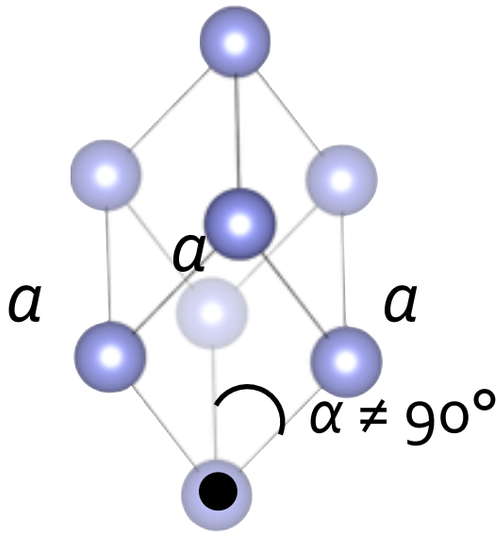

$\alpha = \beta = \gamma = 90°$

**tetragonal**

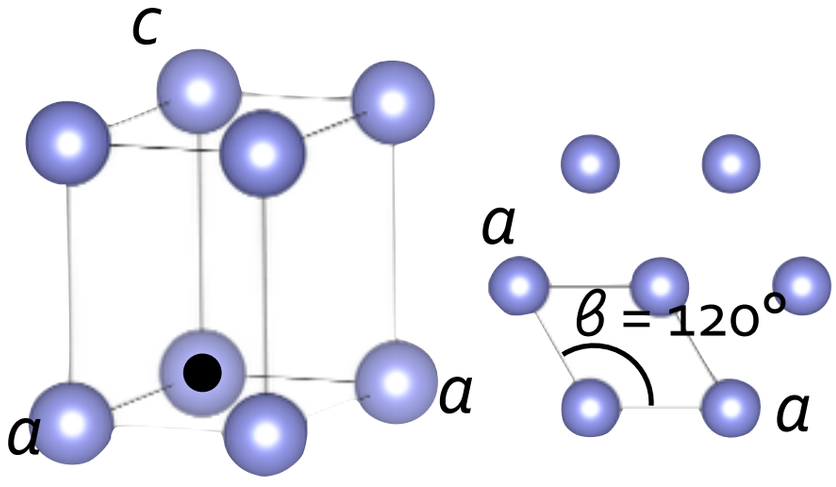



$\alpha = \beta = \gamma = 90°$

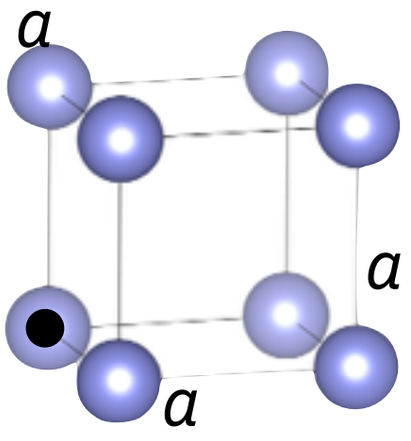
**rhombohedral**




**hexagonal**



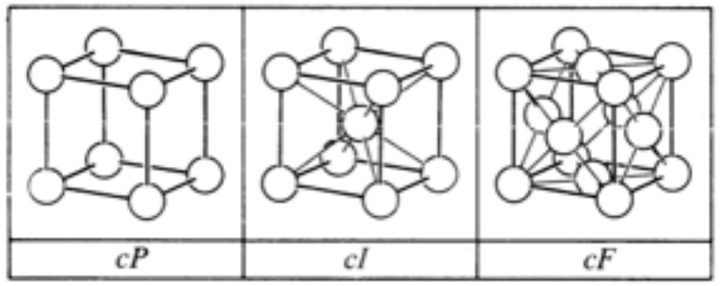

**cubic**



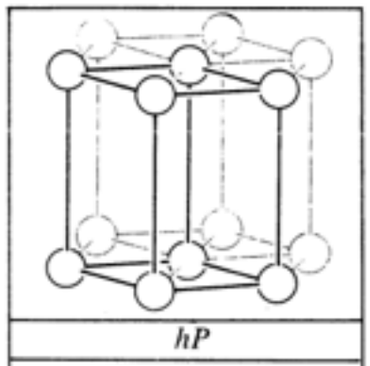

$\alpha = \beta = \gamma = 90°$

# symmetry in three dimensions:
# crystal systems (7) and **Bravais Lattices (14)**

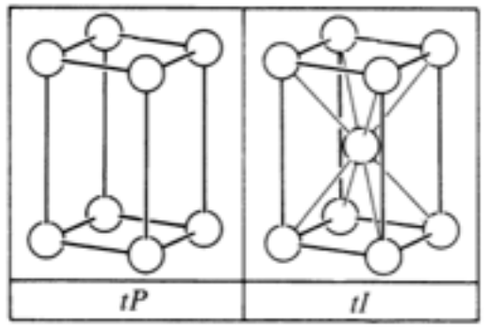
cubic



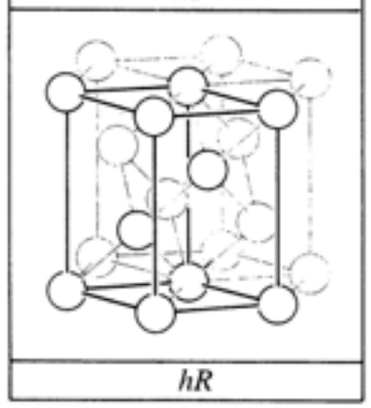

hexagonal



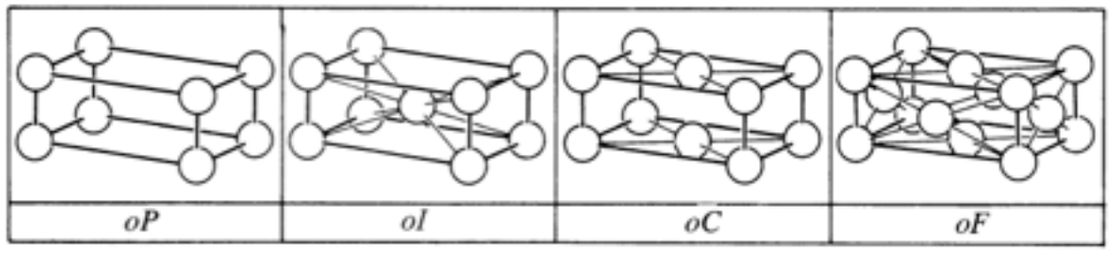

tetragonal



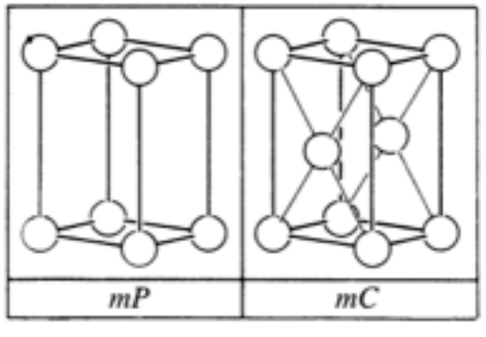

rhombohedral



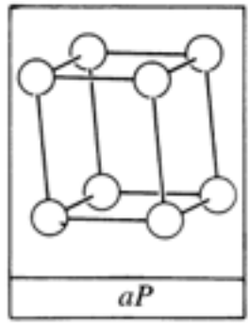

orthorhombic




monoclinic




triclinic



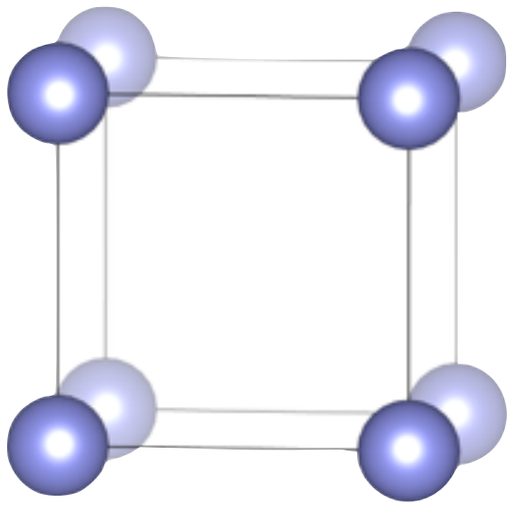

Bravais lattice: combine crystal systems and centering operations

International Tables of Crystallography, *Vol A*

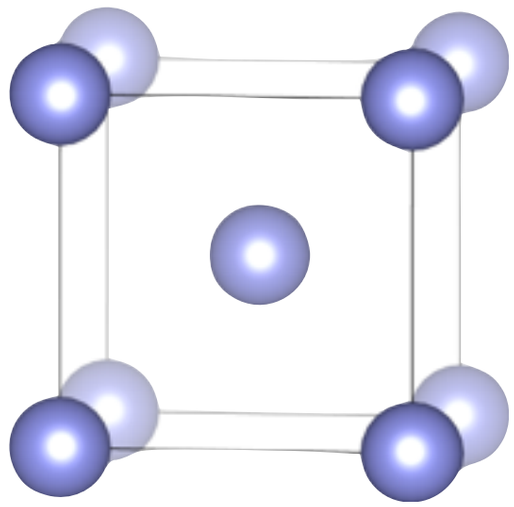
# symmetry in three dimensions: 7 crystal systems; 14 Bravais Lattices

| Crystal System | Bravais Lattices | Axial lengths and angles |
|---|---|---|
| cubic | *P, I, F* | $a = b = c;\ \alpha = \beta = \gamma = 90°$ |
| tetragonal | *P, I* | $a = b \neq c;\ \alpha = \beta = \gamma = 90°$ |
| orthorhombic | *P, I, C, F* | $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$ |
| trigonal | *P, R* | $a = b = c;\ \alpha = \beta = \gamma \neq 90°$ |
| hexagonal | *P* | $a = b \neq c;\ \alpha = \beta = 90°, \gamma = 120°$ |
| monoclinic | *P, C* | $a \neq b \neq c;\ \alpha = \gamma = 90°, \beta \neq 90°$ |
| triclinic | *P* | $a \neq b \neq c;\ [\alpha \neq \beta \neq \gamma] \neq 90°$ |

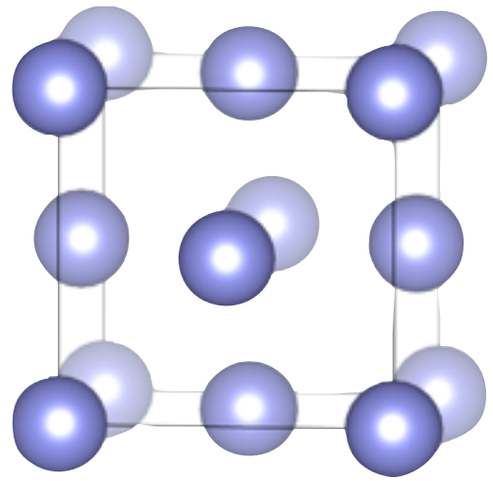
# common structures of the elements



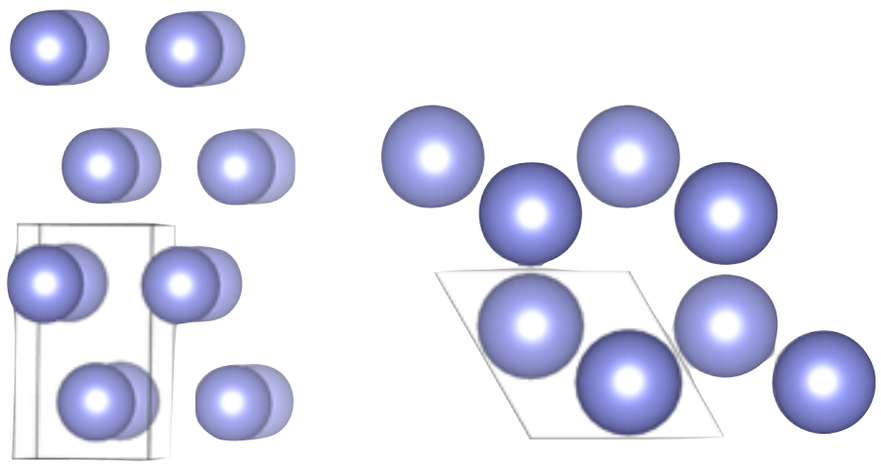
simple cubic: α-Po



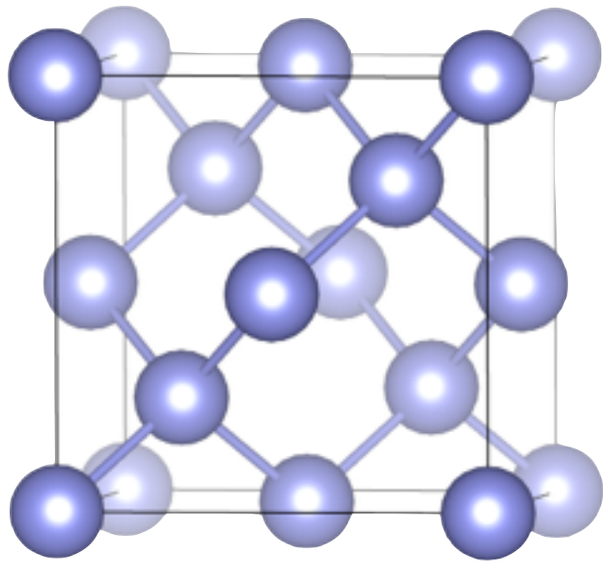
body-centered cubic: α-Fe



face-centered cubic: Cu

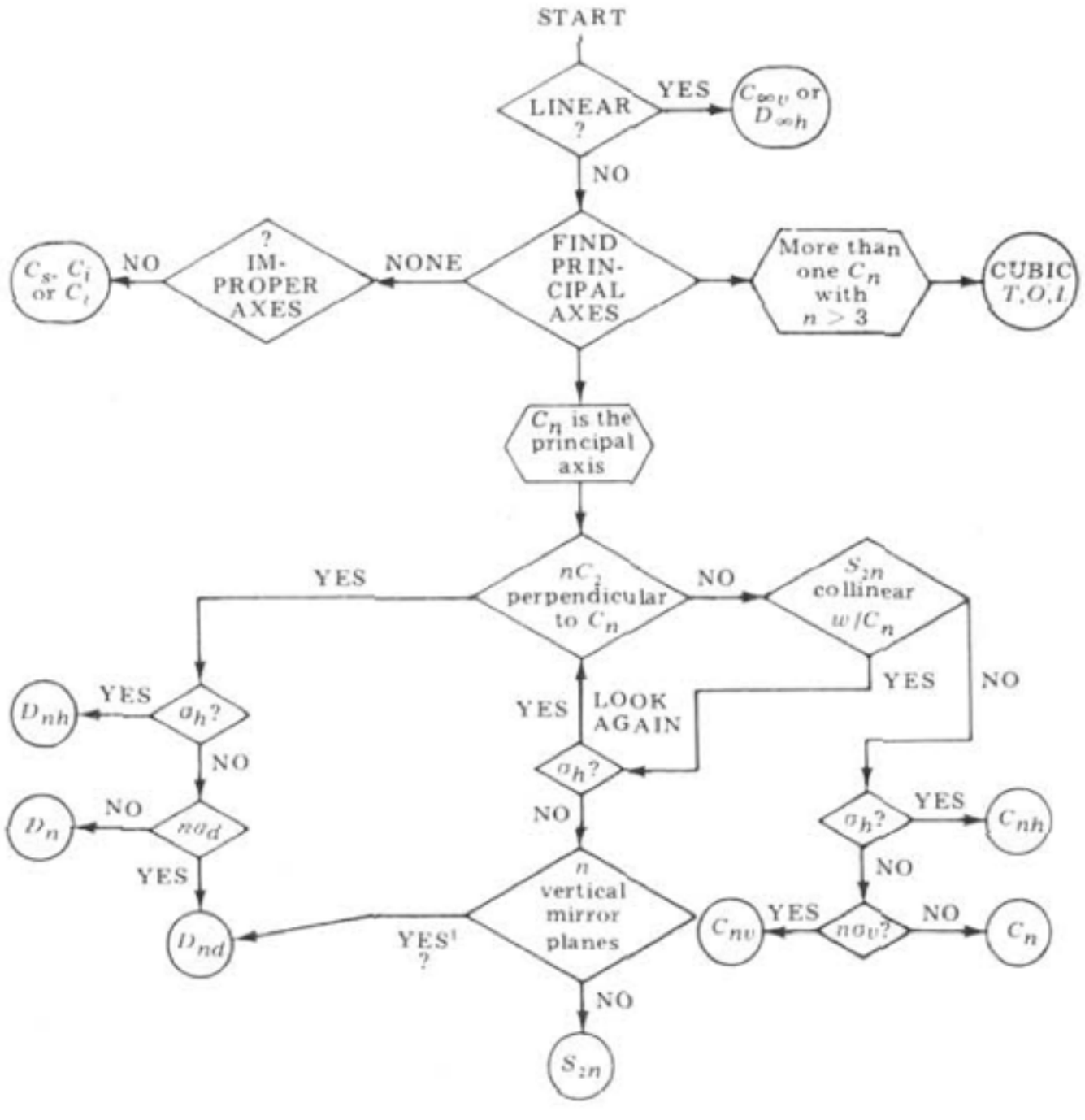


hexagonal-close-packed: Mg



diamond lattice: C, Si

# point group identification




"Flow chart for identification of Schoenfliess point groups." *J. Chem. Ed.*, 53, 3 (1976): 190.

# plane group identification

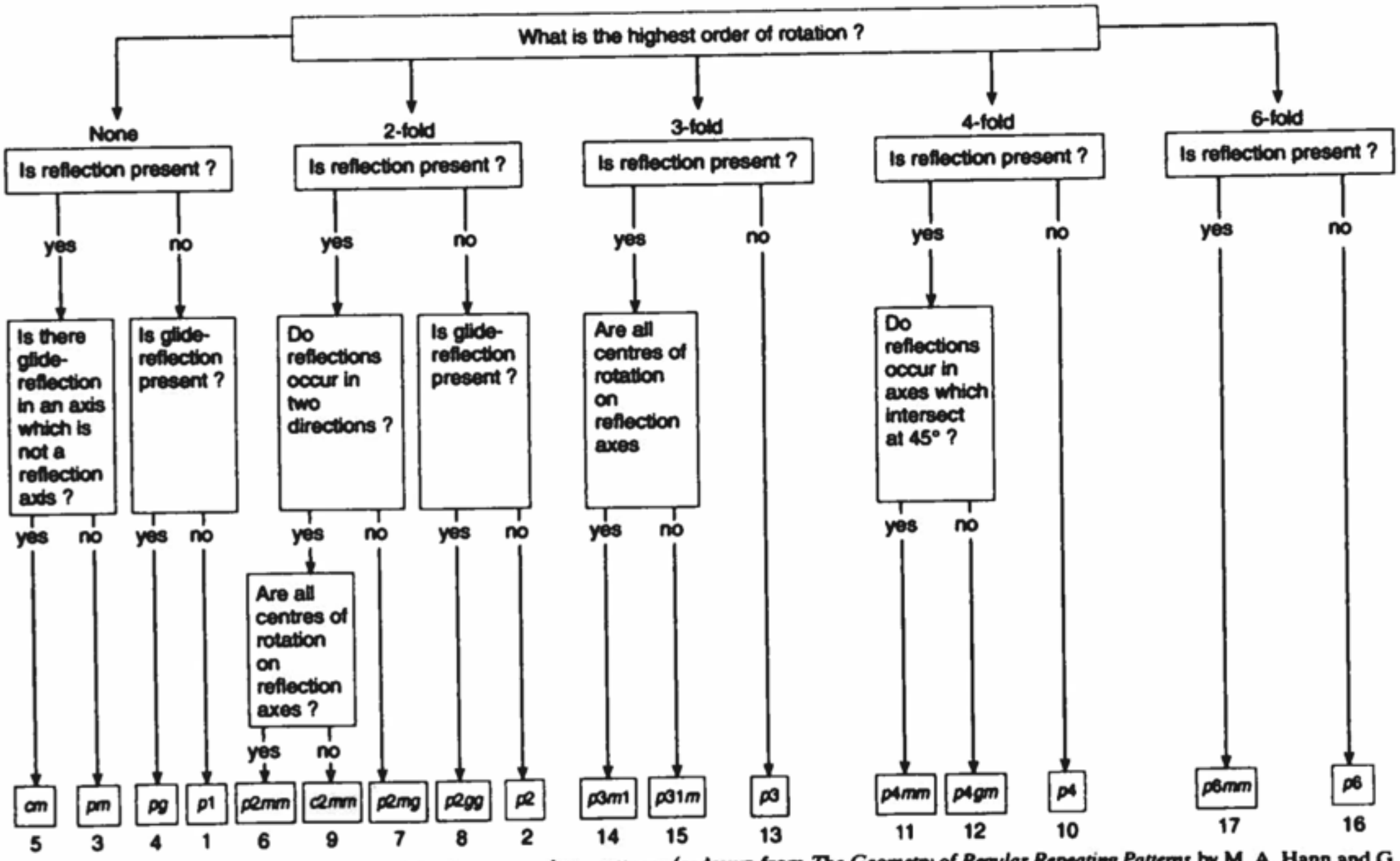
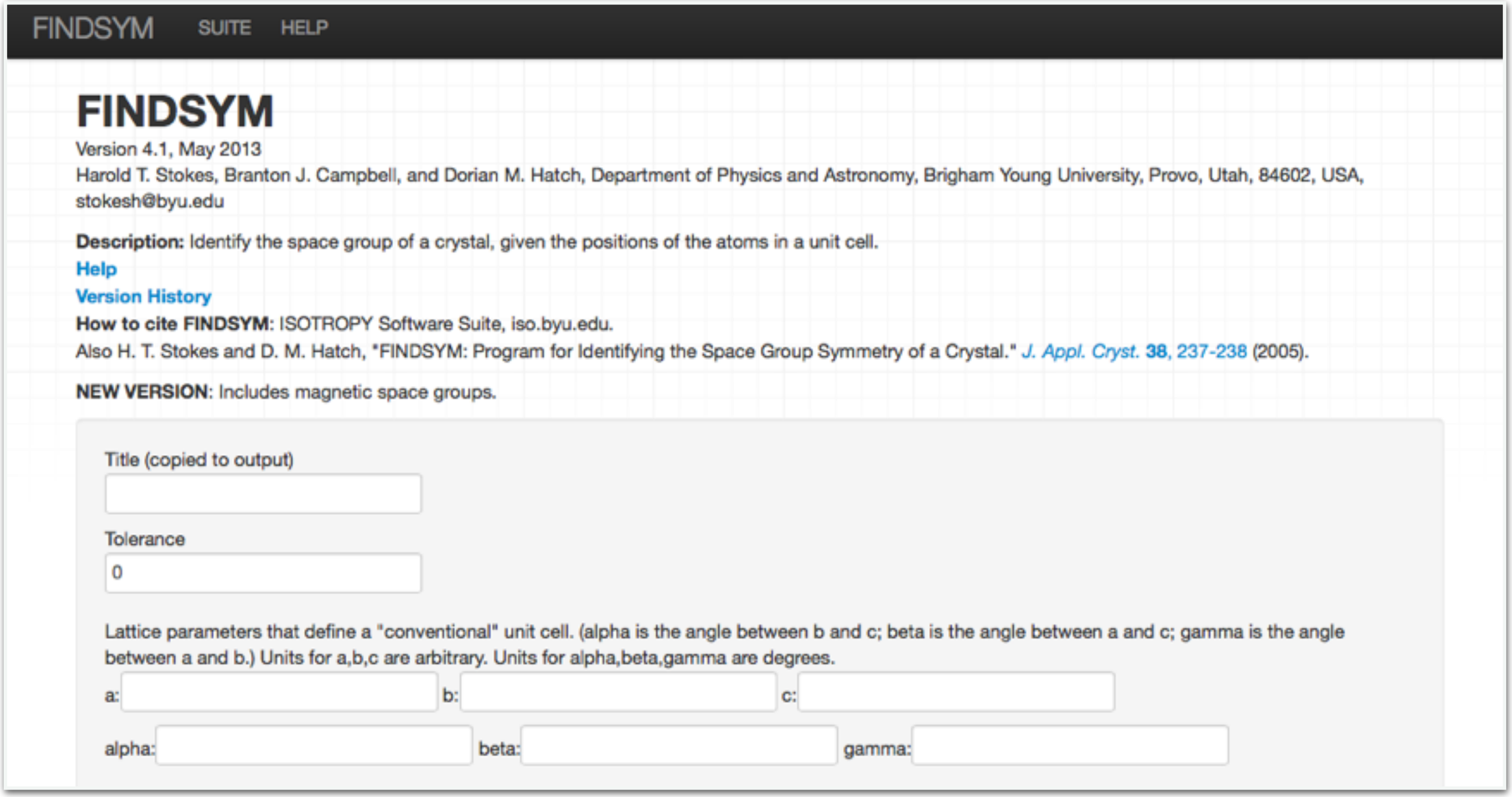



**Fig. 2.8.** Flow diagram for identifying one of the seventeen plane patterns (redrawn from *The Geometry of Regular Repeating Patterns* by M. A. Hann and G. M. Thomson, the Textile Institute, Manchester, 1992). The numbering is that which is arbitrarily assigned in the International Tables (see Fig 2.6).

