The Take Home Message

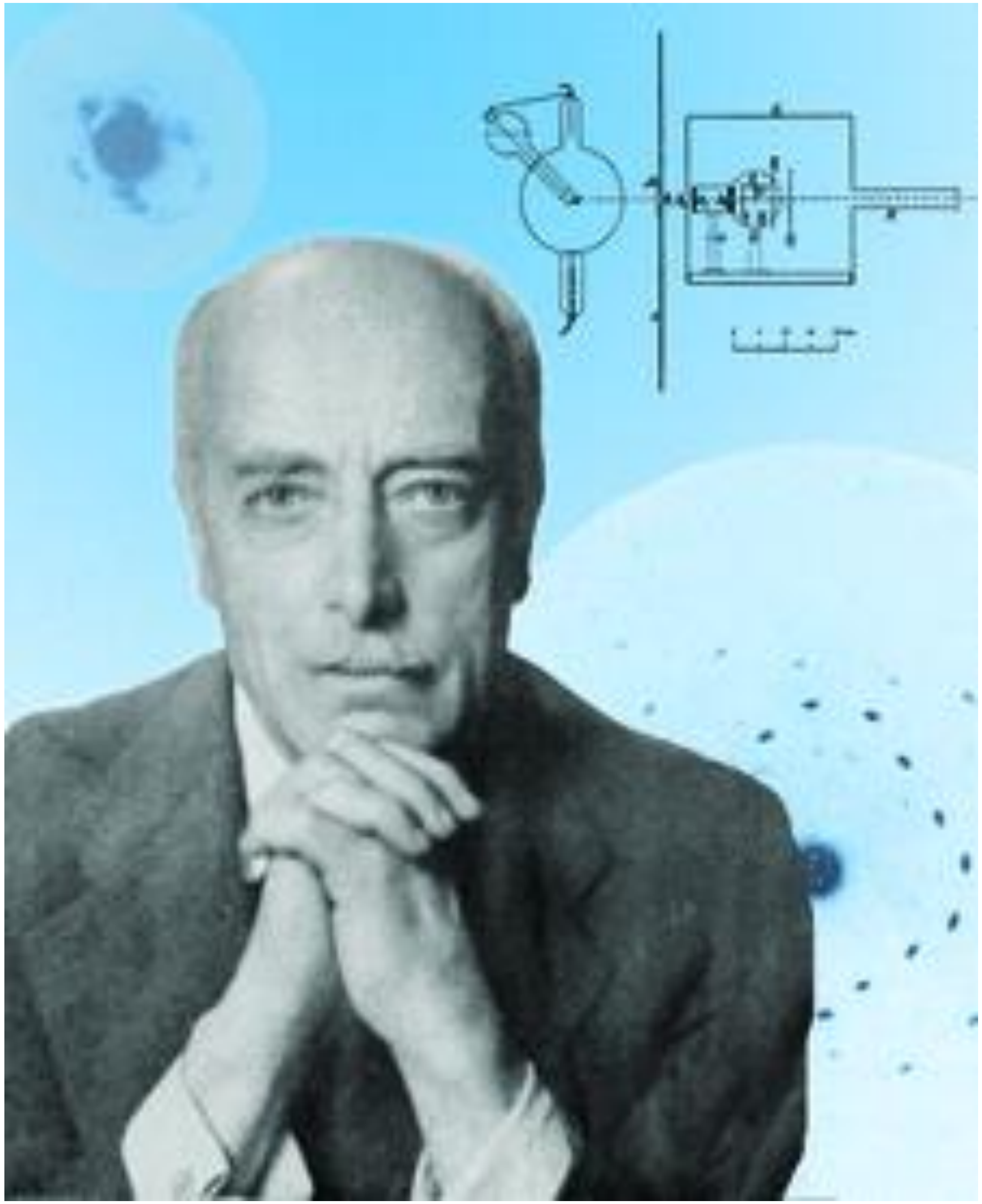
- The electrons scatter the x-ray radiation. Each atom scatters proportional to its atomic number
- The scattered waves interfere with each other because of the periodic nature of the crystal.
- The distance between the spots is inversely related to the repeat distance.
- The pattern of the individual scatterers is contained in the intensity of each spot.
- By applying a Fourier series the intensity can be converted to the scattering arrangement.

