Crystal Structure

thelecture thenextlecture

SOLID STATE PHYSICS
Lecture 5

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Structure & Diffraction

Crystal Diffraction (continued)

### 2.4   Experimental Methods

Notes:

- examples show *photographic film*, for x-rays.

- Can also use electronic detection for x-rays.

- Need counters (e.g. BF_3) for neutrons.

- Information:

  – Positions of lines (geometry)

  – Intensities of lines (electronics, or photogrammetry to measure darkness of lines on films)
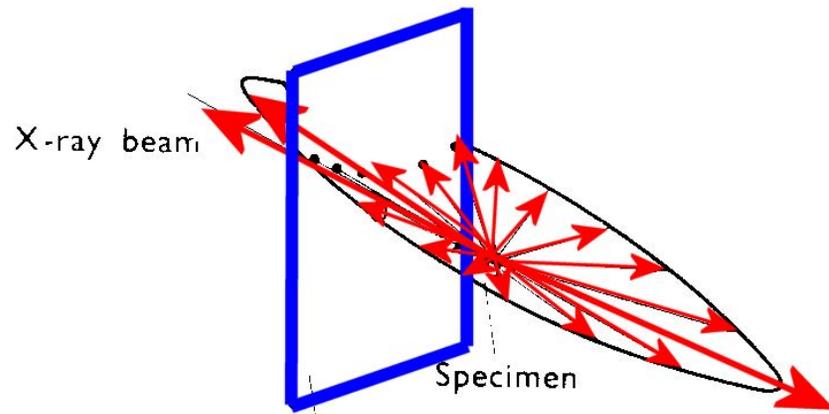
2.4.1 Laue Method

