Lattices, Reciprocal Lattices and Diffraction

Chem 634

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References for this Topic

✿ Clegg, "Crystal Structure Determination".

✿ Stout & Jensen, "X-Ray Structure Determination", 2nd Edition. Instrumentation discussion is completely outdated, but still a good text on the subject.

✿ A more authoritative general reference: Giacovazzo, et al., "Fundamentals of Crystallography", IUCr Texts on Crystallography.

✿ MIT has a good site (MIT Open Courseware): http://ocw.mit.edu/OcwWeb/Chemistry/5-841Fall-2006/LectureNotes/index.htm

Bravais Lattices

• Direct Lattice:
  – A regular, periodic array of points with a spacing commensurate with the unit cell dimensions. The environment around each points in a lattice is identical.

• The set of direct lattice points can be written as (vectors): $\mathbf{R} = t\mathbf{a} + u\mathbf{b} + v\mathbf{c}$ t, u, v integers

• V = volume of unit cell

$$V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) =$$
$$\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$$

Reciprocal Lattices

• Reciprocal Lattice: the basis vectors of the reciprocal lattice are defined as

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}; \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}; \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V}; \quad V = (\mathbf{a} \times \mathbf{b}) \bullet \mathbf{c}$$

(Note: In physics texts, a factor of 2π is usually included

e.g., $\mathbf{a}^* = 2\pi \dfrac{\mathbf{b} \times \mathbf{c}}{V}; \quad \cdots$)

• The set of Reciprocal Lattice Vectors (RLVs) are written as $\mathbf{K}_i = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

h, k, l = integers

Reciprocal Lattices

- Properties of RLVs:

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

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

Alternatively, these can be regarded as *definitions*.

In 2 dimensions, we *define* the RLVs

$$\mathbf{a}^* \perp \mathbf{b} \,, \mathbf{b}^* \perp \mathbf{a} \,, \mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = 1$$

Side by Side (2-D)

Direct Lattice

Reciprocal Lattice

- Although they "live in separate universes", the direct and reciprocal lattices are in rotational "lock-step".

Lattice & Reciprocal Lattice
Example: BCC treated as Primitive

$$\mathbf{a} = \frac{a}{2}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}\right)$$

$$\mathbf{b} = \frac{a}{2}\left(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{c} = \frac{a}{2}\left(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

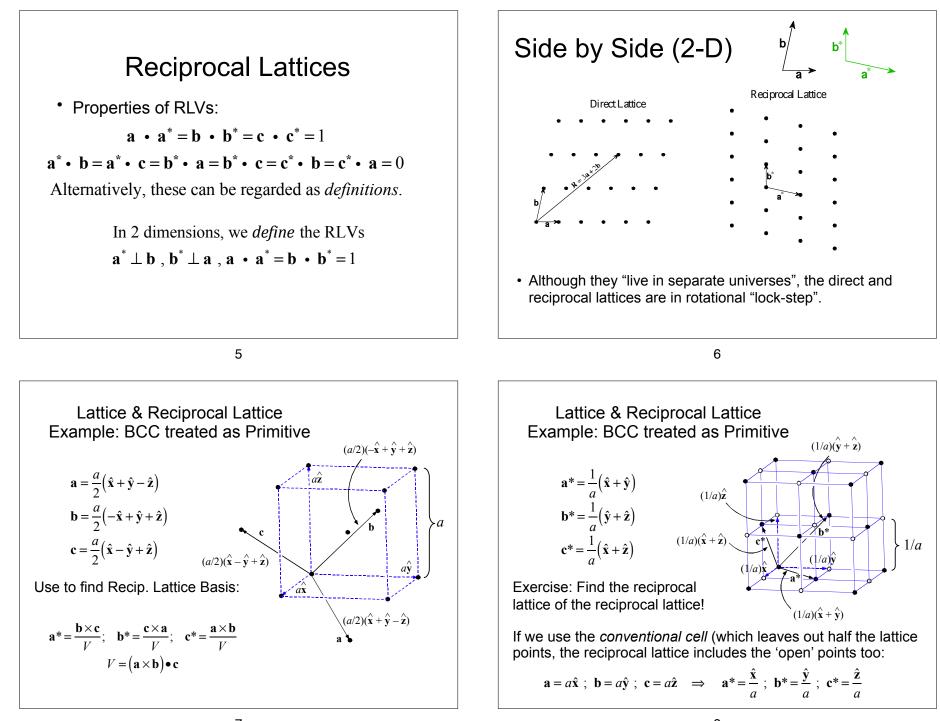Use to find Recip. Lattice Basis:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}; \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}; \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V}$$

