# SOLID STATE PHYSICS

## Lecture 5

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## Crystal Diffraction (continued)

### 2.4 Experimental Methods

**Notes:**

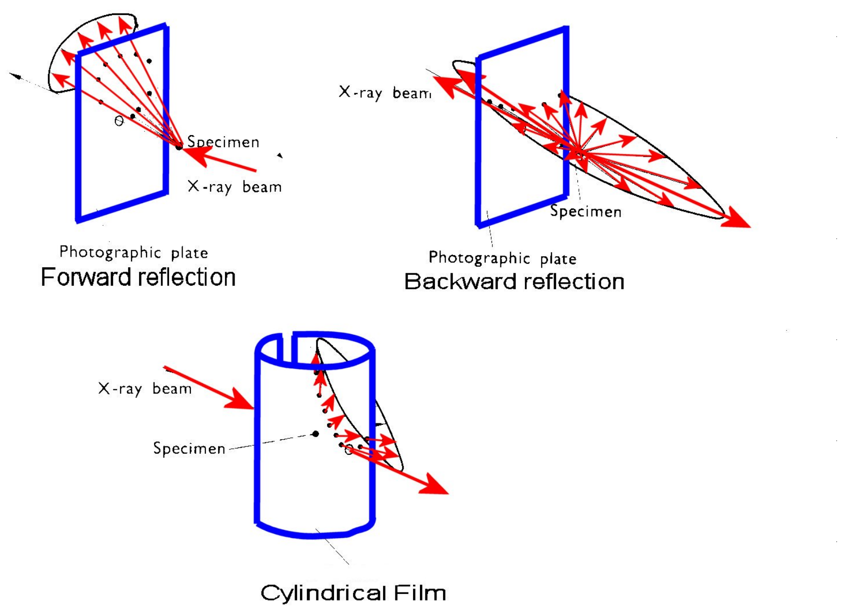
- **examples show *photographic film*, for x-rays.**
- **Can also use electronic detection for x-rays.**
- **Need counters (e.g. $\mathrm{BF_3}$) for neutrons.**
- **Information:**
  - **Positions of lines (geometry)**
  - **Intensities of lines (electronics, or photogrammetry to measure darkness of lines on films)**

