

Experimental Determination of Crystal Structure

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PHYS 624: Introduction to Solid State Physics

<http://www.physics.udel.edu/~bnikolic/teaching/phys624/phys624.html>



Principles of Diffraction

- How do we learn about crystalline structures?

Answer:

Diffraction: Send a beam of particles (of de Broglie wavelength $\lambda = h/p$ or radiation with a wavelength $\lambda \approx a$ comparable to characteristic length scale of the lattice ($a \approx$ twice the atomic or molecular radii of the constituents)).

- **EXPERIMENT:** Identify Bragg peaks which originate from a coherent addition of scattering events in multiple planes within the bulk of the solid.

Principles of Diffraction in Pictures

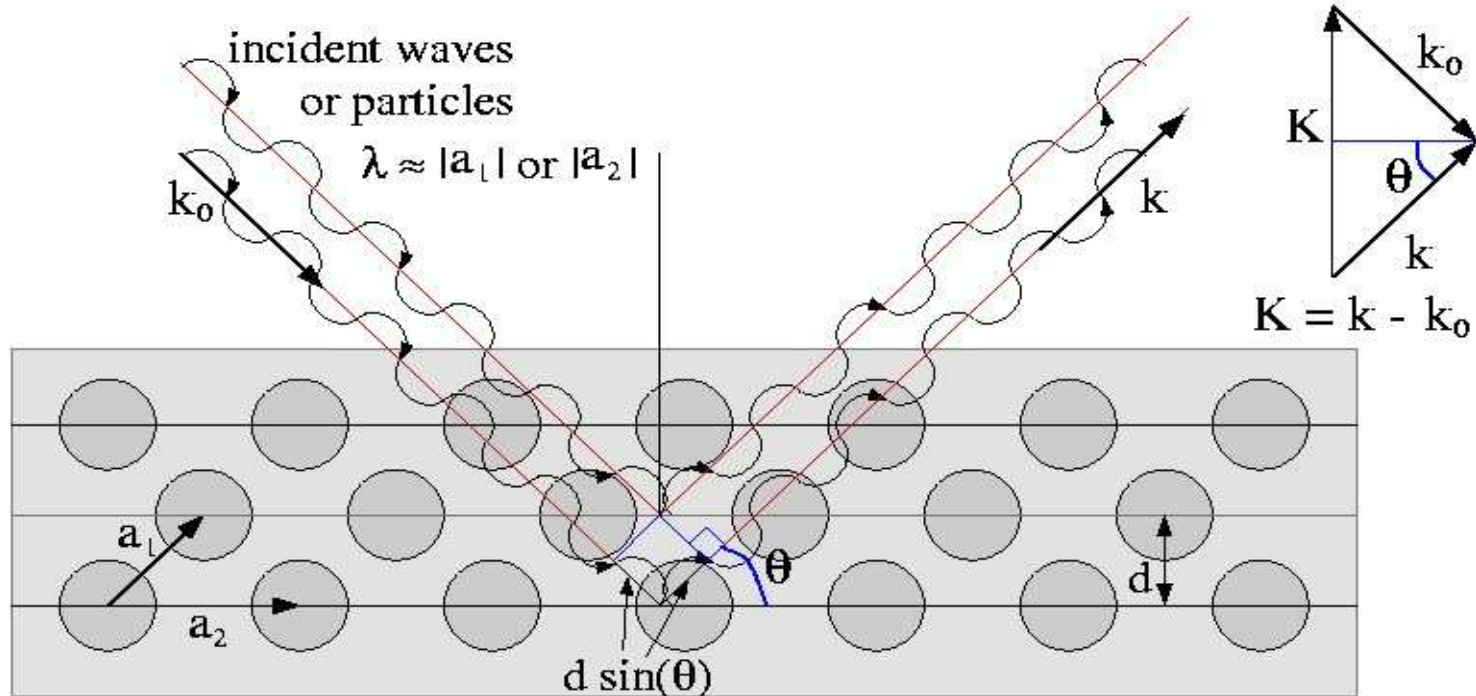


Figure 1: Scattering of waves or particles with wavelength of roughly the same size as the lattice repeat distance allows us to learn about the lattice structure. Coherent addition of two particles or waves requires that $2d \sin \theta = \lambda$ (the Bragg condition), and yields a scattering maximum on a distant screen.

Available Particles for Diffraction Experiments

	X-rays	Neutrons	Electrons
Charge	0	0	$-e$
Mass	0	$1.67 \cdot 10^{-27}$ kg	$9.11 \cdot 10^{-31}$ kg
Typical energy	10 keV	0.03 eV	100 keV
Typical wavelength	1 Å	1 Å	0.05 Å
Typical attenuation length	100 μm	5 cm	1 μm
Typical atomic form factor, f	10^{-3} Å	10^{-4} Å	10 Å

Bad Particles for Diffraction

- Not all particles with de Broglie wavelength $\lambda \approx a$ will work for this application → For example, most charged particles cannot probe the bulk properties of the crystal, since they lose energy to the scatterer very quickly:

$$\frac{dE}{dx} \approx -\frac{4\pi nq^2 e^2}{mv^2} \ln\left(\frac{m\gamma v^3}{qe\omega_0}\right) \sim \frac{q^2}{v^2}$$

- For non-relativistic electron scattering into a solid with $a \approx 2\text{\AA}$

$$a = \lambda = \frac{h}{p} = 12.3 \cdot 10^{-8} \text{ cm} / \sqrt{E} \Rightarrow E = 50 \text{ eV}$$

- The distance at which initial energy is lost is:

$$\delta E = E, n = 10^{23} \text{ cm}^{-3} \Rightarrow \delta x = 100 \text{\AA}$$

- NOTE: Low energy electron diffraction can be used to study the surface of **extremely clean** samples.

Electron Probe Sees only Surface

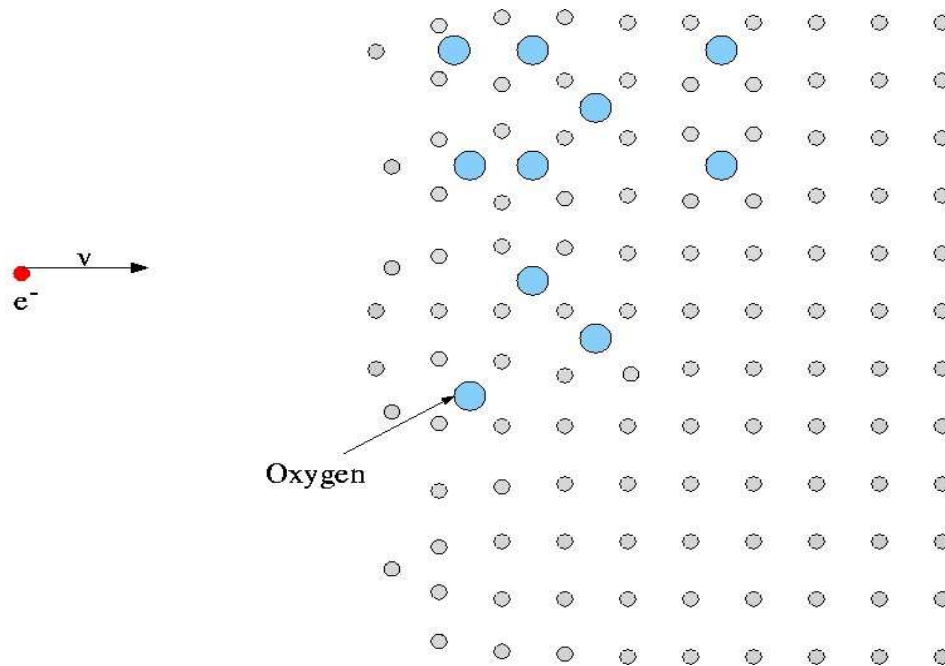
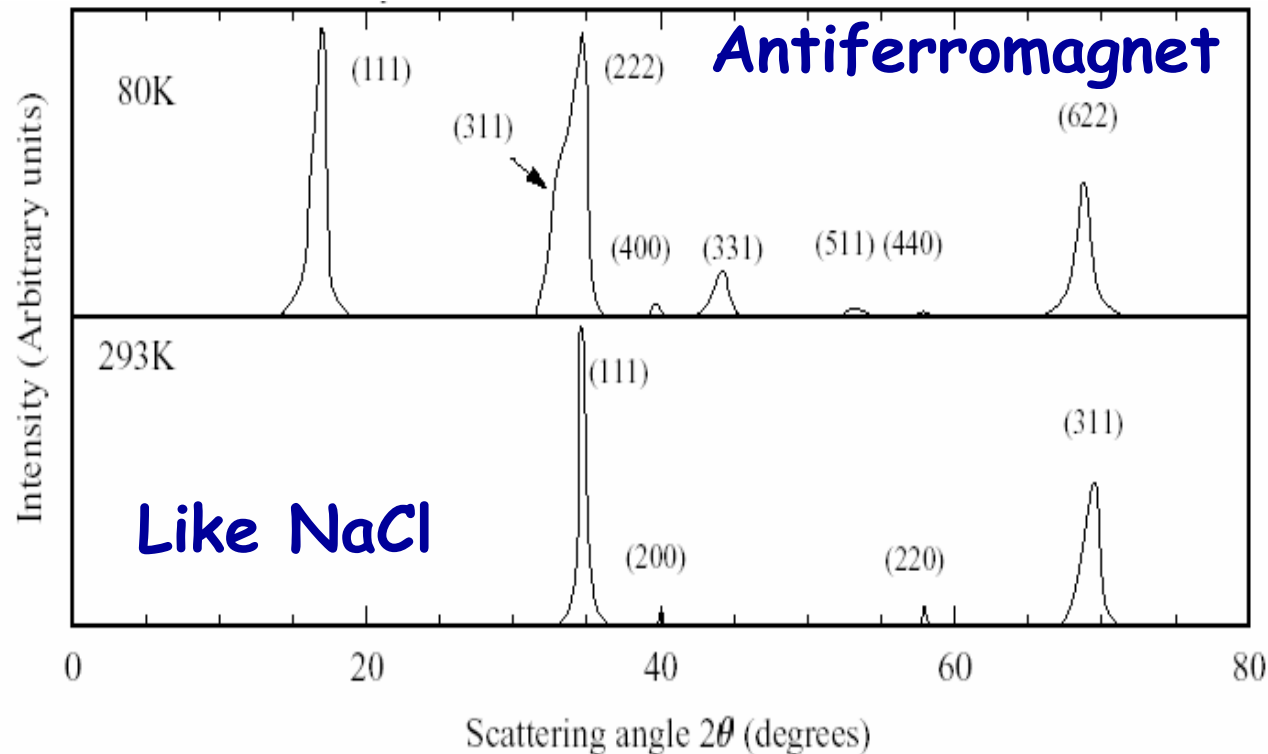