Lesson 6

- Some history
- The reciprocal lattice and cell

History of Diffraction

- Starts in Munich, Germany about 1910
- Involves 3 German physicists
- One is a professor, one an instructor, and one a graduate student.
- Several articles in Acta Cryst. Section A, Vol 68, January 2012.



Arnold Summerfield

Summerfield

- Full Professor in Munich
- Very Good Classical Physicist (at a time when physics was greatly changing)
- Very good pianist.
- Today most remembered for suggesting that electron levels were elliptical and not spherical.

Paul Peter Ewald

Ewald

- Ewald was a student of Summerfield.
- His thesis dealt with calculating the pattern from a regular two and three dimensional grid of radiation emitters. The interest at the time was in radio waves whose wavelengths are in meters but it could be applied to any radiation
- Left Germany and was a professor at the Brooklyn Institute of Technology for many years.

Max von Laue

von Laue

- Was a student of Einstein's
- Was German nobility(?)
- Was in Munich as a lecturer.
- Put the following ideas together
  - X-rays are radiation with Å wavelength
  - Crystals are regular arrays with Å separation
  - The interference reported in Ewald's thesis should therefore be observed using crystals and x-rays.

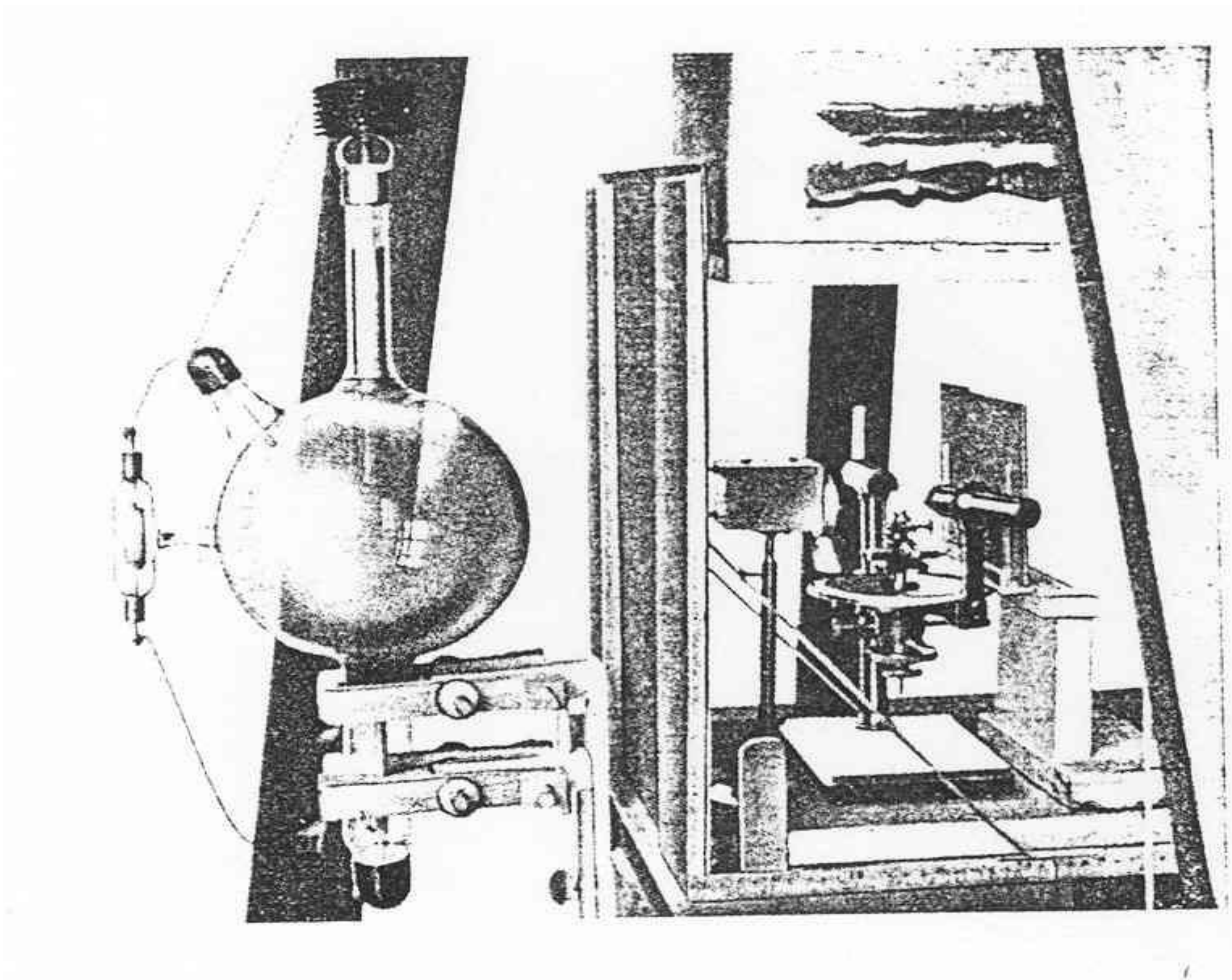
Onward

- Von Laue is not easily discouraged
- He decides that if a crystal is exposed to white radiation then the atoms will fluoresce at their characteristic wavelengths
- He decides to do the experiment to see if it works
- Only one problem—von Laue does not dirty his hands with experiments.

The experiment

- Von Laue recruits a Sommerfields x-ray assistant named Walter Frederick.