# space group identification

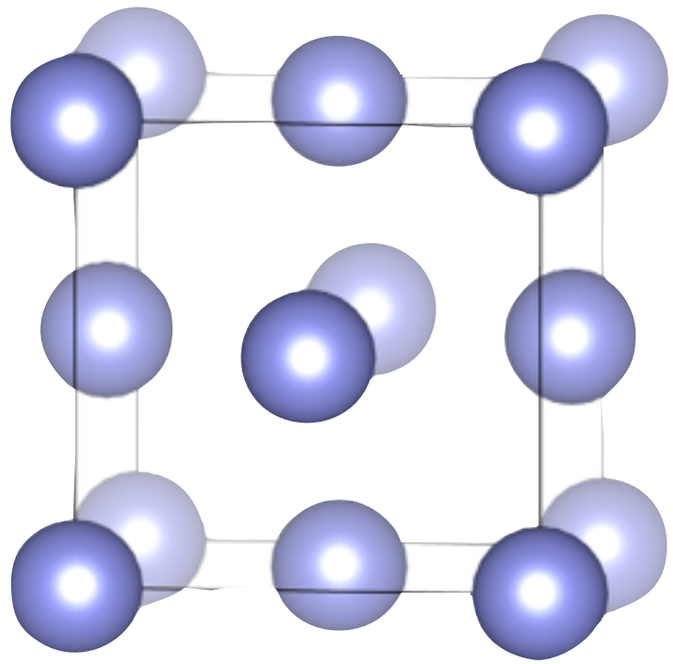



*(use a computer)*

http://stokes.byu.edu/iso/findsym.php

# Let's build a structure

face-centered cubic: Cu
Cubic, $a$ = 3.60 Å
Space-group: 225 $Fm\bar{3}m$



| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | 0 | 0 | 0 |

*(fractional coordinates)*

We only describe the symmetry inequivalent atoms;
let symmetry do the rest.

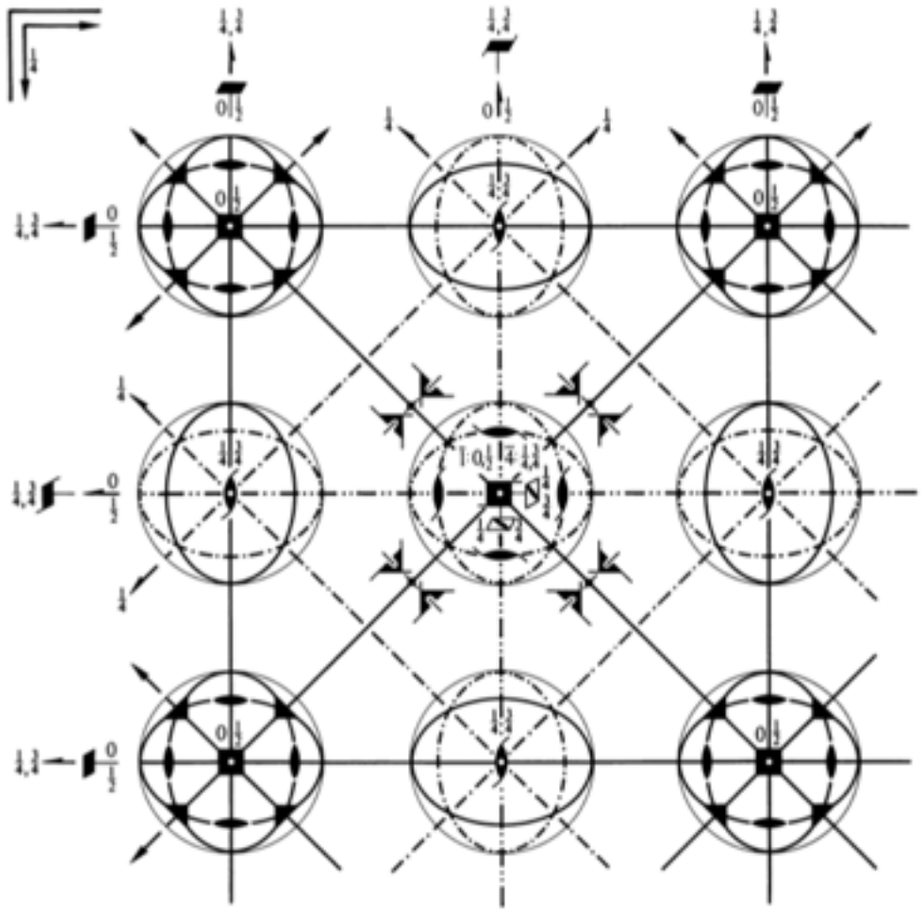
**How many atoms are in a face-centered cubic, close-packed unit cell?**

# Consulting the Int'l Tables of Crystall.

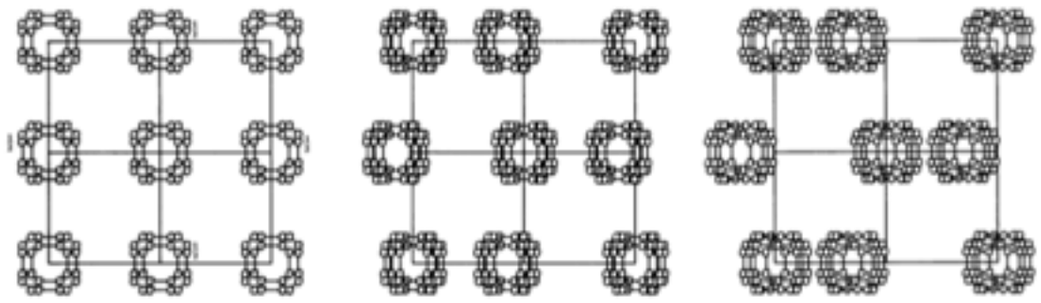
*International Tables for Crystallography* (2006). Vol. A, Space group 225, pp. 688–691.

$F\,m\bar{3}\,m$ $O_h^5$ $m\bar{3}\,m$ Cubic

No. 225 $F\ 4/m\ \bar{3}\ 2/m$ Patterson symmetry $F\,m\bar{3}\,m$



Upper left quadrant only

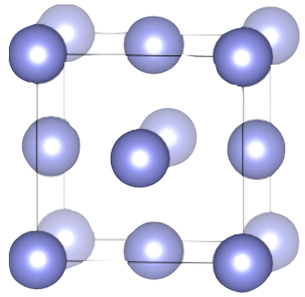


**Positions**

| Multiplicity, Wyckoff letter, Site symmetry | Coordinates | | | | Reflection conditions |
|---|---|---|---|---|---|
| | $(0,0,0)+$ | $(0,\frac{1}{2},\frac{1}{2})+$ | $(\frac{1}{2},0,\frac{1}{2})+$ | $(\frac{1}{2},\frac{1}{2},0)+$ | |
| 192 $l$ 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{x},y,\bar{z}$ | (4) $x,\bar{y},\bar{z}$ | $h,k,l$ permutable |
| | (5) $z,x,y$ | (6) $z,\bar{x},\bar{y}$ | (7) $\bar{z},\bar{x},y$ | (8) $\bar{z},x,\bar{y}$ | General: |
| | (9) $y,z,x$ | (10) $\bar{y},z,\bar{x}$ | (11) $y,\bar{z},\bar{x}$ | (12) $\bar{y},\bar{z},x$ | $hkl$ : $h+k,h+l,k+l=2n$ |
| | (13) $y,x,\bar{z}$ | (14) $\bar{y},\bar{x},\bar{z}$ | (15) $y,\bar{x},z$ | (16) $\bar{y},x,z$ | $0kl$ : $k,l=2n$ |
| | (17) $x,z,\bar{y}$ | (18) $\bar{x},z,y$ | (19) $\bar{x},\bar{z},\bar{y}$ | (20) $x,\bar{z},y$ | $hhl$ : $h+l=2n$ |
| | (21) $z,y,\bar{x}$ | (22) $z,\bar{y},x$ | (23) $\bar{z},y,x$ | (24) $\bar{z},\bar{y},\bar{x}$ | $h00$ : $h=2n$ |
| | (25) $\bar{x},\bar{y},\bar{z}$ | (26) $x,y,\bar{z}$ | (27) $x,\bar{y},z$ | (28) $\bar{x},y,z$ | |
| | (29) $\bar{z},\bar{x},\bar{y}$ | (30) $\bar{z},x,y$ | (31) $z,x,\bar{y}$ | (32) $z,\bar{x},y$ | |
| | (33) $\bar{y},\bar{z},\bar{x}$ | (34) $y,\bar{z},x$ | (35) $\bar{y},z,x$ | (36) $y,z,\bar{x}$ | |
| | (37) $\bar{y},\bar{x},z$ | (38) $y,x,z$ | (39) $\bar{y},x,\bar{z}$ | (40) $y,\bar{x},\bar{z}$ | |
| | (41) $\bar{x},\bar{z},y$ | (42) $x,\bar{z},\bar{y}$ | (43) $x,z,y$ | (44) $\bar{x},z,\bar{y}$ | |
| | (45) $\bar{z},\bar{y},x$ | (46) $\bar{z},y,\bar{x}$ | (47) $z,\bar{y},\bar{x}$ | (48) $z,y,x$ | |
| | | | | | Special: as above, plus |
| 96 $k$ . . $m$ | $x,x,z$ $\bar{z},\bar{x},x$ $x,x,\bar{z}$ $\bar{x},\bar{z},\bar{x}$ | $\bar{x},\bar{x},z$ $\bar{z},x,\bar{x}$ $\bar{x},\bar{x},\bar{z}$ $x,\bar{z},x$ | $\bar{x},x,\bar{z}$ $x,z,x$ $x,\bar{x},z$ $z,x,\bar{x}$ | $x,\bar{x},\bar{z}$ $\bar{x},z,\bar{x}$ $\bar{x},x,z$ $z,\bar{x},x$ | $z,x,x$ $x,\bar{z},\bar{x}$ $x,z,\bar{x}$ $\bar{z},x,x$ | $z,\bar{x},\bar{x}$ $\bar{x},\bar{z},x$ $\bar{x},z,x$ $\bar{z},\bar{x},\bar{x}$ | no extra conditions |
| 96 $j$ $m$ . . | $0,y,z$ $\bar{z},0,y$ $y,0,\bar{z}$ $0,\bar{z},\bar{y}$ | $0,\bar{y},z$ $\bar{z},0,\bar{y}$ $\bar{y},0,\bar{z}$ $0,\bar{z},y$ | $0,y,\bar{z}$ $y,z,0$ $y,0,z$ $z,y,0$ | $0,\bar{y},\bar{z}$ $\bar{y},z,0$ $\bar{y},0,z$ $z,\bar{y},0$ | $z,0,y$ $y,\bar{z},0$ $0,z,\bar{y}$ $\bar{z},y,0$ | $z,0,\bar{y}$ $\bar{y},\bar{z},0$ $0,z,y$ $\bar{z},\bar{y},0$ | no extra conditions |
| 48 $i$ $m$ . $m2$ | $\frac{1}{2},y,y$ $\bar{y},\frac{1}{2},y$ | $\frac{1}{2},\bar{y},y$ $\bar{y},\frac{1}{2},\bar{y}$ | $\frac{1}{2},y,\bar{y}$ $y,y,\frac{1}{2}$ | $\frac{1}{2},\bar{y},\bar{y}$ $\bar{y},y,\frac{1}{2}$ | $y,\frac{1}{2},y$ $y,\bar{y},\frac{1}{2}$ | $y,\frac{1}{2},\bar{y}$ $\bar{y},\bar{y},\frac{1}{2}$ | no extra conditions |
| 48 $h$ $m$ . $m2$ | $0,y,y$ $\bar{y},0,y$ | $0,\bar{y},y$ $\bar{y},0,\bar{y}$ | $0,y,\bar{y}$ $y,y,0$ | $0,\bar{y},\bar{y}$ $\bar{y},y,0$ | $y,0,y$ $y,\bar{y},0$ | $y,0,\bar{y}$ $\bar{y},\bar{y},0$ | no extra conditions |
| 48 $g$ 2 . $mm$ | $x,\frac{1}{4},\frac{1}{4}$ $\frac{1}{4},x,\frac{3}{4}$ | $\bar{x},\frac{3}{4},\frac{1}{4}$ $\frac{3}{4},\bar{x},\frac{3}{4}$ | $\frac{1}{4},x,\frac{1}{4}$ $x,\frac{1}{4},\frac{3}{4}$ | $\frac{1}{4},\bar{x},\frac{3}{4}$ $\bar{x},\frac{1}{4},\frac{1}{4}$ | $\frac{1}{4},\frac{1}{4},x$ $\frac{1}{4},\frac{1}{4},\bar{x}$ | $\frac{3}{4},\frac{1}{4},\bar{x}$ $\frac{1}{4},\frac{3}{4},x$ | $hkl$ : $h=2n$ |
| 32 $f$ . 3 $m$ | $x,x,x$ $x,x,\bar{x}$ | $\bar{x},\bar{x},x$ $\bar{x},\bar{x},\bar{x}$ | $\bar{x},x,\bar{x}$ $x,\bar{x},x$ | $x,\bar{x},\bar{x}$ $\bar{x},x,x$ | | | no extra conditions |
| 24 $e$ 4 $m$ . $m$ | $x,0,0$ | $\bar{x},0,0$ | $0,x,0$ | $0,\bar{x},0$ | $0,0,x$ | $0,0,\bar{x}$ | no extra conditions |
| 24 $d$ $m$ . $mm$ | $0,\frac{1}{4},\frac{1}{4}$ | $0,\frac{3}{4},\frac{1}{4}$ | $\frac{1}{4},0,\frac{1}{4}$ | $\frac{1}{4},0,\frac{3}{4}$ | $\frac{1}{4},\frac{1}{4},0$ | $\frac{3}{4},\frac{1}{4},0$ | $hkl$ : $h=2n$ |
| 8 $c$ $\bar{4}$ 3 $m$ | $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ | $\frac{1}{4},\frac{1}{4},\frac{3}{4}$ | | | | | $hkl$ : $h=2n$ |
| 4 $b$ $m\bar{3}m$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | | | | | | no extra conditions |
| 4 $a$ $m\bar{3}m$ | $0,0,0$ | | | | | | no extra conditions |

face centering operations

our 1 symm. inequiv. atom



Symmetry inequivalent atoms:

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu | 0 | 0 | 0 |

Multiplicity: **4** *(face centering)*

All atoms:

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu1 | 0 | 0 | 0 |
| Cu2 | 0 | 0.5 | 0.5 |
| Cu3 | 0.5 | 0 | 0.5 |
| Cu4 | 0.5 | 0.5 | 0 |

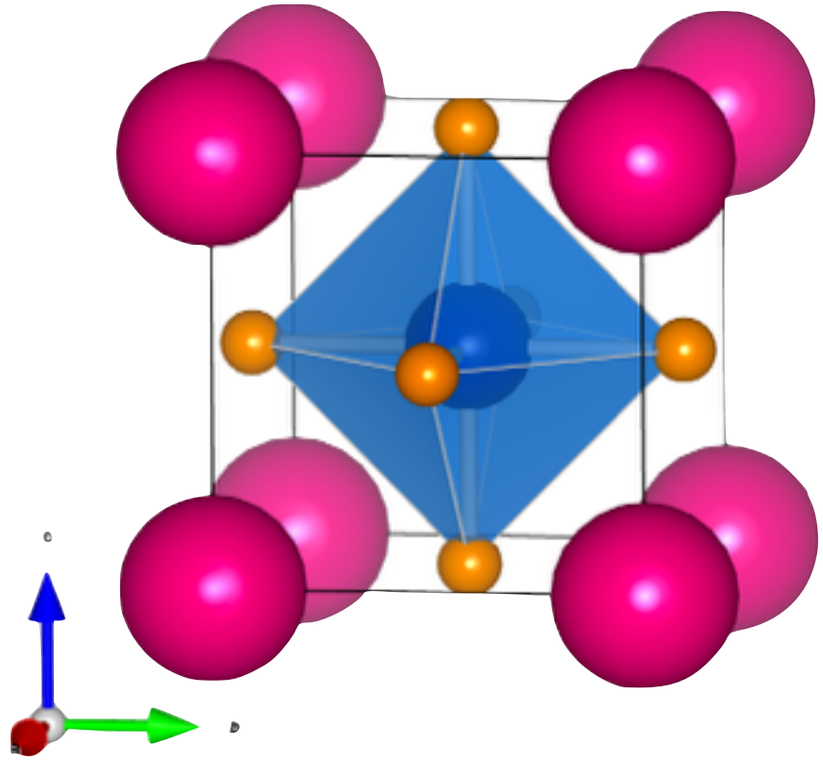
Now we have all 4 atoms

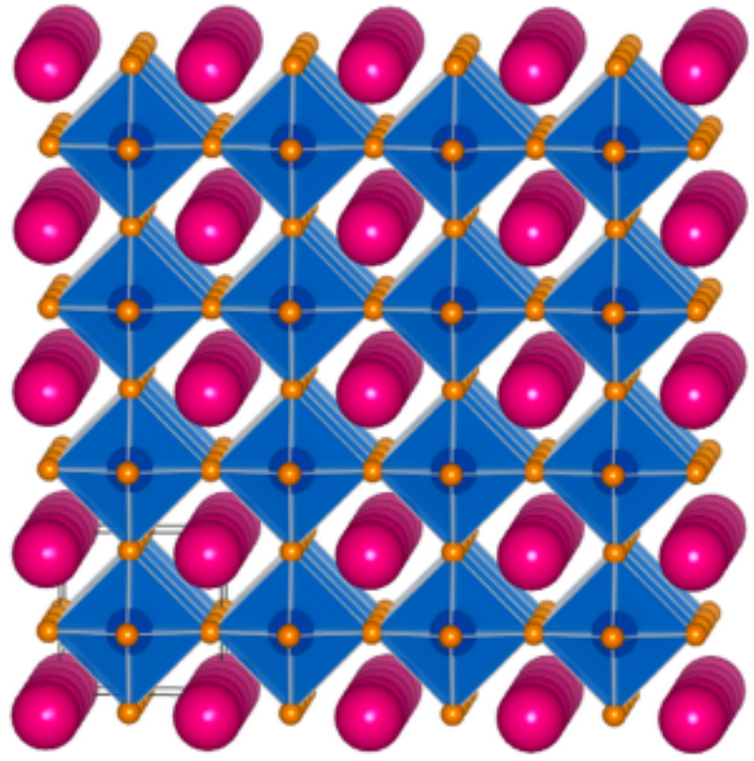
# Let's build another structure: a perovskite!