Figure 2: *An electron about to scatter from a typical material. However, at the surface of the material, oxidation and surface reconstruction distort the lattice. If the electron scatters from this region, we cannot learn about the structure of the bulk.*

CONCLUSION: *Use neutral particles or electromagnetic radiation which scatter only from nuclei → NEUTRONS or X-rays.*

Neutron Scattering Experiments

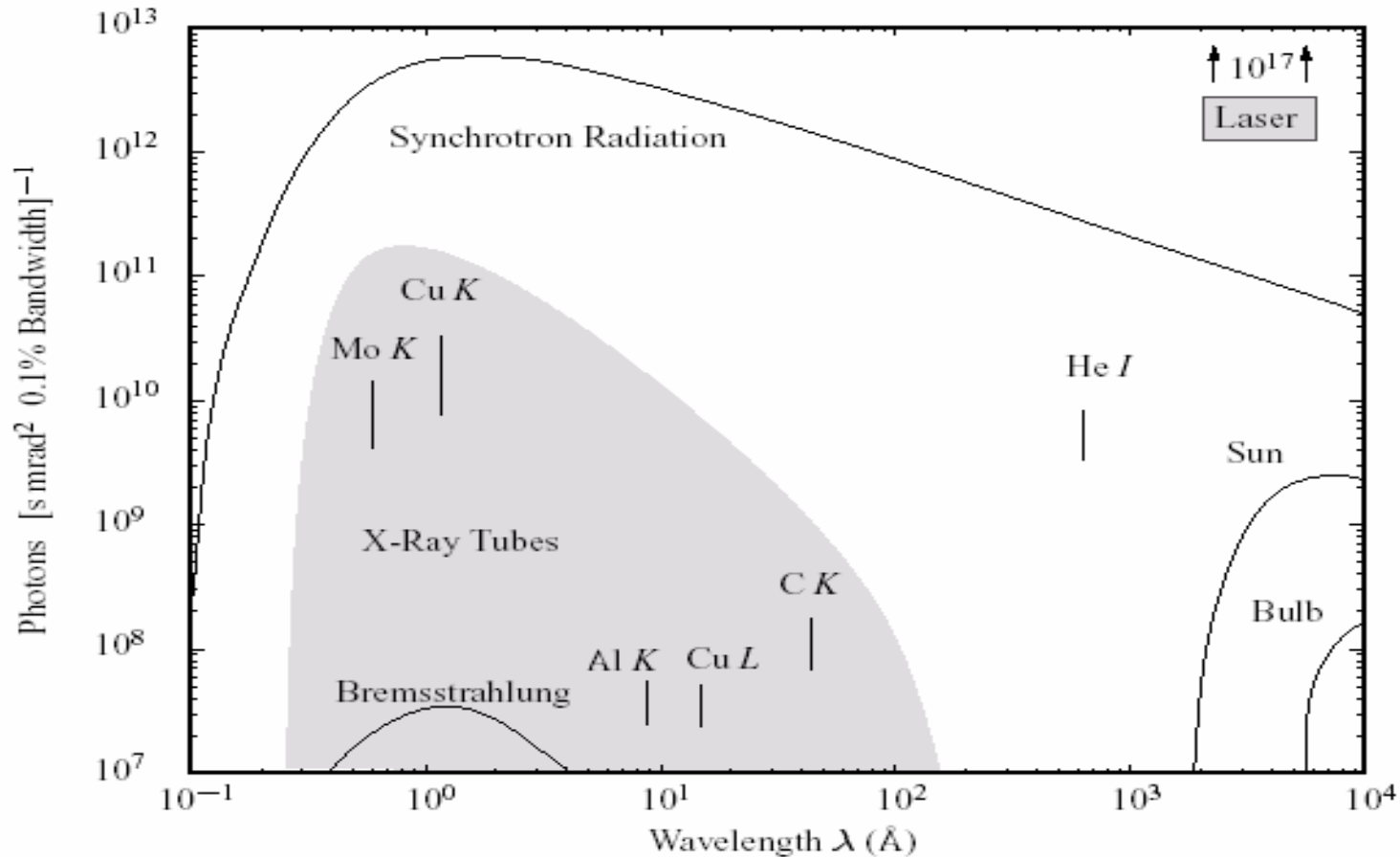
□ Neutrons scatter almost completely **isotropic**: **Elastic** scattering gives precise information about the static lattice structure while **Inelastic** scattering allows one to study lattice vibrations.



Spin-Spin
Interactions

MnO

Sources of Photons (EM Radiation)



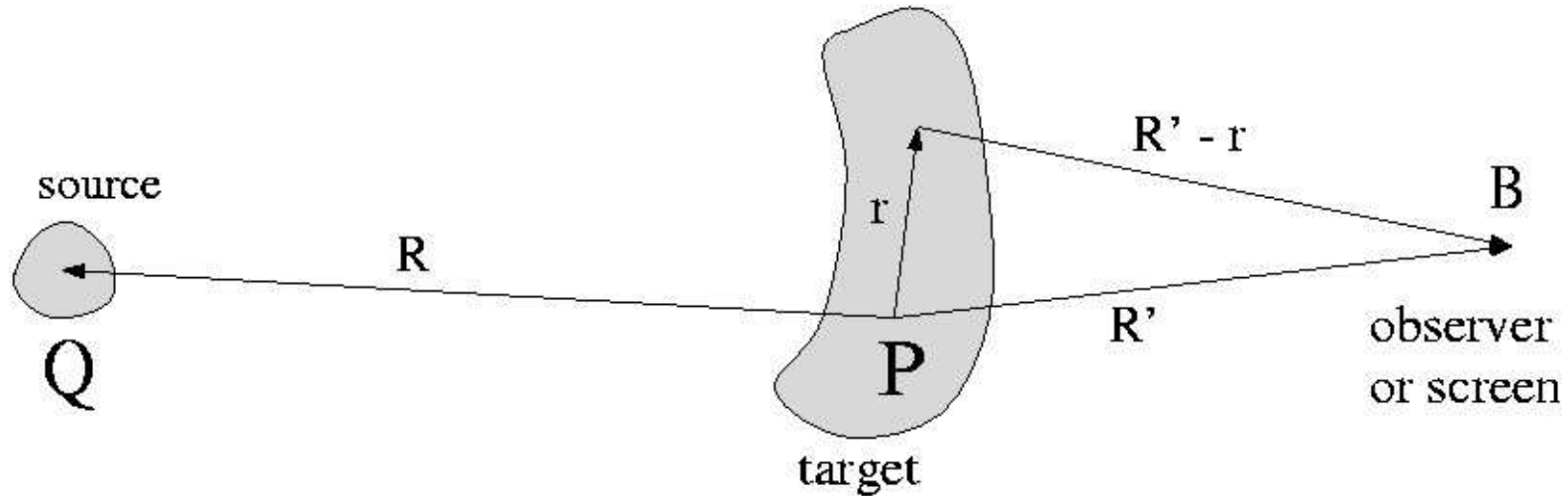
❑ **Interaction of X-rays with condensed matter:** charged particle (electron density) vibrates at the frequency of the incoming radiation.

Classical Theory of Diffraction

- **Three basic assumptions:**

1. The operator which describes the coupling of the target to the scattered "object" (in this case the operator is the density) commutes with the Hamiltonian → realm of classical physics.
2. Huygens principle: Every radiated point of the target will serve as a secondary source spherical waves of the same frequency as the source and the amplitude of the diffracted wave is the sum of the wavelengths considering their amplitudes and relative phases.
3. Resulting spherical waves are not scattered again. For example, in the fully quantum theory for neutron scattering this will correspond to approximating the scattering rate by Fermi golden rule, i.e., the so-called first-order Born approximation.