$$V = (\mathbf{a} \times \mathbf{b}) \bullet \mathbf{c}$$

$(a/2)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$

$a\hat{\mathbf{z}}$

$(a/2)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$

$a\hat{\mathbf{y}}$

$a\hat{\mathbf{x}}$

$(a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$

Lattice & Reciprocal Lattice
Example: BCC treated as Primitive

$$\mathbf{a}^* = \frac{1}{a}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}}\right)$$

$$\mathbf{b}^* = \frac{1}{a}\left(\hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{c}^* = \frac{1}{a}\left(\hat{\mathbf{x}} + \hat{\mathbf{z}}\right)$$

Exercise: Find the reciprocal lattice of the reciprocal lattice!

$(1/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}})$

$(1/a)\hat{\mathbf{z}}$

$(1/a)(\hat{\mathbf{x}} + \hat{\mathbf{z}})$

$(1/a)\hat{\mathbf{x}}$

$(1/a)\hat{\mathbf{y}}$

$(1/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}})$

If we use the *conventional cell* (which leaves out half the lattice points, the reciprocal lattice includes the 'open' points too:

$$\mathbf{a} = a\hat{\mathbf{x}} \,;\ \mathbf{b} = a\hat{\mathbf{y}} \,;\ \mathbf{c} = a\hat{\mathbf{z}} \quad \Rightarrow \quad \mathbf{a}^* = \frac{\hat{\mathbf{x}}}{a} \,;\ \mathbf{b}^* = \frac{\hat{\mathbf{y}}}{a} \,;\ \mathbf{c}^* = \frac{\hat{\mathbf{z}}}{a}$$
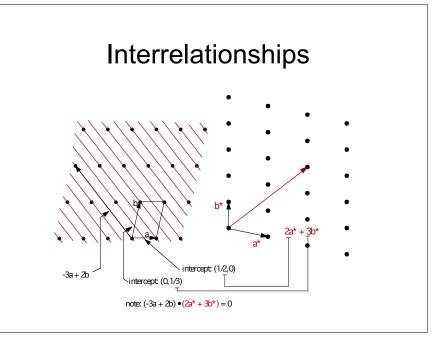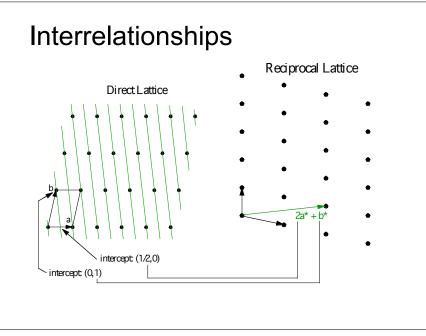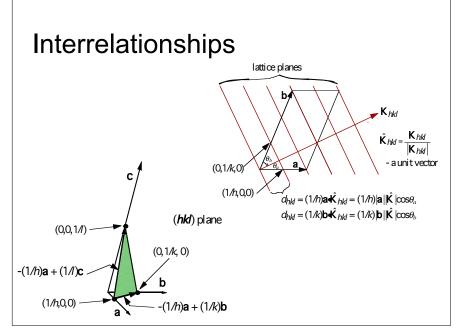
Interrelationships