General formula: $ABX_3$

Primitive cubic: $SrTiO_3$
Cubic, $a$ = 4.00 Å
Space-group: **221** $Pm\bar{3}m$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sr | 0 | 0 | 0 |
| Ti | 0.5 | 0.5 | 0.5 |
| O | 0.5 | 0.5 | 0 |





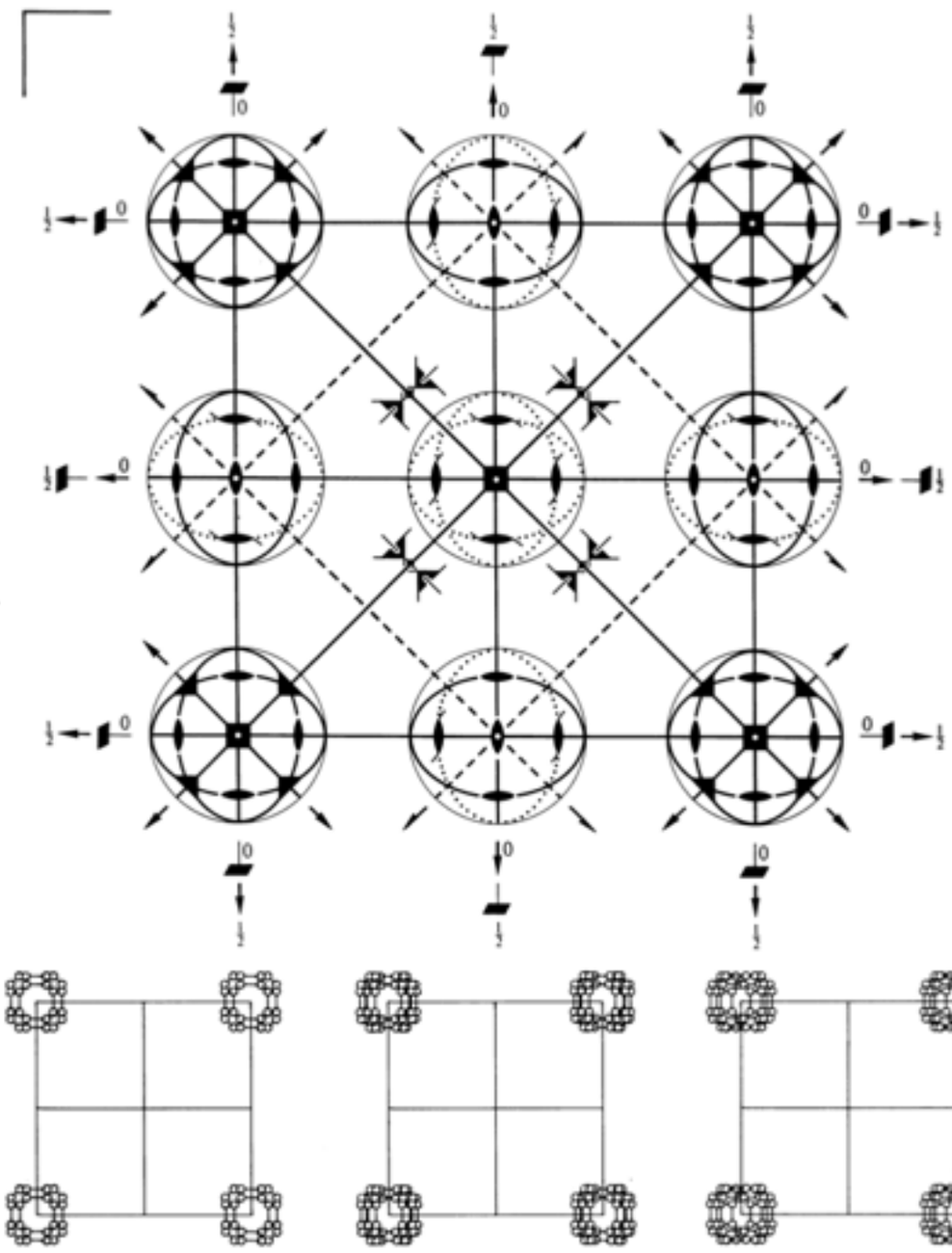
Corner-linked $TiO_6$ octahedra

# Consulting the Int'l Tables of Crystall.

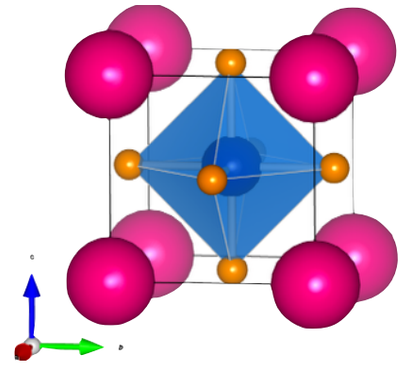
*International Tables for Crystallography* (2006). Vol. A, Space group 221, pp. 672–674.

$Pm\bar{3}m$ $O_h^1$ $m\bar{3}m$ Cubic

No. 221 $P\ 4/m\ \bar{3}\ 2/m$ Patterson symmetry $Pm\bar{3}m$



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 48 | *n* | 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{x},y,\bar{z}$ | (4) $x,\bar{y},\bar{z}$ | | no conditions |
| | | | (5) $z,x,y$ | (6) $z,\bar{x},\bar{y}$ | (7) $\bar{z},\bar{x},y$ | (8) $\bar{z},x,\bar{y}$ | | |
| | | | (9) $y,z,x$ | (10) $\bar{y},z,\bar{x}$ | (11) $y,\bar{z},\bar{x}$ | (12) $\bar{y},\bar{z},x$ | | |
| | | | (13) $y,x,\bar{z}$ | (14) $\bar{y},\bar{x},\bar{z}$ | (15) $y,\bar{x},z$ | (16) $\bar{y},x,z$ | | |
| | | | (17) $x,z,\bar{y}$ | (18) $\bar{x},z,y$ | (19) $\bar{x},\bar{z},\bar{y}$ | (20) $x,\bar{z},y$ | | |
| | | | (21) $z,y,\bar{x}$ | (22) $z,\bar{y},x$ | (23) $\bar{z},y,x$ | (24) $\bar{z},\bar{y},\bar{x}$ | | |
| | | | (25) $\bar{x},\bar{y},\bar{z}$ | (26) $x,y,\bar{z}$ | (27) $x,\bar{y},z$ | (28) $\bar{x},y,z$ | | |
| | | | (29) $\bar{z},\bar{x},\bar{y}$ | (30) $\bar{z},x,y$ | (31) $z,x,\bar{y}$ | (32) $z,\bar{x},y$ | | |
| | | | (33) $\bar{y},\bar{z},\bar{x}$ | (34) $y,\bar{z},x$ | (35) $\bar{y},z,x$ | (36) $y,z,\bar{x}$ | | |
| | | | (37) $\bar{y},\bar{x},z$ | (38) $y,x,z$ | (39) $\bar{y},x,\bar{z}$ | (40) $y,\bar{x},\bar{z}$ | | |
| | | | (41) $\bar{x},\bar{z},y$ | (42) $x,\bar{z},\bar{y}$ | (43) $x,z,y$ | (44) $\bar{x},z,\bar{y}$ | | |
| | | | (45) $\bar{z},\bar{y},x$ | (46) $\bar{z},y,\bar{x}$ | (47) $z,\bar{y},\bar{x}$ | (48) $z,y,x$ | | |
| | | | | | | | | Special: no extra conditions |
| 24 | *m* | . . *m* | $x,x,z$ | $\bar{x},\bar{x},z$ | $\bar{x},x,\bar{z}$ | $x,\bar{x},\bar{z}$ | $z,x,x$ | $z,\bar{x},\bar{x}$ |
| | | | $\bar{z},\bar{x},x$ | $\bar{z},x,\bar{x}$ | $x,z,x$ | $\bar{x},\bar{z},x$ | $x,\bar{z},\bar{x}$ | $\bar{x},z,x$ |
| | | | $x,x,\bar{z}$ | $\bar{x},\bar{x},\bar{z}$ | $x,\bar{x},z$ | $\bar{x},x,z$ | $x,z,\bar{x}$ | $\bar{x},z,x$ |
| | | | $\bar{x},\bar{z},\bar{x}$ | $x,\bar{z},x$ | $z,x,\bar{x}$ | $z,\bar{x},x$ | $\bar{z},x,x$ | $\bar{z},\bar{x},\bar{x}$ |
| 24 | *l* | *m* . . | $\frac{1}{2},y,z$ | $\frac{1}{2},\bar{y},z$ | $\frac{1}{2},y,\bar{z}$ | $\frac{1}{2},\bar{y},\bar{z}$ | $z,\frac{1}{2},y$ | $z,\frac{1}{2},\bar{y}$ |
| | | | $\bar{z},\frac{1}{2},y$ | $\bar{z},\frac{1}{2},\bar{y}$ | $y,z,\frac{1}{2}$ | $\bar{y},z,\frac{1}{2}$ | $y,\bar{z},\frac{1}{2}$ | $\bar{y},\bar{z},\frac{1}{2}$ |
| | | | $y,\frac{1}{2},\bar{z}$ | $\bar{y},\frac{1}{2},\bar{z}$ | $y,\frac{1}{2},z$ | $\bar{y},\frac{1}{2},z$ | $\frac{1}{2},z,\bar{y}$ | $\frac{1}{2},z,y$ |
| | | | $\frac{1}{2},\bar{z},\bar{y}$ | $\frac{1}{2},\bar{z},y$ | $z,y,\frac{1}{2}$ | $z,\bar{y},\frac{1}{2}$ | $\bar{z},y,\frac{1}{2}$ | $\bar{z},\bar{y},\frac{1}{2}$ |
| 24 | *k* | *m* . . | $0,y,z$ | $0,\bar{y},z$ | $0,y,\bar{z}$ | $0,\bar{y},\bar{z}$ | $z,0,y$ | $z,0,\bar{y}$ |
| | | | $\bar{z},0,y$ | $\bar{z},0,\bar{y}$ | $y,z,0$ | $\bar{y},z,0$ | $y,\bar{z},0$ | $\bar{y},\bar{z},0$ |
| | | | $y,0,\bar{z}$ | $\bar{y},0,\bar{z}$ | $y,0,z$ | $\bar{y},0,z$ | $0,z,\bar{y}$ | $0,z,y$ |
| | | | $0,\bar{z},\bar{y}$ | $0,\bar{z},y$ | $z,y,0$ | $z,\bar{y},0$ | $\bar{z},y,0$ | $\bar{z},\bar{y},0$ |
| 12 | *j* | *m* . *m*2 | $\frac{1}{2},y,y$ | $\frac{1}{2},\bar{y},y$ | $\frac{1}{2},y,\bar{y}$ | $\frac{1}{2},\bar{y},\bar{y}$ | $y,\frac{1}{2},y$ | $y,\frac{1}{2},\bar{y}$ |
| | | | $\bar{y},\frac{1}{2},y$ | $\bar{y},\frac{1}{2},\bar{y}$ | $y,y,\frac{1}{2}$ | $\bar{y},y,\frac{1}{2}$ | $y,\bar{y},\frac{1}{2}$ | $\bar{y},\bar{y},\frac{1}{2}$ |
| 12 | *i* | *m* . *m*2 | $0,y,y$ | $0,\bar{y},y$ | $0,y,\bar{y}$ | $0,\bar{y},\bar{y}$ | $y,0,y$ | $y,0,\bar{y}$ |
| | | | $\bar{y},0,y$ | $\bar{y},0,\bar{y}$ | $y,y,0$ | $\bar{y},y,0$ | $y,\bar{y},0$ | $\bar{y},\bar{y},0$ |
| 12 | *h* | *m m* 2 . . | $x,\frac{1}{2},0$ | $\bar{x},\frac{1}{2},0$ | $0,x,\frac{1}{2}$ | $0,\bar{x},\frac{1}{2}$ | $\frac{1}{2},0,x$ | $\frac{1}{2},0,\bar{x}$ |
| | | | $\frac{1}{2},x,0$ | $\frac{1}{2},\bar{x},0$ | $x,0,\frac{1}{2}$ | $\bar{x},0,\frac{1}{2}$ | $0,\frac{1}{2},\bar{x}$ | $0,\frac{1}{2},x$ |
| 8 | *g* | . 3 *m* | $x,x,x$ | $\bar{x},\bar{x},x$ | $\bar{x},x,\bar{x}$ | $x,\bar{x},\bar{x}$ | | |
| | | | $x,x,\bar{x}$ | $\bar{x},\bar{x},\bar{x}$ | $x,\bar{x},x$ | $\bar{x},x,x$ | | |
| 6 | *f* | 4 *m* . *m* | $x,\frac{1}{2},\frac{1}{2}$ | $\bar{x},\frac{1}{2},\frac{1}{2}$ | $\frac{1}{2},x,\frac{1}{2}$ | $\frac{1}{2},\bar{x},\frac{1}{2}$ | $\frac{1}{2},\frac{1}{2},x$ | $\frac{1}{2},\frac{1}{2},\bar{x}$ |
| 6 | *e* | 4 *m* . *m* | $x,0,0$ | $\bar{x},0,0$ | $0,x,0$ | $0,\bar{x},0$ | $0,0,x$ | $0,0,\bar{x}$ |
| 3 | *d* | 4/*m m* . *m* | $\frac{1}{2},0,0$ | $0,\frac{1}{2},0$ | $0,0,\frac{1}{2}$ | | | |
| 3 | *c* | 4/*m m* . *m* | $0,\frac{1}{2},\frac{1}{2}$ | $\frac{1}{2},0,\frac{1}{2}$ | $\frac{1}{2},\frac{1}{2},0$ | | | O(1), O(2), O(3) |
| 1 | *b* | *m* $\bar{3}$ *m* | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | | | | | Ti(1) |
| 1 | *a* | *m* $\bar{3}$ *m* | $0,0,0$ | | | | | Sr(1) |



Symmetry inequivalent atoms:

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sr | 0 | 0 | 0 |
| Ti | 0.5 | 0.5 | 0.5 |
| O | 0.5 | 0.5 | 0 |

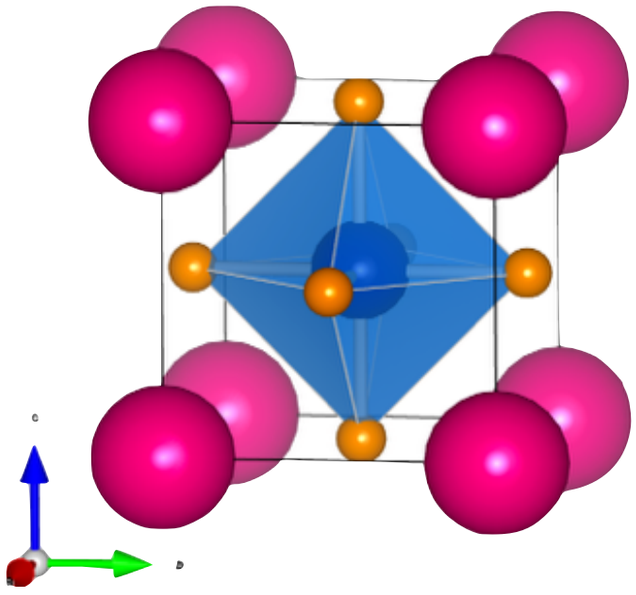
No centering operations

All atoms:

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sr1 | 0 | 0 | 0 |
| Ti1 | 0.5 | 0.5 | 0.5 |
| O1 | 0.5 | 0.5 | 0 |
| O2 | 0.5 | 0 | 0.5 |
| O3 | 0.5 | 0.5 | 0 |

# tiling with abandon...

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| **Sr1** | **0** | **0** | **0** |
| *Ti1* | *0.5* | *0.5* | *0.5* |
| **O1** | **0.5** | **0.5** | **0** |
| *O2* | *0.5* | *0* | *0.5* |
| **O3** | **0.5** | **0.5** | **0** |



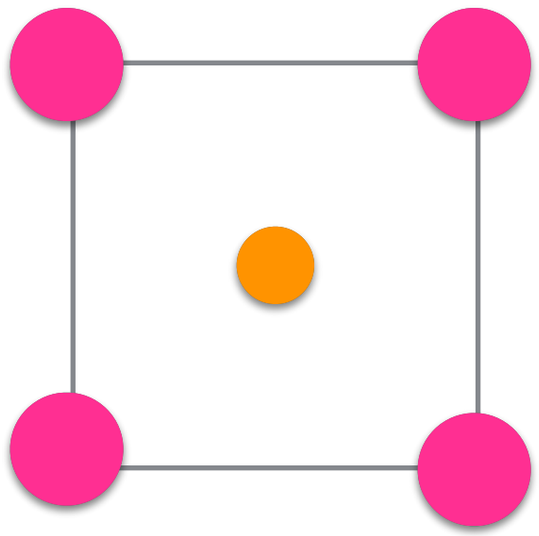
sanity check, coordination numbers:

O: 2

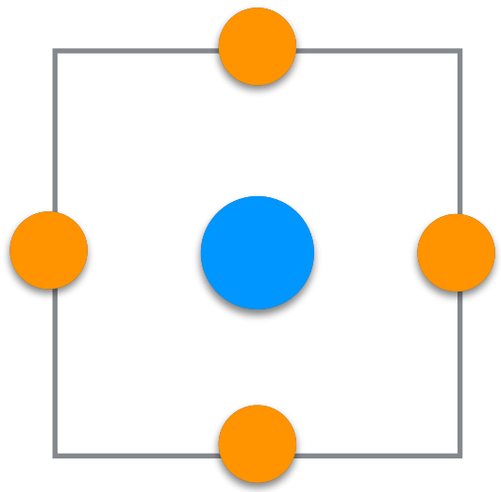
Ti: 6

Sr: 12

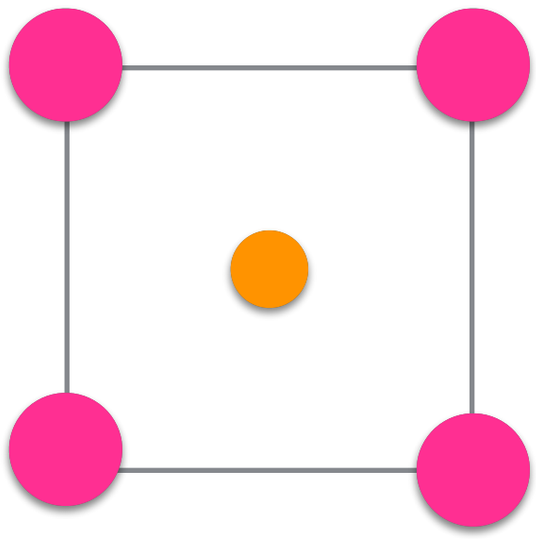
z = 0



z = 0.5



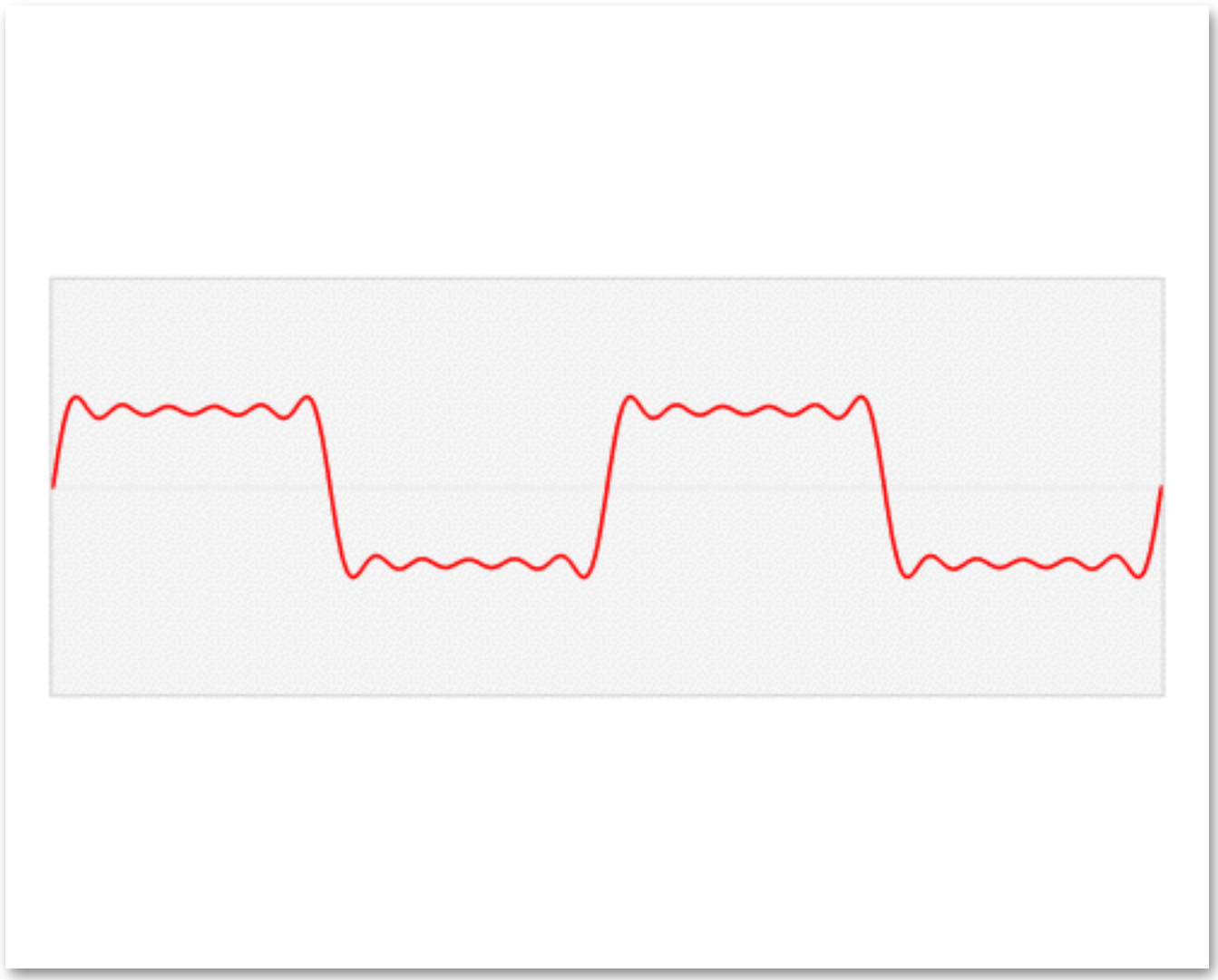
z = 1



entering into reciprocal space

# Fourier transforms

mathematical operations that identify repeating patterns



http://en.wikipedia.org/wiki/Fourier_transform

***Key:***

$f$

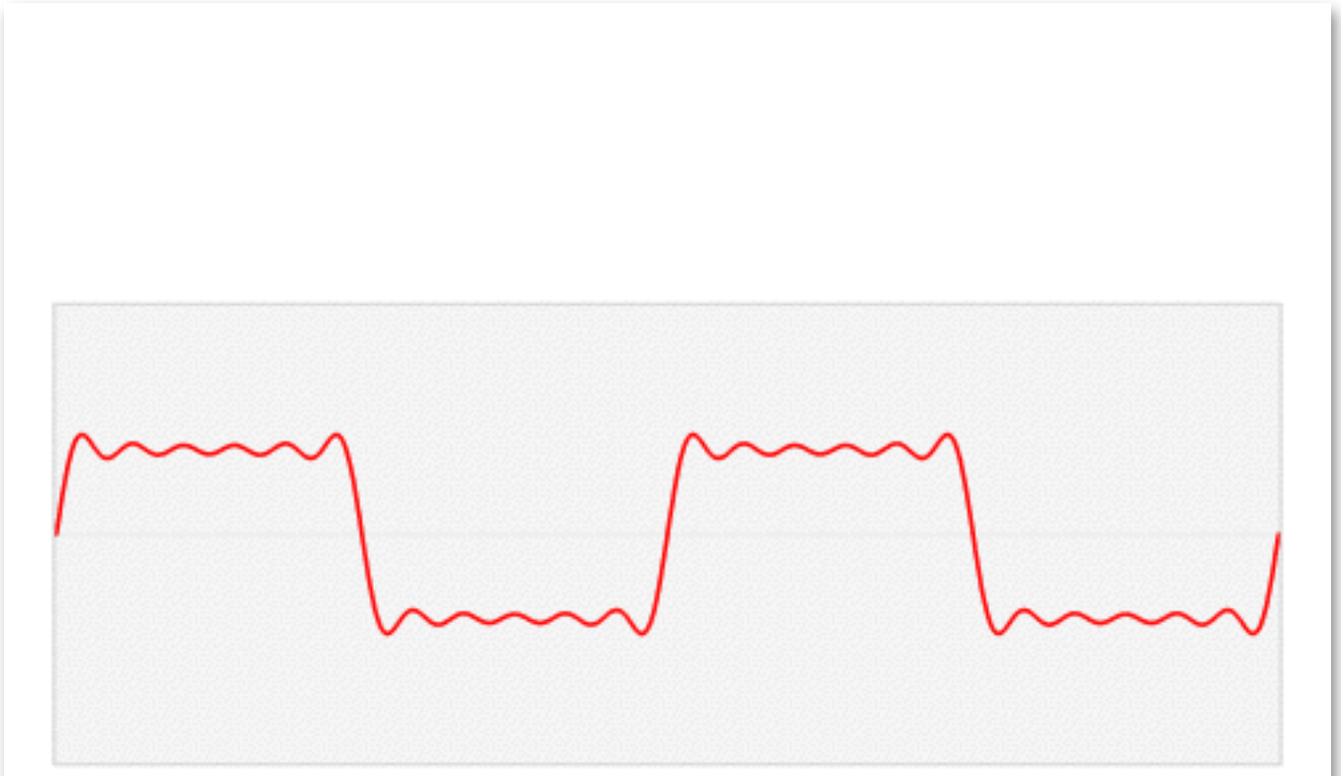
Original function
(direct space)