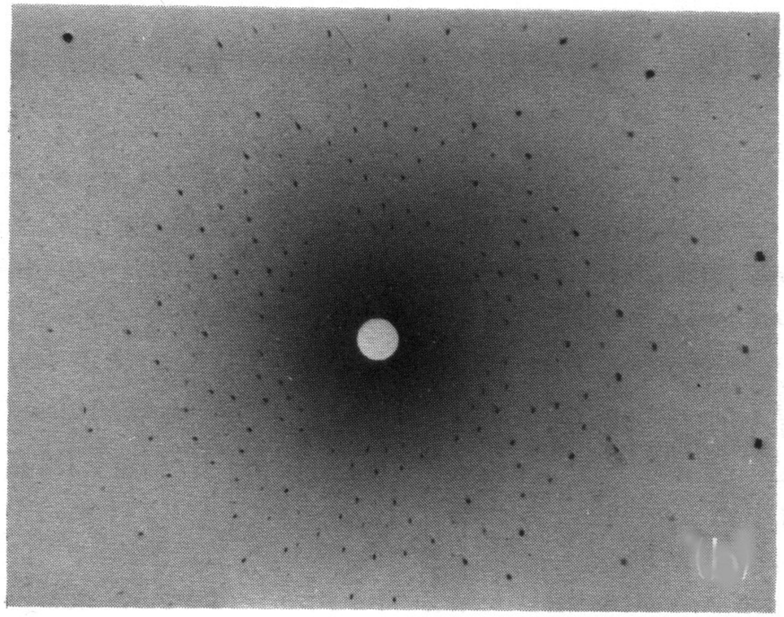


#### 2.4.1 Laue Method

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







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

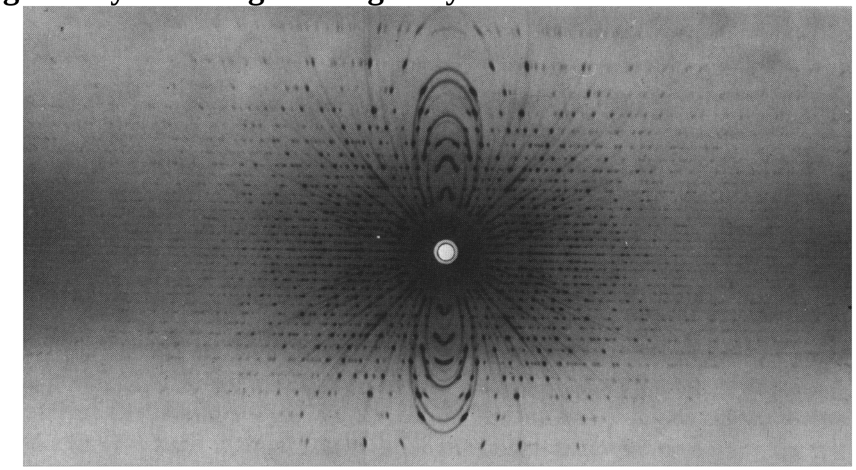


**Shows crystal symmetry – when crystal appropriately oriented.**
**Use for aligning crystal for other methods.**
**Range of $\lambda$, so cannot determine $a$ from photographic image, but if outgoing wavelengths can be measured, *can* use to find lattice parameters.**



### 2.4.2 Rotating Crystal Method

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

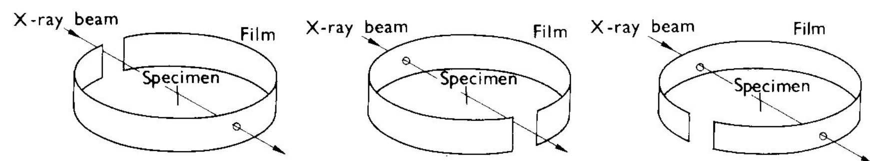


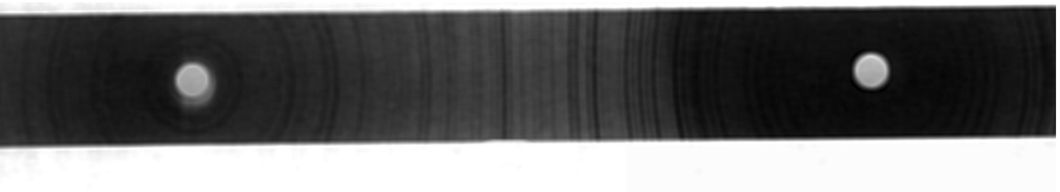
**Either full $360^\circ$ rotation (as above) or small (5 to $15^\circ$) oscillations.**



### 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 $\mathrm{NaClO_3}$ taken with Cu$K\alpha$ radiation.**

**X-ray powder diffraction pattern of $\mathrm{SiO_2}$ 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 $\mathrm{r}_I$.**
**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, $\mathrm{k}_f$, so from the atom to a point $\mathrm{r}$ its phase changes by $\mathrm{k}_f.(\mathbf{r} - \mathbf{r}_I)$.**
**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 $\mathrm{k}_f$ is scattered from the crystal, it is the sum of the waves scattered by all the atoms, or**

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

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

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

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

$$\mathrm{Total\ \ Amplitude} \propto S \sum_I \exp[-i\Delta\mathbf{k}.\mathbf{r}_I]. \qquad (1)$$



### 2.5.2 The Reciprocal Lattice

**Define a new set of vectors $(\mathrm{A}, \mathrm{B}, \mathrm{C})$ with which to define $\Delta\mathrm{k}$.**
**Require**

$$\begin{array}{ccccc} \mathbf{a}.\mathbf{A} = 2\pi & , & \mathbf{a}.\mathbf{B} = 0 & , & \mathbf{a}.\mathbf{C} = 0 \\ \mathbf{b}.\mathbf{A} = 0 & , & \mathbf{b}.\mathbf{B} = 2\pi & , & \mathbf{b}.\mathbf{C} = 0 \\ \mathbf{c}.\mathbf{A} = 0 & , & \mathbf{c}.\mathbf{B} = 0 & , & \mathbf{c}.\mathbf{C} = 2\pi \end{array} \qquad (2)$$