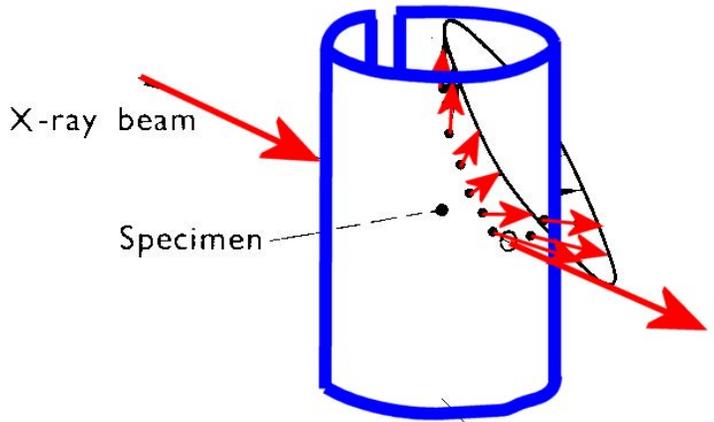**1912: Max von Laue (assisted by Paul Knipping and Walter Friedrich).**
$CuSO_4$ **and ZnS.**
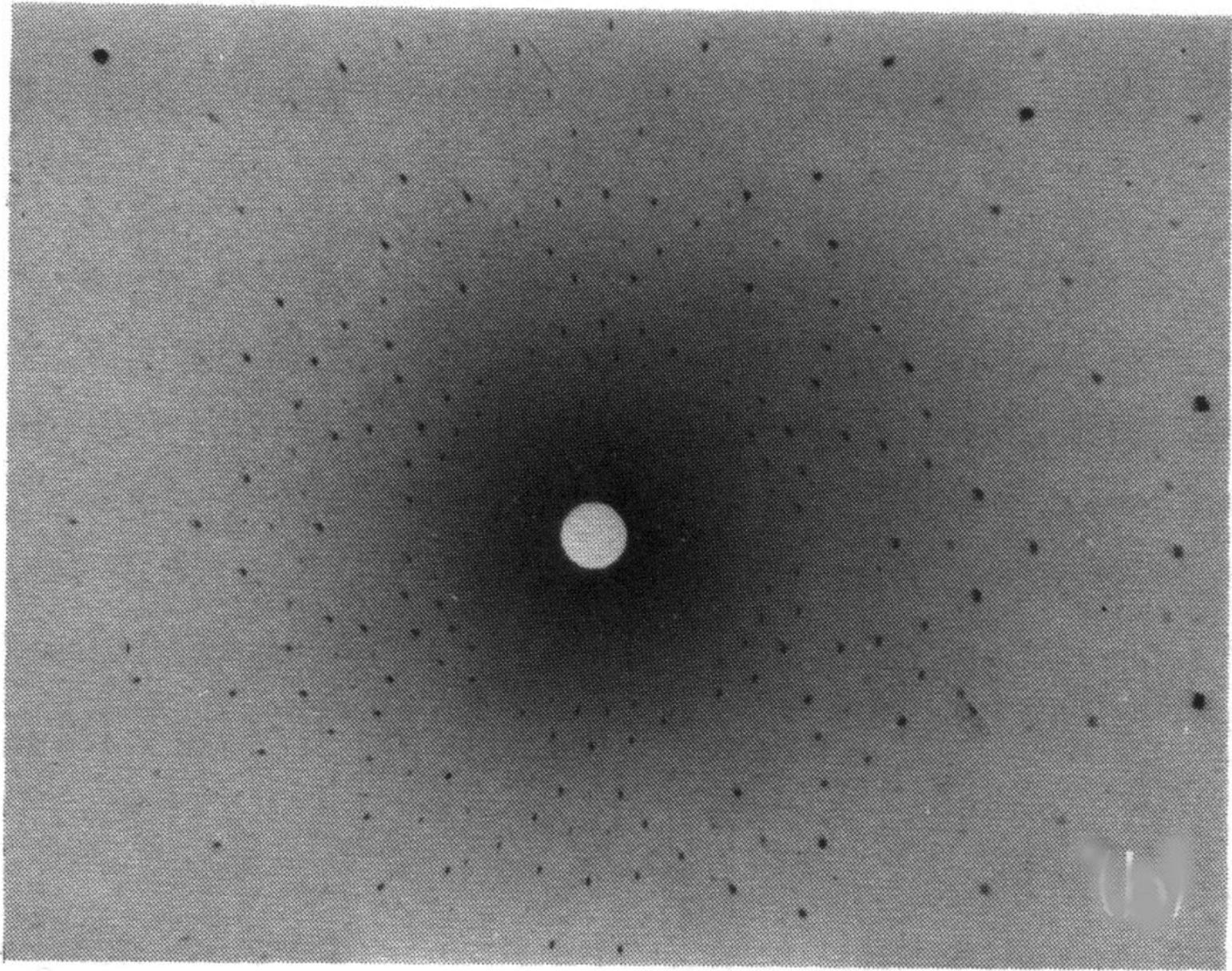**Broad x-ray spectrum – single crystal**

Specimen

X-ray beam
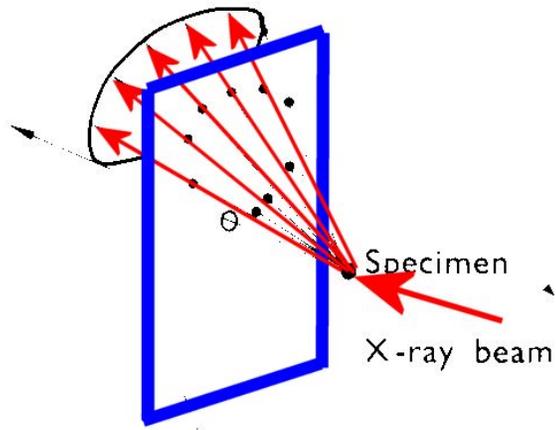
Photographic plate

Forward reflection

X-ray beam

Specimen

Photographic plate

Backward reflection

X-ray beam

Specimen

Cylindrical Film

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**Forward scattering Laue image of hexagonal crystal.**

Shows crystal symmetry – when crystal appropriately oriented.
Use for aligning crystal for other methods.
Range of λ, so cannot determine a from photographic image, but if outgoing wavelengths can be measured, *can* use to find lattice parameters.