$\hat{f}$

Fourier transform
(reciprocal space)

# Fourier transforms

mathematical operations that identify repeating patterns



http://en.wikipedia.org/wiki/Fourier_transform

***Key:***

$$f(\mathbf{r}) = \int_{-\infty}^{\infty} \hat{f}(\mathbf{q}) e^{2\pi i \mathbf{q}\cdot\mathbf{r}} d\mathbf{q}$$

Inverse transform
(direct space)

$$\hat{f}(\mathbf{q}) = \int_{-\infty}^{\infty} f(\mathbf{r}) e^{-2\pi i \mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

Fourier transform
(reciprocal space)

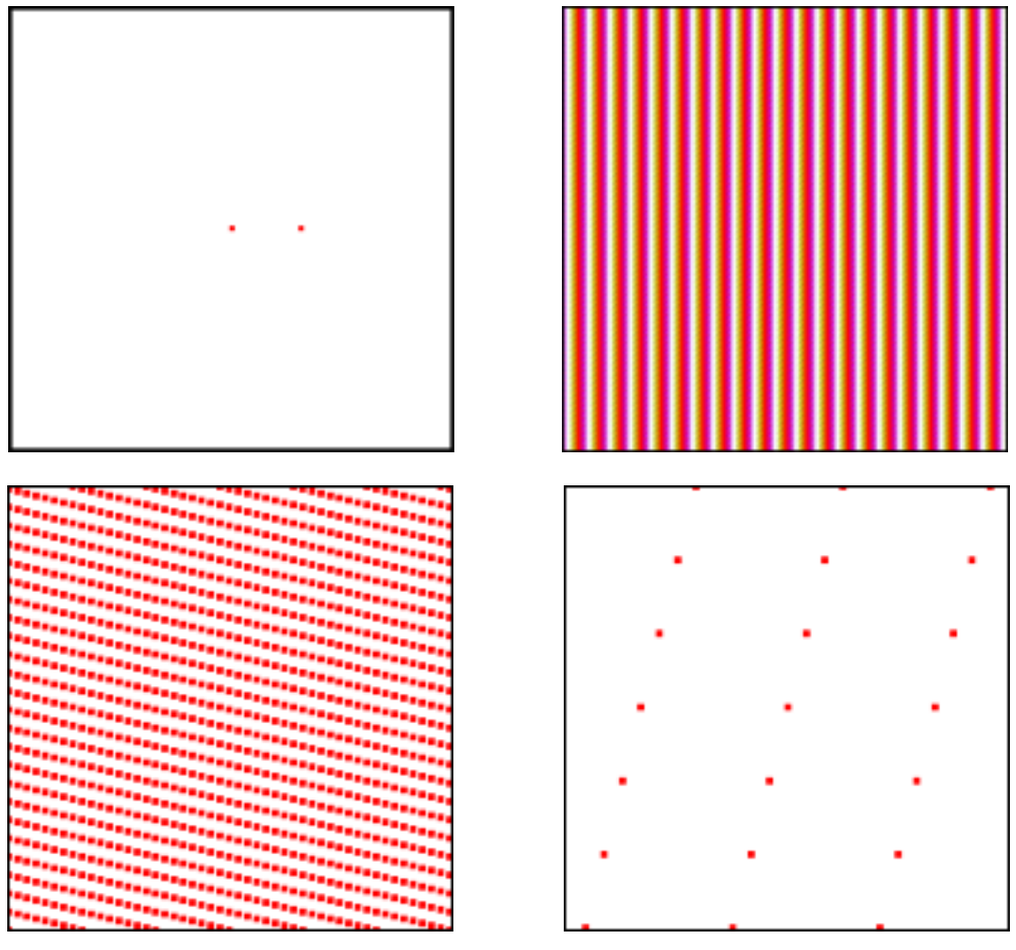
*Remember:* $e^{ix} = \cos(x) + i\sin(x)$

# Crystals have repeating patterns

- For each plane of atoms, you have a characteristic periodicity (or frequency).
- What are the units? *inverse length*
- **Reciprocal space**

# Fourier transforms of periodic structures: **diffraction**

object → Fourier transform



We can do this with two-dimensional objects. Two slits will produce a grating interference pattern.

A grating will produce a lattice of points.

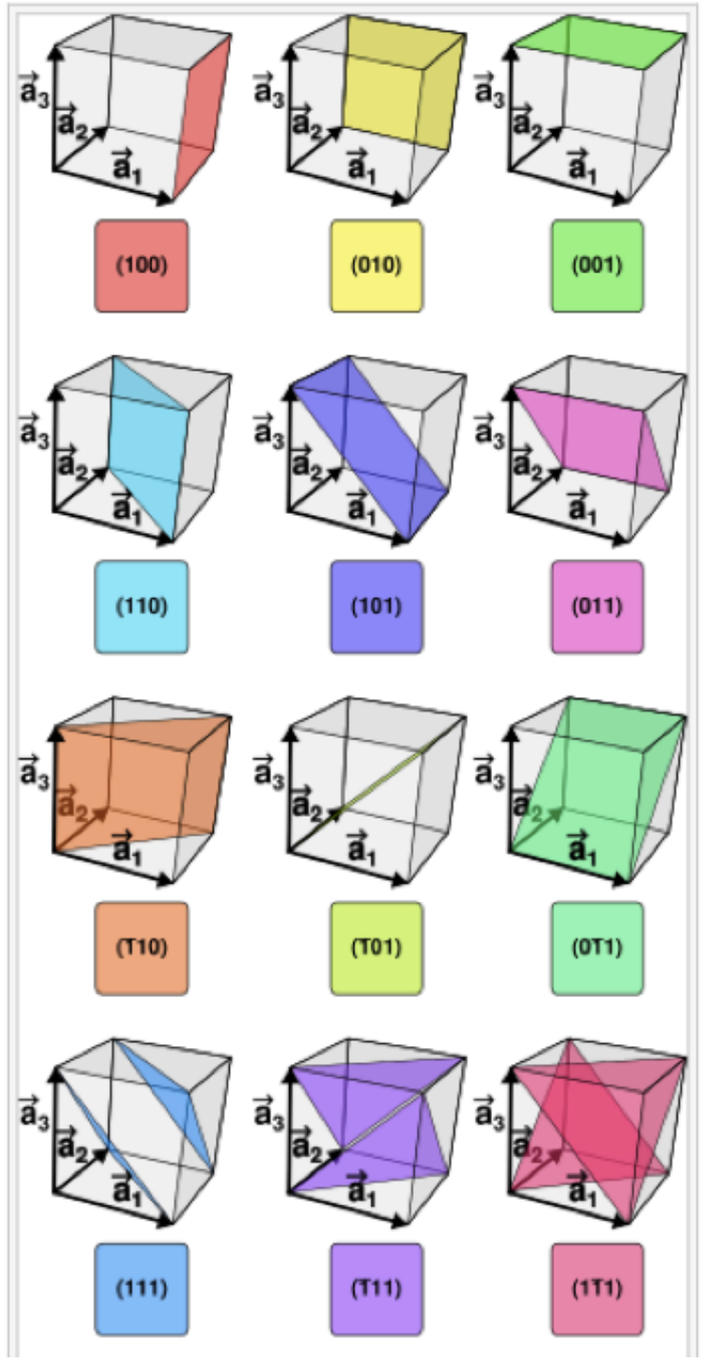
Images taken from Kevin Cowtan's Picture Book of Fourier Transforms:

http://www.ysbl.york.ac.uk/~cowtan/fourier/fourier.html

Visit for more (and interactive) examples.

# Miller indices: labels for sets of planes

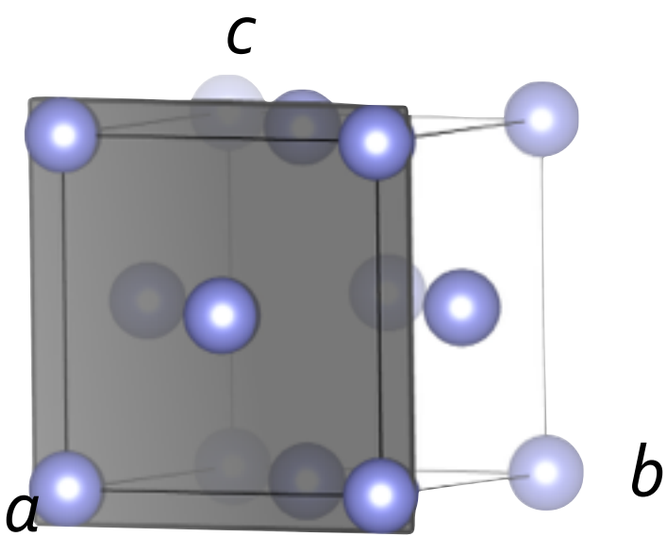
- the indices: (*hkl*)
  - *h* : (intercept with *a*)$^{-1}$
  - *k* : (intercept with *b*)$^{-1}$
  - *l* : (intercept with *c*)$^{-1}$
- Convention dictates that we use integers; therefore, multiply if needed.



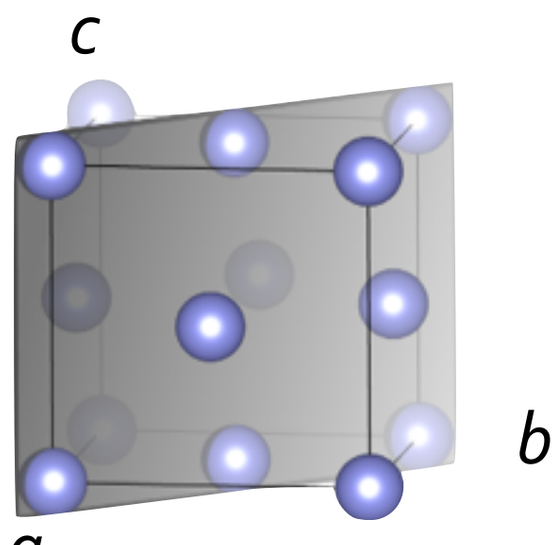

http://en.wikipedia.org/wiki/Miller_index

# Examples of Miller Indices

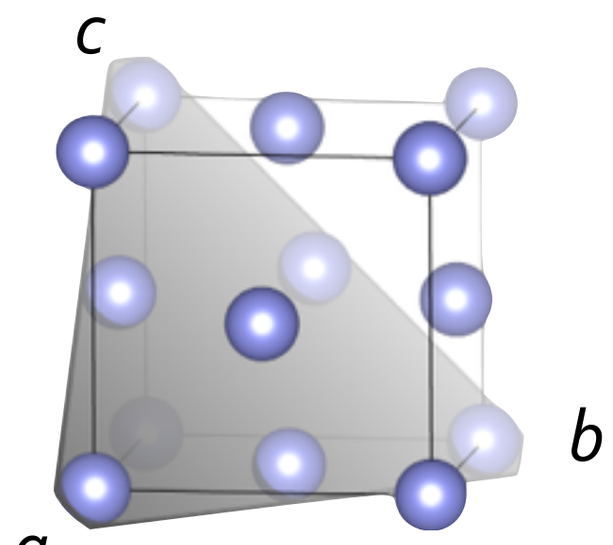
(100)

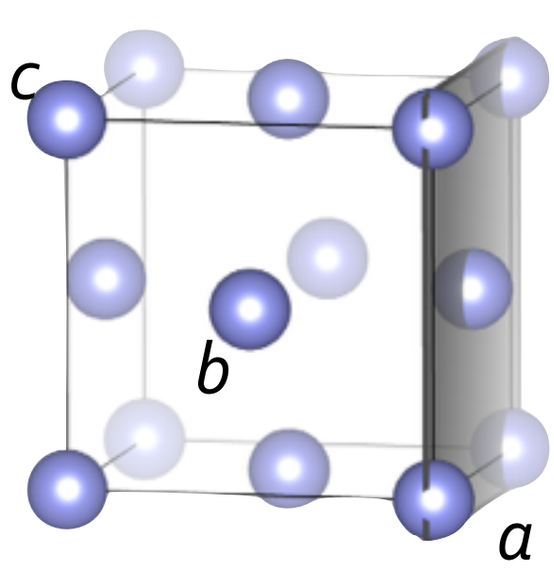


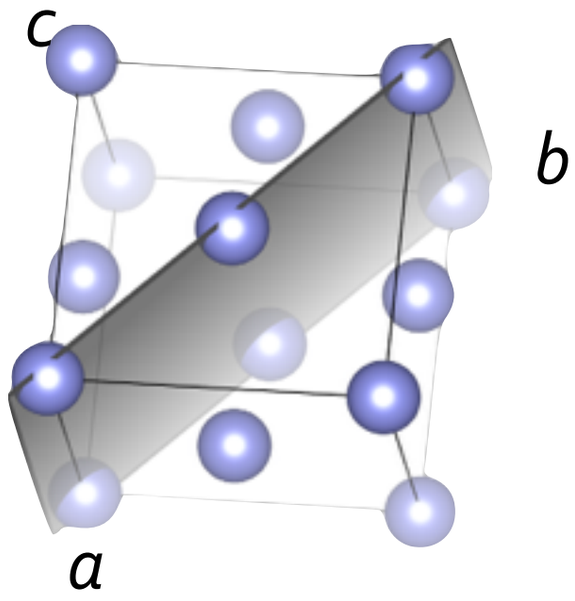

(110)

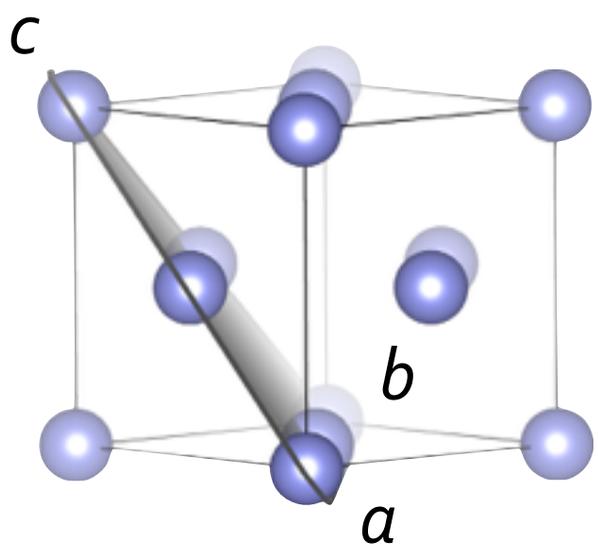



(111)



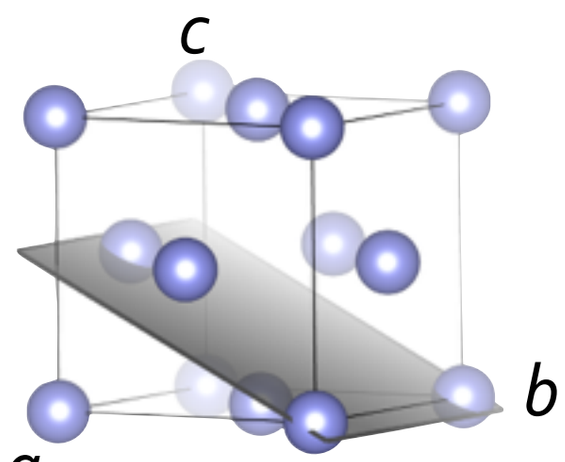



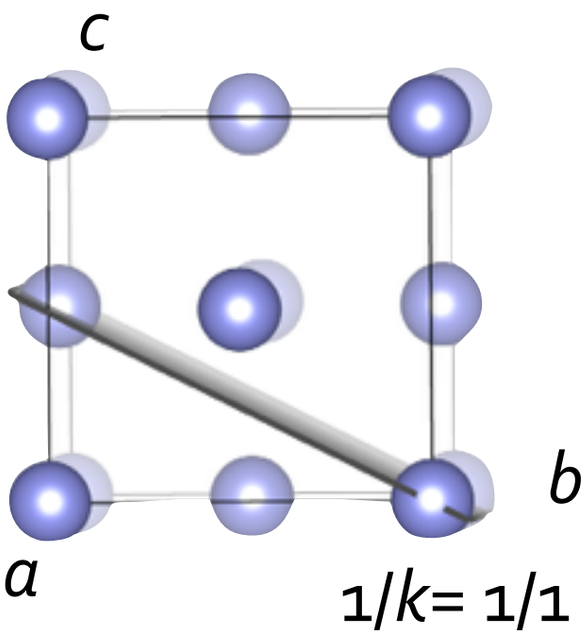




for no intercept: we take the intercept as ∞; the index is then zero

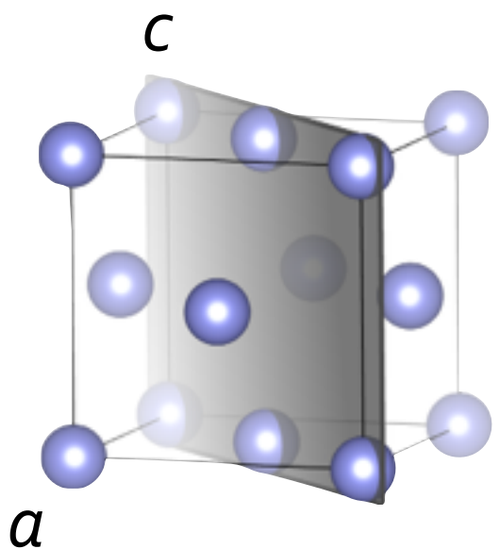
# More examples of Miller Indices

$(012)$



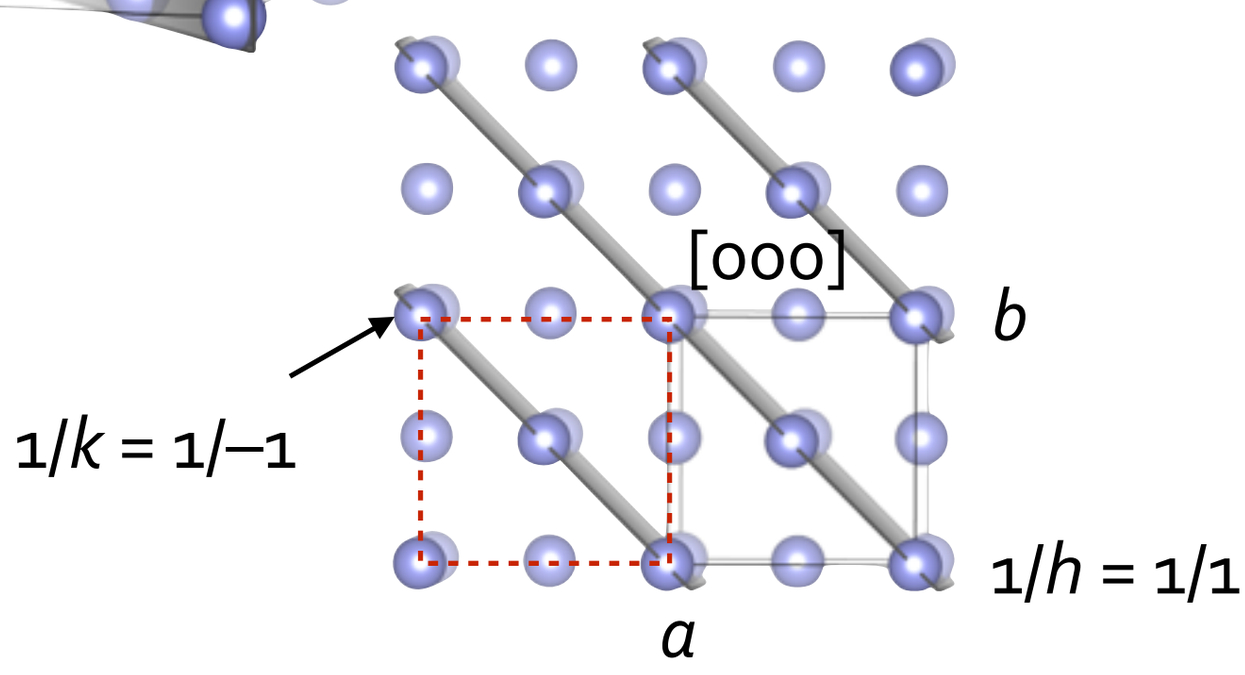




$(1\bar{1}0)$




negative index?

