COMMONWEALTH OF AUSTRALIA

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Measuring Crystal Structures

Lecture 5

Space Groups

Ionic Crystals

Lecture 6

Diffraction

Miller Indices

Bragg's Law

Lecture 7

Solid State Materials

Ionic vs Covalent Bonding

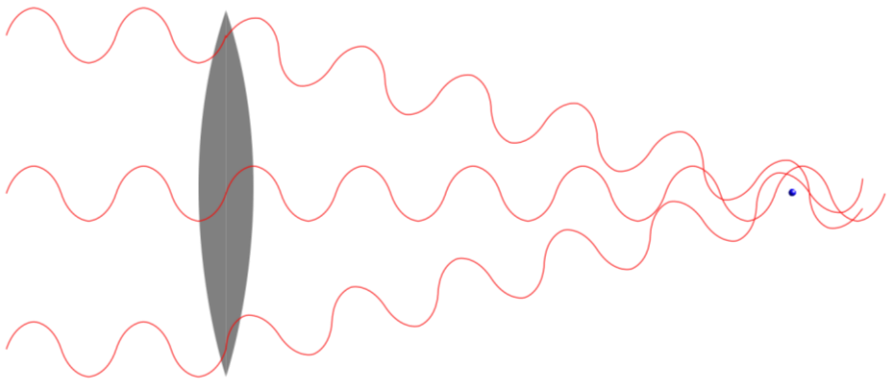
Ionic Radii

Lattice Enthalpy

Where are the atoms?

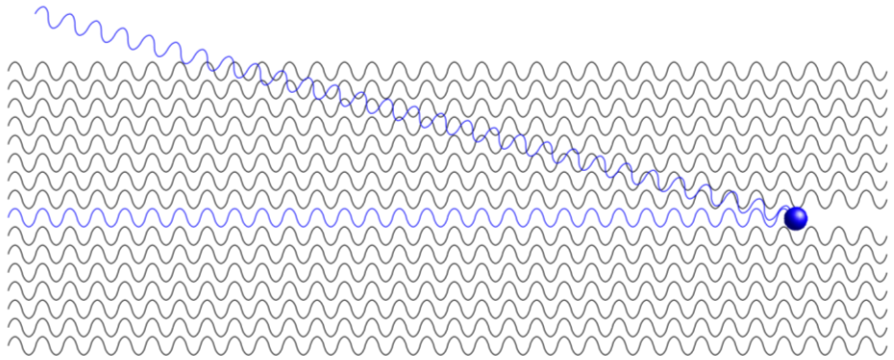
Ideally, we could 'see' atoms in a microscope by focusing visible light on them.

- But the sizes of atoms are in the order of Ångstroms (Å, 10^{-10} m), while visible light has wavelengths close to a micron (µm, 10^{-6} m), so this doesn't work.



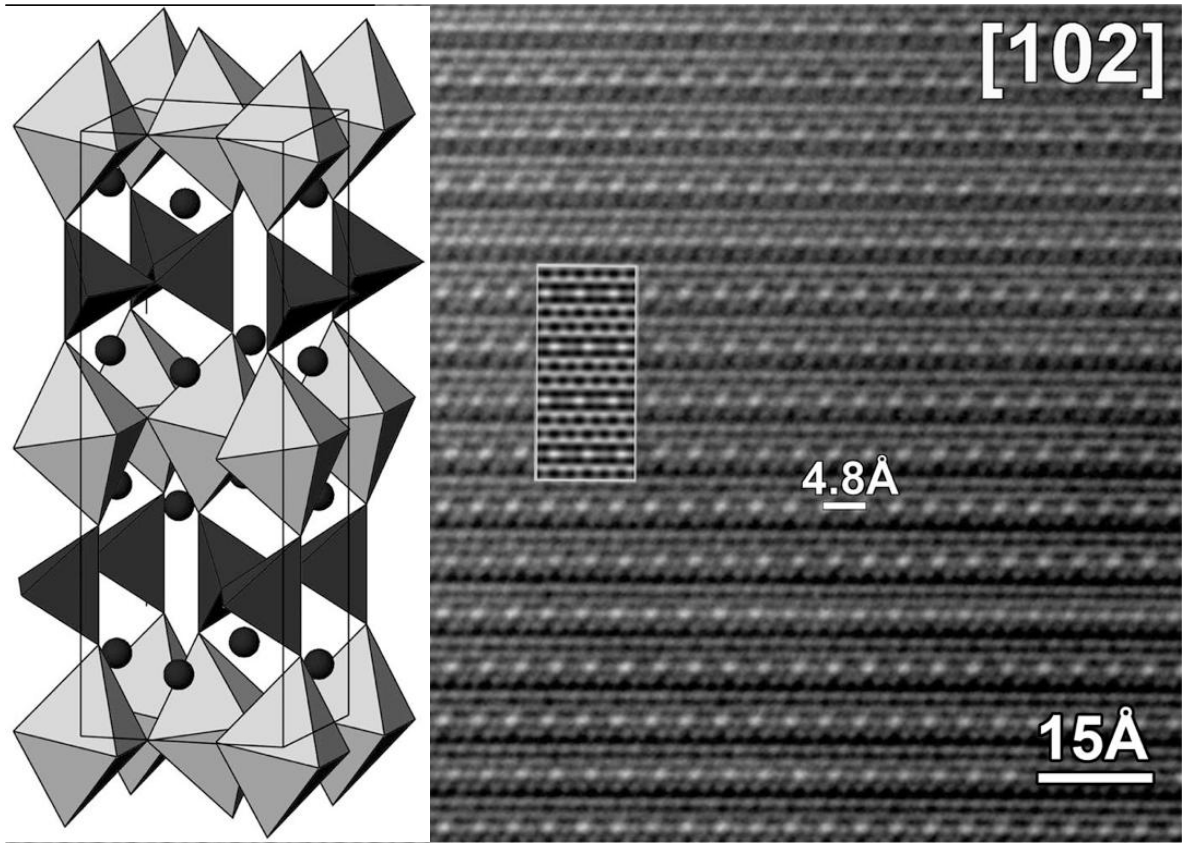
Electromagnetic waves with wavelengths in the order of Ångstroms are X-rays.

- But we cannot focus X-rays with a lens, so we could never get a signal strong enough to detect.



Visualising Atoms with Electron Microscopy

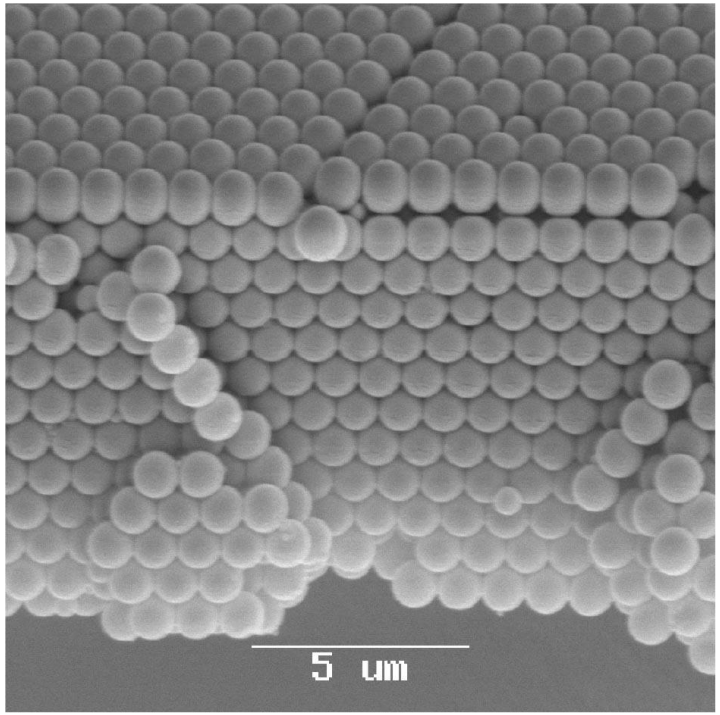
Electrons – with wave and particle behaviours (wave-particle duality) – can be focused by an electric field to resolve individual atoms. But microscopy has limitations in locating all atoms and how they are arranged.



Diffraction of Light

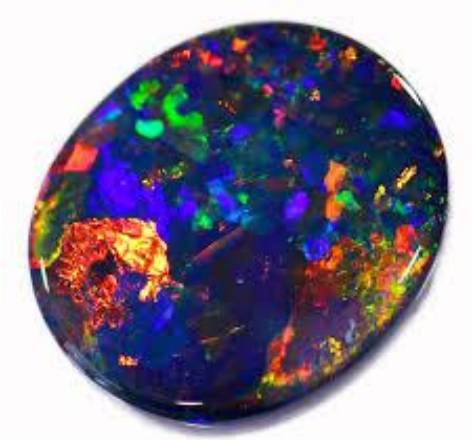
Q: Why does the colour of an opal depend on its viewing angle?