- The direct lattice can be partitioned such that all of the lattice points lie on sets of planes. Crystallographers classify these sets of planes using the intercepts on the unit cell axes cut by the plane adjacent to the plane through the origin.
- The intercepts are of the form $(1/h, 0, 0)$, $(0, 1/k, 0)$, and $(0, 0, 1/l)$.
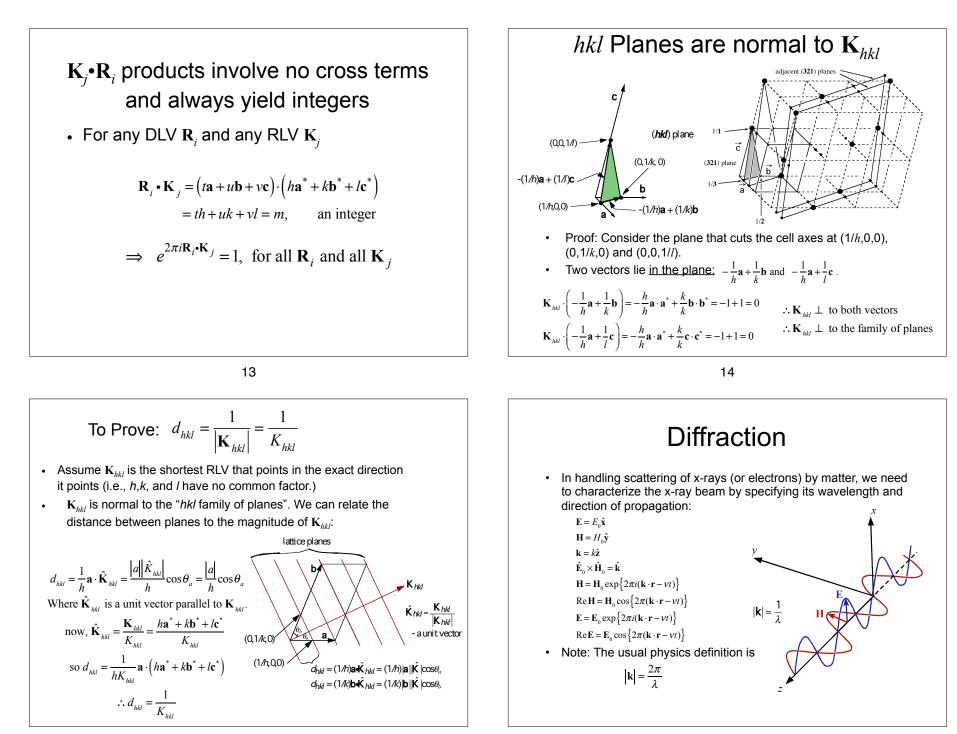- These planes are normal to the RLVs

$$\mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

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Interrelationships

-3a + 2b

intercept: (1/2, 0)

intercept: (0, 1/3)

$2a^* + 3b^*$

note: $(-3a + 2b) \cdot (2a^* + 3b^*) = 0$

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Interrelationships

Direct Lattice

Reciprocal Lattice

$2a^* + b^*$

intercept: (1/2, 0)

intercept: (0, 1)

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Interrelationships

lattice planes

$\mathbf{K}_{hkl}$

$\hat{\mathbf{K}}_{hkl} = \dfrac{\mathbf{K}_{hkl}}{|\mathbf{K}_{hkl}|}$

- a unit vector

$(0, 1/k, 0)$

$(1/h, 0, 0)$

$d_{hkl} = (1/h)\mathbf{a} \cdot \hat{\mathbf{K}}_{hkl} = (1/h)|\mathbf{a}||\hat{\mathbf{K}}|\cos\theta_a$

$d_{hkl} = (1/k)\mathbf{b} \cdot \hat{\mathbf{K}}_{hkl} = (1/k)|\mathbf{b}||\hat{\mathbf{K}}|\cos\theta_b$