***tile with abandon***




**For animations, see:**

http://www.doitpoms.ac.uk/tlplib/miller_indices/lattice_index.php

# index notation (for completeness)

- (*hkl*)
  - indexes a ***specific*** lattice plane
- {*hkl*}
  - indexes all ***symmetry-related*** lattice planes
  - In a cubic system,

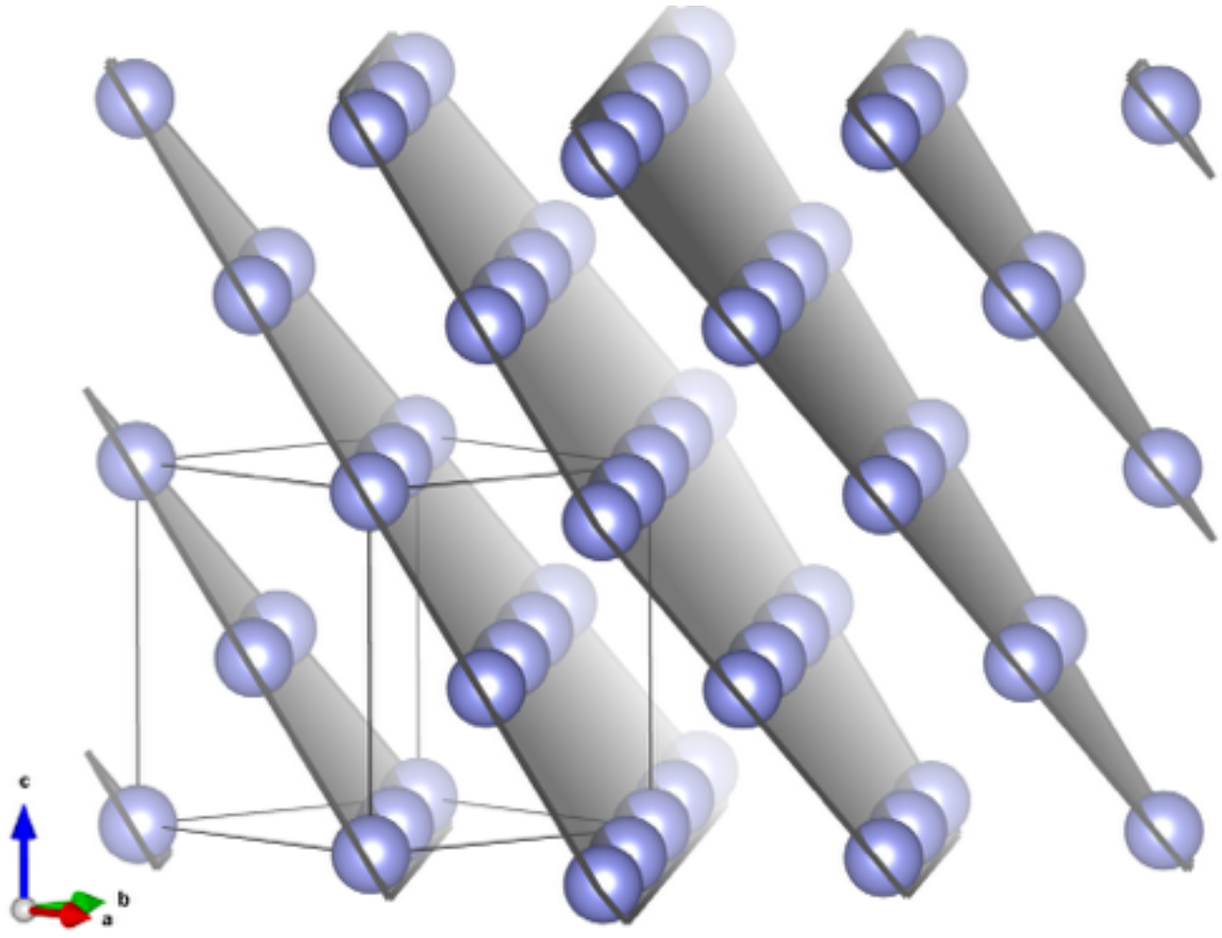
$$\{100\} \ni (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$$

- [uvw]
  - indexes a ***specific*** lattice vector
- ⟨*uvw*⟩
  - indexes all ***symmetry-related*** lattice vectors
  - In a cubic system,

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

# Miller indices index all sets of planes

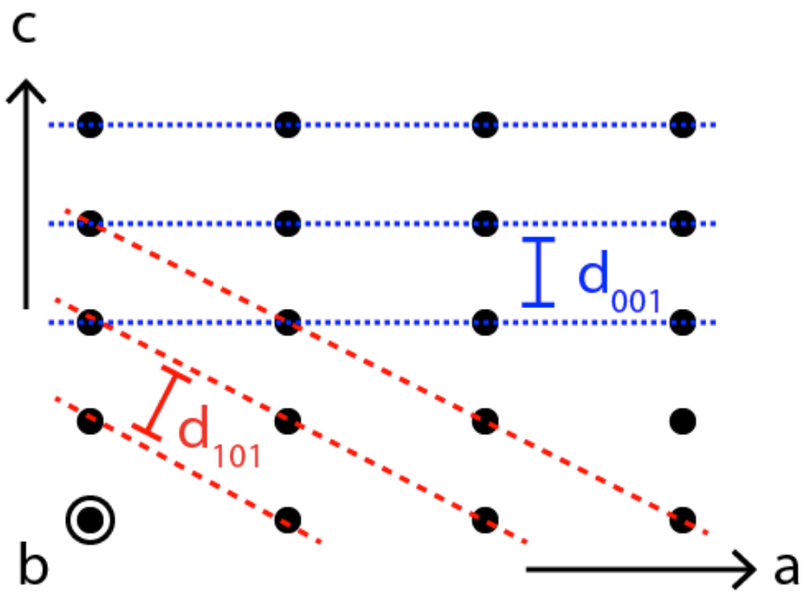
$(111)$ = all of the planes drawn

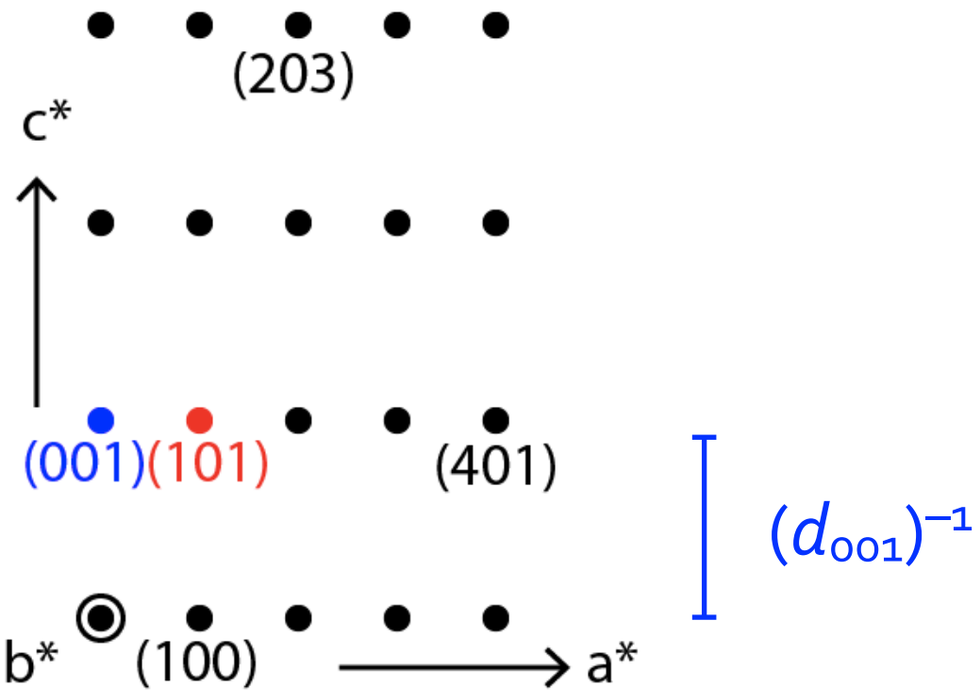



***maybe there is an easier way to describe ALL of the planes of atoms?***

# reciprocal space and the reciprocal lattice

$d_{hkl}$-spacing: distance between planes




**atoms:**
direct space (Å)

**recip. lattice points:**
reciprocal space ($Å^{-1}$)

Fourier transform

sets of planes in direct space become points in reciprocal space;
they form the basis of the reciprocal lattice.
*note the inverse relationship*: big $\boldsymbol{a}$, small $\boldsymbol{a}^*$

# Reciprocal space

$V = a \cdot (b \times c)$ volume of the unit cell

Reciprocal lattice vectors, $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, and $\boldsymbol{c}^*$:

$$a^* = \frac{b \times c}{a \cdot (b \times c)}; b^* = \frac{c \times a}{a \cdot (b \times c)}; c^* = \frac{a \times b}{a \cdot (b \times c)};$$

Reciprocal lattice comprised of:

$\mathbf{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$

where $h$, $k$, and $l$ are the Miller indices (integers).

# what can you learn about **crystals** from **diffraction**?

***electron***

- Lattice constants
  - **locations** of points in *reciprocal space*
- Symmetry
  - **arrangement** and **presence** of points in *reciprocal space*
- Atom positions
  - **intensity** of points in *reciprocal space* [***caveat for electron diffraction***]
- Orientation
  - **intensity** and **arrangement** of points in reciprocal space

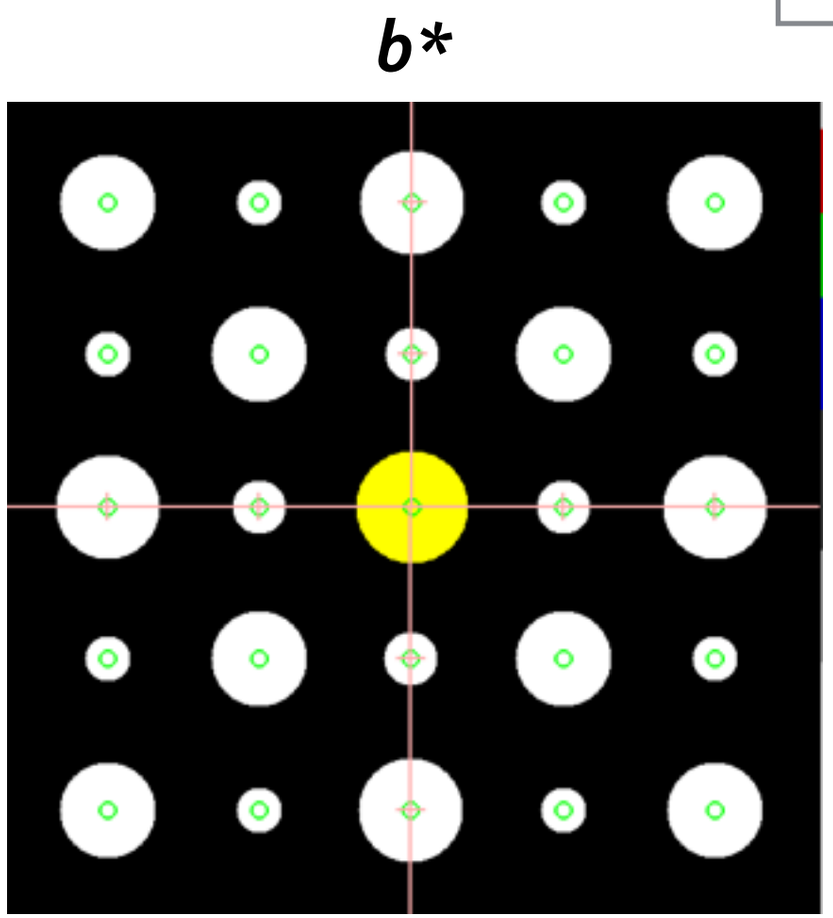
To learn about orientation, you need to know the underlying lattice structure