2.4.2   Rotating Crystal Method

Single x-ray wavelength – single crystal rotated in beam.
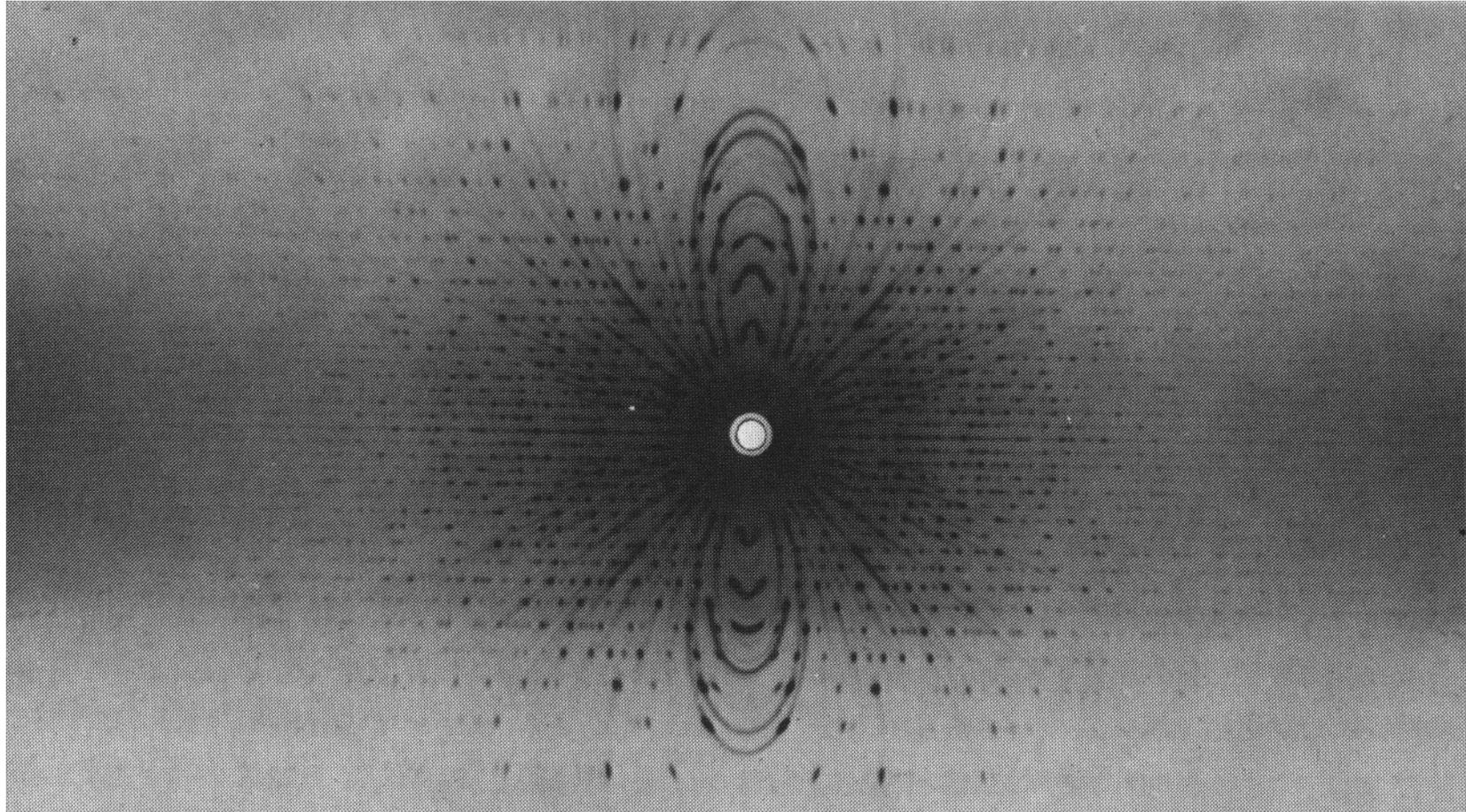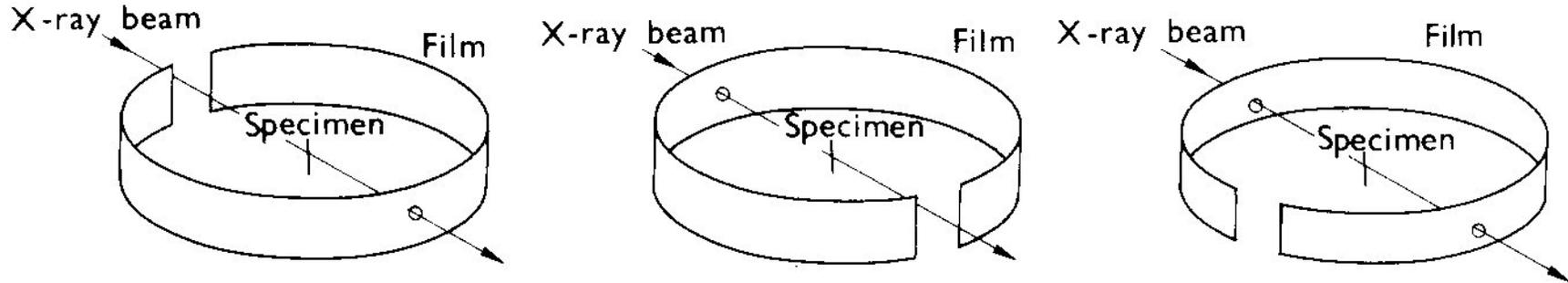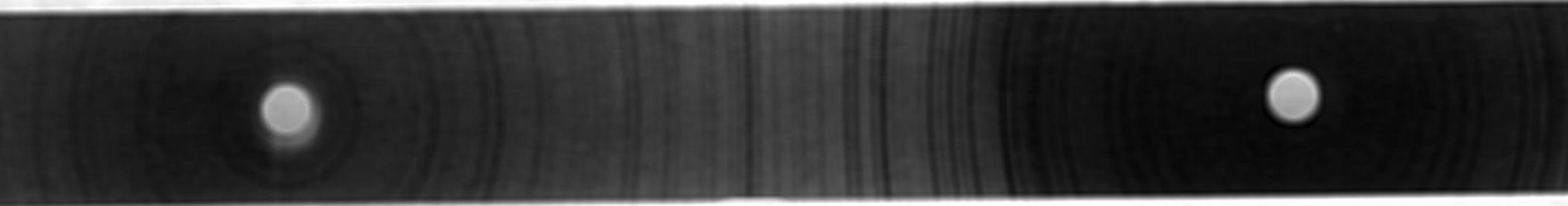