A: Because the colour arises not from light absorption in the visible region, but from the diffraction of light.



Electron microscope image of opal

Opal consists of the close packing of silica spheres of uniform size, with diameters in the range 130 to 300 nm. Visible light has a wavelength range of ~400-700 nm.

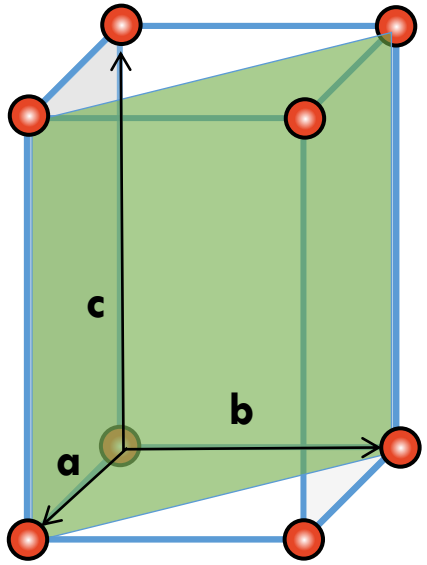


Because the *d*-spacings (the spacing between equivalent layers) in the opal lattice are on a similar length scale to visible light, the light is diffracted by the opal lattice.
(This is a 3D analogue of diffraction by an oil film on water giving a rainbow.)

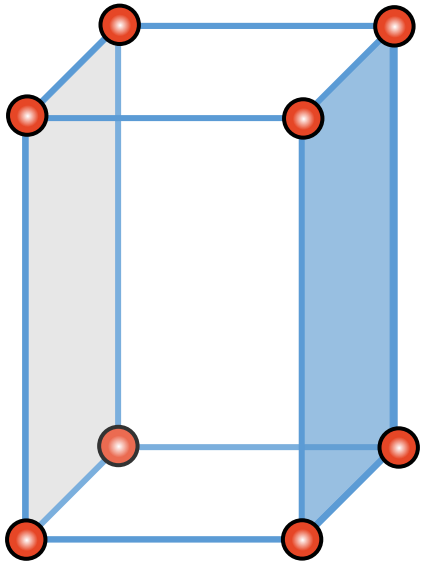
See pre-lecture video for more details

Miller Indices Define Planes in a Crystal Lattice

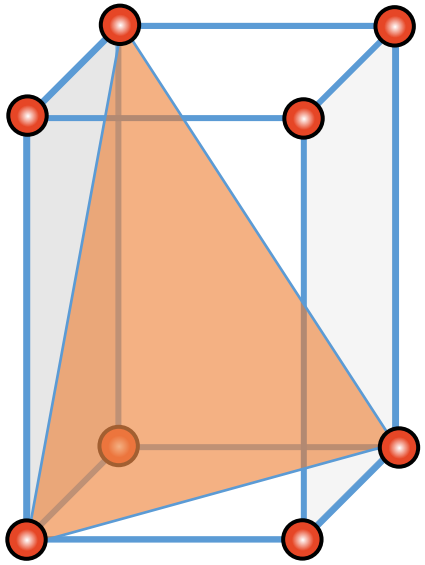
- (*h k l*) for *h*, *k*, *l* integers defines the plane *h* **a** + *k* **b** + *l* **c**
- The reciprocal of the Miller index (1/h) gives the axis intercept
- Negative integers are written as $\bar{h}$
- Typical interatomic distances in a crystal lattice are ~1-3 Å



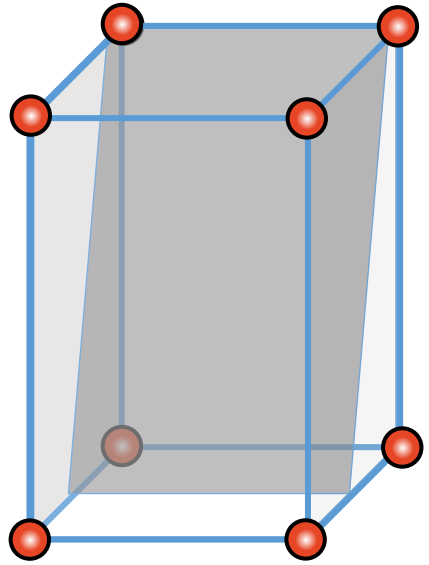
(110)



(010)



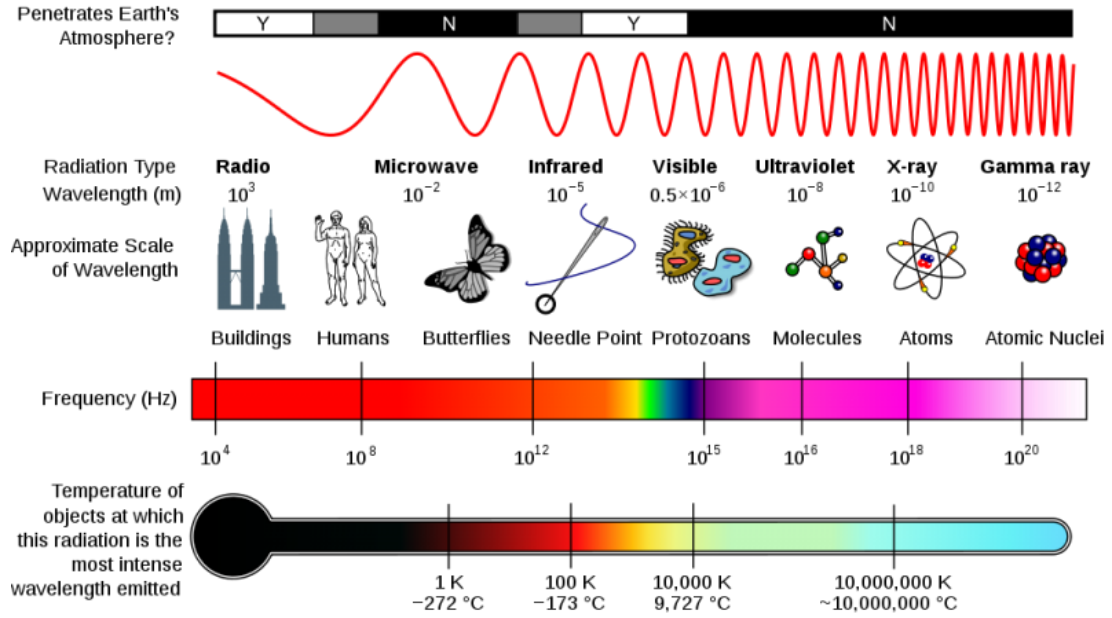
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(201)

What type of radiation will diffract off Miller planes?

- The Electromagnetic Spectrum



In crystallography we are looking ***ordering at the atomic length scale***

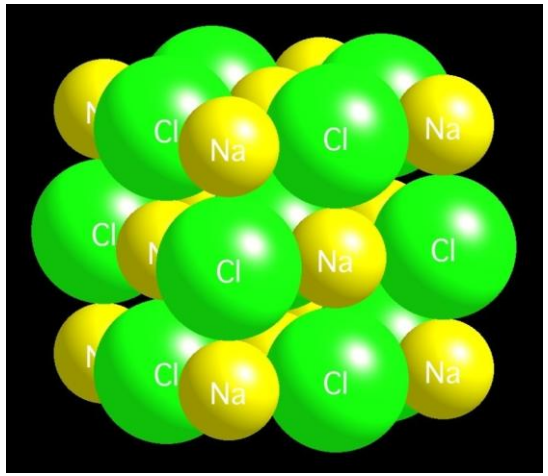
- typical interatomic distances are ~1-3 Å
- this is in the same length scale as **X-rays** – this is why we use X-ray crystallography
- we can also use **neutron** and **electron** beams for diffraction due to their wave-like properties

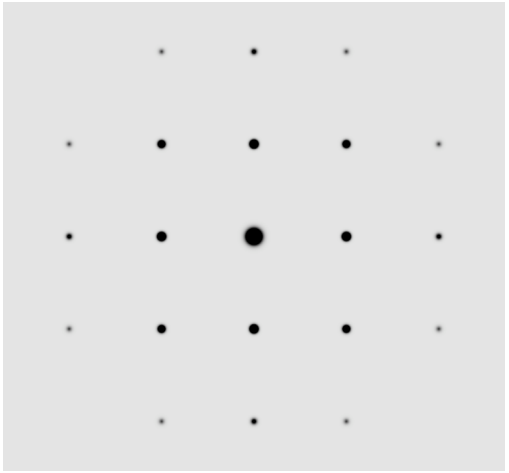
X-ray Diffraction

- Wilhelm Röntgen – discovers X-rays in 1895
- Max von Laue – confirms wavelength by diffraction experiment
- William H. & William L. Bragg – solve first crystal structure