$(0, 0, 1/l)$

(hkl) plane

$(0, 1/k, 0)$

$-(1/h)\mathbf{a} + (1/l)\mathbf{c}$

$-(1/h)\mathbf{a} + (1/k)\mathbf{b}$

$(1/h, 0, 0)$

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$\mathbf{K}_j \cdot \mathbf{R}_i$ products involve no cross terms and always yield integers

- For any DLV $\mathbf{R}_i$ and any RLV $\mathbf{K}_j$

$$\mathbf{R}_i \cdot \mathbf{K}_j = \left(t\mathbf{a} + u\mathbf{b} + v\mathbf{c}\right) \cdot \left(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right)$$
$$= th + uk + vl = m, \qquad \text{an integer}$$

$$\Rightarrow \quad e^{2\pi i \mathbf{R}_i \cdot \mathbf{K}_j} = 1, \text{ for all } \mathbf{R}_i \text{ and all } \mathbf{K}_j$$

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hkl Planes are normal to $\mathbf{K}_{hkl}$

- Proof: Consider the plane that cuts the cell axes at $(1/h,0,0)$, $(0,1/k,0)$ and $(0,0,1/l)$.
- Two vectors lie <u>in the plane</u>: $-\dfrac{1}{h}\mathbf{a} + \dfrac{1}{k}\mathbf{b}$ and $-\dfrac{1}{h}\mathbf{a} + \dfrac{1}{l}\mathbf{c}$.

$$\mathbf{K}_{hkl} \cdot \left(-\frac{1}{h}\mathbf{a} + \frac{1}{k}\mathbf{b}\right) = -\frac{h}{h}\mathbf{a}\cdot\mathbf{a}^* + \frac{k}{k}\mathbf{b}\cdot\mathbf{b}^* = -1 + 1 = 0 \qquad \therefore \mathbf{K}_{hkl} \perp \text{ to both vectors}$$

$$\mathbf{K}_{hkl} \cdot \left(-\frac{1}{h}\mathbf{a} + \frac{1}{l}\mathbf{c}\right) = -\frac{h}{h}\mathbf{a}\cdot\mathbf{a}^* + \frac{k}{k}\mathbf{c}\cdot\mathbf{c}^* = -1 + 1 = 0 \qquad \therefore \mathbf{K}_{hkl} \perp \text{ to the family of planes}$$

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To Prove: $d_{hkl} = \dfrac{1}{\left|\mathbf{K}_{hkl}\right|} = \dfrac{1}{K_{hkl}}$

- Assume $\mathbf{K}_{hkl}$ is the shortest RLV that points in the exact direction it points (i.e., h, k, and l have no common factor.)
- $\mathbf{K}_{hkl}$ is normal to the "hkl family of planes". We can relate the distance between planes to the magnitude of $\mathbf{K}_{hkl}$:

$$d_{hkl} = \frac{1}{h}\mathbf{a}\cdot\hat{\mathbf{K}}_{hkl} = \frac{|a||\hat{K}_{hkl}|}{h}\cos\theta_a = \frac{|a|}{h}\cos\theta_a$$

Where $\hat{\mathbf{K}}_{hkl}$ is a unit vector parallel to $\mathbf{K}_{hkl}$.

$$\text{now, } \hat{\mathbf{K}}_{hkl} = \frac{\mathbf{K}_{hkl}}{K_{hkl}} = \frac{h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*}{K_{hkl}}$$

$$\text{so } d_{hkl} = \frac{1}{hK_{hkl}}\mathbf{a}\cdot\left(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right)$$

$$\therefore d_{hkl} = \frac{1}{K_{hkl}}$$

$d_{hkl} = (1/h)\mathbf{a}\cdot\hat{\mathbf{K}}_{hkl} = (1/h)|\mathbf{a}||\hat{K}|\cos\theta_a$
$d_{hkl} = (1/k)\mathbf{b}\cdot\hat{\mathbf{K}}_{hkl} = (1/k)|\mathbf{b}||\hat{K}|\cos\theta_b$