Either full $360°$ rotation (as above) or small (5 to $15°$) oscillations.

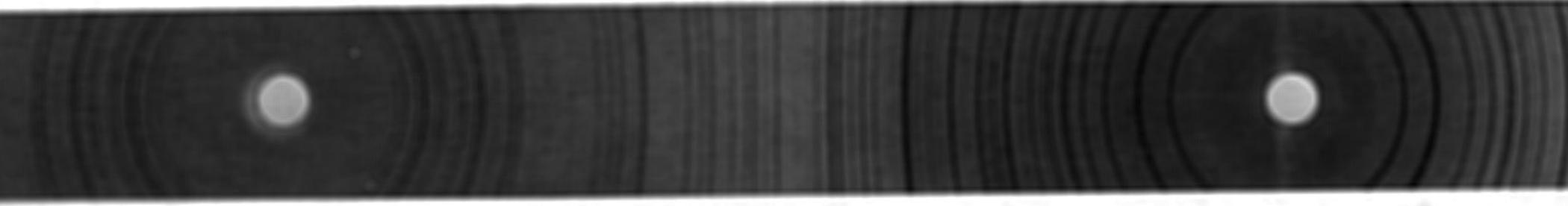## 2.4.3   Powder Methods

Single x-ray wavelength – finely powdered sample.
Effect similar to rotating crystal, but rotated about all possible axes.