Nobel prizes for Physics in 1901, 1914 and 1915

Structure of NaCl



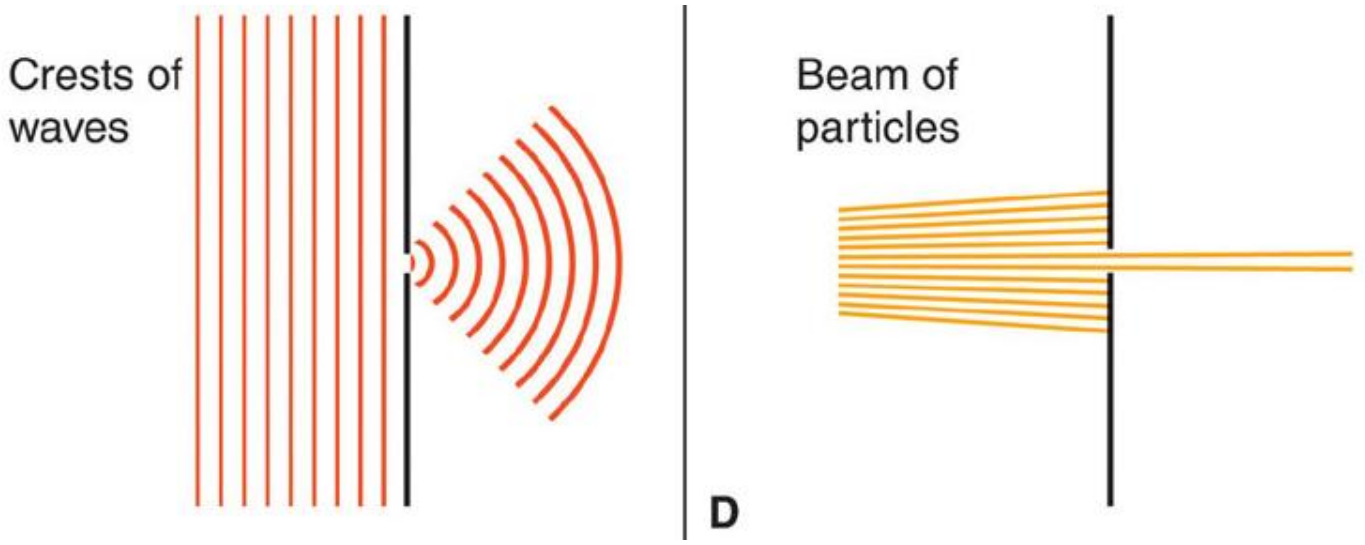


Diffraction pattern of NaCl

Diffraction

In crystallography, we take a large number of atoms arranged in a crystal and diffract X-rays off them, which combine to form a single image that conveys information about the average structure of all atoms.

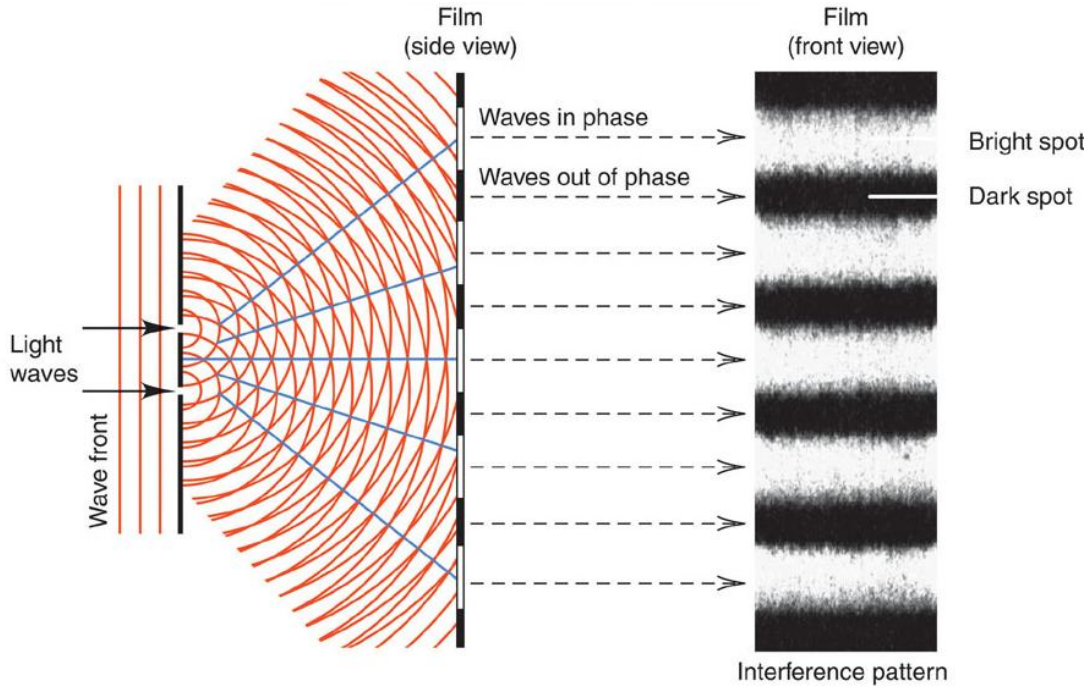
Diffraction is an inherent property of waves.



Diffraction by Optical Gratings (1D)

Consider the diffraction of coherent waves by two slits:

Constructive and destructive interference at the crests and troughs of diffracted waves creates a diffraction pattern that conveys information about the distance between the slits.

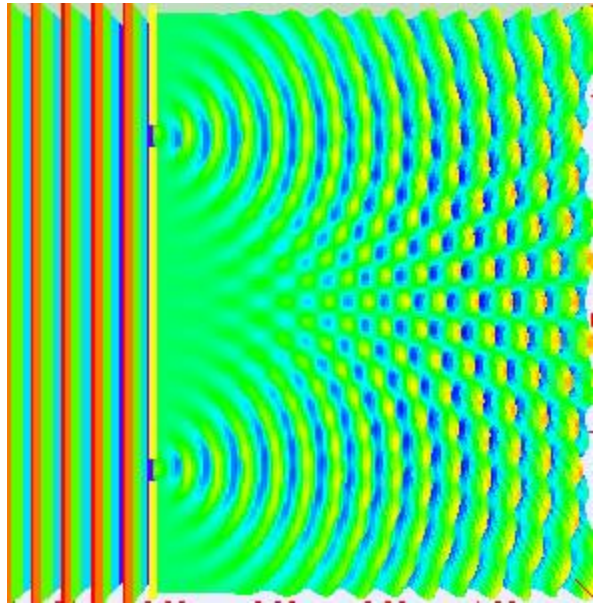


Figures from Silberberg, "The Molecular Nature of Matter and Change" 3rd Edition (2003), McGraw-Hill

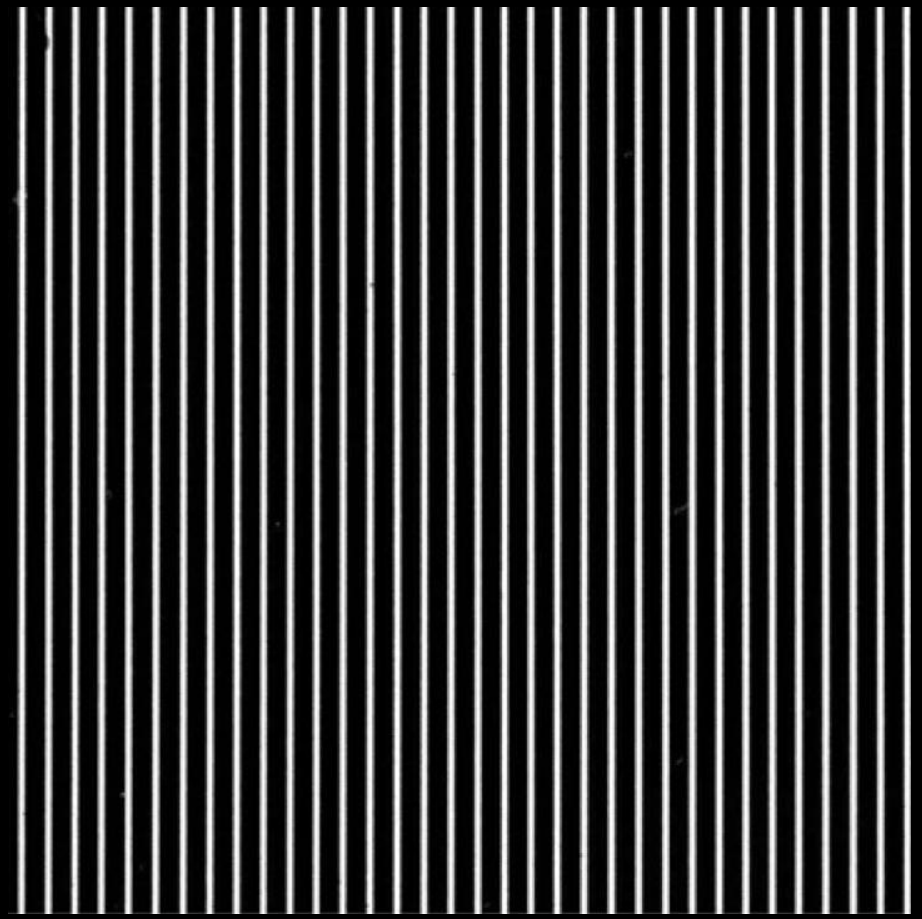
Diffraction by Optical Gratings (1D)