- Since the atoms will be producing the x-rays, an atom with an easily detected wavelength should be used.
- They chose copper and use $CuSO_4 \cdot 12H_2O$
- Since the pattern should come off in all directions the film is placed on the incoming x-ray side
- The result—a blank film

The Apparatus



One Further Comment

- At time von Laue appears to be haughty
- After Hitler comes to power he brings the Dutch physicist Peter Debye (another Summerfield student) to Germany.
- Debye for a while becomes the chief spokesman for Nazi physics and its attempt to disprove “Jewish physics” (Einstein).
- Von Laue bitterly fights the Nazi's and Debye
- He is kept out of the concentration camps because of his nobility.

What von Laue Proved

1. That x-rays were waves

2. That their wavelength was on the order of Angstroms.

3. That the distance between atoms in a crystal was also on the order of Angstroms

What von Laue never understood.

He never understood that the process was not fluorescence.

He never understood why white radiation produced the result as he never characterized the wavelength of the diffracted beam.

He understood the interference effect but not how it related to the unit cell.

The Braggs

Father and son William and William Lawerence

Bragg senior built the crystal diffractometer. Showed that each Laue spot consisted of only one x-ray wavelength (the end of the particle idea).

Larry figured out that this was diffraction of scattered x-rays and derived the famous Bragg equation.

Ewald's Contirbutions

While the idea of Bragg planes is useful it does not explain their relation to the crystal itself.

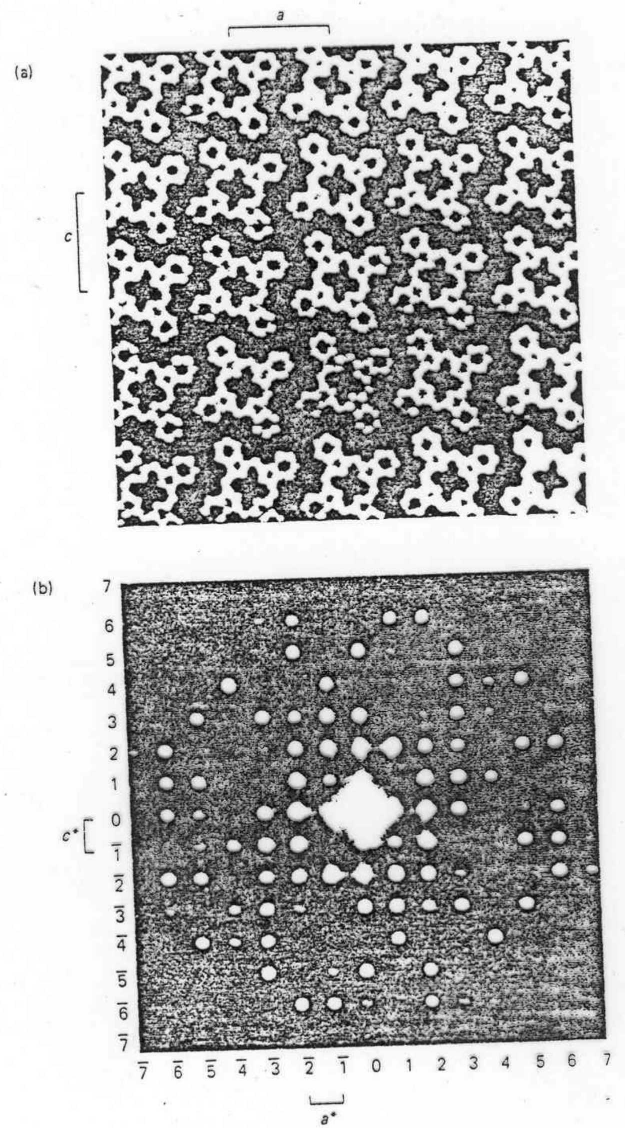
Develops the dynamic theory of diffraction.