Setup of Scattering Experiment



$$|R| \gg |r| \Rightarrow A_P = A_0 e^{i(\mathbf{k}_0(\mathbf{R}+\mathbf{r})-\omega_0 t)} \quad (\text{incident wave})$$

$$\text{Hygens: } A_B(R') \propto \int d\mathbf{r} A_P \rho(\mathbf{r}) \frac{e^{i\mathbf{k}(\mathbf{R}'-\mathbf{r})}}{|\mathbf{R}'-\mathbf{r}|}$$

$$A_B(R') \propto A_0 e^{i(\mathbf{k}_0\mathbf{R}+\mathbf{k}\mathbf{R}'-\omega_0 t)} \int d\mathbf{r} \rho(\mathbf{r}) \frac{e^{i-(\mathbf{k}-\mathbf{k}_0)\mathbf{r}}}{|\mathbf{R}'-\mathbf{r}|}$$

The Role of Fourier Transforms in Diffraction Pattern Analysis

- At very large R' , i.e., in the so-called radiation or far zone:

$$A_B(R') \propto \frac{A_0 e^{i(\mathbf{k}_0 \mathbf{R} + \mathbf{k} \mathbf{R}' - \omega_0 t)}}{R'} \int d\mathbf{r} \rho(\mathbf{r}) e^{-i(\mathbf{k} - \mathbf{k}_0) \mathbf{r}}$$

- In terms of the scattered intensity $I_B \propto |A_B|^2$

$$I_B \propto \frac{|A_0|^2}{R'^2} \left| \int d\mathbf{r} \rho(\mathbf{r}) e^{-i(\mathbf{k} - \mathbf{k}_0) \mathbf{r}} \right|^2$$

$$I_B(\mathbf{K}) \propto \frac{|A_0|^2}{R'^2} \left| \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{K} \mathbf{r}} \right|^2 = \frac{|A_0|^2}{R'^2} |\rho(\mathbf{K})|^2$$

Fourier transform of the density of scatterers

Patterson Function

$$I(\mathbf{K}) \propto |\rho(\mathbf{K})|^2 \propto \int \rho(\mathbf{r}) e^{-i\mathbf{K}\mathbf{r}} d\mathbf{r} \int \rho(\mathbf{r}') e^{-i\mathbf{K}\mathbf{r}'} d\mathbf{r}'$$

$$\mathbf{r} \rightarrow \mathbf{r}' + \mathbf{r}$$

$$I(\mathbf{K}) \propto \int e^{i\mathbf{K}\mathbf{r}'} d\mathbf{r}' \int \rho(\mathbf{r}) \rho(\mathbf{r}' + \mathbf{r}) d\mathbf{r}$$

- The Patterson function is the autocorrelation function of the scattering density (it has maximum whenever \mathbf{r}' corresponds to a vector between two atoms in the structure):

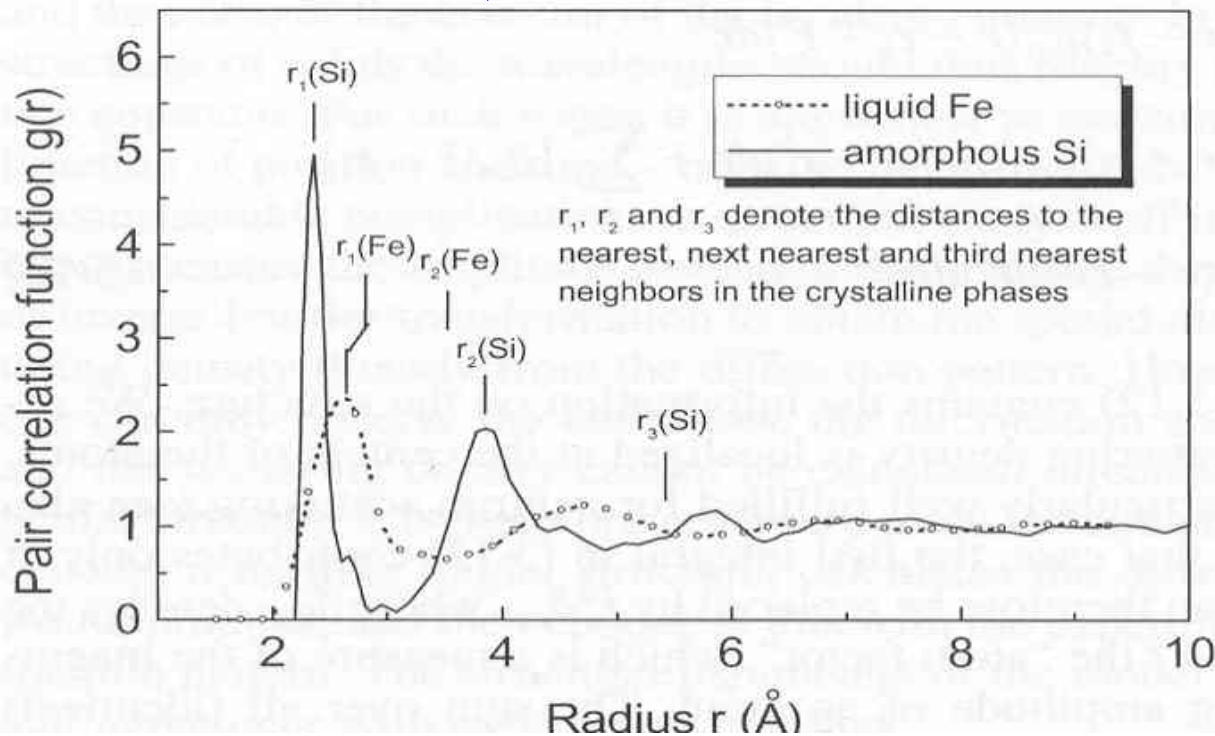
$$P(\mathbf{r}') = \int \rho(\mathbf{r}) \rho(\mathbf{r}' + \mathbf{r}) d\mathbf{r}$$

Vocabulary: Patterson Function, Structure Factor, Pair Correlation Function

Patterson: $P(\mathbf{r}') = Nf^2\delta_{0,r'} + N \int \rho(\mathbf{r})\bar{\rho}(\mathbf{r}'+\mathbf{r})d\mathbf{r}$, $\bar{\rho}(r) = \left\langle \sum_{j \neq i} \rho_{atom}(r-r_j) \right\rangle$

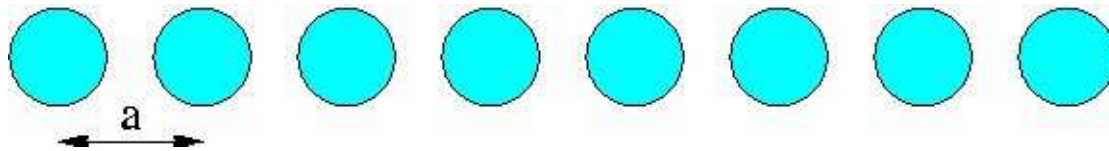
Pair Correlation: $\frac{N}{V} f^2 g(r') = \int \rho(r)\bar{\rho}(r+r')dr$

Structure Factor: $I(\mathbf{K}) \propto S(\mathbf{K}) = 1 + \frac{N}{V} \int g(r)e^{i\mathbf{K}\cdot\mathbf{r}} dr$



Scattering From 1D Periodic Structures

- Density of periodic crystal:



$$\rho(x+ma) = \rho(x) \Rightarrow \rho(x) = \sum_n \rho_n e^{iG_n x}$$

$$\rho(x+ma) = \sum_n \rho_n e^{iG_n(x+ma)} = \sum_n \rho_n e^{iG_n x} e^{iG_n ma} = \rho(x)$$

$$e^{iG_n ma} = 1 \Rightarrow G_n = \frac{2n\pi}{a}$$

Scattering from 3D Periodic Structures

- Generalization to three-dimensional structures:

$$\rho(\mathbf{r} + \mathbf{r}_n) = \rho(\mathbf{r}), \mathbf{r} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3; n_1, n_2, n_3 \in \mathbb{Z}$$

$$\mathbf{G} \cdot \mathbf{r}_n = 2m\pi, m \in \mathbb{Z}$$

$$\mathbf{G} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3 \Rightarrow (h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3) \cdot n_1 \mathbf{a}_1 = 2m\pi, m \in \mathbb{Z}$$

$$\mathbf{g}_1 \cdot \mathbf{a}_1 = 2\pi, \mathbf{g}_2 \cdot \mathbf{a}_1 = \mathbf{g}_3 \cdot \mathbf{a}_1 = 0$$

Reciprocal Lattice (in Reciprocal Space)

- The orthonormal set $(\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3)$ forms the basis of the reciprocal lattice:

$$\mathbf{g}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \mathbf{g}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \mathbf{g}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

http://www.matter.org.uk/diffraction/geometry/sperposition_of_waves_exercises.htm

$$\Omega_{BZ} = |\mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3)| = \frac{(2\pi)^3}{|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|} = \frac{(2\pi)^3}{\Omega_{PUC}}$$

- Real-space and reciprocal lattice have the same point group symmetry (but do not necessarily have the same Bravais lattice: example **FCC** and **BCC** are reciprocal to each other with point group symmetry O_h).