# $BaTiO_3$ <001>

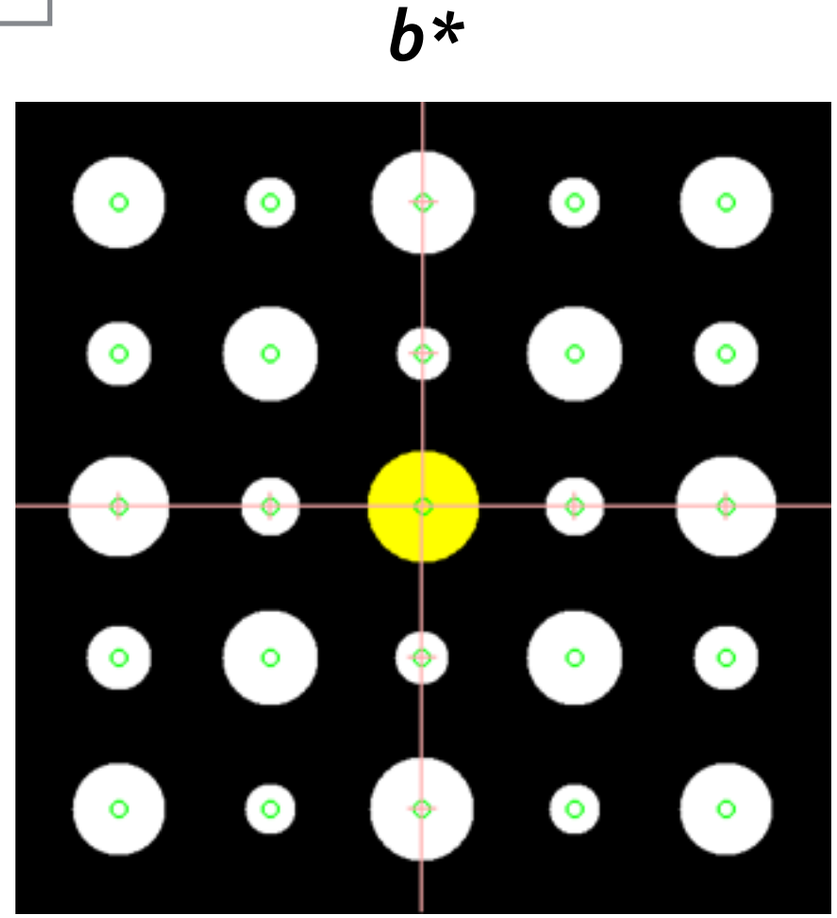
cubic - paraelectric

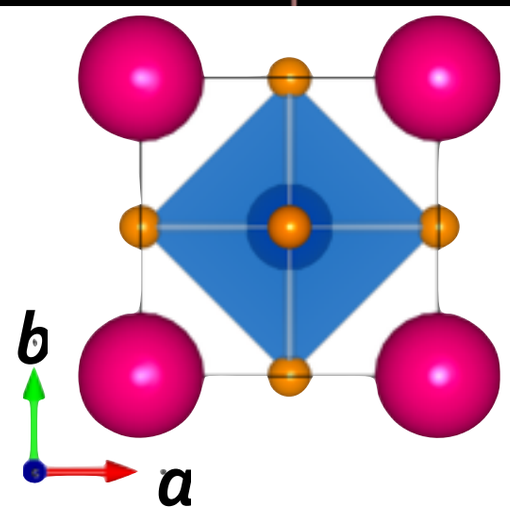
**what changed?**

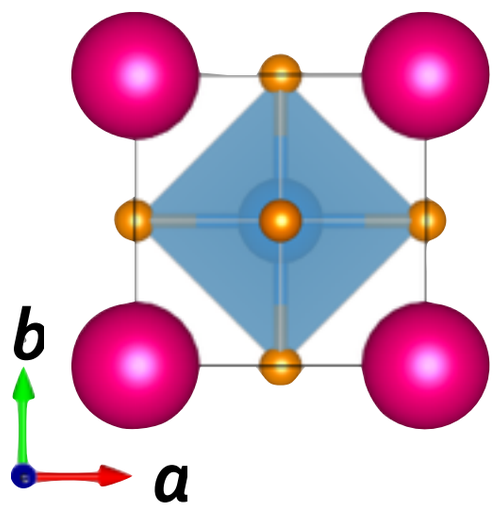
tetragonal - ferroelectric




*(nothing perceptible here)*



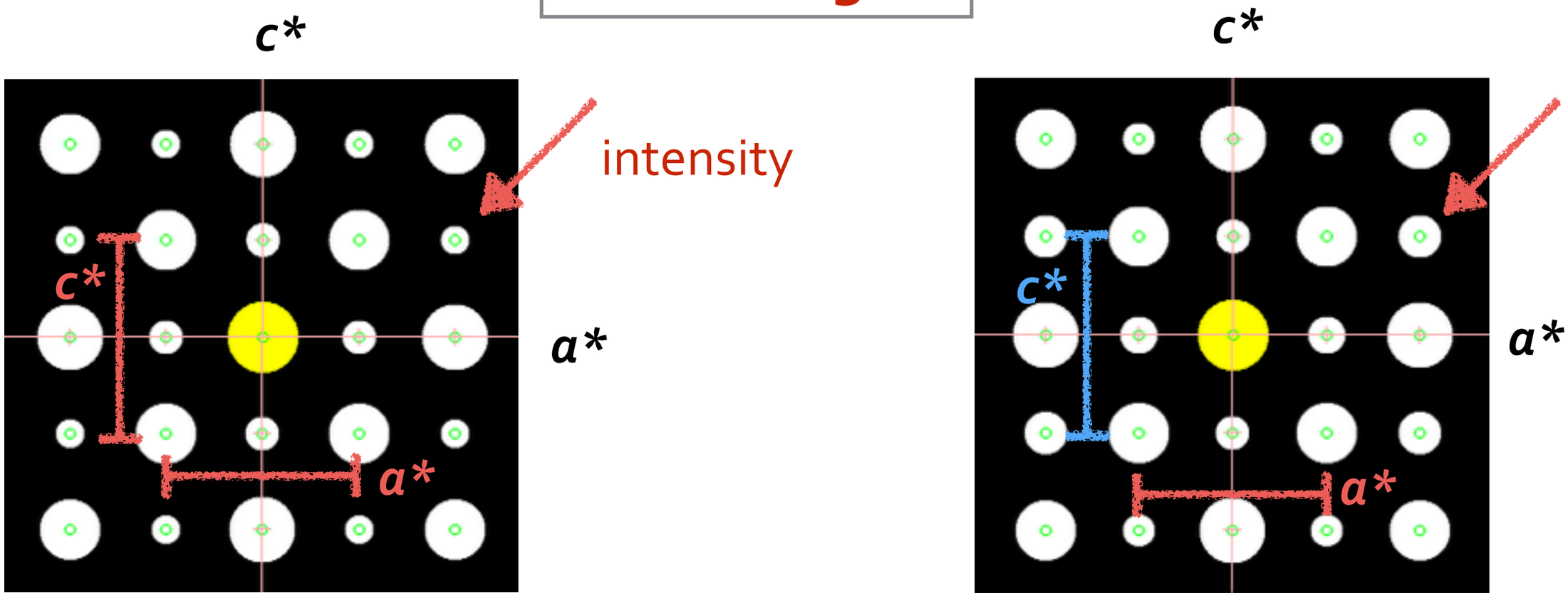

simulated with ISODISTORT and VESTA

# $BaTiO_3$ <010>

cubic - paraelectric

**what changed?**

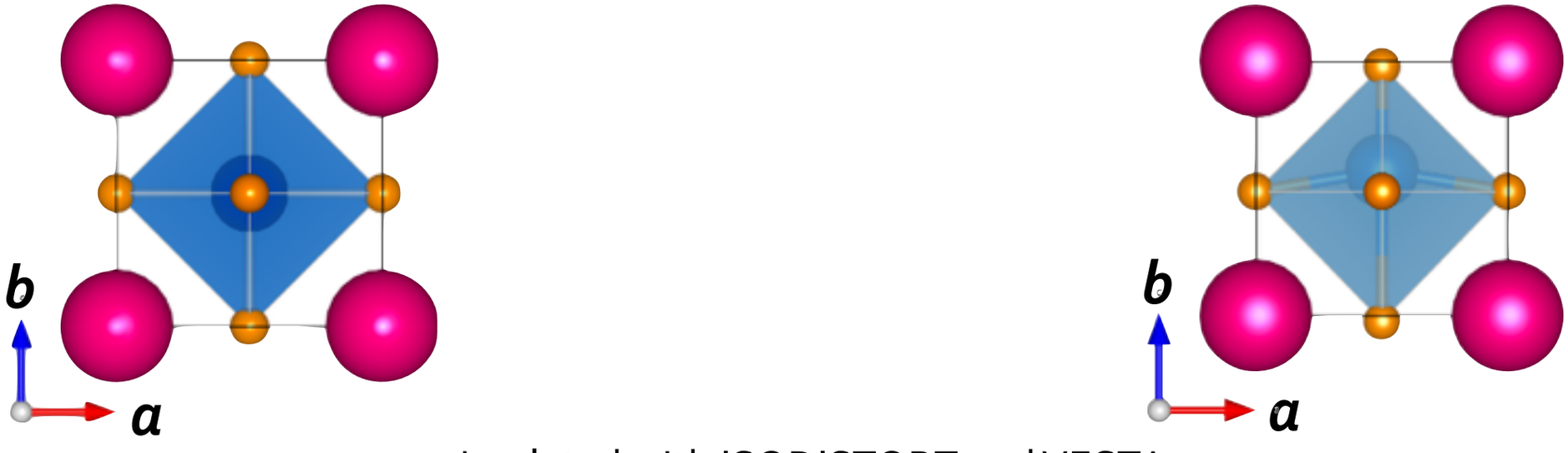
tetragonal - ferroelectric




$a^* = c^*$

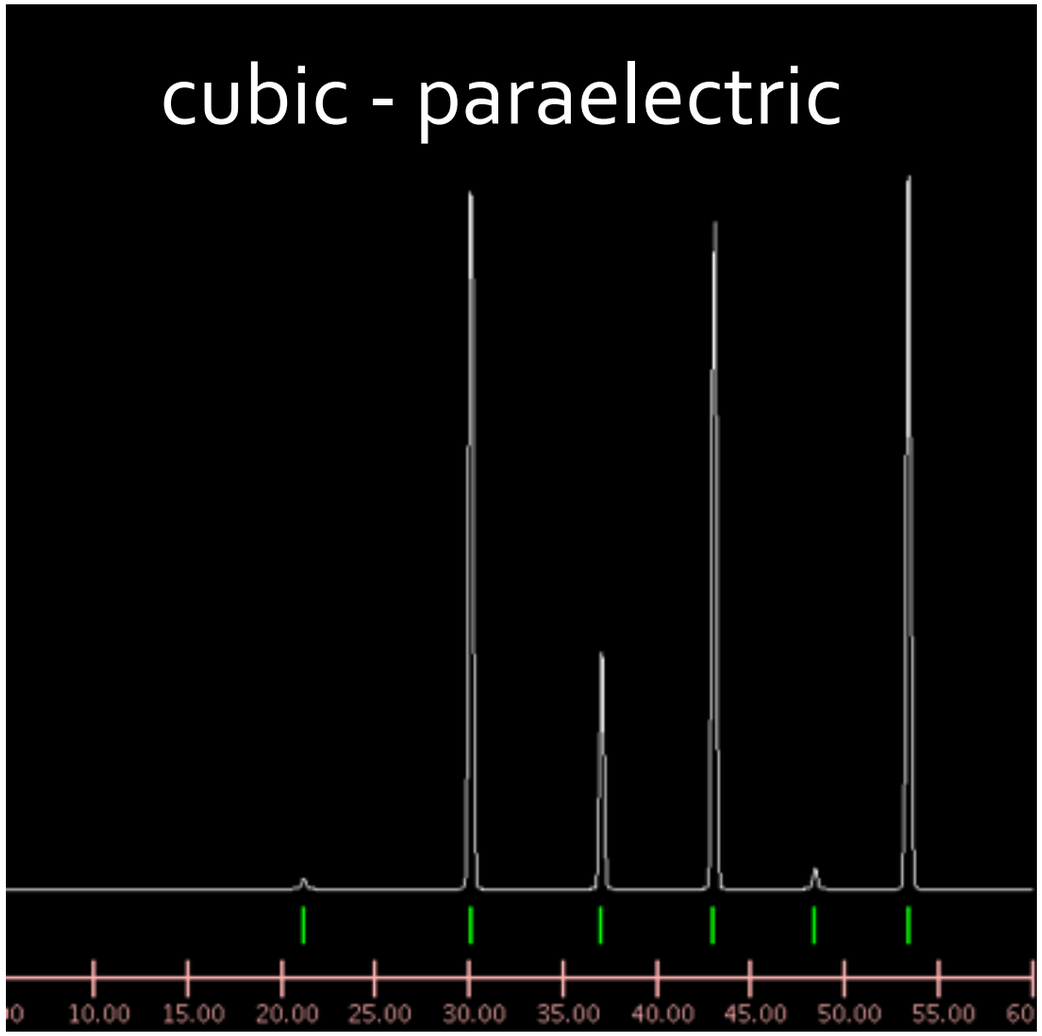
cell dimensions

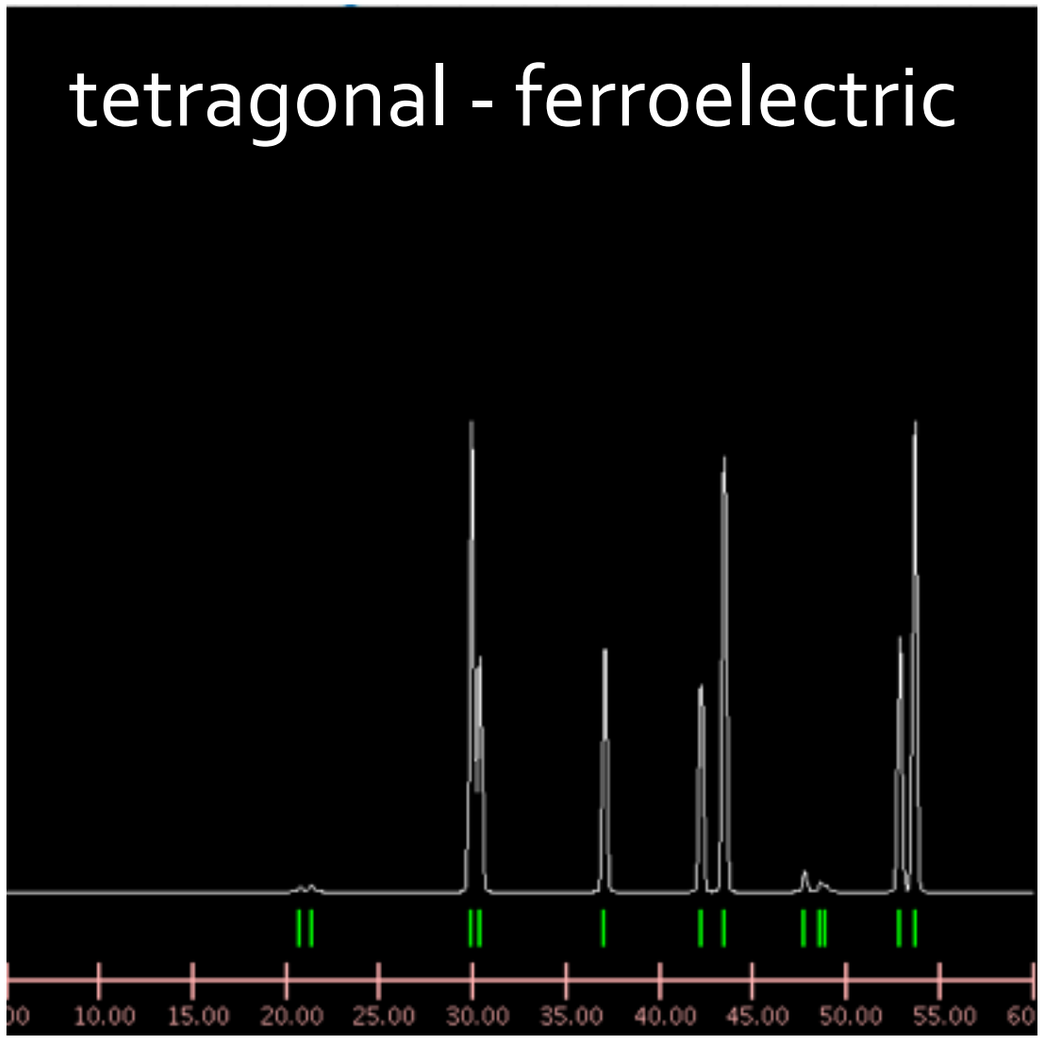
$a^* \neq c^*$

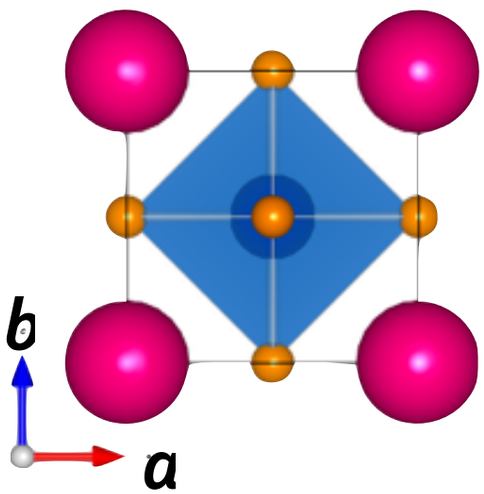



simulated with ISODISTORT and VESTA

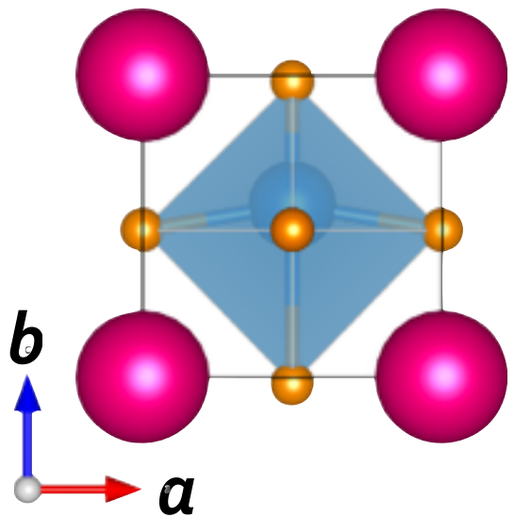
# $BaTiO_3$ powder x-ray diffraction




distinct peak splitting
and intensity differences




simulated with ISODISTORT and VESTA

# Why do crystallography in the TEM?

**take advantage of the 'local' probe!**

- Phase identification (lattice or point group)
- Orientation of crystals
- Finite sizes precludes macroscopic crystallography
  - *the nanostructure problem; challenges in crystal growth.*
- Supersymmetry: strong electron contrast
  - *modulated structures, charge density wave materials (e.g., $TaS_2$, $LiFeBO_3$)*
- Disorder: domains and local distortions
  - *e.g., metal-insulator transitions, ferroelectrics, superconductors*

# Disorder: distortions and metal-insulator transitions

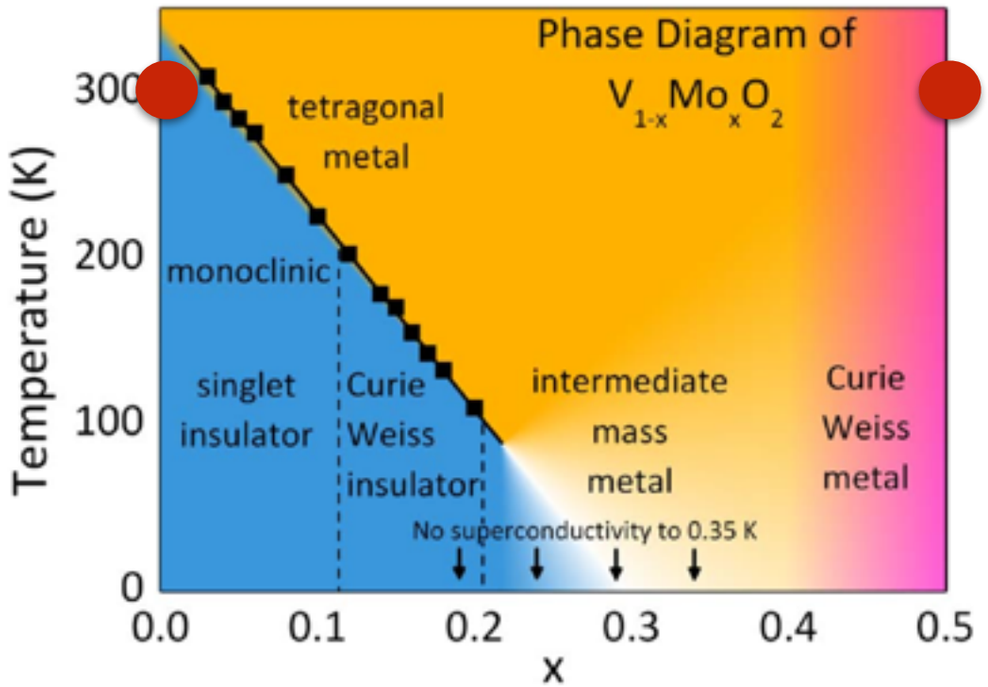
**$V_{1-x}Mo_xO_2$**

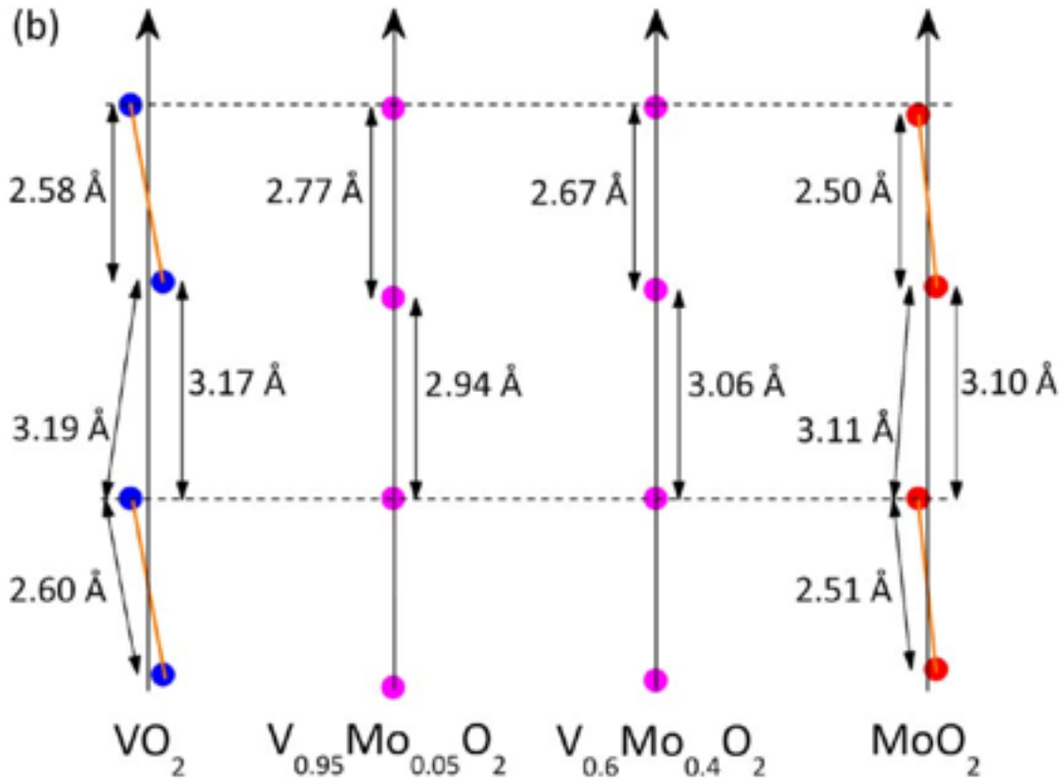
At $T$ = 300 K:

Monoclinic for $VO_2$
– **insulator**

Tetragonal for $V_{0.5}Mo_{0.5}O_2$
– ***weird*** **metal**

**modulation of *M–M* distances within the material**



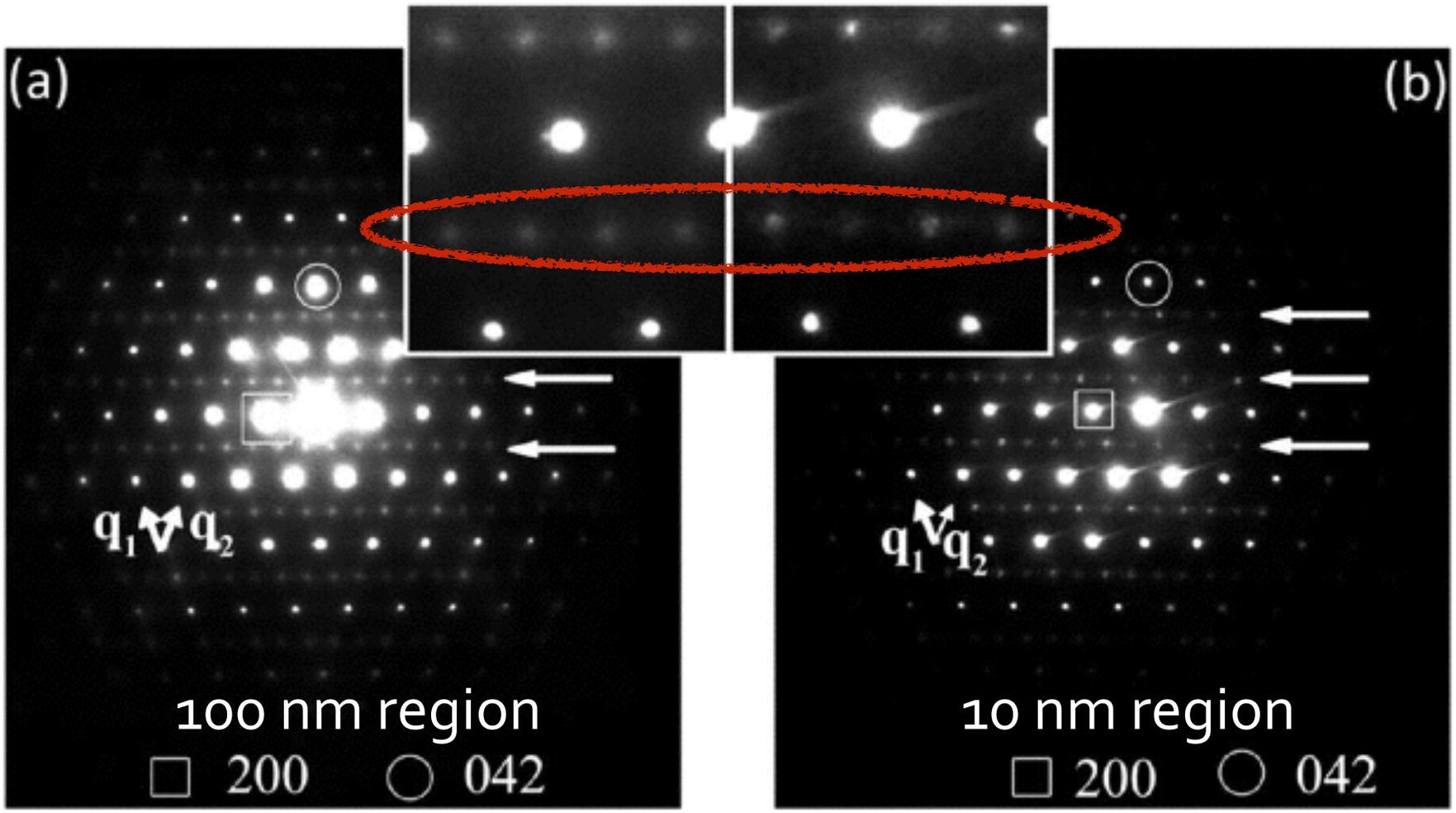




Holman, McQueen, Williams, Klimczuk, Stephens, Zandbergen, Xu, Ronning, Cava, Insulator to correlated metal transition in $V_{1-x}Mo_xO_2$, *Phys. Rev. B*, 2009, **79**, 245114

# Local distortions in $V_{0.5}Mo_{0.5}O_2$

X-ray crystallography: tetragonal *on average*

Zooming into a small region of the sample with TEM:




Extra reflections: broken tetragonal symmetry!

***monoclinic on a short length scale***

**yet still metallic**

Holman, McQueen, Williams, Klimczuk, Stephens, Zandbergen, Xu, Ronning, Cava, Insulator to correlated metal transition in $V_{1-x}Mo_xO_2$, *Phys. Rev. B*, 2009, **79**, 245114

# Kinematic theory for diffraction

- Main assumptions:
    - single scattering (no multiple scattering)
    - elastic scattering
    - monochromatic incident beam
    - distortion free crystal
    - only a small fraction of e's scattered
    - no absorption

# Kinematic theory for diffraction

- Main assumptions: (**non-ideal assumptions for the TEM**)
  - single scattering (no multiple scattering)
    *except maybe for very thin samples*
  - elastic scattering
  - monochromatic incident beam
  - distortion free crystal
  - only a small fraction of e's scattered
  - no absorption

# intensities: structure factor (kinematic scattering)

- $F_{hkl}$ = structure factor

$$F_{hkl} = \sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)]$$

  - atom positions are at $x_n$,$y_n$, and $z_n$. $f_n$ is the atomic scattering factor. The summation is taken over all atoms in the unit cell.

- We actually measure intensity that is proportional to $|F_{hkl}|^2$

    - Since we measure the square, we loose the relative phases of the periodic components: "the crystallographic phase problem"

# systematic absences from the structure factor

Consider a body-centered cell, with identical atoms at (0,0,0) and (1/2, 1/2, 1/2)

$$F_{hkl} = \sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)]$$

$$F_{hkl}/f_n = \exp[2\pi i(h0 + k0 + l0)] + \exp[2\pi i(1/2h + 1/2k + 1/2l)]$$

$$F_{hkl}/f_n = 1 + \exp[\pi i(h + k + l)]$$

**if h + k + l = even:**

$$F_{hkl}/f_n = 1 + 1 + 0 = 2$$

***intensity is observed***

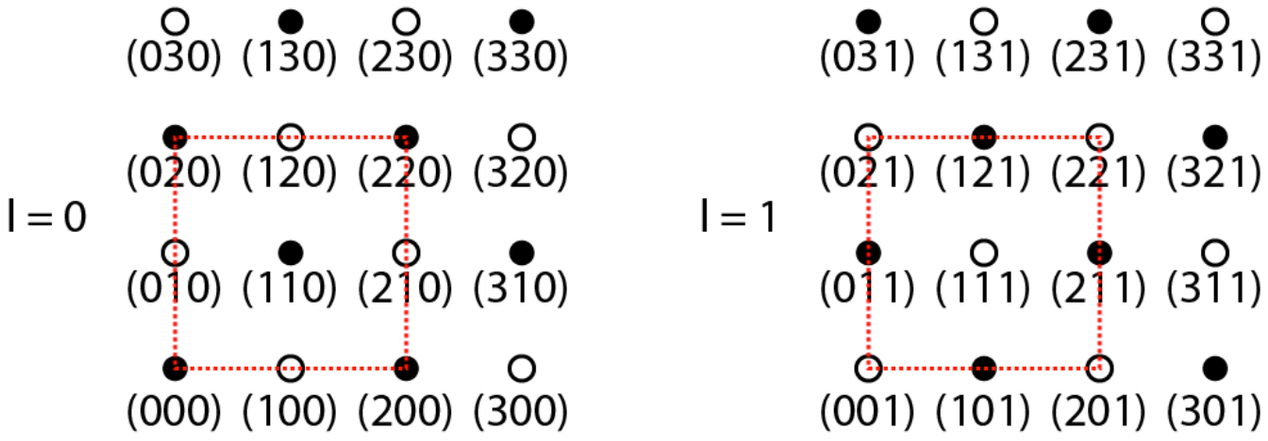
**if h + k + l = odd:**

$$F_{hkl}/f_n = 1 - 1 + 0 = 0$$

***these reflections are absent***

# systematic absences from the structure factor

A consequence of this is that a BCC crystal has a FCC reciprocal lattice.




Other translation operations create different systematic absences.

*Translational symmetry elements and their systematic absences*

| Symmetry element | Affected reflection | Condition for systematic absence |
|---|---|---|
| *Centred-cells:* | | |
| Body-centred (I) | *hkl* | $(h+k+l)$ odd |
| Face-centred (A) | *hkl* | $(k+l)$ odd |
| Face-centred (B) | *hkl* | $(h+l)$ odd |
| Face-centred (C) | *hkl* | $(h+k)$ odd |
| Face-centred (F) | *hkl* | $(h+k)$ odd |
| | | $(h+l)$ odd |
| | | $(k+l)$ odd |
| *Screw axes:* | | |
| Two-fold screw ($2_1$) along *a* | *h*00 | *h* odd |
| $2_1$ along *b* | 0*k*0 | *k* odd |
| $2_1$ along *c* | 00*l* | *l* odd |
| *Glide planes* $\perp b$*:* | | |
| Translation ($a/2$) (*a*-glide) | *h*0*l* | *h* odd |
| Translation ($c/2$) | *h*0*l* | *l* odd |
| Translation ($a/2+c/2$)(*n*-glide) | *h*0*l* | $(h+l)$ odd |
| Translation ($a/4+c/4$)(*d*-glide) | *h*0*l* | $(h+l)=4n+1, 2, 3$ |

# other examples

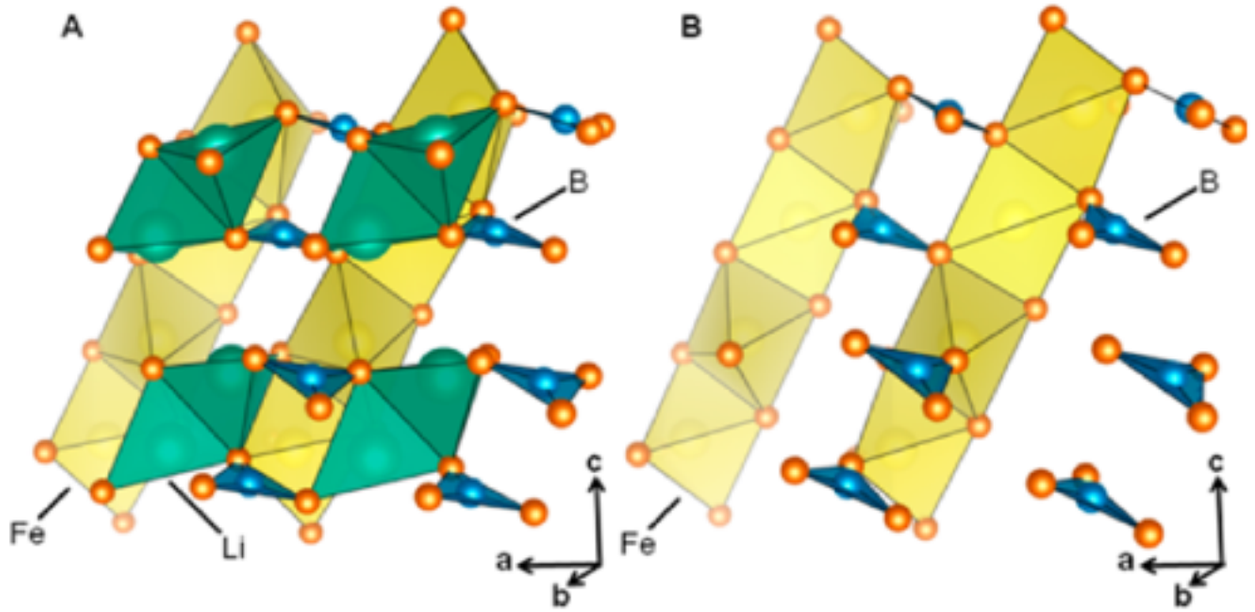
# Why do crystallography in the TEM?