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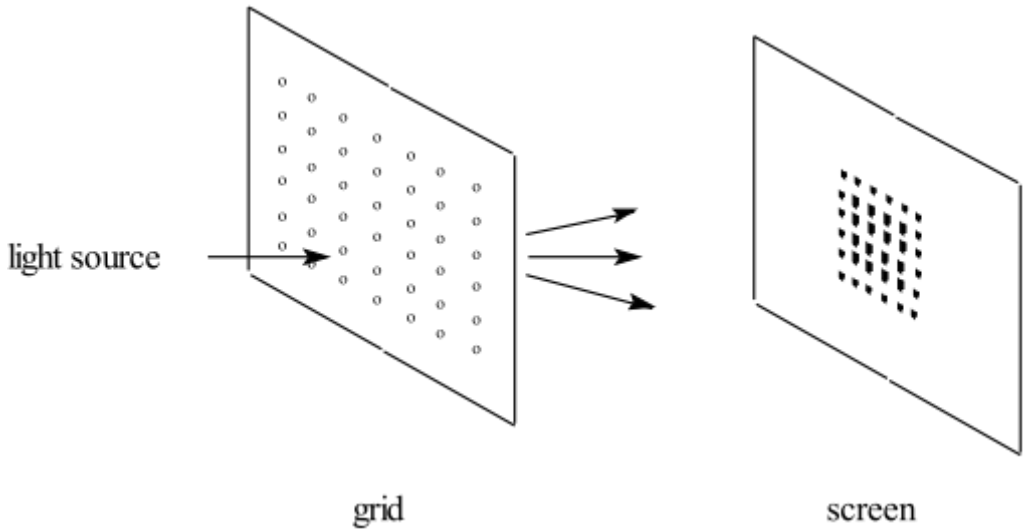


Diffraction by Optical Gratings (2D)

When more than two slits are placed in a regular array, the diffraction pattern conveys more information about their disposition.

While a one-dimensional array of slits gives a one-dimensional diffraction pattern, a two-dimensional array of slits gives a two-dimensional diffraction pattern.

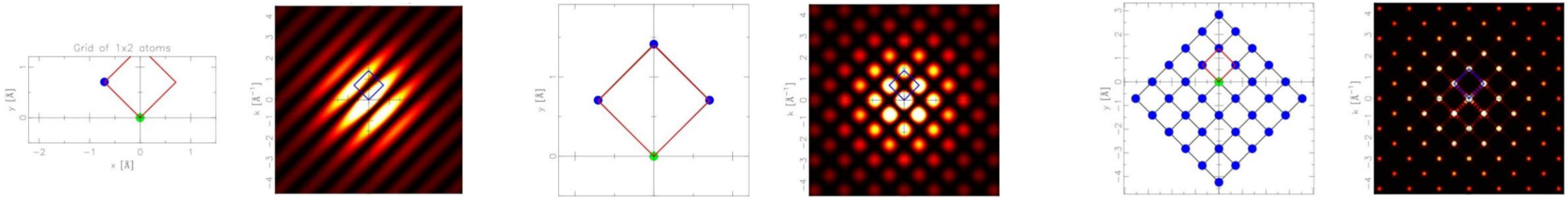
When coherent visible light (i.e., a laser) is shone through a slide imprinted with an opaque grid of similar dimensions to its wavelength, a diffraction pattern is observed.



Diffraction by Optical Gratings

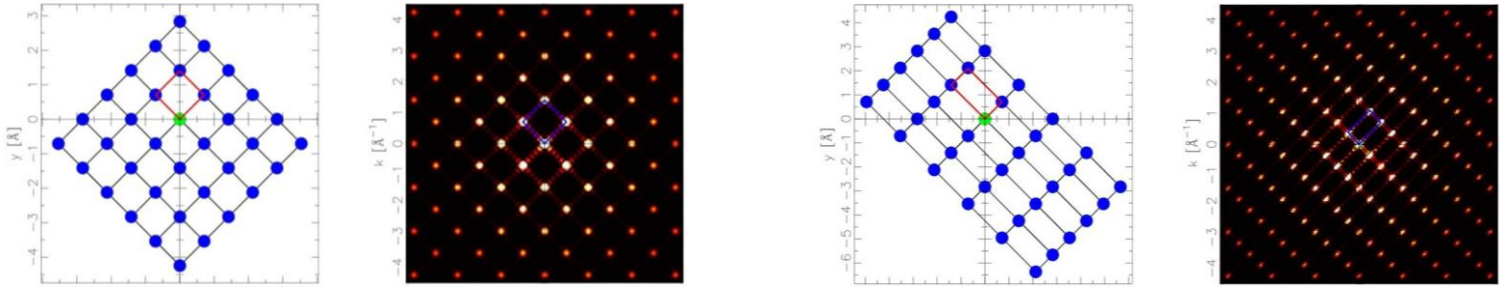
The patterns produced are similar to these simulated ones.

- The diffraction pattern is not simply a projected image of the grid;
- The more spots are included in the beam (i.e., the bigger the beam size), the better the diffraction pattern is resolved;

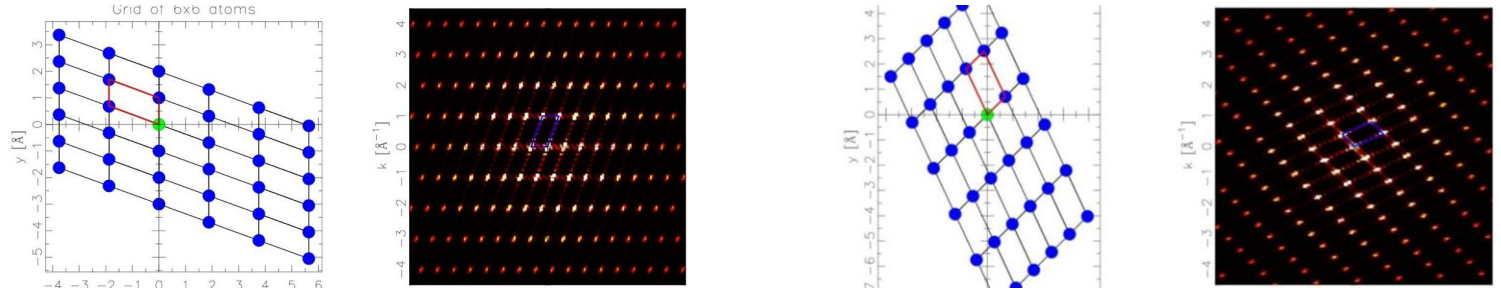


Diffraction by Optical Gratings

- The diffraction pattern changes for different grids.



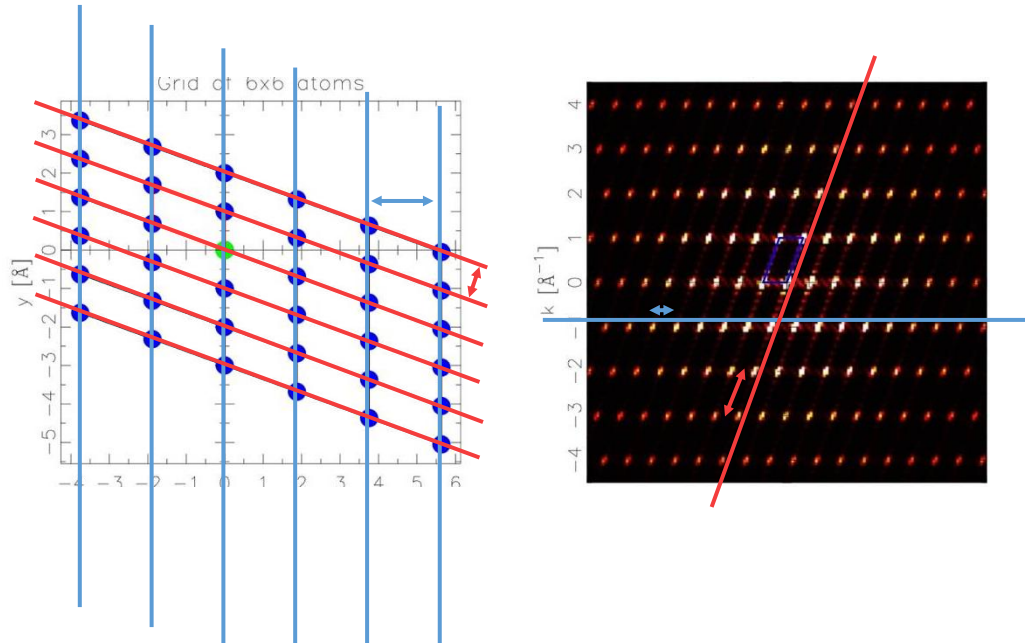
- The diffraction pattern rotates with the grid.