Scattering intensity for a crystal: Laue

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \Rightarrow I_B(K) \propto \frac{|A_0|^2}{R'^2} \left| \int d\mathbf{r} \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{-i(\mathbf{K}-\mathbf{G})\mathbf{r}} \right|^2$$

$$\int e^{-i(\mathbf{K}-\mathbf{G})\mathbf{r}} d\mathbf{r} = \begin{cases} V, & \mathbf{G} = \mathbf{K} \\ 0, & \mathbf{G} \neq \mathbf{K} \end{cases} \quad V - \text{lattice volume}$$

$$I_B(K) \propto \frac{|A_0|^2}{R'^2} |\rho_{\mathbf{G}}|^2 V^2 \delta_{\mathbf{G},\mathbf{K}}$$

This is called **Laue condition for scattering**. The fact that this is proportional to V^2 rather than V indicates that the diffraction spots, in this approximation, are infinitely bright (for a sample in thermodynamic limit) \rightarrow when real broadening is taken into account, $I_B(K) \propto V$

Freidel Rule

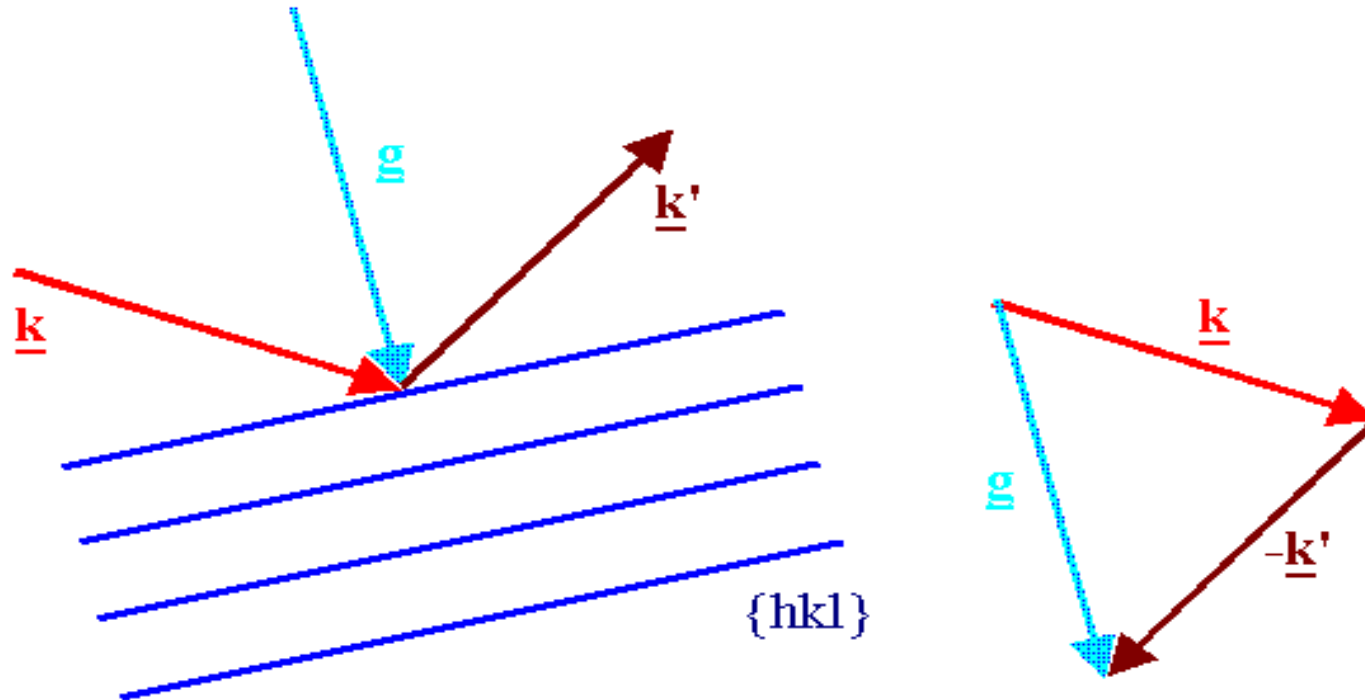
$$I_{hkl} \propto |\rho_{hkl}|^2$$

$$\rho(\mathbf{r}) \in \mathbb{R} \Leftrightarrow \rho_{\mathbf{G}} = \rho_{-\mathbf{G}}^*$$

$$I_{-h-k-l} \equiv I_{\overline{hkl}} = I_{hkl}$$

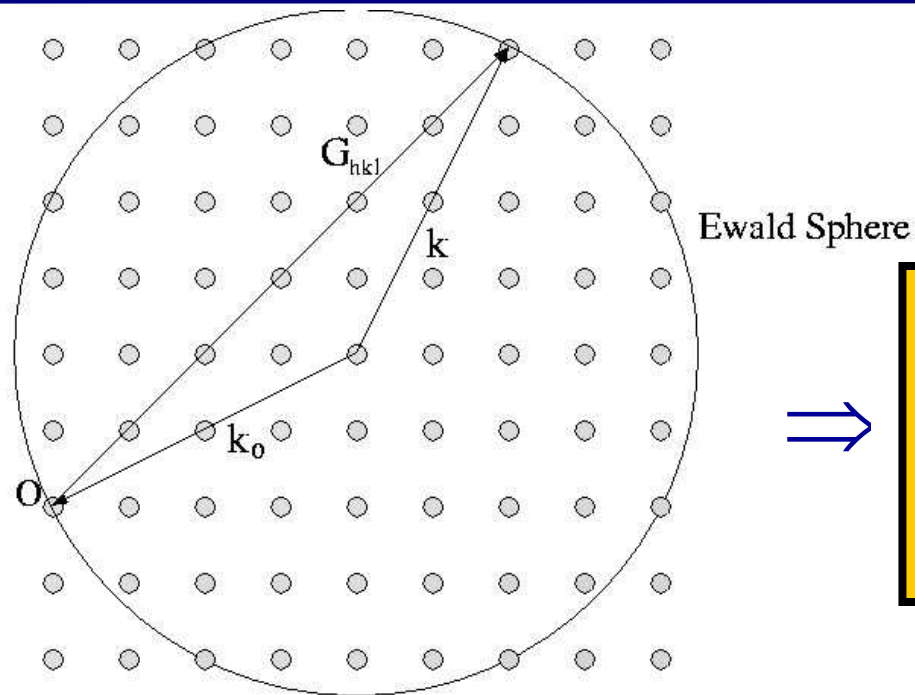
- For every spot at $\mathbf{k}' - \mathbf{k}_0 = \mathbf{G}$, there will be one at $\mathbf{k} - \mathbf{k}_0 = \mathbf{G}$. Thus, for example, if we scatter from a crystal with a 3-fold symmetry axis, we will get a 6-fold scattering pattern.
- The scattering pattern always has an inversion center even if none is present in the target! $\mathbf{G} \rightarrow -\mathbf{G}$

Graphical Laue



- ***If***, and only ***if*** the three vectors involved form a ***closed triangle***, is the Laue condition met. If the Laue condition is ***not*** met, the incoming wave just moves through the lattice and emerges on the other side of the crystal (**neglecting absorption**).

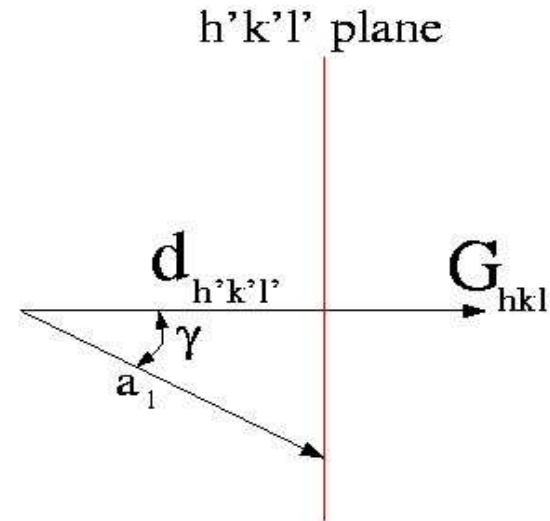
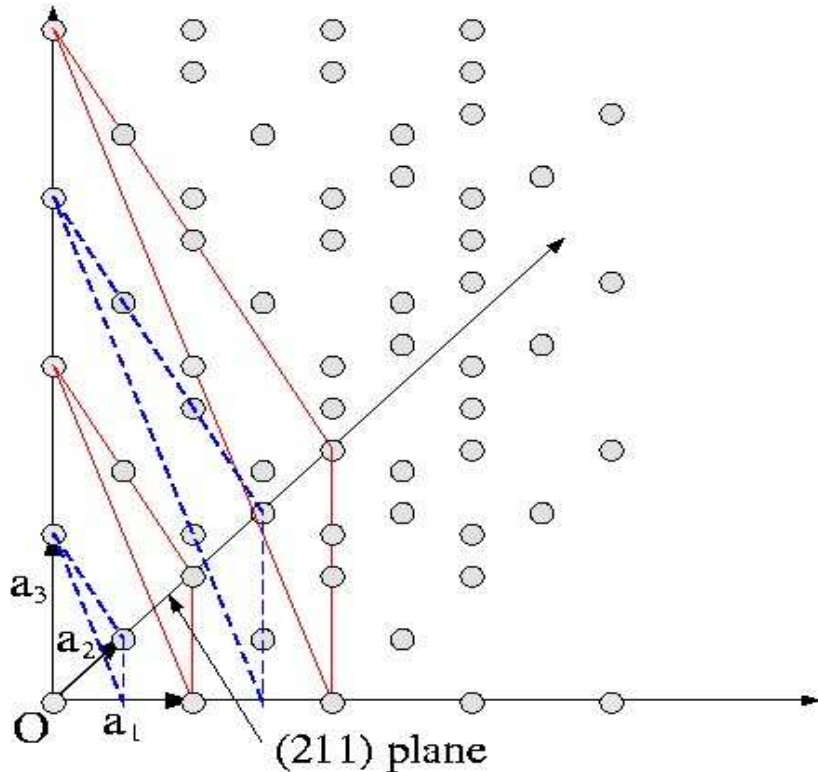
Graphical Laue: Ewald sphere



Use powder X-ray Diffraction (powdered sample corresponds to averaging over all orientations of the reciprocal lattice – will observe all peaks that lie within the radius $2|\mathbf{k}_0|$ of the origin of reciprocal lattice.