Introduces the idea of reciprocal space.

Reciprocal Space

- This is the Fourier transform of the electron density in the crystal.
- There is a certain irony—the real space is inside the crystal and we cannot directly experience it. Reciprocal space is what we see in the diffraction pattern.
- Note real space is continuous while reciprocal space is discrete.

Real and Reciprocal Space



Some Nomenclature

All reciprocal vectors will be labeled with a superscript * and have units of length^{-1}.

The three basis vectors of the reciprocal unit cell are labeled **a*, b*** and **c***

There are also three angles which are **α*, β*,** and **γ***

Any vector with * will assumed to be defined in reciprocal space

Reciprocal Indices

- In real space used x, y, and z which are real numbers.
- Since reciprocal space is discrete need different indices which will be integers.
- Use h,k,l where h is along **a***, k along **b*** and l along **c***
- For cells with 3-fold or 6-fold axes use hkil where i=-(h+k)
- hkl have many meaings in crystallography

What do these mean

- An index of 1 means that this is a full translation along real space
- An index of 2 represents a translation of ½ way across the cell.
- Translation is along the reciprocal coordinates to be defined later.
- Note the longer the reciprocal vector the shorter the corresponding real vector.

What does it mean for hkl to be non-integral

- Cell is too small –if axis is 1/2 times the correct repeat distance than index ½ = 1
- Supercell—long range ordering
- Crystal is a twin (more than one crystal) and non-integral index represents the other crystal.
- High order diffraction effects. This is a Bragg reflection where n is > 1.

How does the Reciprocal Relate to the Real Cell

- By definition

$\mathbf{a}\cdot\mathbf{a^*} = 1 \quad \mathbf{a}\cdot\mathbf{b^*} = 0 \quad \mathbf{a}\cdot\mathbf{c^*} = 0$

$\mathbf{b}\cdot\mathbf{b^*} = 1 \quad \mathbf{b}\cdot\mathbf{c^*} = 0 \quad \mathbf{c}\cdot\mathbf{c^*} = 1$

- This means **a*** is perpendicular to the **bc** face
  b* is perpendicular to the **ac** face and
  c* is perpendicular to the **ab** face.

Orthogonal Coordinates

- If a real basis vector is perpendicular to the other two real basis vectors than the real and reciprocal vectors are parallel
- This means **|v|** = 1.0/**|v*|** and vice versa
- This applies for all orthogonal cell systems.
- Also applies to the **b** axis in a monoclinic cell and the **c** axis in a hexagonal/trigonal cell.
- The magnitude of **|v|** is always 1/d where d is the distance between planes.