**take advantage of the 'local' probe!**

- Phase identification (lattice or point group)
- Orientation of crystals
- Finite sizes precludes macroscopic crystallography
  - *the nanostructure problem; challenges in crystal growth.*
- Supersymmetry: strong electron contrast
  - *modulated structures, charge density wave materials (e.g., $TaS_2$, $LiFeBO_3$)*
- Disorder: domains and local distortions
  - *e.g., metal-insulator transitions, ferroelectrics, superconductors*

# what is a modulated, supersymmetric structure?

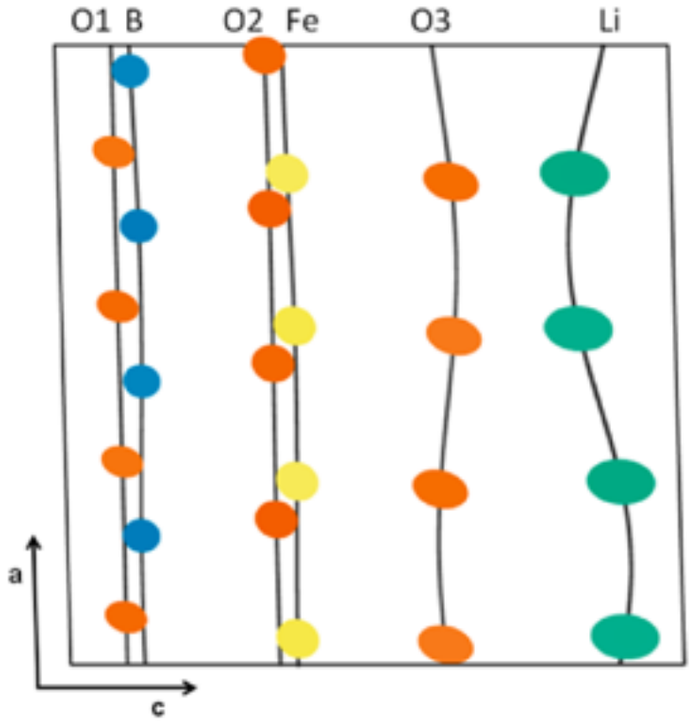
- example: $LiFeBO_3$
- Li-ion battery cathode material



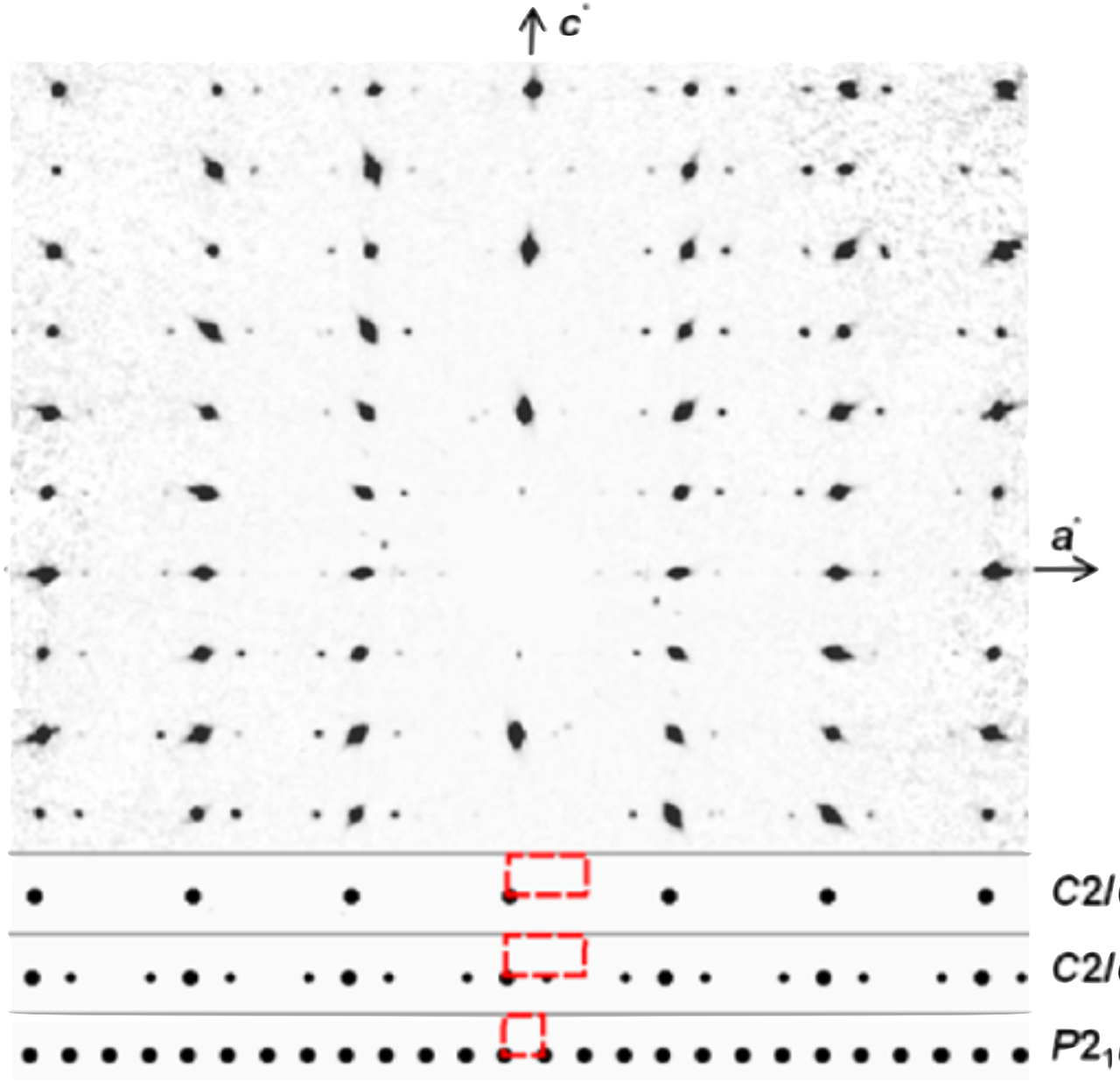

Y. Janssen, D. S. Middlemiss, S.-H. Bo, C. P. Grey, P. G. Khalifah, Structural Modulation in the High Capacity Battery Cathode Material , *J. Am. Chem. Soc*., 2012, **134**, 12516–12527.

# what is a modulated, supersymmetric structure?

- example: $LiFeBO_3$
- Li-ion battery cathode material




modulation of Li position

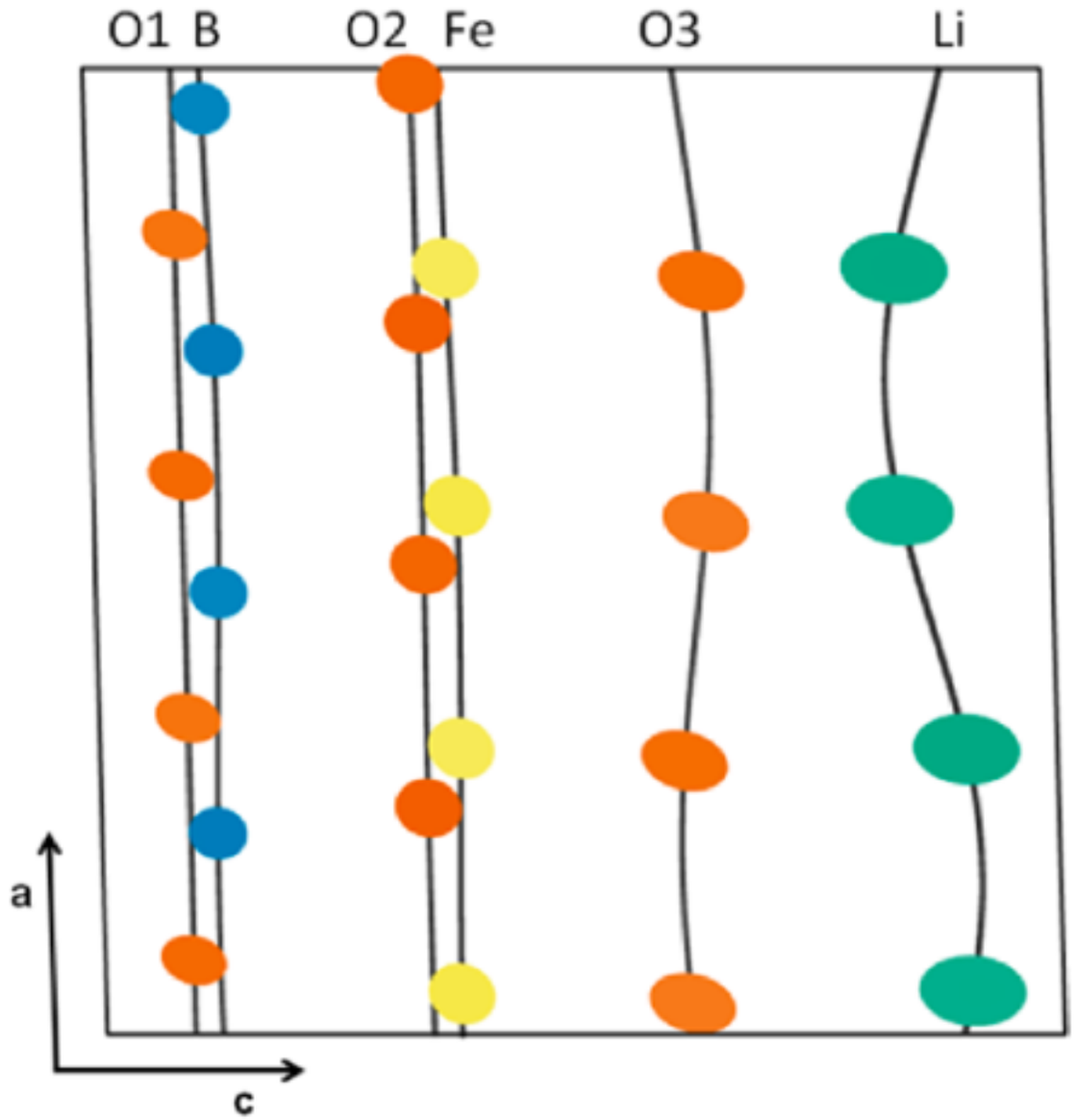



extra, weak reflections observed
at 1/2 **a*** , or 2**a** !!!

Y. Janssen, D. S. Middlemiss, S.-H. Bo, C. P. Grey, P. G. Khalifah, Structural Modulation in the High Capacity Battery Cathode Material , *J. Am. Chem. Soc*., 2012, **134**, 12516–12527.

# what is a modulated, supersymmetric structure?

- example: $LiFeBO_3$
- Li-ion battery cathode material
- Periodicity of the Li positions is **commensurate** with the underlying reciprocal lattice but has longer-range order.

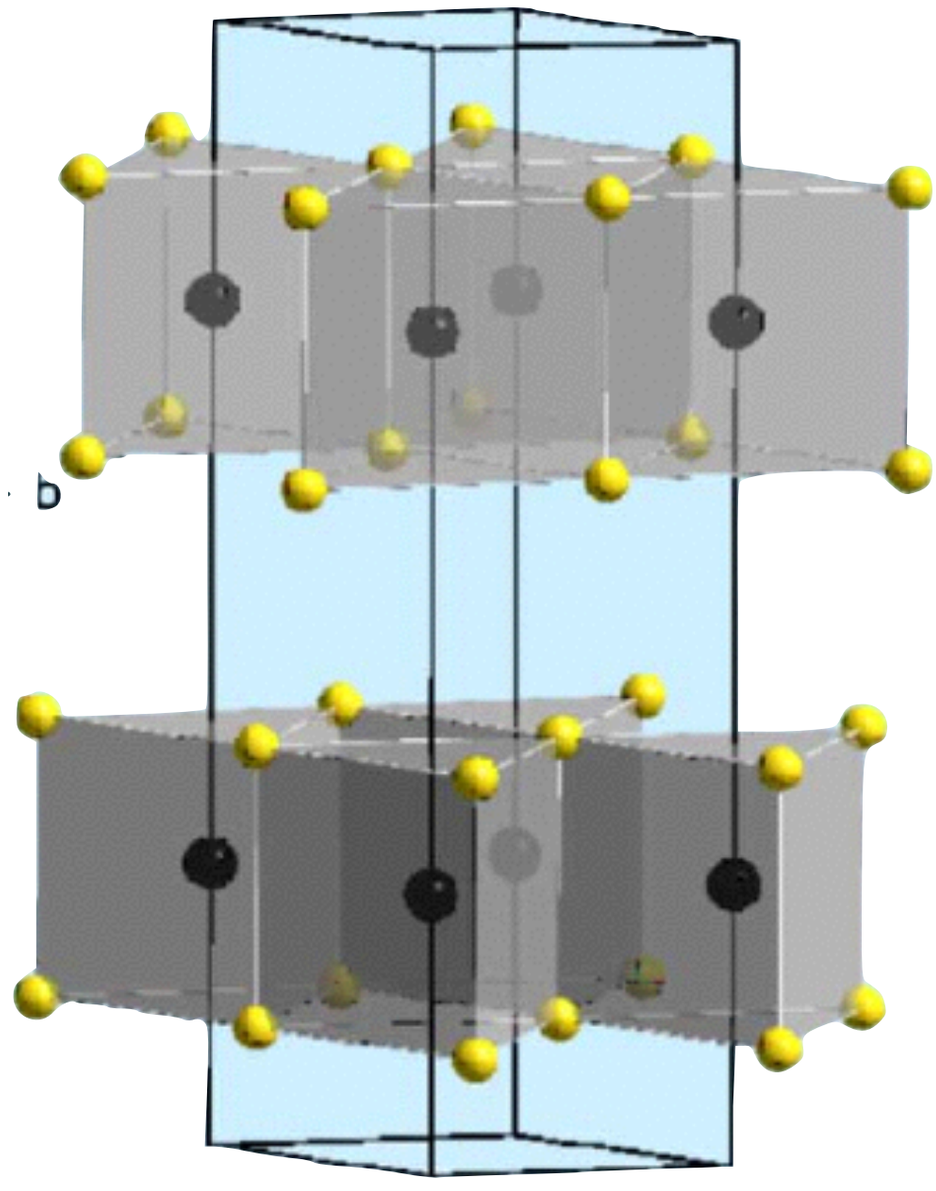



modulation of Li position

Y. Janssen, D. S. Middlemiss, S.-H. Bo, C. P. Grey, P. G. Khalifah, Structural Modulation in the High Capacity Battery Cathode Material , *J. Am. Chem. Soc*., 2012, **134**, 12516–12527.

# supersymmetry: higher dimensional crystallography

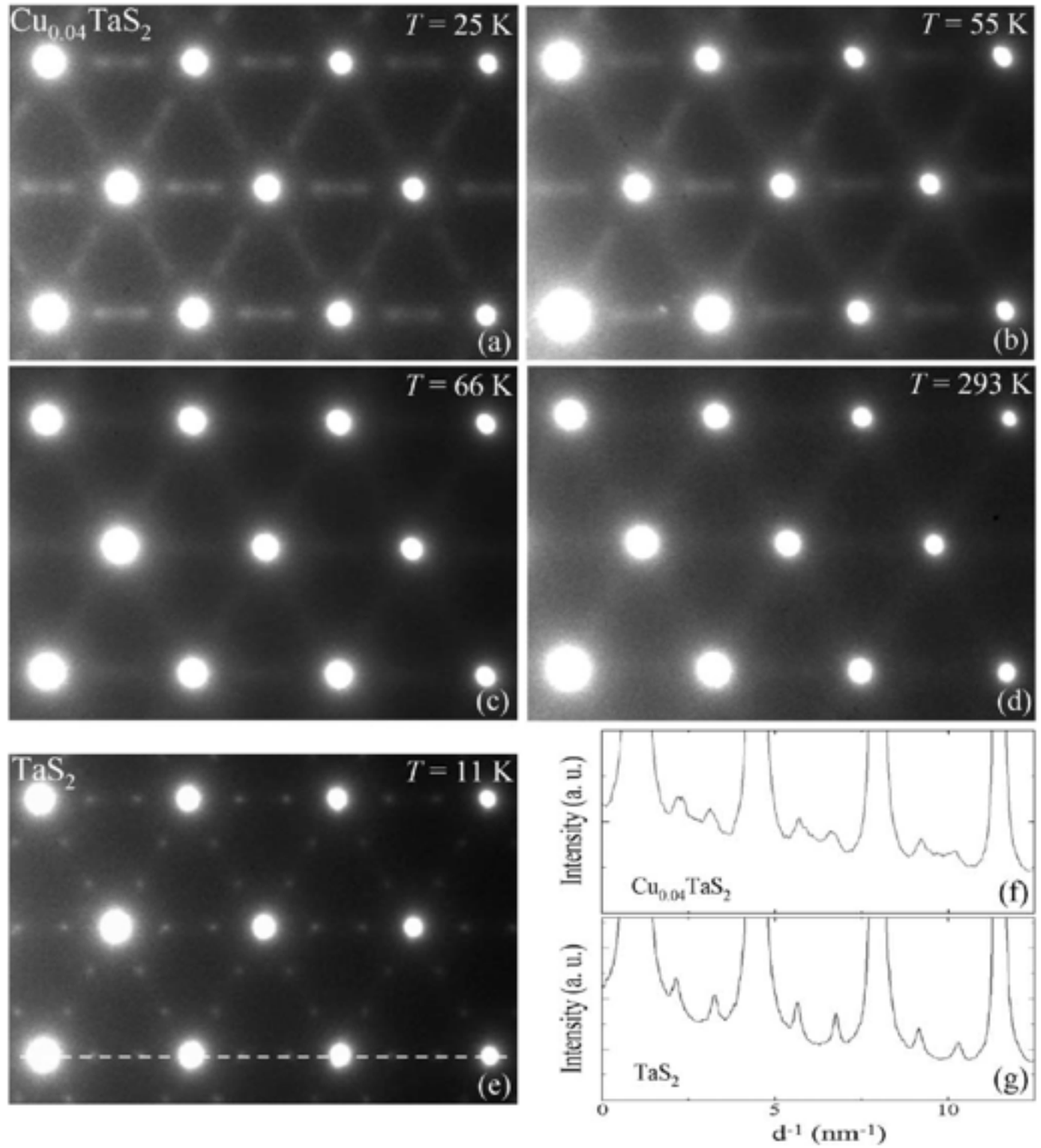
- example: charge-density wave order in $TaS_2$
  - $q$ = [0.341, 0, 0]
- that is, the actual unit cell is $(0.341)^{-1}$ times longer along $\boldsymbol{a}$!



Wagner, Morosan, Hor, Tao, Zhu, Sanders, McQueen, Zandbergen, Williams, West, Cava, "Tuning the charge density wave and superconductivity in CuxTaS2", *Phys. Rev. B*, 2008, **78**, 104520

# supersymmetry: higher dimensional crystallography

- example: charge-density wave order in $TaS_2$
  - $q$ = [0.341, 0, 0]
- that is, the actual unit cell is $(0.341)^{-1}$ times longer along $\boldsymbol{a}$!




Wagner, Morosan, Hor, Tao, Zhu, Sanders, McQueen, Zandbergen, Williams, West, Cava, "Tuning the charge density wave and superconductivity in CuxTaS2", *Phys. Rev. B*, 2008, **78**, 104520

# additional crystallography resources:

http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/Introduction_to_Crystallography/

*Web-based video lectures and other resources*

http://www.doitpoms.ac.uk/tlplib/crystallography3/index.php

*great animations and illustrations*

http://www.iucr.org/education/pamphlets

*handouts from the International Union on Crystallography*

http://jp-minerals.org/vesta/en/

*software for visualizing crystal structures and lattice planes (VESTA)*

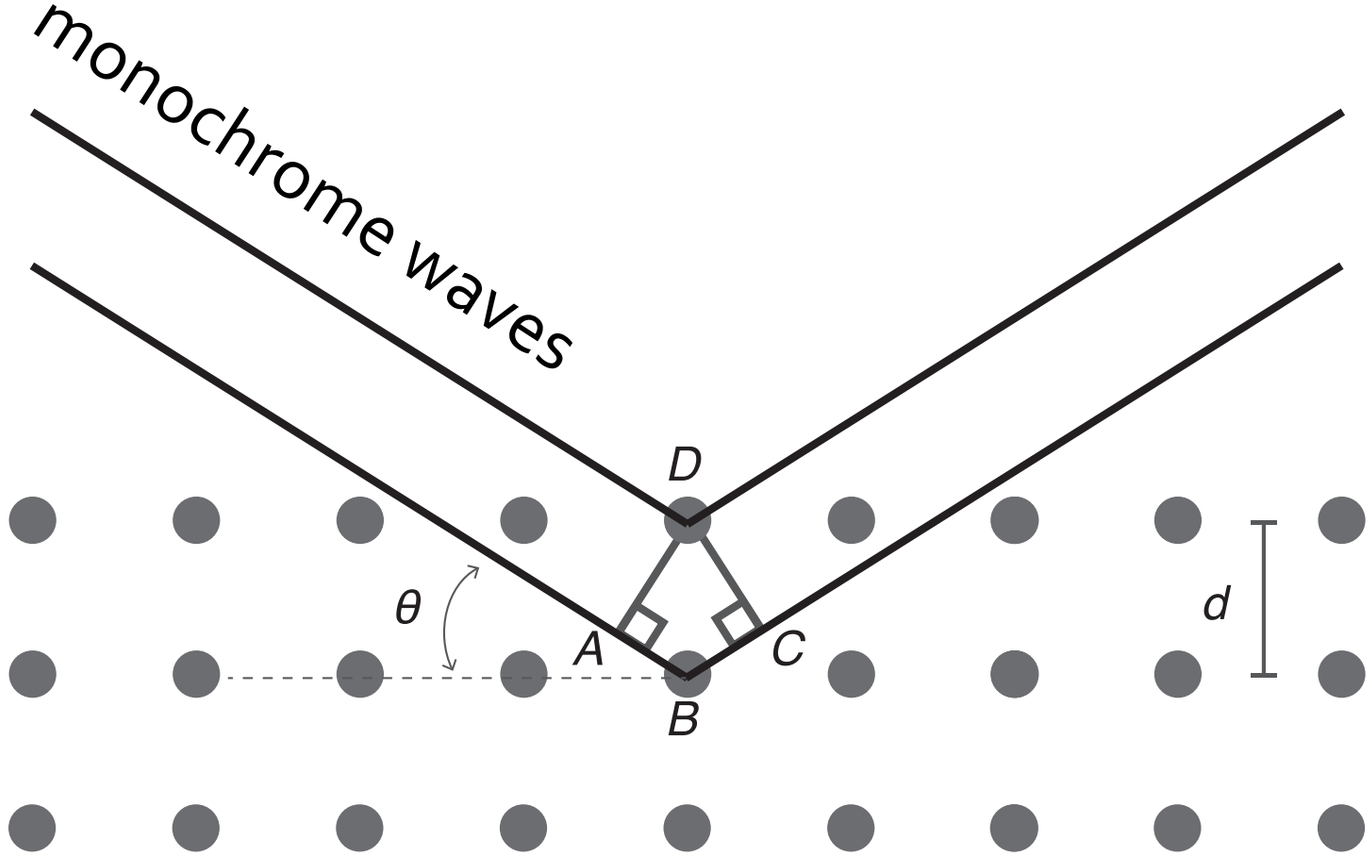
http://stokes.byu.edu/iso/isodistortform.php