Figure 1: The *Ewald Construction* to determine if the conditions are correct for obtaining a **Bragg peak**: Select a point in *k-space* as the origin. Draw the incident wavevector \mathbf{k}_0 to the origin. From the base of \mathbf{k}_0 spin \mathbf{k} (remember, that for elastic scattering $|\mathbf{k}| = |\mathbf{k}_0|$) in all possible directions to form a sphere. At each point where this sphere intersects a lattice point in *k-space*, there will be a Bragg peak with $\mathbf{G} = \mathbf{k} - \mathbf{k}_0$. In the example above we find 8 Bragg peaks. **If however, we change \mathbf{k}_0 by a small amount, then we have none!**

Miller Indices



$$\frac{1}{u} : \frac{1}{v} : \frac{1}{w} = h : k : l \Rightarrow (hkl), -h \equiv \bar{h}$$

$$g_1 : g_2 : g_3 = h : k : l \rightarrow \text{Miller indices} \Leftrightarrow \mathbf{G}$$

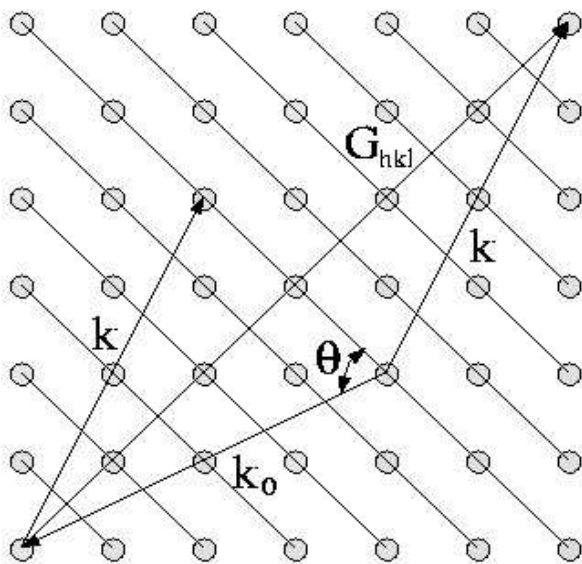
$$\mathbf{G} \cdot \mathbf{r}_n = 2\pi m \Leftrightarrow \mathbf{q} = (n_1 - pg_3)\mathbf{a}_1 + (n_2 - pg_3)\mathbf{a}_2 + [n_3 + p(g_1 + g_2)]\mathbf{a}_3, \mathbf{G} \cdot \mathbf{q} = 2\pi m$$

$$d_m = \frac{2\pi m}{|\mathbf{G}|}$$

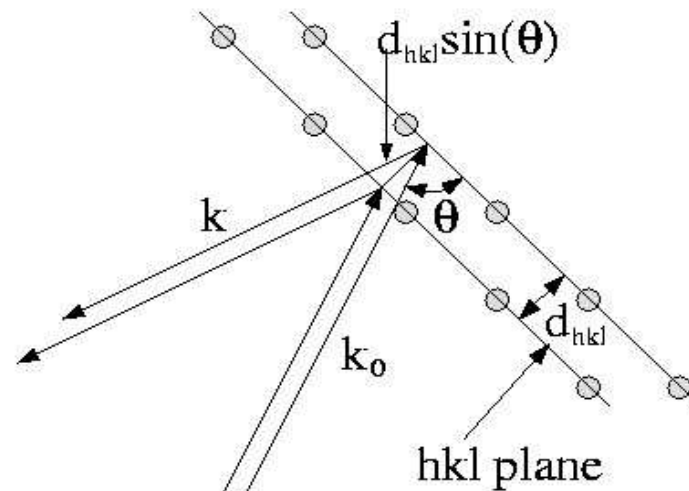
Conventions: hkl , $[hkl]$, (hkl) , $\{hkl\}$, $\langle hkl \rangle$

Bragg vs. Laue = Reciprocal vs. Real Space Analysis

Laue Condition
(in reciprocal space)
 $\mathbf{K} = \mathbf{k} - \mathbf{k}_0 = \mathbf{G}_{hkl}$



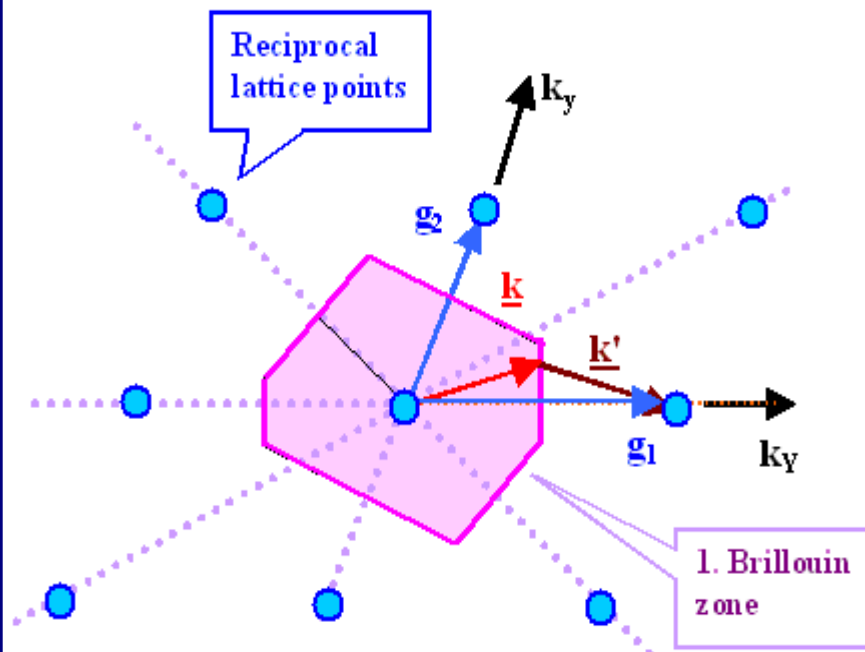
Bragg Condition
(in real space)
 $2d_{hkl} \sin(\theta) = \lambda$



$$|\mathbf{K}| = K = |\mathbf{k} - \mathbf{k}_0| = G_{hkl}$$

$$K = 2k_0 \sin \theta = \frac{4\pi}{\lambda} \sin \theta = \frac{2\pi}{d_{hkl}} \Rightarrow \lambda = 2d_{hkl} \sin \theta$$

Brillouin Zone Interpretation of Bragg and Laue Diffraction Conditions



□ We want to know which particular wave vectors out of many (**an infinite set, in fact**) meet the diffraction (Bragg & Laue) condition for a given crystal lattice plane.

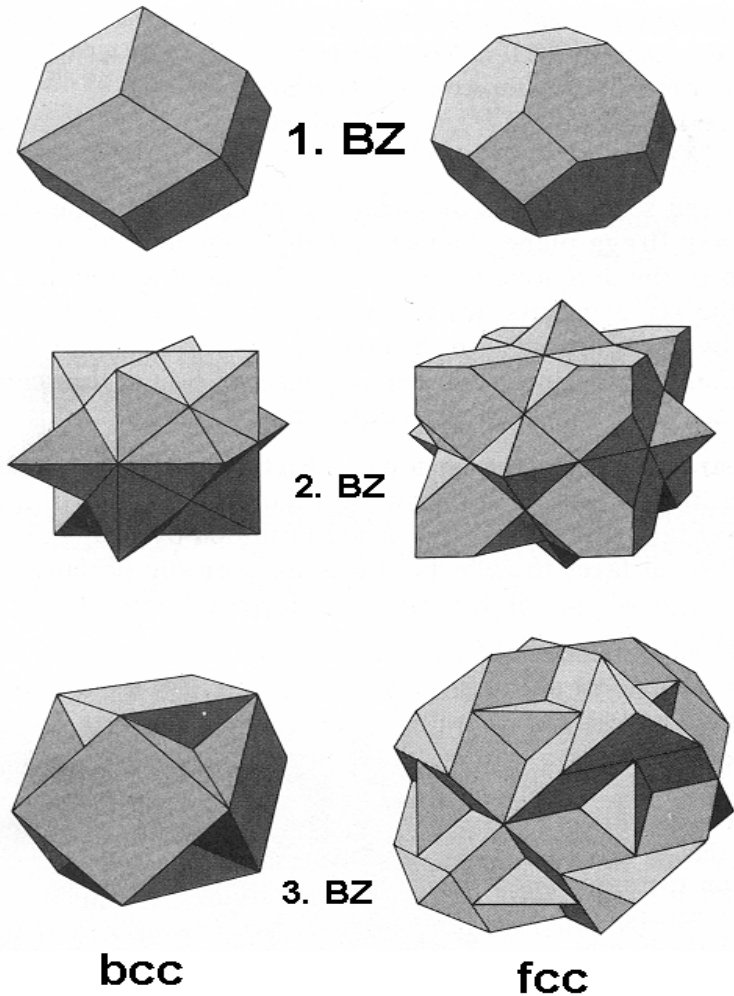
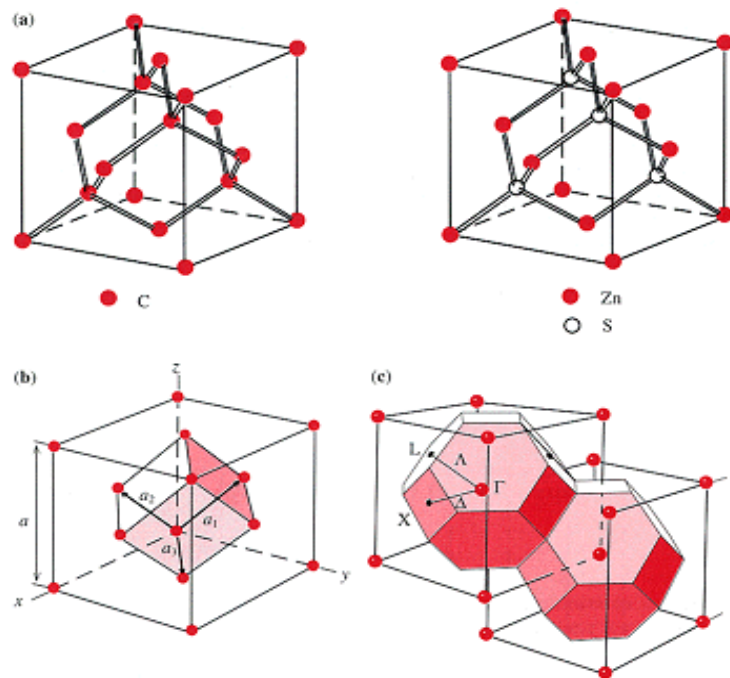
□ If we construct **Wigner-Seitz cells** in the reciprocal lattice, all wave vectors ending on the Wigner-Seitz cell walls will meet the Bragg condition for the set of lattice planes represented by the cell wall.