Monoclinic Cell

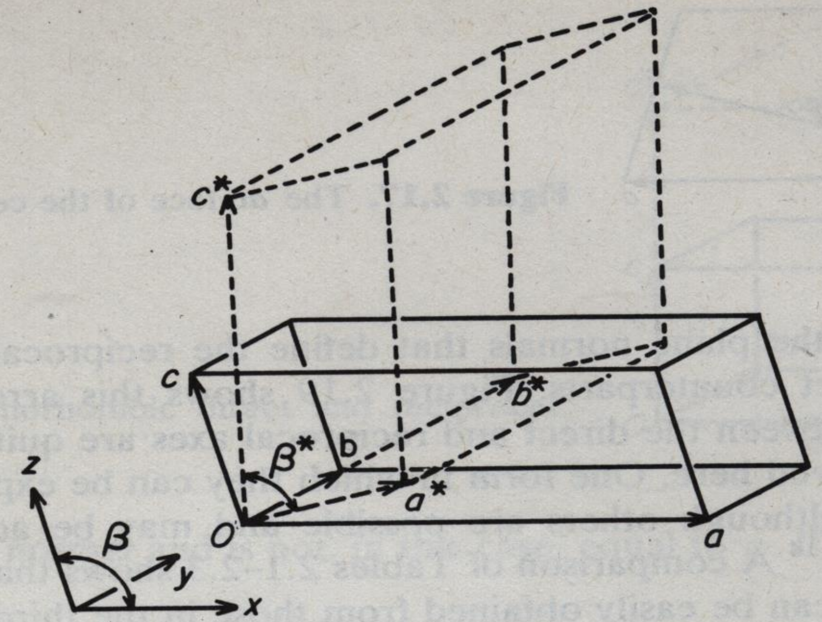


Figure 2.18. Monoclinic direct and reciprocal cells.

Triclinic Cell

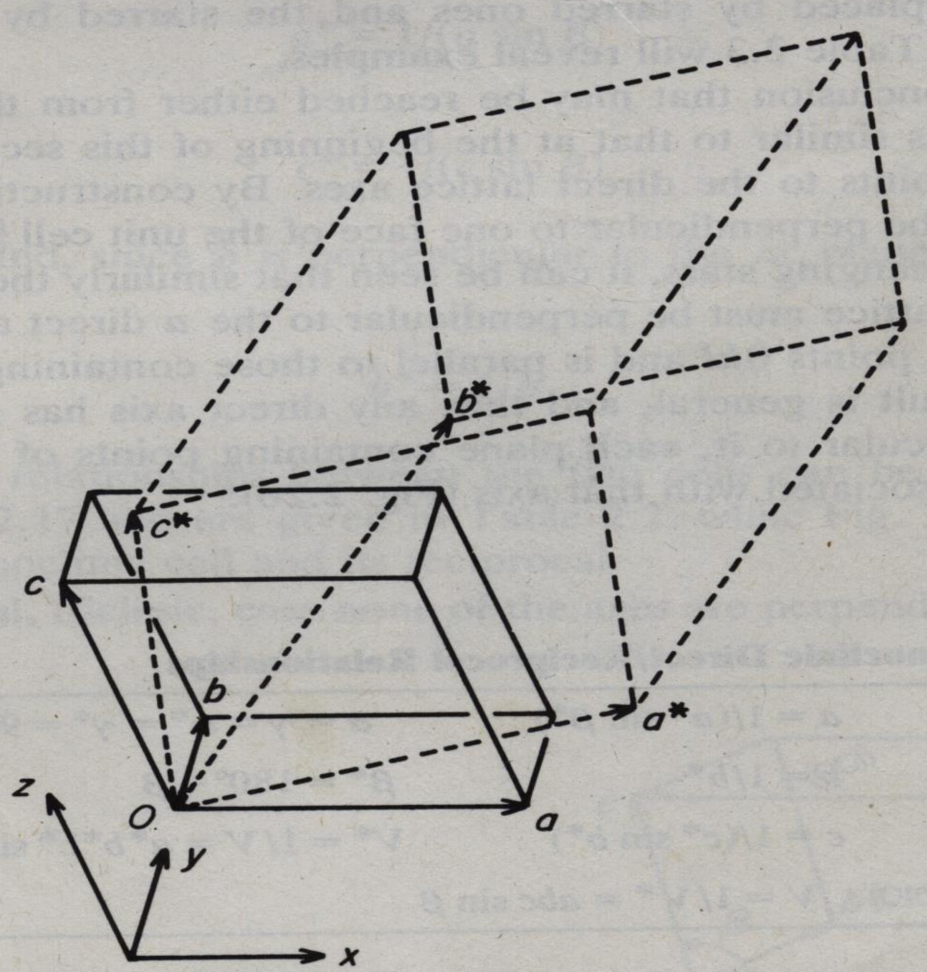


Figure 2.19. Triclinic direct and reciprocal cells.

Formulas for Conversion

TABLE 2.3 Triclinic Direct and Reciprocal Relationships

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^* c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^* c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^* b^* \sin \gamma^*}{V^*}$$

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

$$V^* = \frac{1}{V} = a^* b^* c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \qquad \cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma} \qquad \cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \qquad \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$