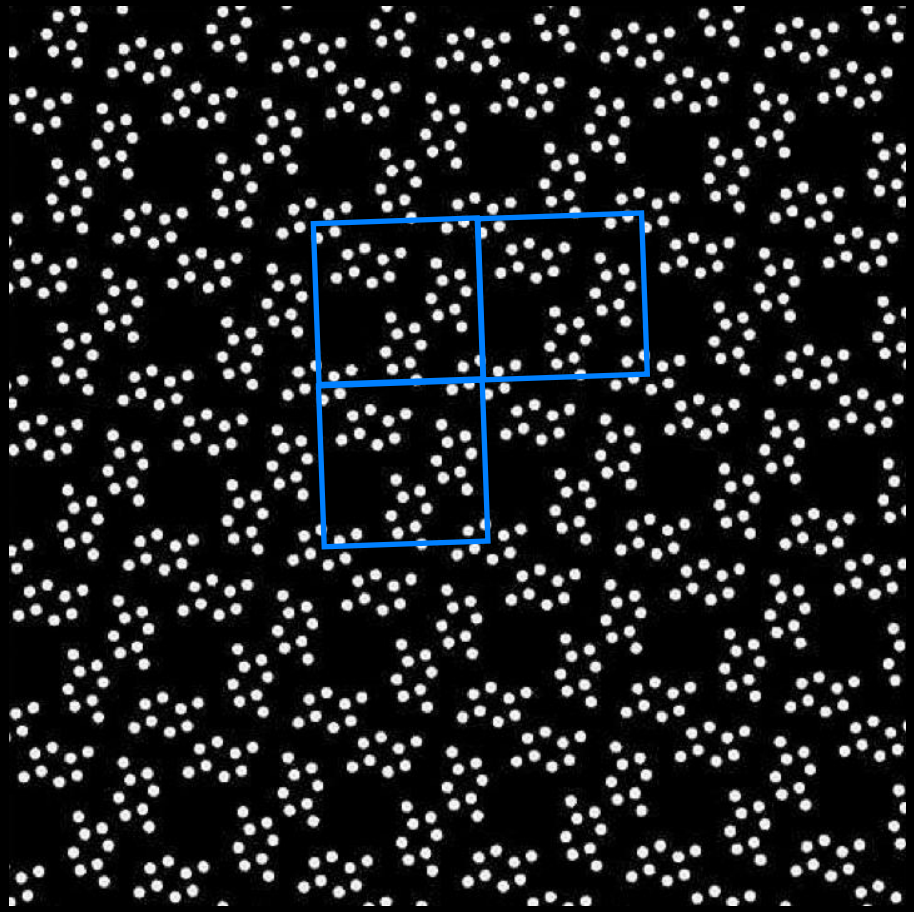


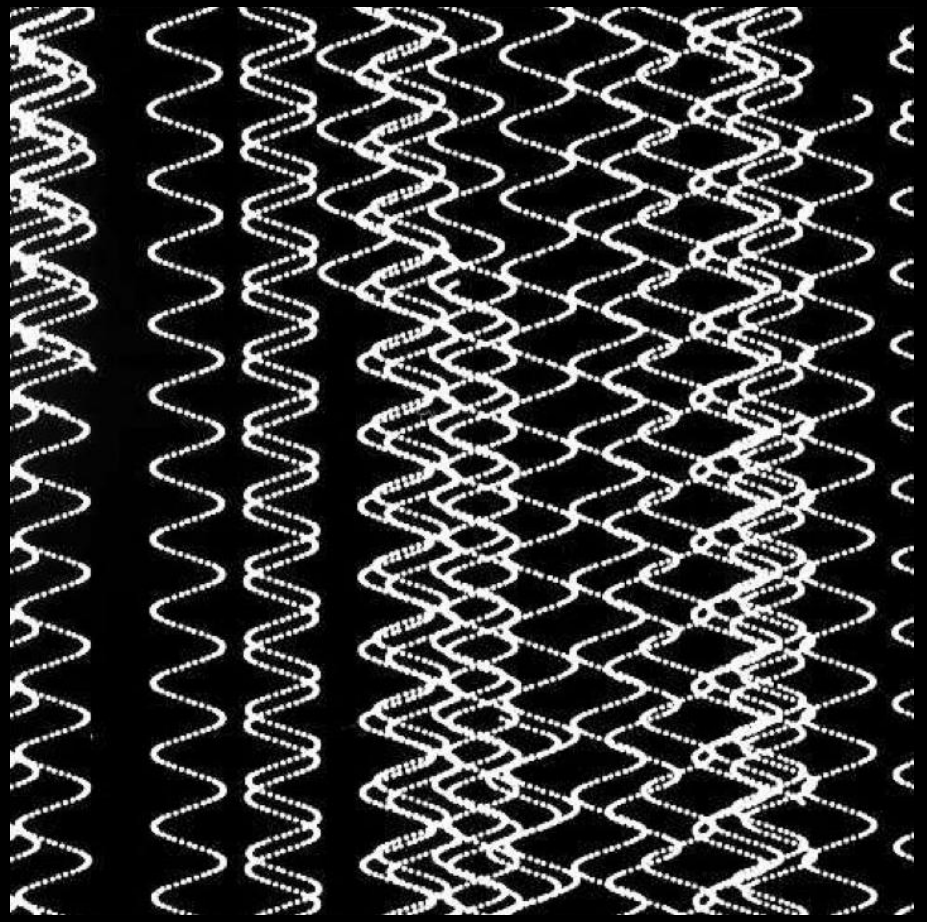
Diffraction by Optical Gratings

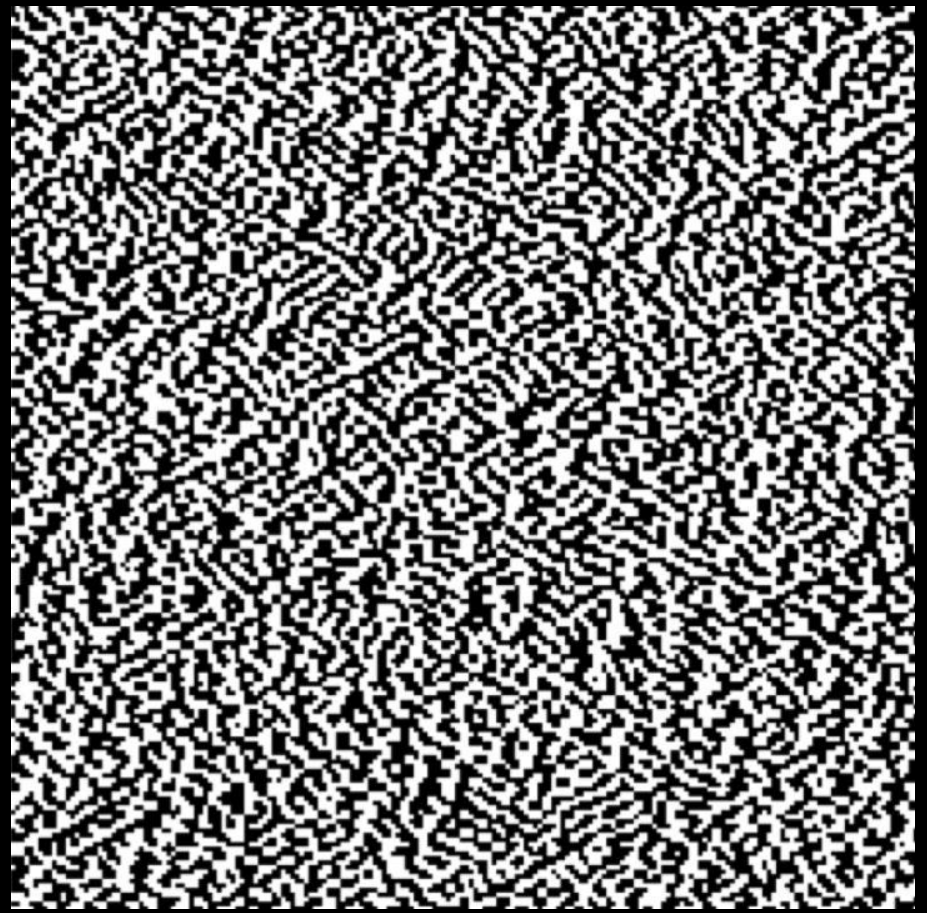
The object in real space creates a pattern in reciprocal space.