**In general,**

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

**The vectors $(\mathrm{A}, \mathrm{B}, \mathrm{C})$ 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**

$$\Delta\mathbf{k} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C},$$

**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**

$$\Delta\mathbf{k}.\mathbf{r}_I = 2\pi(hn_1 + kn_2 + ln_3).$$

**So**

$$\begin{aligned}\sum_I \exp[-i\Delta\mathbf{k}.\mathbf{r}_I] &= \sum_{n_1}\sum_{n_2}\sum_{n_3} \exp[-2\pi i(hn_1 + kn_2 + ln_3)] \\ &= \left\{\sum_{n_1} e^{-2\pi i h n_1}\right\}\left\{\sum_{n_2} e^{-2\pi i k n_2}\right\}\left\{\sum_{n_3} e^{-2\pi i l n_3}\right\}.\end{aligned}$$

**Sums, in principle, go over $-\infty < n_i < \infty$, or at least over a very large range $1 \le n_i \le N_i$.**
**Phases lead to cancellation unless $h$, $k$ and $l$ are integers, when each term is 1 and total amplitude is $SN_1N_2N_3$.**

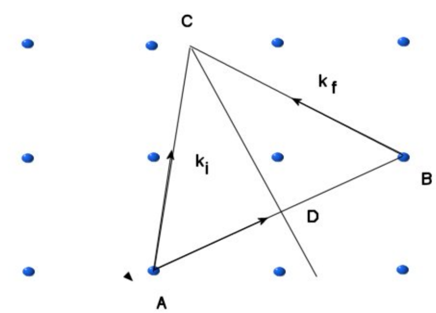


**So we see**

- **we have a strong reflection when $\Delta\mathrm{k}$ is a reciprocal lattice vector;**
- **remembering that $\Delta\mathrm{k}$ is perpendicular to the reflecting plane, an $(hkl)$ reflection has $\Delta\mathrm{k} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$.**

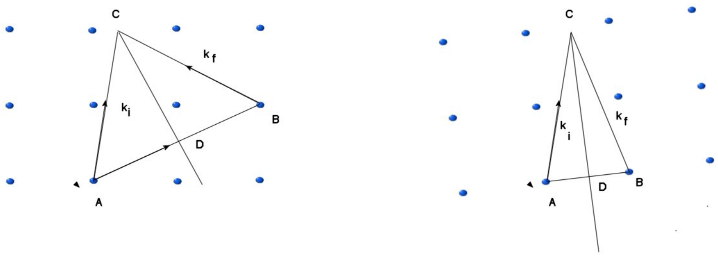


## 2.6 The Laue Construction




**This is a diagram in the *reciprocal lattice*.**
**Just as the lattice is an abstract mathematical object, so is the reciprocal lattice.**
**Neither $\mathrm{k}_i$ nor $\mathrm{k}_f$ need to be reciprocal lattice vectors, but $\mathrm{k}_f - \mathrm{k}_i$ is.**

Note that only certain special incident directions of $\mathrm{k}_i$ will give a diffracted signal.

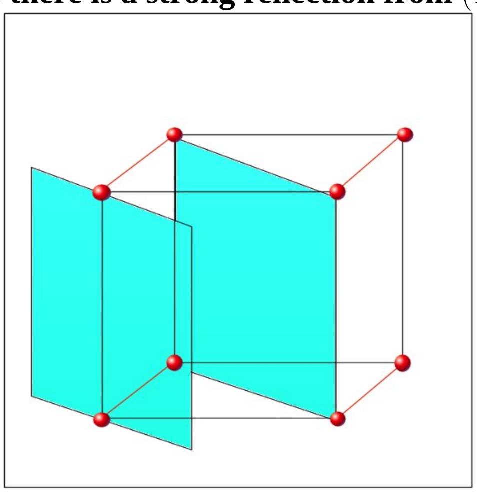





## 2.7 Non-Monatomic Structures

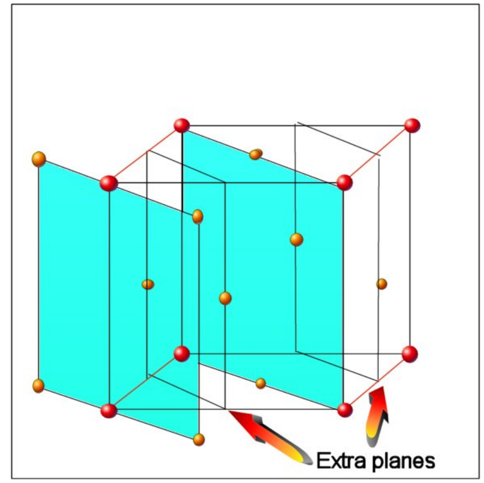
### 2.7.1 Simple Treatment

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 between them:




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 $\lambda$, 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.**