$$\mathbf{G}_{hkl} \left(\frac{\mathbf{G}_{hkl}}{2} + \mathbf{k} \right) = 0$$

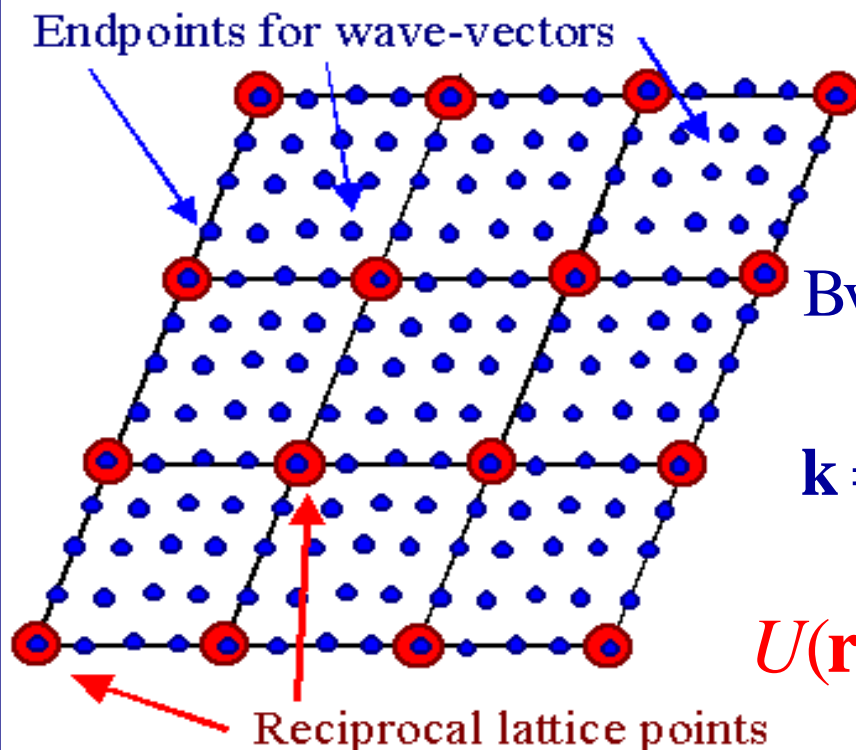
$$(\mathbf{k})^2 = (\mathbf{k}_0)^2 = (\mathbf{G}_{hkl} + \mathbf{k})^2 = \mathbf{G}_{hkl}^2 + \mathbf{k}^2 + 2\mathbf{G}_{hkl} \cdot \mathbf{k}$$

3D Brillouin Zones

• Constructing Brillouin zones is a good example for the evolution of complex systems from the repeated application of simple rules to simple starting conditions - any **12-year old** can do it in two dimensions, but in 3D, ... Ph.D. thesis in 1965 ...



Reciprocal vs. k-vectors



$$|d^3\mathbf{k}| = \frac{(2\pi)^3}{N\Omega_{PUC}}$$

$$\text{BvK: } \Psi_{n\mathbf{k}}(\mathbf{r}) = \Psi_{n\mathbf{k}}(\mathbf{r} + N_j \mathbf{a}_j)$$

$$\mathbf{k} = \left(\frac{\pm 2\pi n_x}{L_x}, \frac{\pm 2\pi n_y}{L_y}, \frac{\pm 2\pi n_z}{L_z} \right), L_x = N_1 a$$

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}) \Rightarrow U(\mathbf{r}) = \sum_{\mathbf{G}} U(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

□ Arbitrary wave vector \mathbf{k} can be written as a sum of some reciprocal lattice vector \mathbf{G} plus a suitable wave vector \mathbf{k}' ; i.e. we can always write $\mathbf{k} = \mathbf{G} + \mathbf{k}'$ and \mathbf{k}' can always be confined to the **first Brillouin zone**, i.e. the **elementary cell of the reciprocal lattice**.

Fourier Analysis in Solid State Physics of Crystals

□ **Periodic Function**, with the same periodicity as the lattice, expanded in Fourier series:

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}) \Rightarrow U(\mathbf{r}) = \sum_{\mathbf{G}} U(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

□ **Arbitrary wave function** expanded in plane waves:

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

□ **Bloch wavefunctions** (eigenstates of crystal Hamiltonian) expansion:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} = \Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$

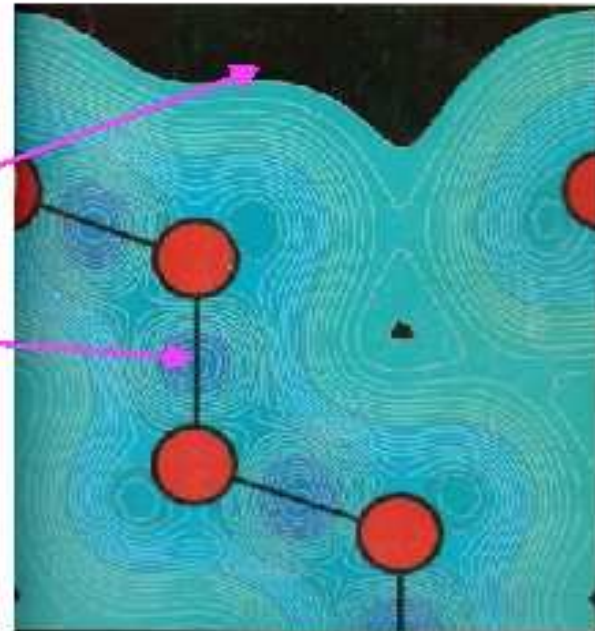
Nearly-free-electron-like?

Density of valence electrons
is rather smoothly varying

Minimum at holes in structure

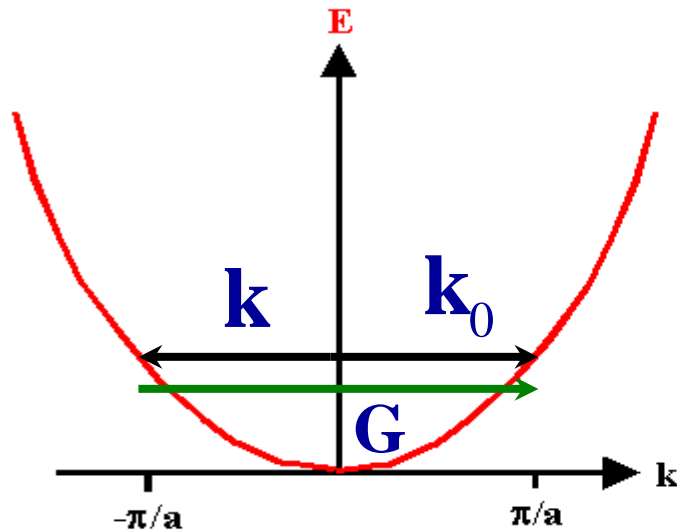
Peaked at bonds

Reasonable to consider as
a perturbation starting
from uniform system
just like the 1d problem that
we solved

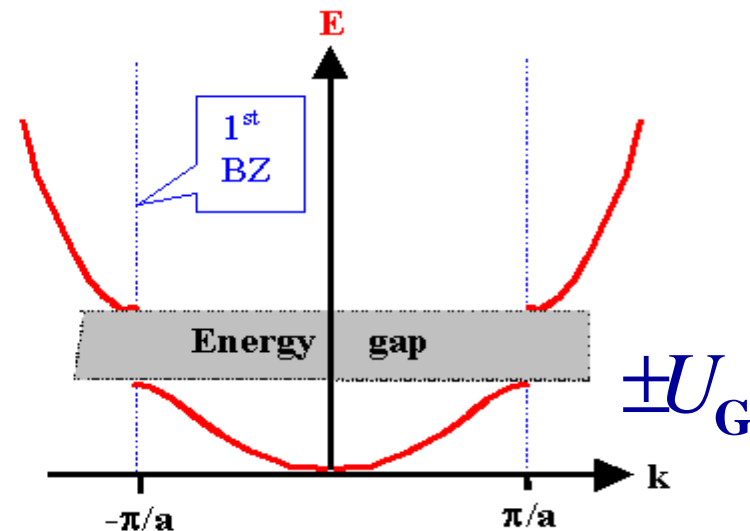


Calculated valence electron density
in a (110) plane in a Si crystal
(Cover of Physics Today, 1970)