- Diffraction spots run perpendicular to their corresponding Bragg planes. I.e., planes running vertically give rise to spots running horizontally (blue).
- The distance between the spots is inversely proportional to the d-spacing between the planes. I.e., planes that are further apart give rise to spots that are closer together. Planes that are closer together give rise to spots that are farther away.





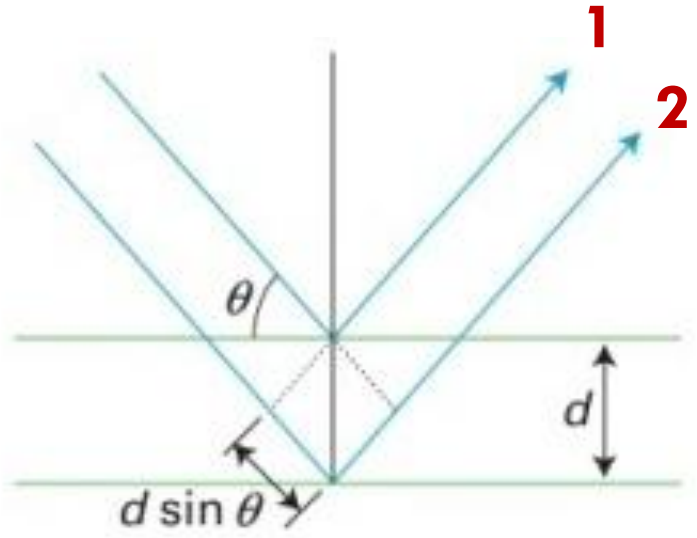




Bragg Diffraction

The Braggs explained diffraction by suggesting that X-rays behave as if they are reflected by planes of the crystal lattice.

If the angle of incidence of the X-rays with respect to the planes is such that constructive interference occurs, then a diffraction spot is observed.



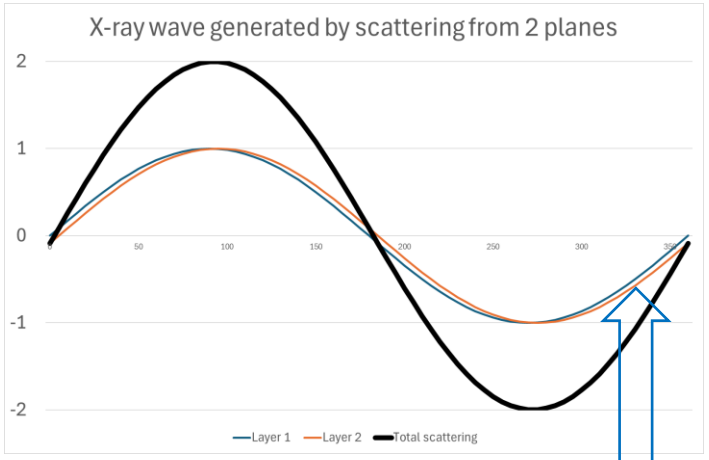
The extra distance travelled by beam **2** is $2d\sin\theta$. Thus, if constructive interference is to occur then this distance must correspond to an integral number (n) of wavelengths, i.e., $n\lambda = 2d\sin\theta$.

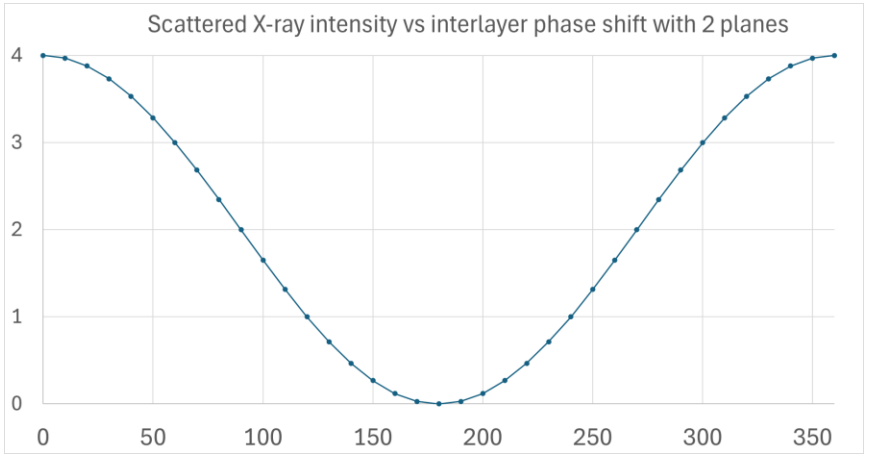
See also https://www.youtube.com/watch?v=QHMzFUo0NL8

See 'diffraction' spreadsheet on Canvas (bottom of week 2 page) if you want to play with the phase shift to see what this does.

Simulating Constructive and Destructive Interference

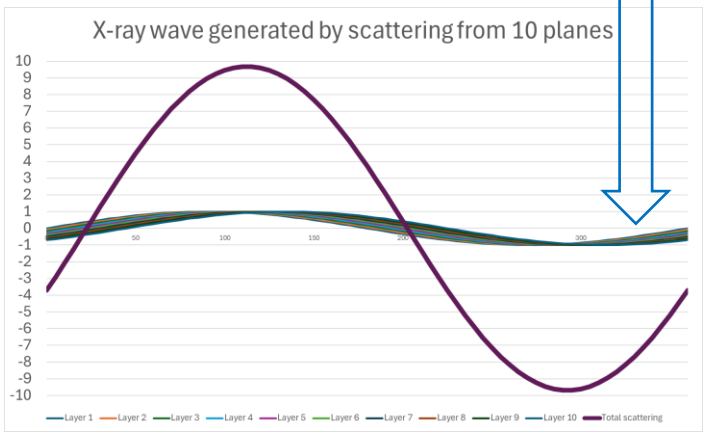
2 planes

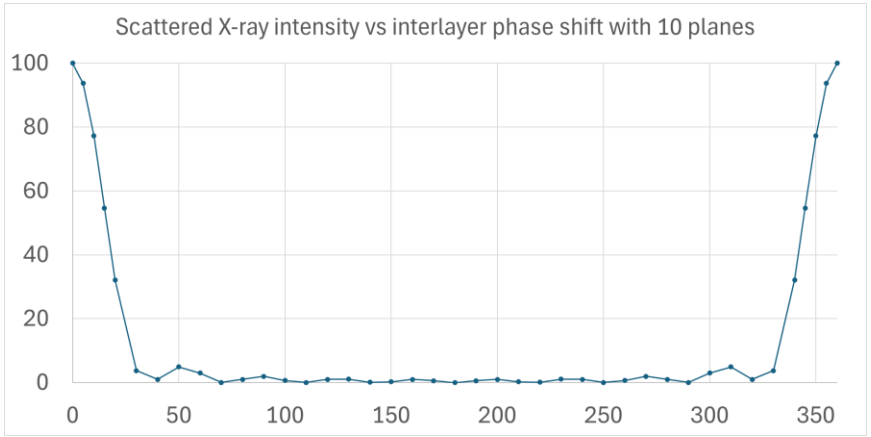




Scattered waves 5° out of phase

10 planes





How would adding more crystal planes change things?

Measuring Diffraction Patterns

When an X-ray beam hits a crystal, it only 'sees' a 2D *projection* of the 3D real lattice.

Consequently, the observed diffraction pattern will only be a (curved) 2D *slice* through the 3D reciprocal lattice.

To measure a complete diffraction pattern, we need to rotate the crystal through all possible (unique) orientations.