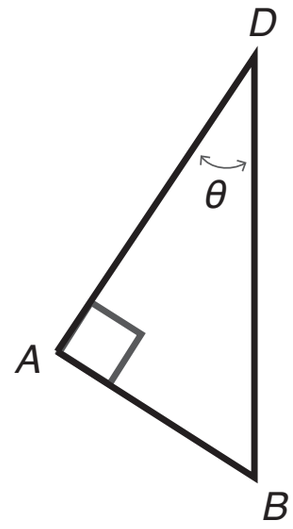
ISODISTORT: *online tool for simulating crystals, their distortions, and their diffraction patterns*

# more on diffraction

# Diffraction: Bragg's Law

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




if the path-length difference of the two waves is equal to an integer multiple of the wavelength, then constructive interference

$\sin\vartheta = AB/BD = AB/d$

$AB = BC$

constructive if $2AB = n\lambda$

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

# Diffraction: the Laue Equations

Instead, we can use vector notation

$| \mathbf{s} - \mathbf{s_0} | = 2 \sin\vartheta$

and

$| \boldsymbol{d}^*_{hkl} | = 1/d_{hkl}$

Their ratio is λ:

$( \mathbf{s} - \mathbf{s_0} ) / \lambda = \boldsymbol{d}^*_{hkl}$

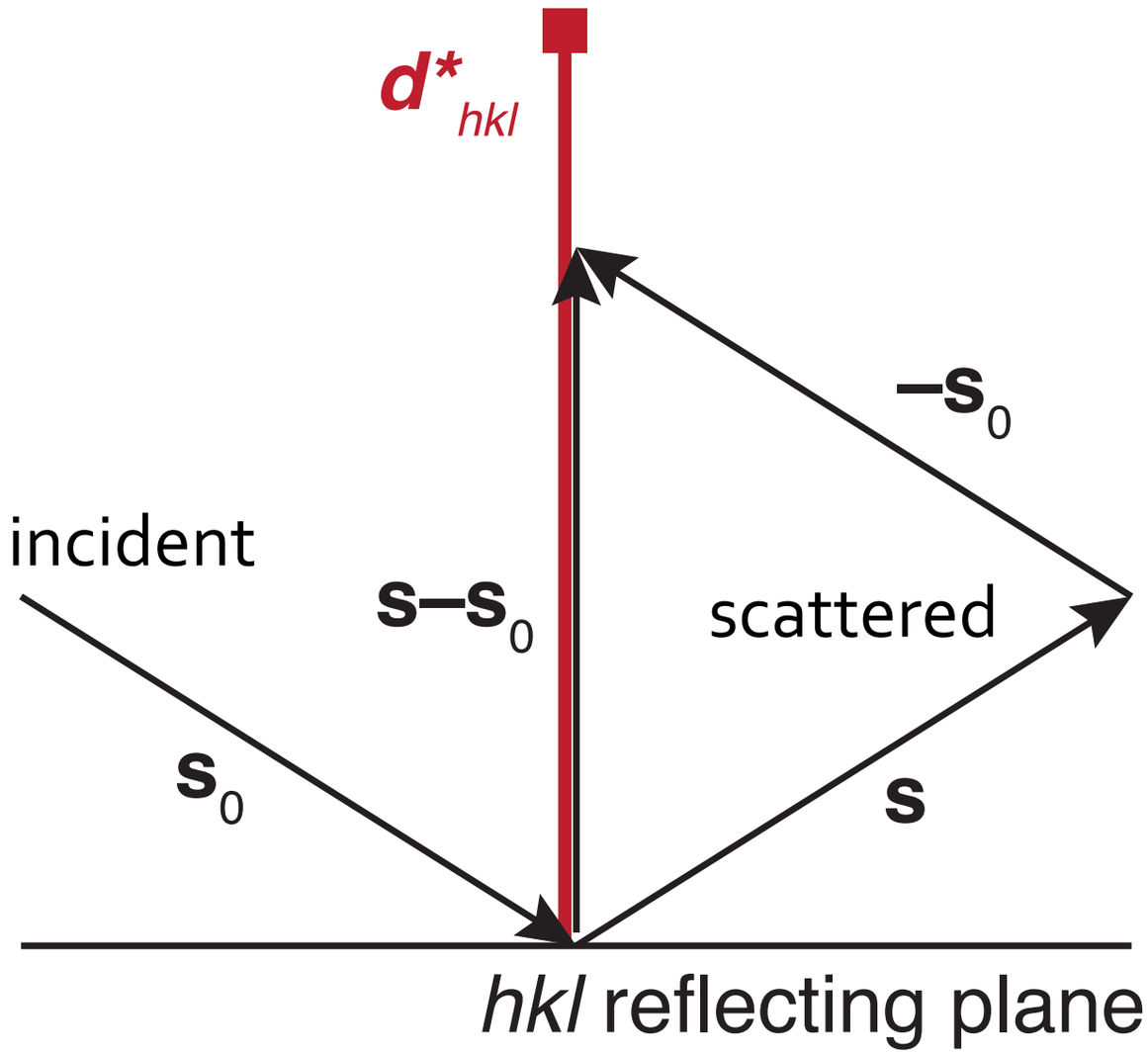
Because:

$\boldsymbol{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

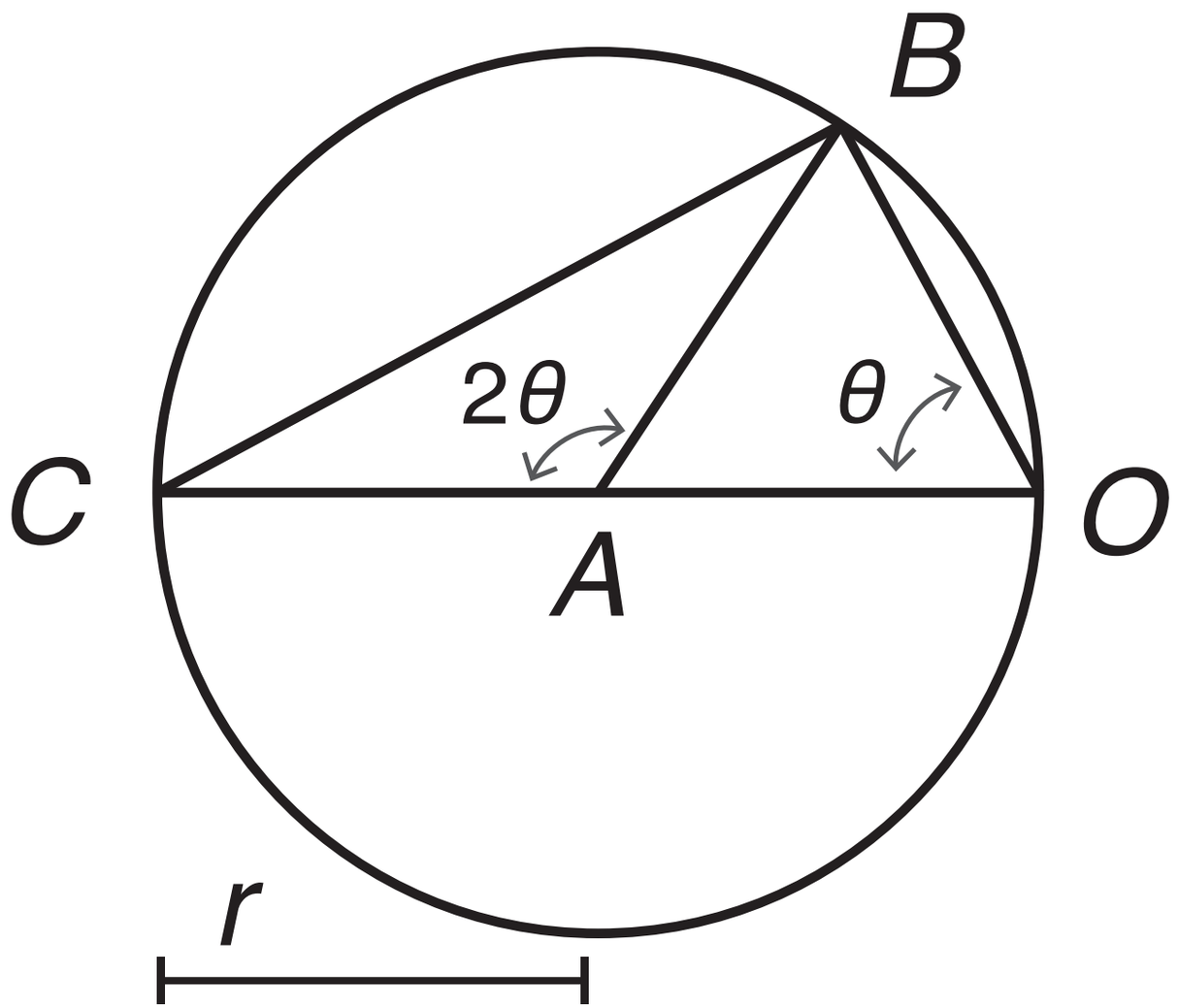
The first Laue equation is:

$\mathbf{a} ( \mathbf{s} - \mathbf{s_0} ) = n_x \lambda$

then repeat for **b**, $n_y$; **c**, $n_z$.



# Diffraction: The Ewald Sphere




From trigonometry:

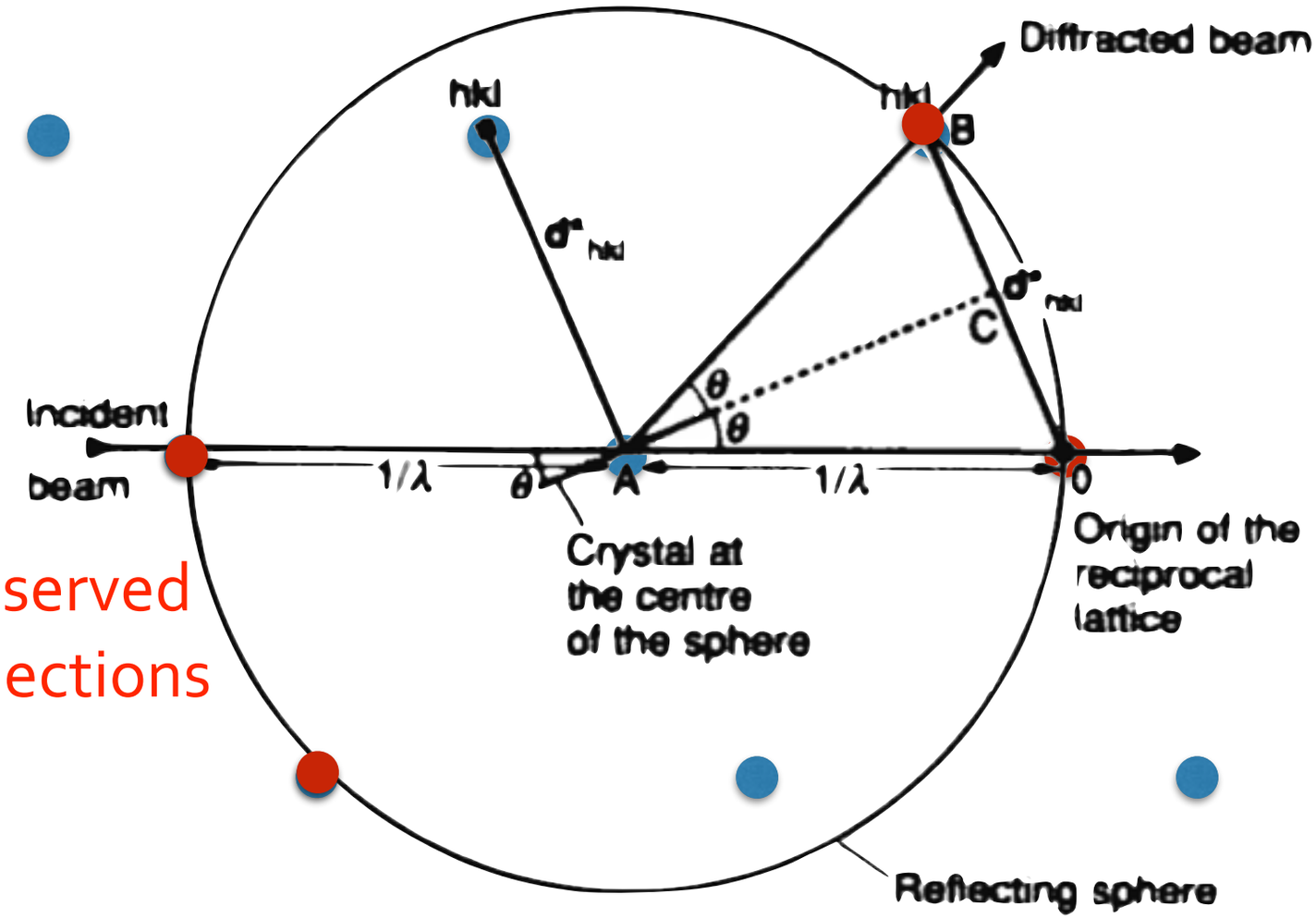
$$\sin\theta = \frac{OB}{2r}$$

In reciprocal space, we can set ***r* = 1/λ**. If *O* is the origin in reciprocal space, and *B* falls on a reciprocal lattice point, then:

$$\sin\theta = \frac{\frac{1}{d_{hkl}}}{\frac{2}{\lambda}}$$

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

# Diffraction: The Ewald Sphere



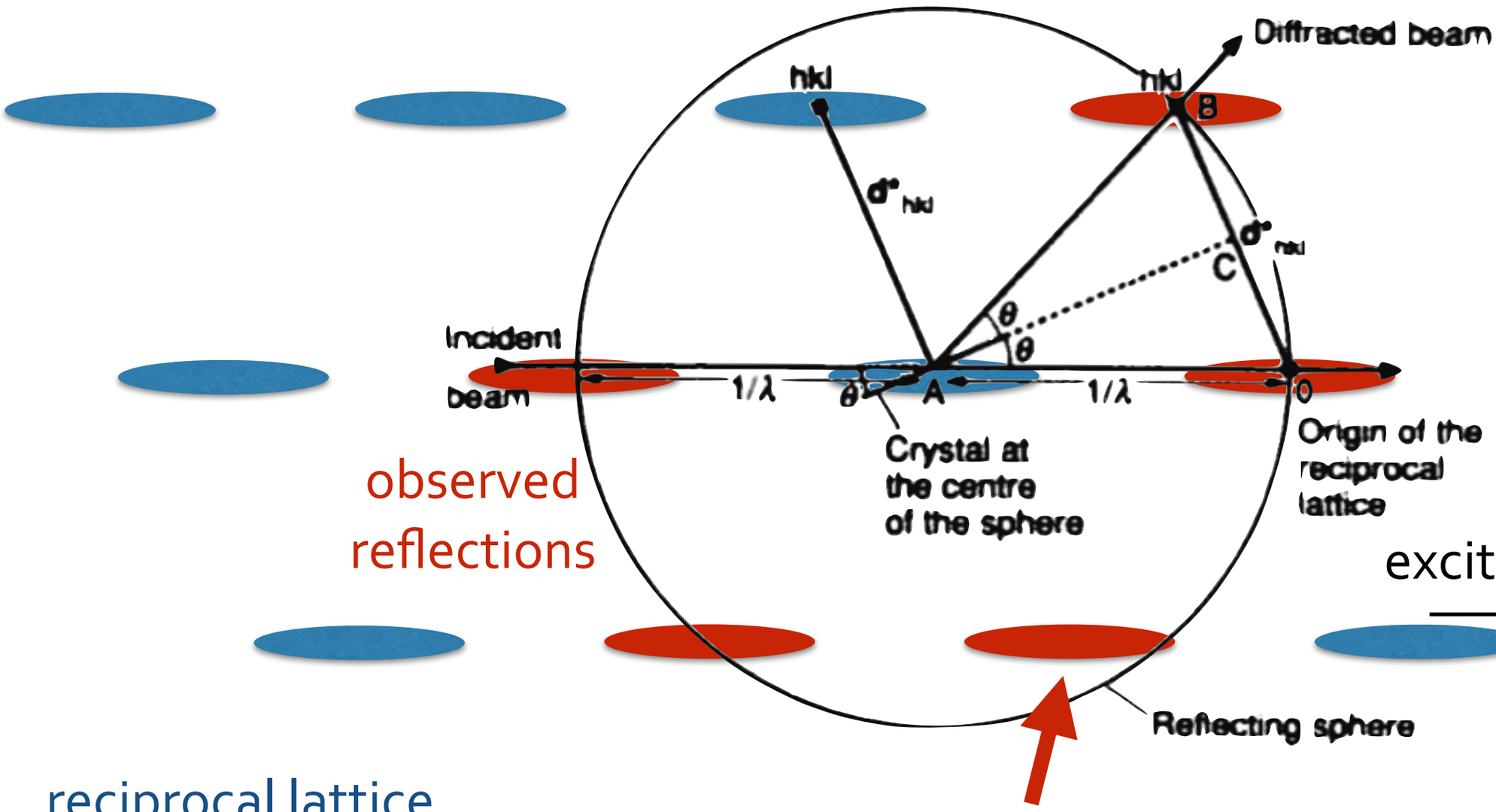

observed reflections

reciprocal lattice

*Basics of Crystallography and Diffraction*, C. Hammond

# the Ewald sphere in the TEM

relrods: **re**ciprocal **l**attice **rods**  *finite size effect of a thin sample*

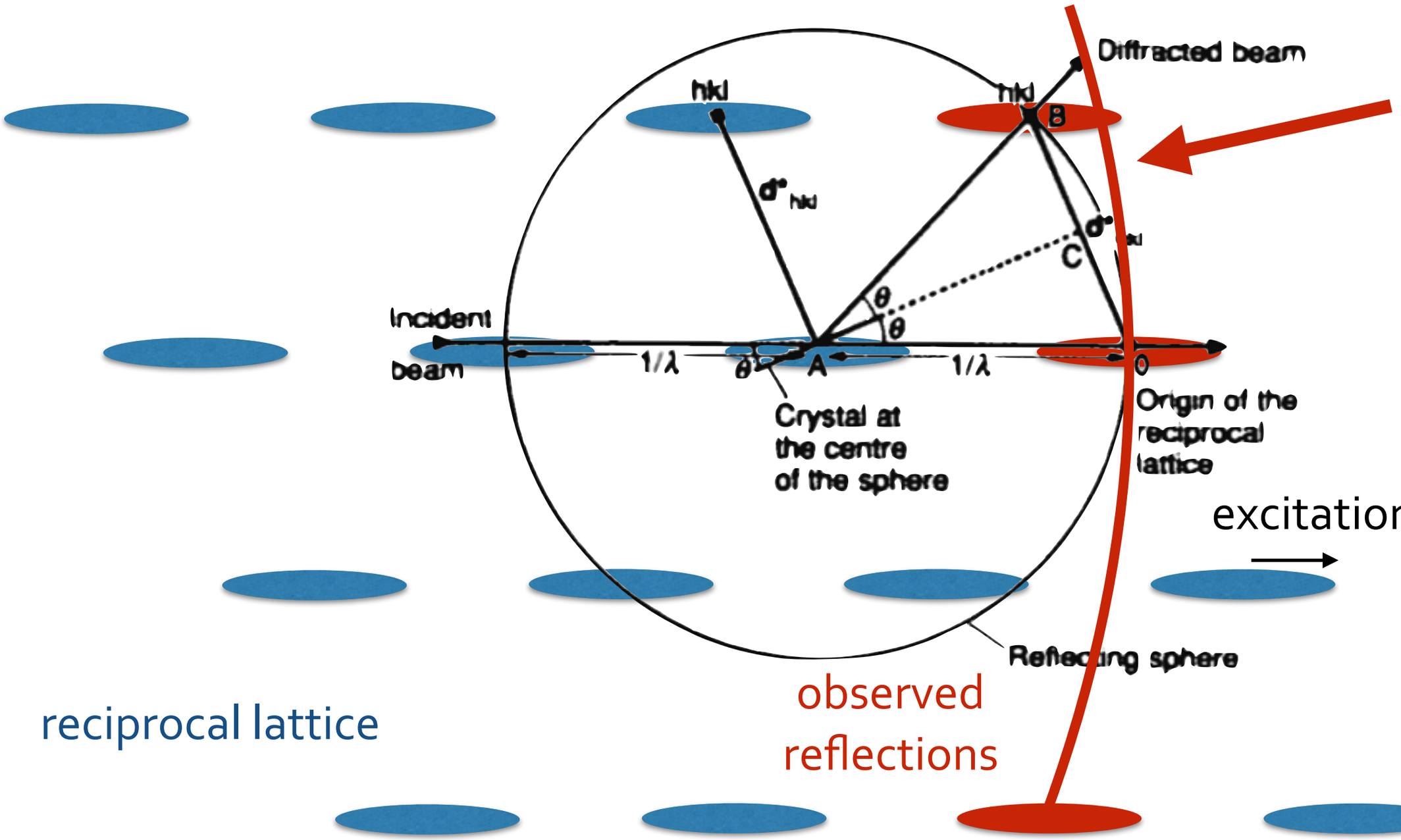



*Basics of Crystallography and Diffraction*, C. Hammond

# the Ewald sphere in the TEM

relrods: **re**ciprocal **l**attice **rods** *finite size effect of a thin sample*

**the Ewald sphere appears flat! (λ ~ 0.05 Å *vs.* 1.54 Å for Cu Kα X-rays)**




*Basics of Crystallography and Diffraction*, C. Hammond

# deviations from kinematic theory in electron diffraction

- **multiple scattering - dynamical diffraction**
  - need to use the "Howie-Whelan equations"
  - simultaneous equations that describe the direct beam and scattered beam
- **"relrods"**
  - thin samples cause reciprocal lattice points to be streaked (think nanoparticle broadening)
  - "excitation error"

# Diffraction in the Electron Microscope

| V (kV) | λ (Å) |
|---|---|
| 20 | 0.086 |
| 100 | 0.037 |
| 1000 | 0.009 |

# structure factor in the TEM

- In the TEM, because we have *multiple scattering*, we often **see reflections that should be systematically absent**.
  - ***This is a breakdown of the kinematic approximation.***
    - Electrons strongly interact with matter because they are charged particles; therefore, they often scatter many times.
    - Electrons and X-rays scatter $\propto$(atomic number)$^2$; however, X-rays interact much less.
- **Conclusion: intensities in electron diffraction patterns require non-trivial analysis to solve atomic structures**

# Diffraction in the Electron Microscope

- observable patterns:
  - amorphous ring pattern
  - single crystal SAED pattern
  - polycrystalline SAED pattern
  - CBED pattern
  - Kikuchi patterns