X-ray powder diffraction pattern of $NaClO_3$ **taken with Cu$K\alpha$ radiation.**

X-ray powder diffraction pattern of SiO_2 **taken with Cu$K\alpha$ radiation.**
Powder diffraction patterns are often used for identifying materials.

2.5 Mathematics of Diffraction

2.5.1 Monatomic Structure

Incoming plane wave

$$\psi_i = A \exp[i(\mathbf{k}_i.\mathbf{r} - \omega t)]$$

Scattered by the atom in unit cell I at $\mathbf{r}_I$.
Assume scattered amplitude is $S\,A$ – all the unit cells are the same,
so independent of I.
When incident wave hits atom, it is

$$A \exp[i(\mathbf{k}_i.\mathbf{r}_I - \omega t)].$$

It is scattered with a different wave-vector, $\mathbf{k}_f$, so from the atom to a
point $\mathbf{r}$ its phase changes by $\mathbf{k}_f.(\mathbf{r} - \mathbf{r}_I)$.
The scattered wave is thus

$$S\,A\,\exp[i(\mathbf{k}_i.\mathbf{r}_I - \omega t)]\exp[i\mathbf{k}_f.(\mathbf{r} - \mathbf{r}_I)]$$

or

$$S\,A\,\exp[i(\mathbf{k}_f.\mathbf{r} - \omega t)]\exp[i(\mathbf{k}_i - \mathbf{k}_f).\mathbf{r}_I].$$

So if a plane wave with wavevector k_f is scattered from the crystal, it is the sum of the waves scattered by all the atoms, or

$$\text{Total Wave} = S\,A\,\exp[i(\mathbf{k}_f.\mathbf{r} - \omega t)] \sum_I \exp[i(\mathbf{k}_i - \mathbf{k}_f).\mathbf{r}_I].$$

Write $\Delta k = \mathbf{k}_f - \mathbf{k}_i$:

$$\text{Total Wave} = S\,A\,\exp[i(\mathbf{k}_f.\mathbf{r} - \omega t)] \sum_I \exp[-i\Delta\mathbf{k}.\mathbf{r}_I],$$

and as the amplitude of the outgoing wave $\exp[i(\mathbf{k}_f.\mathbf{r} - \omega t)]$ is 1,

$$\text{Total Amplitude} \propto S \sum_I \exp[-i\Delta\mathbf{k}.\mathbf{r}_I]. \tag{1}$$

2.5.2   The Reciprocal Lattice

Define a new set of vectors (A, B, C) with which to define $\triangle k$. Require

$$
\begin{aligned}
\mathbf{a}.\mathbf{A} = 2\pi \ , \quad \mathbf{a}.\mathbf{B} = 0 \ , \quad \mathbf{a}.\mathbf{C} = 0 \\
\mathbf{b}.\mathbf{A} = 0 \ , \quad \mathbf{b}.\mathbf{B} = 2\pi \ , \quad \mathbf{b}.\mathbf{C} = 0 \\
\mathbf{c}.\mathbf{A} = 0 \ , \quad \mathbf{c}.\mathbf{B} = 0 \ , \quad \mathbf{c}.\mathbf{C} = 2\pi
\end{aligned}
\tag{2}
$$

In general,

$$
\begin{aligned}
\mathbf{A} &= \frac{2\pi \mathbf{b} \times \mathbf{c}}{\mathbf{a}.\mathbf{b} \times \mathbf{c}} \\
\mathbf{B} &= \frac{2\pi \mathbf{c} \times \mathbf{a}}{\mathbf{a}.\mathbf{b} \times \mathbf{c}} \\
\mathbf{C} &= \frac{2\pi \mathbf{a} \times \mathbf{b}}{\mathbf{a}.\mathbf{b} \times \mathbf{c}}
\end{aligned}
\tag{3}
$$

The vectors (A, B, C) define the *reciprocal lattice*.
For simple cubic system, reciprocal lattice vectors are just $2\pi/a$ along the x, y and z axes.