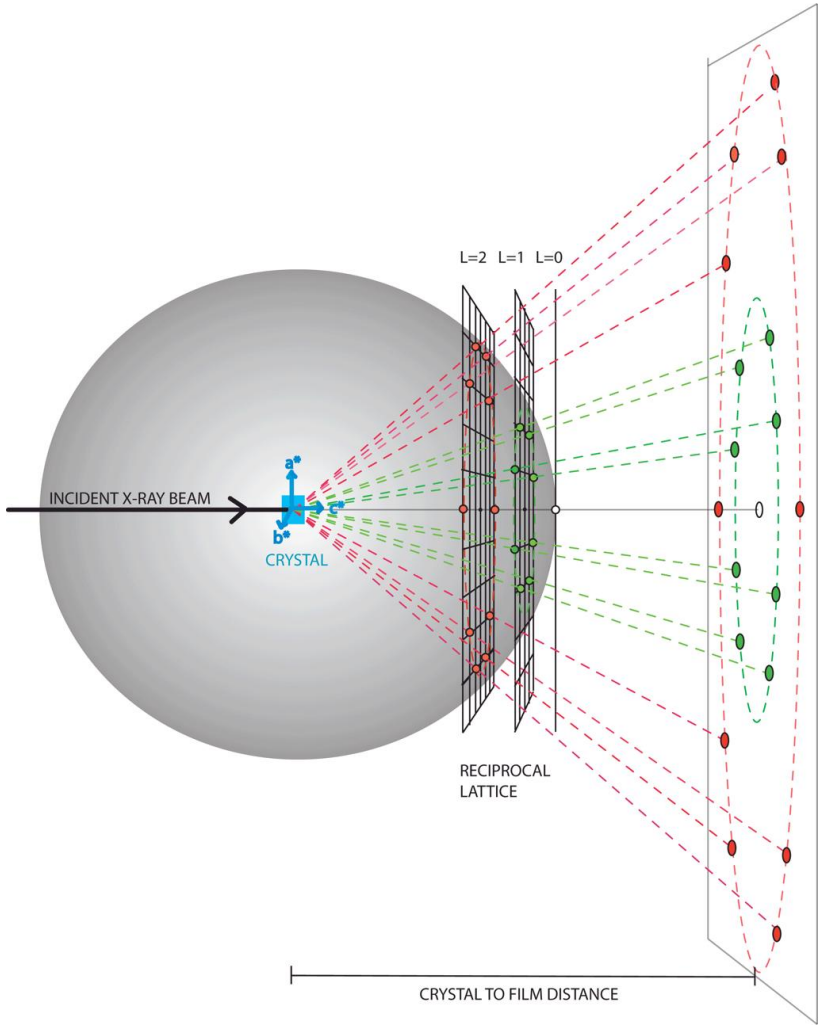
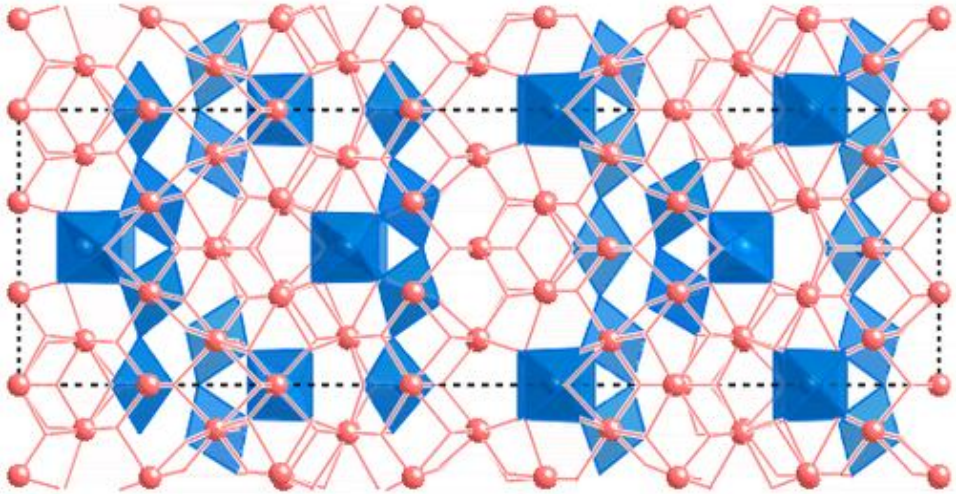
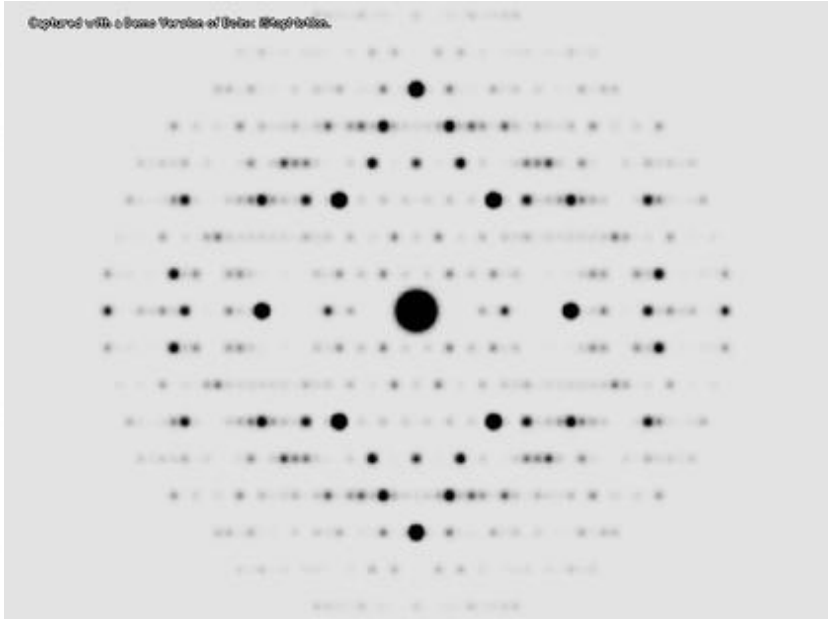


Figure from http://www.doe-mbi.ucla.edu/~sawaya/m230d/Data/data.html

Effect of Rotating Structure



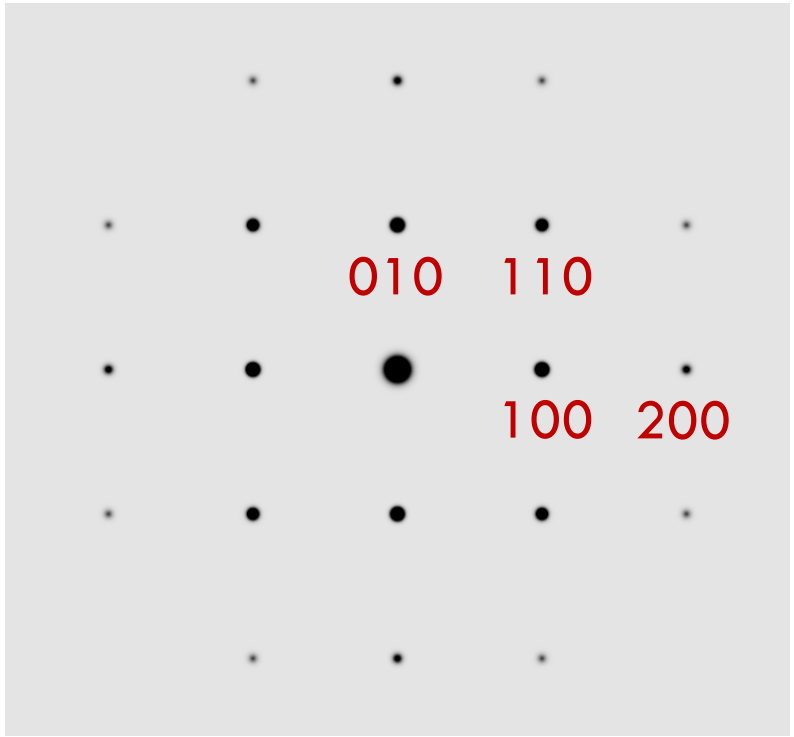


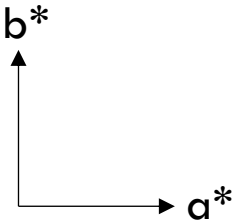
Indexing Diffraction Patterns with Miller Indices

In single crystal diffraction we measure the intensities of many (thousands) of **reflections** which we index to a ***reciprocal lattice*** in terms of the ***Miller indices*** (***h k l***).

Projection perpendicular to [0 0 1]:
(diffraction pattern in 2D)

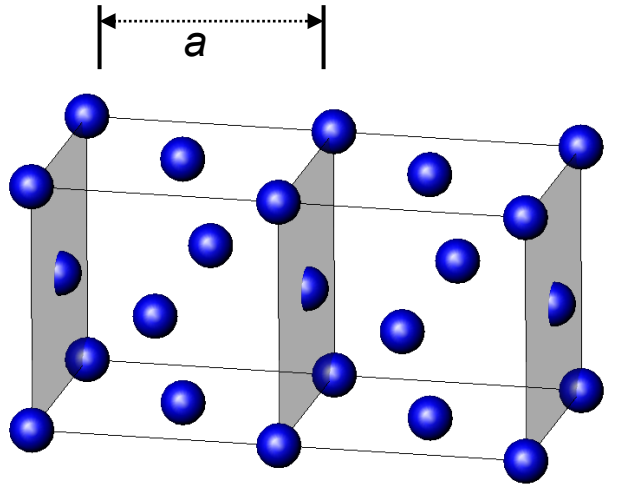
The position and distance between spots is used to determine the unit cell type.