Crystal Electrons in the BZ-realm



Free electron gas



Free electron gas and diffraction at Brillouin zones

- All wave vectors that end on a **BZ**, will fulfill the Bragg condition and thus are diffracted – states with $+\frac{\pi}{a}$ is Bragg reflected into state with $-\frac{\pi}{a}$ (and vice versa)
- Wave vectors a completely in the interior of the 1. **BZ**, or well in between any two **BZs**, will never get diffracted; they move pretty much as if the potential would be constant, i.e. *they behave very close to the solutions of the free electron gas.*

Crystal Electrons in the BZ-realm

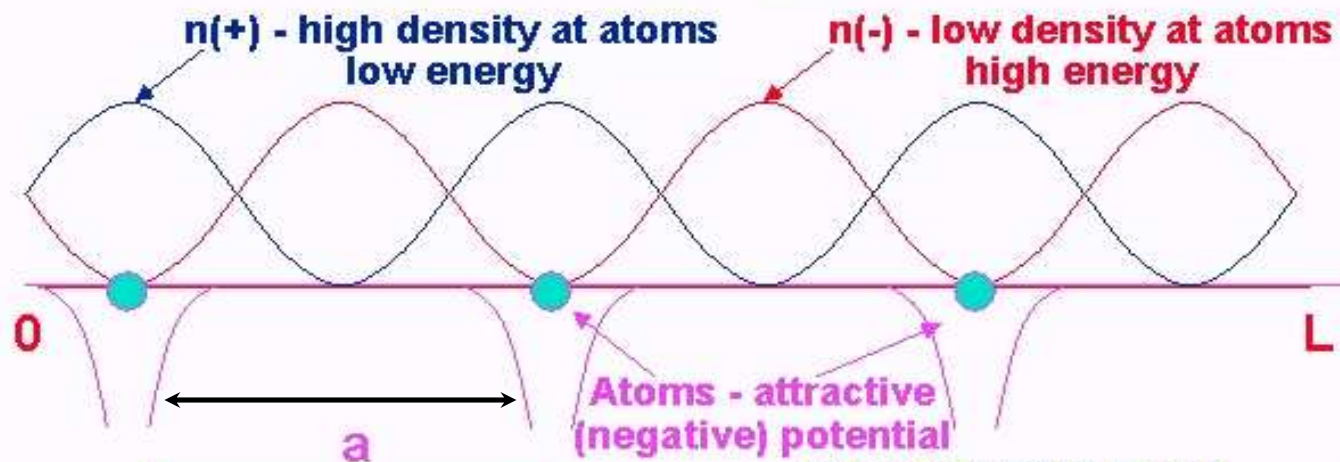
Interpretation of Standing waves at Brillouin Zone boundary

- Bragg scattering at $k = \pi/a$ leads to the two possible combinations of the right and left going waves:

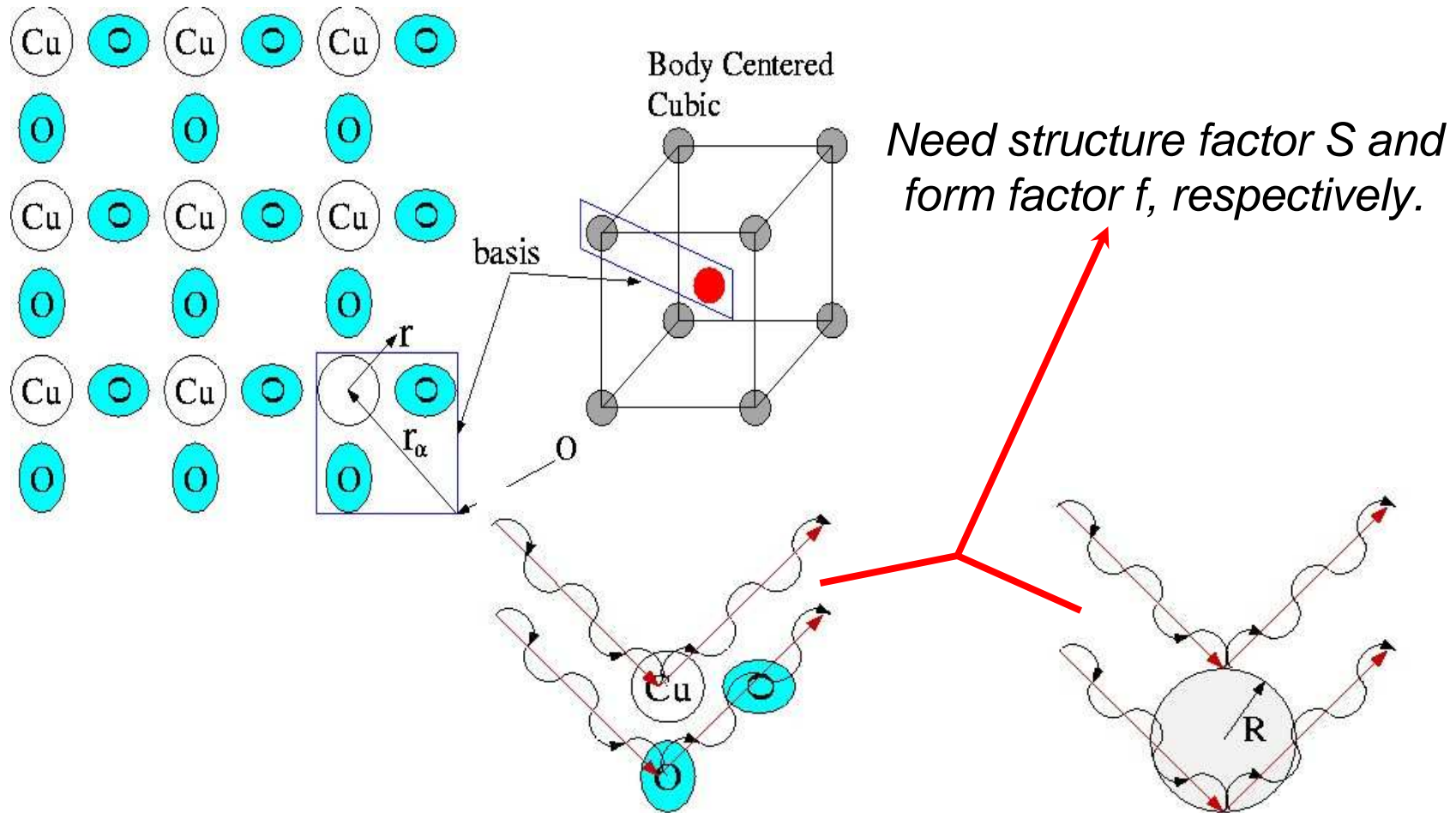
$$\Psi (+) = \exp(i \pi x/a) + \exp(-i \pi x/a) = 2 \cos(\pi x/a)$$

$$\Psi (-) = \exp(i \pi x/a) - \exp(-i \pi x/a) = 2i \sin(\pi x/a),$$

with density $n(+)$ = $4 \cos^2(\pi x/a)$; $n(-)$ = $4 \sin^2(\pi x/a)$



Scattering From a Lattice with a Basis



Structure and Form factors

$$I_{hkl} \propto |\rho_{hkl}|^2, \rho_{hkl} = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{G}_{hkl}\mathbf{r}} = \frac{1}{V} \sum_{\text{cells}} \int_{\text{cell}} d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{G}_{hkl}\mathbf{r}}$$

$$\rho_{hkl} = \frac{1}{V} \sum_{N_1, N_2, N_3} \int_{\text{cell}} d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{G}(\mathbf{r}_n + \mathbf{r}_\alpha + \mathbf{r}')} \text{ since } \mathbf{r} = \mathbf{r}_n + \mathbf{r}_\alpha + \mathbf{r}'$$

$$\rho_{hkl} = \frac{1}{V_{\text{cell}}} \sum_{\alpha} e^{-i\mathbf{G}_{hkl}\mathbf{r}_\alpha} \int d\mathbf{r}' \rho_{\alpha}(\mathbf{r}') e^{-i\mathbf{G}_{hkl}\mathbf{r}'}$$

Atomic
Scattering Form
Factor

$$\longrightarrow f_{\alpha} = \int d\mathbf{r}' \rho_{\alpha}(\mathbf{r}') e^{-i\mathbf{G}_{hkl}\mathbf{r}'} \propto Z \Rightarrow I \propto Z^2$$

Structure Factor



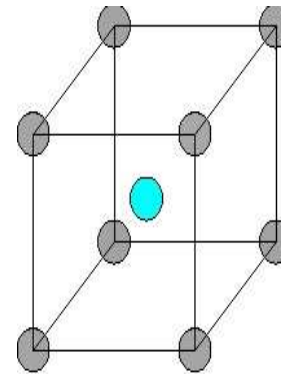
$$S = f \Leftrightarrow \text{One atom per unit cell } \rho_{hkl} = \frac{1}{V_c} \sum_{\alpha} e^{-i\mathbf{G}_{hkl}\mathbf{r}_\alpha} f_{\alpha} = \frac{S_{hkl}}{V_c}$$