Lattice	Reciprocal Lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Hexagonal	Hexagonal

2.5.3 The Scattered Amplitude

Let
$$\triangle \mathbf{k} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C},$$
and remember that our structure is periodic:
$$\mathbf{r}_I = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}.$$
Immediately we have
$$\triangle \mathbf{k}.\mathbf{r}_I = 2\pi(hn_1 + kn_2 + ln_3).$$
So
$$\sum_I \exp[-i\triangle \mathbf{k}.\mathbf{r}_I] = \sum_{n_1}\sum_{n_2}\sum_{n_3} \exp[-2\pi i(hn_1 + kn_2 + ln_3)]$$
$$= \left\{\sum_{n_1} e^{-2\pi i h n_1}\right\}\left\{\sum_{n_2} e^{-2\pi i k n_2}\right\}\left\{\sum_{n_3} e^{-2\pi i l n_3}\right\}.$$

Sums, in principle, go over $-\infty < n_i < \infty$, or at least over a very large range $1 \leq n_i \leq N_i$.

Phases lead to cancellation unless h, k and l are integers, when each term is 1 and total amplitude is $SN_1N_2N_3$.

So we see

- **we have a strong reflection when $\triangle k$ is a reciprocal lattice vector;**

- **remembering that $\triangle k$ is perpendicular to the reflecting plane, an (hkl) reflection has $\triangle \mathbf{k} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$.**
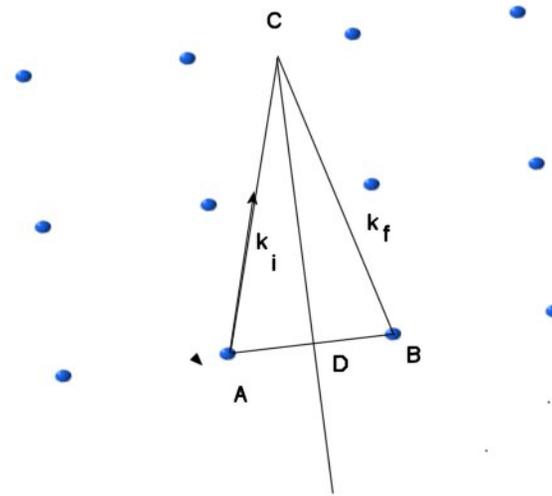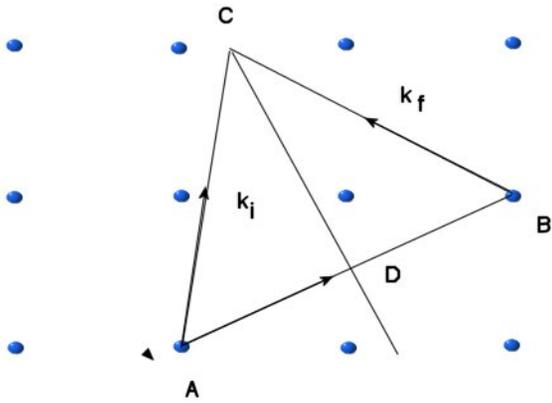
2.6   The Laue Construction
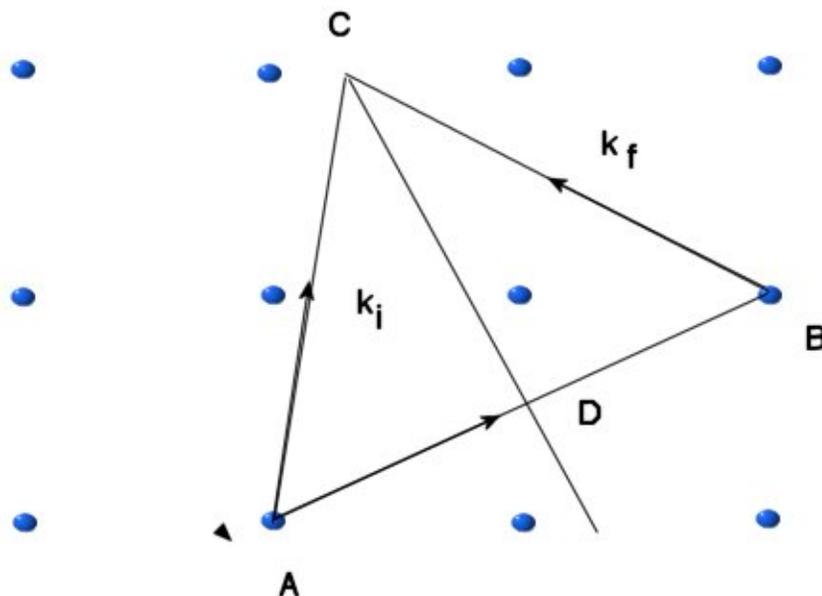
This is a diagram in the *reciprocal lattice*.
Just as the lattice is an abstract mathematical object, so is the recip-
rocal lattice.
Neither k_i nor k_f need to be reciprocal lattice vectors, but $k_f - k_i$ is.
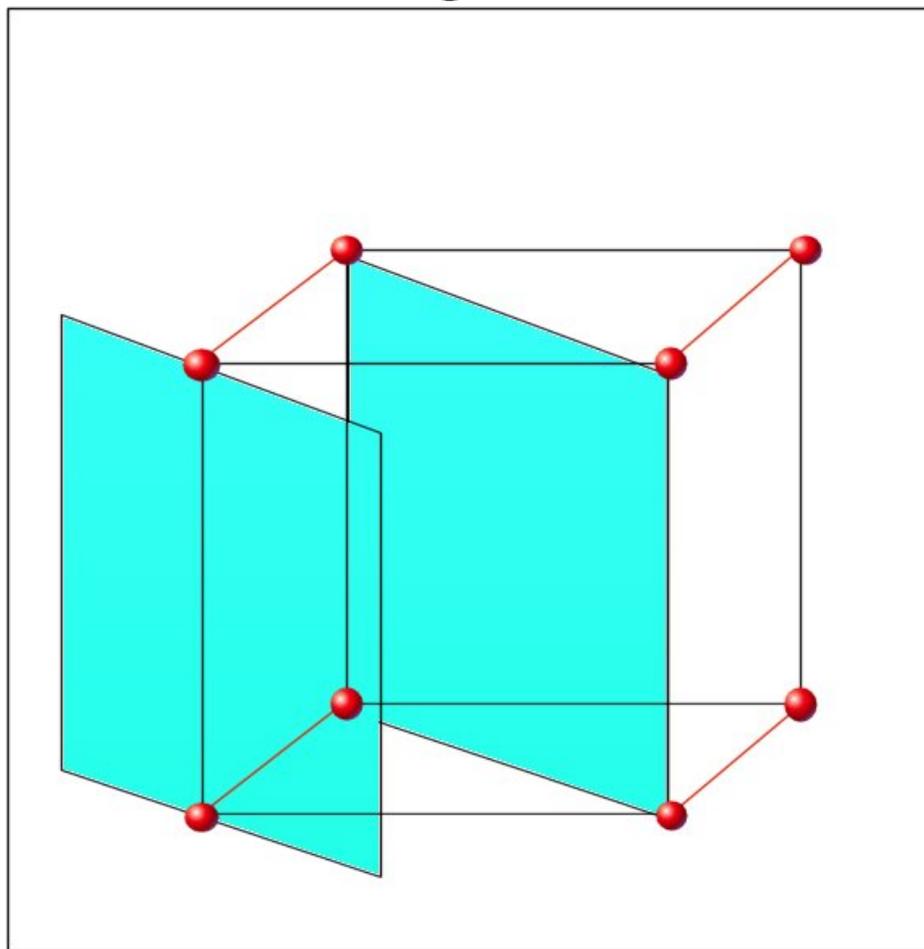
Note that only certain special incident directions of k_i will give a diffracted signal.
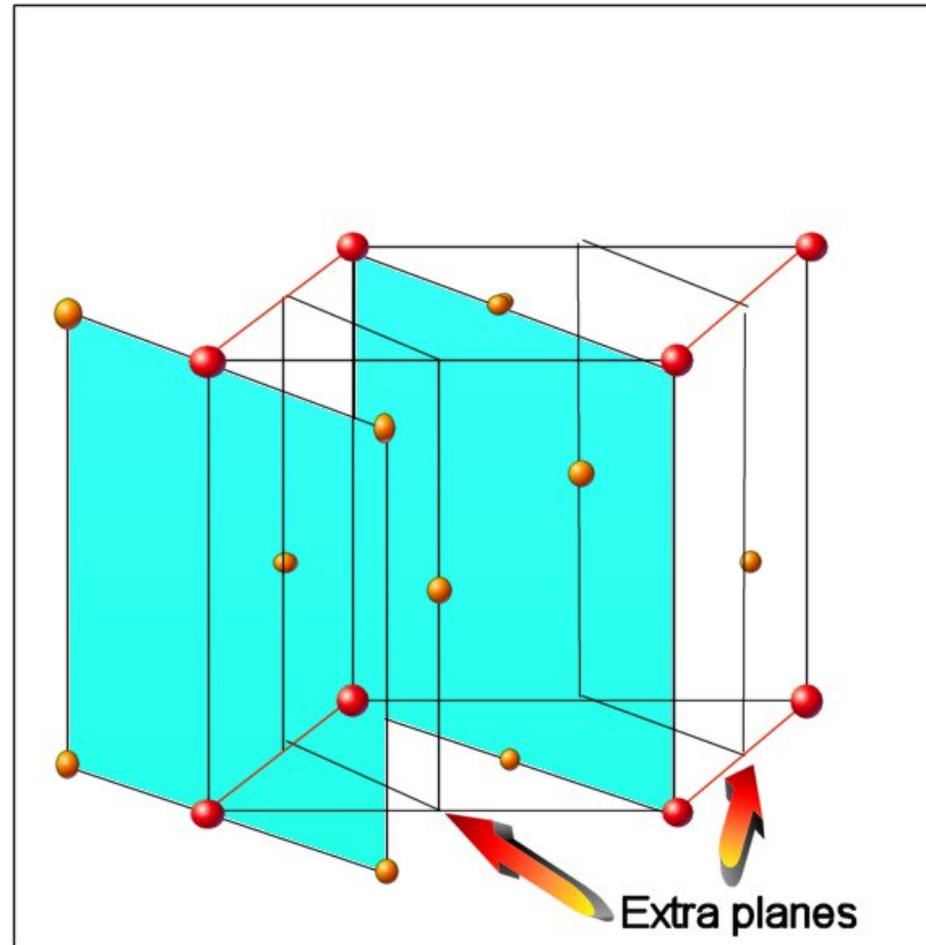
2.7   Non-Monatomic Structures

2.7.1   Simple Treatment

Example: an FCC structure (thought of as simple cubic with a basis of two atoms, one at $(0, 0, 0)$, three more at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $0, \frac{1}{2}, \frac{1}{2})$. For simple cubic, there is a strong reflection from (110) planes:

**but face-centred cubic has extra atoms in the orginal planes and be-
tween them:**

Extra planes

**These extra planes have the same number of atoms as the original
(110) planes. But if the original planes correspond to a path length
difference of λ, these have path length difference of $\lambda/2$ – their signals
will be *out of phase*. If the atoms are all the same, the (110) reflection
will be missing. If the atoms are different, the amplitude of the (110)**

reflection will be reduced.

These *missing orders* tell us something about the structures:

- simple cubic – no missing orders;

- fcc – only see (hkl) where h, k and l are all even OR all odd.

- bcc – only see (hkl) where $h + k + l$ is even.

Summary

- Experimental methods – broad-band or single-wavelength;

- Bragg's law explained by von Laue's treatment;

- Scattering treatment;

- The reciprocal lattice;

- Effect of atomic basis.

Next:

- Detailed treatment of structure with a basis;

- Other information from diffraction;

- Binding of crystals.