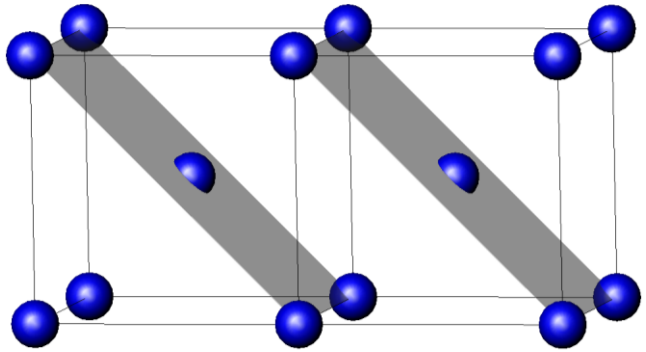
Indexing Diffraction Patterns with Miller Indices

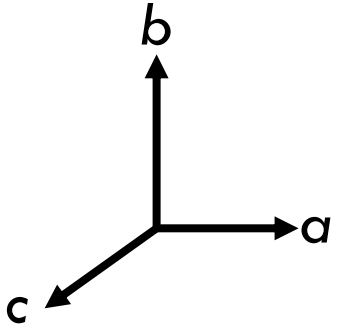
The ***Miller indices*** (***h k l***) of a reflection correspond to the Miller indices of the set of lattice planes that produce that reflection by Bragg's Law.

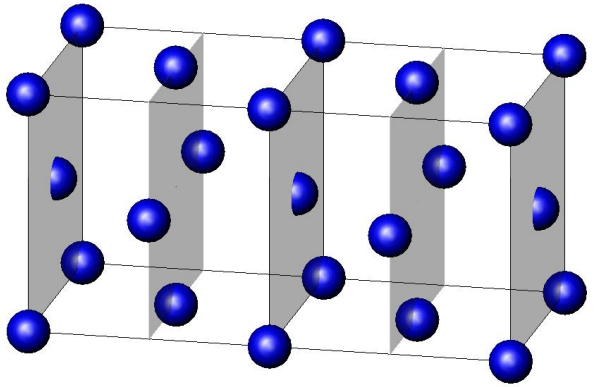


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(110)



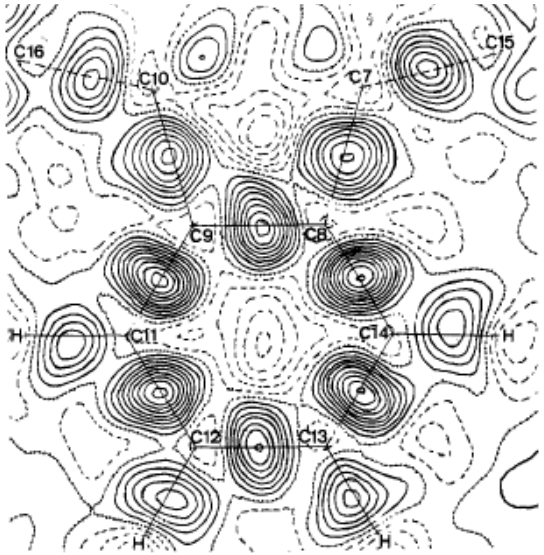




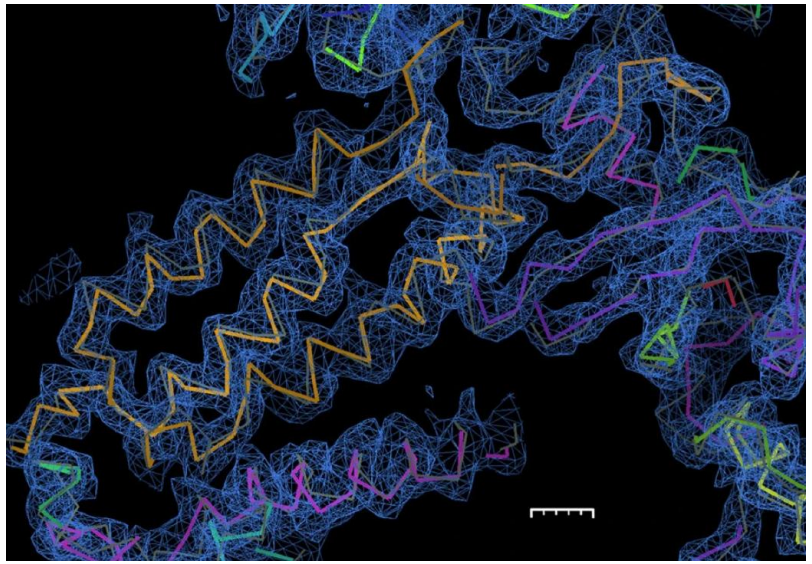
(200)

Electron Density Maps from X-ray Scattering

X-rays scatter off electrons, so analysis of X-ray scattering patterns provides a 3D map of electron density. This can provide extremely accurate pictures of geometry and chemical bonding in chemical structures (see left, showing bonding electron density) and enable the structure determination of highly complex biological molecules (see right; RNA polymerase II).



doi: 10.1021/ja00414a077



doi: 10.1038/ncomms3777

Learning Outcomes

After this lecture and pre-lecture video you should be able to

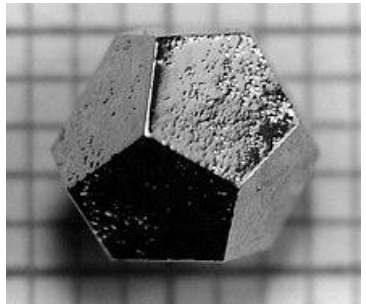
- Define Bragg diffraction.
- Describe the principles of a diffraction experiment.
- Relate Miller indices and lattice planes.
- Determine Miller indices and *d*-spacings of lattice planes.
- Complete the lecture worksheet and Q4 of Tutorial 2 (week 4).

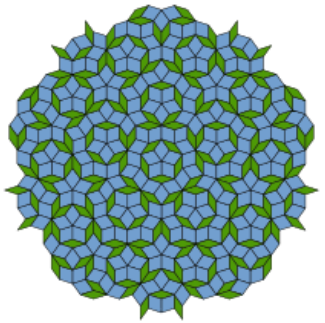
Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed., OUP, 2014, Chapter 3.1–3.5; Blackman, Bottle, Schmid, Mocerino & Wille, Chemistry, 2nd Ed. Wiley & Sons, 2012, Chapter 7.4-7.5.

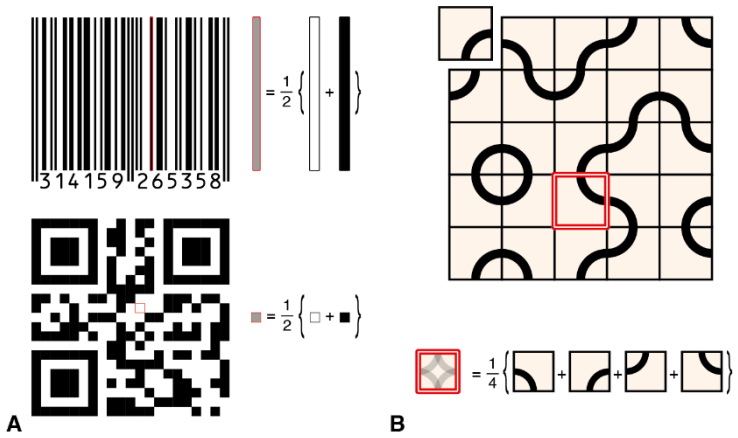
Aperiodic periodic structures

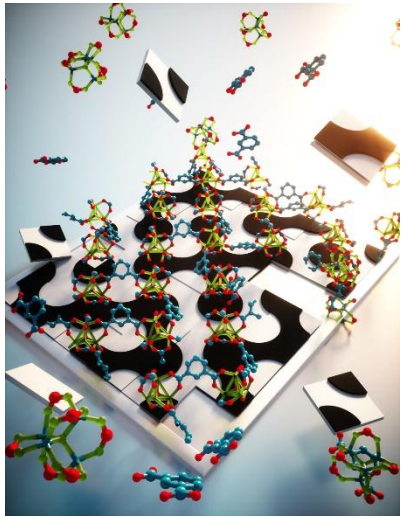
In very special cases it's possible to have periodic structures with no long-range periodicity. DNA is one example (see L4 worksheet) – it stores information by encoding molecular bits (base pairs) onto a periodic template (double helix); if it was entirely periodic it would store no information (like a string of zeroes).

A range of different classes of crystals also adopt this special arrangement. One now well-established category is quasicrystals (www.nobelprize.org/prizes/chemistry/2011/popular-information; en.wikipedia.org/wiki/Holmium–magnesium–zinc_quasicrystal).









Recently, a new class of aperiodic crystal has been discovered (by Lisa, one of my PhD students) based on what's known as 'Truchet tiling' (see DOI: 10.1126/science.ade5239). These crystals offer future scope for data storage at the nanoscale, potentially superseding the highly inefficient current use of magnetic domains.