Extinctions

$$\mathbf{r}_\alpha = u_\alpha \mathbf{a}_1 + v_\alpha \mathbf{a}_2 + w_\alpha \mathbf{a}_3$$

$$S_{hkl} = \sum_{\alpha} f_{\alpha} \exp \left[-2\pi i (hu_{\alpha} + hv_{\alpha} + wu_{\alpha}) \right]$$

$$\mathbf{r}_1 = (0, 0, 0) \quad \mathbf{r}_2 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right)$$



$$f_{Fe}^{X\text{-ray}} \approx f_{Co}^{X\text{-ray}}$$

$$f_{Fe}^{\text{neutron}} \neq f_{Co}^{\text{neutron}}$$

Unit Cell of BCC ordered FeCo

● Fe

● Co

$$S_{hkl} = f \left(1 + e^{-i\pi(h+k+l)} \right) = \begin{cases} 0, & h+k+l \text{ odd} \\ 2f, & h+k+l \text{ even} \end{cases}$$

Position of Bragg reflection: Shape and dimension of the unit cell

Intensities of reflections: Content of the unit cell

Structure Factor Revisted: Quantum Mechanical Case

Example: Diffraction of electron on crystalline potential $\lambda \sim a = 10^8 \text{ cm} \Rightarrow E \sim 0.1 \text{ eV}$

$$U(\mathbf{r}) = \sum_{\alpha} U_{\alpha}(\mathbf{r} - \mathbf{r}_{\alpha}) \Rightarrow e^{-} \text{ transition from } \Psi_{\mathbf{k}} = \frac{e^{i\mathbf{k}\mathbf{r}}}{\sqrt{V}} \text{ to } \Psi_{\mathbf{k}_1} = \frac{e^{i\mathbf{k}_1\mathbf{r}}}{\sqrt{V}}$$

Quantum-Mechanical Probability Amplitude for this transition:

$$A_{\mathbf{k}_1\mathbf{k}} = \langle \Psi_{\mathbf{k}_1} | \hat{U} | \Psi_{\mathbf{k}} \rangle = \int d\mathbf{r} \Psi_{\mathbf{k}_1}^*(\mathbf{r}) U(\mathbf{r}) \Psi_{\mathbf{k}}(\mathbf{r})$$

$$A_{\mathbf{k}_1\mathbf{k}} = \frac{1}{V} \sum_{\alpha} e^{i(\mathbf{k}-\mathbf{k}_1)\mathbf{r}_{\alpha}} \int e^{i(\mathbf{k}-\mathbf{k}_1)(\mathbf{r}-\mathbf{r}_{\alpha})} U_{\alpha}(\mathbf{r}-\mathbf{r}_{\alpha}) d\mathbf{r} = U_{\alpha}(\mathbf{G}) S(\mathbf{G})$$

$$U_{\alpha}(\mathbf{G}) = \frac{1}{V_0} \int d\mathbf{r} e^{i\mathbf{G}(\mathbf{r}-\mathbf{r}_{\alpha})} U_{\alpha}(\mathbf{r}-\mathbf{r}_{\alpha})$$

$$S(\mathbf{G}) = \frac{1}{N} \sum_{\alpha} e^{i\mathbf{G}\mathbf{r}_{\alpha}}$$

Structure factor is completely determined by geometrical properties of the crystal.

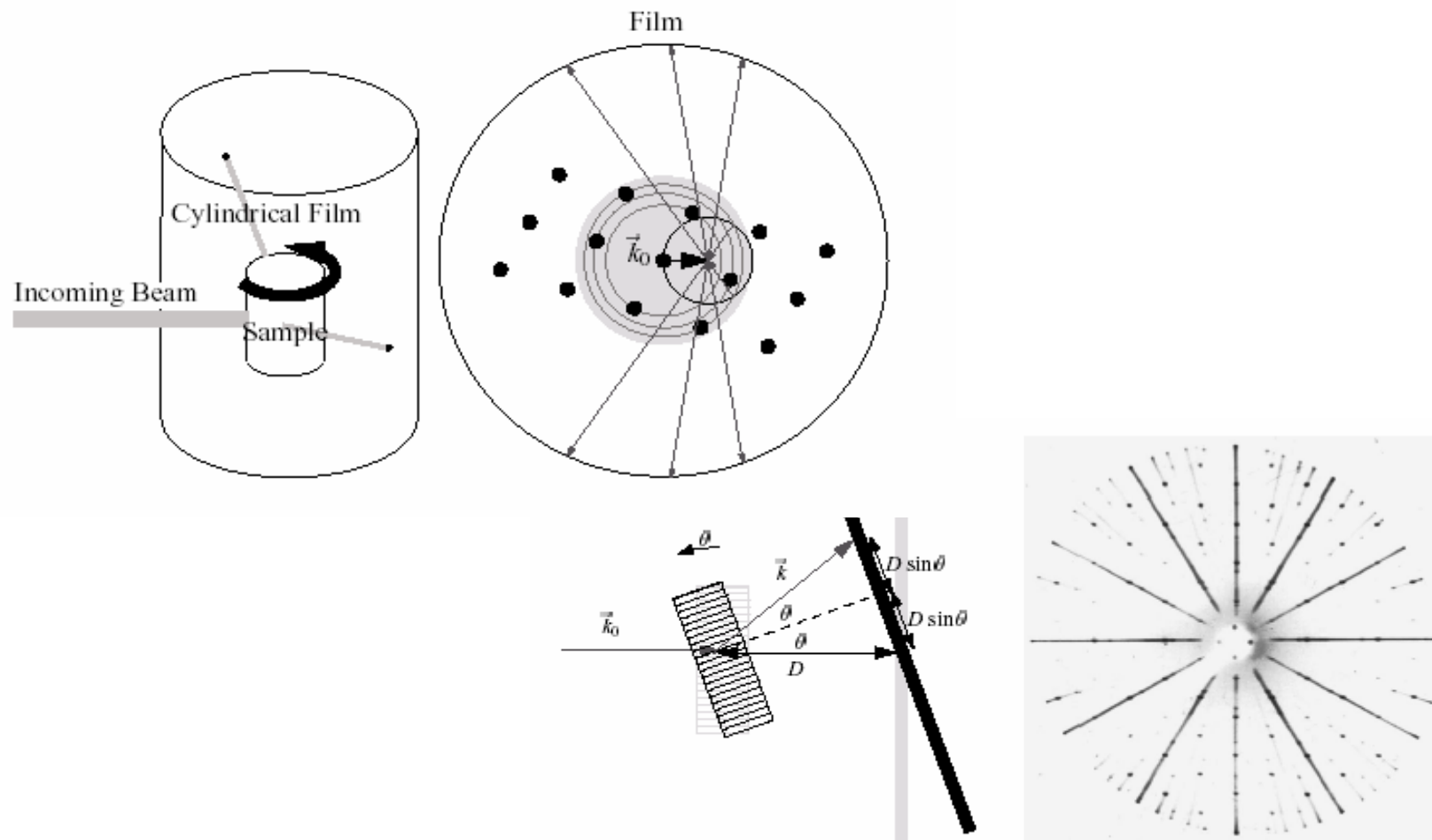
Structure factor: Conclusion

- Any matrix element that describes a transition between two electronic states under the action of crystalline potential will contain a **structure factor**.
- Crystal potential does not have to be necessarily expressed in terms of sum of the atomic potentials; furthermore, the transition do not necessarily involve “external” electrons → everything is valid also for transition between electronic states of a crystal itself.
- Extracting of structure factor reflects how spatial distribution of ions affects dynamics of processes in crystals. **Example:**

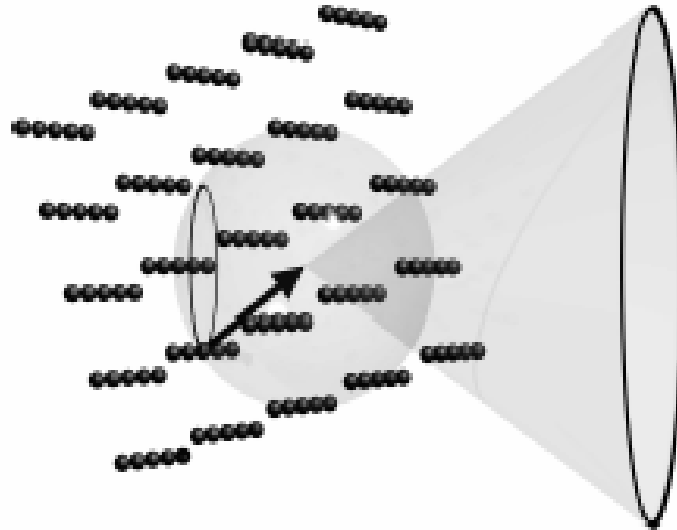
$$\rho(\mathbf{r}) = \sum_{\alpha} \rho(\mathbf{r} - \mathbf{r}_{\alpha}) \Rightarrow \rho(\mathbf{k}) = S(\mathbf{k}) \rho_0(\mathbf{k}) \text{ for electrons}$$

$$\langle \rho(\mathbf{r}) \rho(\mathbf{r}_1) \rangle \Rightarrow S(\mathbf{k}) = \rho(\mathbf{k}) \rho(-\mathbf{k}) \text{ for molecules}$$

Experimental Techniques: Rotating Crystal



Experimental Techniques: Powders



$$\theta = \sin^{-1}(K/2k_0)$$

and the radius r on film of the scattering ring due to reciprocal lattice vector \vec{K} is

$$r = D \tan(2\theta).$$