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Diffraction

- In handling scattering of x-rays (or electrons) by matter, we need to characterize the x-ray beam by specifying its wavelength and direction of propagation:

$$\mathbf{E} = E_0\hat{\mathbf{x}}$$
$$\mathbf{H} = H_0\hat{\mathbf{y}}$$
$$\mathbf{k} = k\hat{\mathbf{z}}$$
$$\hat{\mathbf{E}}_0 \times \hat{\mathbf{H}}_0 = \hat{\mathbf{k}}$$
$$\mathbf{H} = \mathbf{H}_0 \exp\left\{2\pi i(\mathbf{k}\cdot\mathbf{r} - vt)\right\}$$
$$\text{Re }\mathbf{H} = \mathbf{H}_0 \cos\left\{2\pi(\mathbf{k}\cdot\mathbf{r} - vt)\right\}$$
$$\mathbf{E} = \mathbf{E}_0 \exp\left\{2\pi i(\mathbf{k}\cdot\mathbf{r} - vt)\right\}$$
$$\text{Re }\mathbf{E} = \mathbf{E}_0 \cos\left\{2\pi(\mathbf{k}\cdot\mathbf{r} - vt)\right\}$$

$$|\mathbf{k}| = \frac{1}{\lambda}$$

- Note: The usual physics definition is

$$|\mathbf{k}| = \frac{2\pi}{\lambda}$$

Additional Comments

- In order to speak of the localization of an electron (or photon), we must 'blur' the specification of the electron's (photon's) wavelength, and allow that there is some uncertainty in the wavelength (and frequency and energy):

$$E_k(z,t) = \int_{-\infty}^{\infty} E_0(k') \exp\left\{2\pi i(k'z - vt)\right\} dk'$$
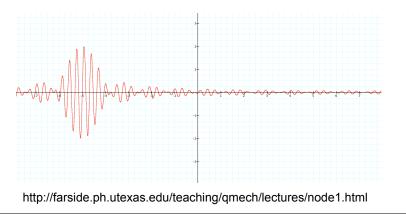
where we have assumed, for simplicity, that the wave is propagating along the z-axis and $E_0(k)$ is a function strongly peaked near a particular 'approximate' wavenumber k.

- Electrons and photons are different in that wave packets for electrons spread out over time, while photon wave packets retain their width as they propagate. For more details, see:

http://farside.ph.utexas.edu/teaching/qmech/lectures/node1.html

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Traveling wave packet

- By "adding" up a narrow range of frequencies, a "wave packet" can be constructed and a photon visualized.

http://farside.ph.utexas.edu/teaching/qmech/lectures/node1.html

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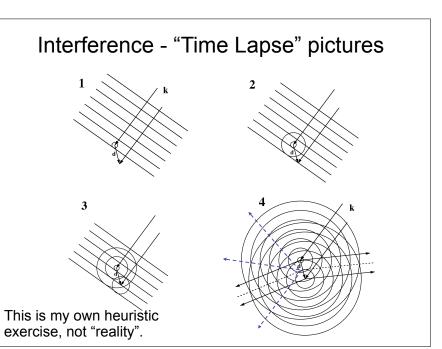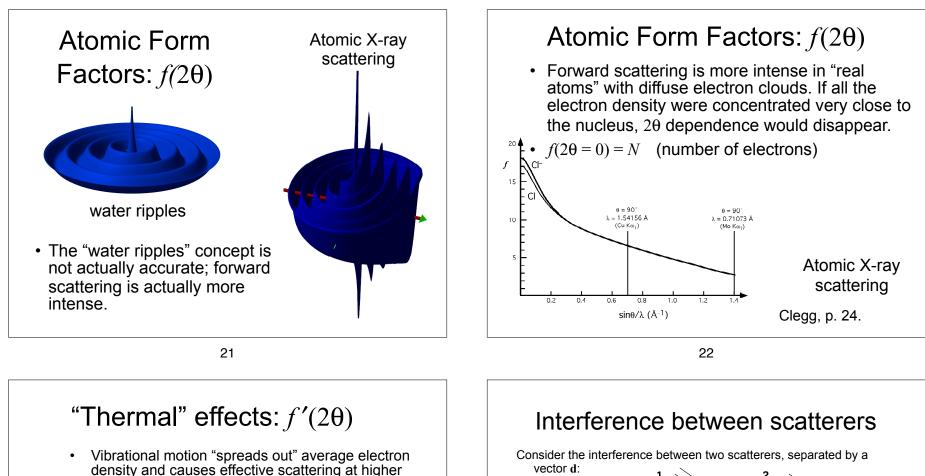
Elastic Scattering
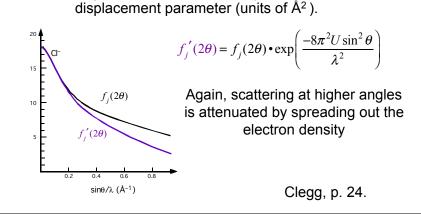
- When an x-ray is scattered by an atom it may emerge in any direction, but unless absorption occurs, it has the same wavelength:

$$\left|\mathbf{k}\right| = \left|\mathbf{k}'\right| = \frac{1}{\lambda}$$
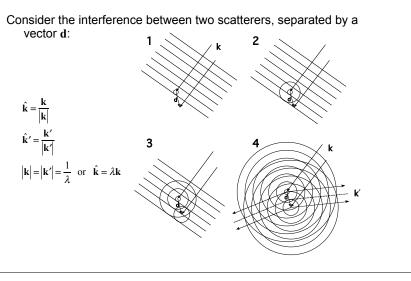
- X-ray diffraction for structure determination is concerned with interference effects that result from scattering by periodic arrays of atoms.

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Interference - "Time Lapse" pictures

This is my own heuristic exercise, not "reality".

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Atomic Form Factors: $f(2\theta)$

Atomic X-ray scattering

water ripples

- The "water ripples" concept is not actually accurate; forward scattering is actually more intense.

Atomic Form Factors: $f(2\theta)$

- Forward scattering is more intense in "real atoms" with diffuse electron clouds. If all the electron density were concentrated very close to the nucleus, 2θ dependence would disappear.
- $f(2\theta = 0) = N$ (number of electrons)

$\theta = 90°$
$\lambda = 1.54156$ Å
(Cu Kα_1)

$\theta = 90°$
$\lambda = 0.71073$ Å
(Mo Kα_1)

sinθ/λ (Å^{-1})

Atomic X-ray scattering

Clegg, p. 24.

"Thermal" effects: $f'(2\theta)$

- Vibrational motion "spreads out" average electron density and causes effective scattering at higher angles to fall off more rapidly; U is the isotropic displacement parameter (units of Å^2).

$$f_j'(2\theta) = f_j(2\theta) \bullet \exp\left(\frac{-8\pi^2 U \sin^2\theta}{\lambda^2} \right)$$

$f_j(2\theta)$

$f_j'(2\theta)$

sinθ/λ (Å^{-1})

Again, scattering at higher angles is attenuated by spreading out the electron density

Clegg, p. 24.

Interference between scatterers

Consider the interference between two scatterers, separated by a vector **d**:

$\hat{\mathbf{k}} = \dfrac{\mathbf{k}}{|\mathbf{k}|}$

$\hat{\mathbf{k}}' = \dfrac{\mathbf{k}'}{|\mathbf{k}'|}$

$|\mathbf{k}| = |\mathbf{k}'| = \dfrac{1}{\lambda}$ or $\hat{\mathbf{k}} = \lambda\mathbf{k}$

1   2   3   4

Interference between scatterers

Consider the interference between two scatterers, separated by a vector **d**:

$$\hat{\mathbf{k}} = \frac{\mathbf{k}}{|\mathbf{k}|}$$

$$\hat{\mathbf{k}}' = \frac{\mathbf{k}'}{|\mathbf{k}'|}$$

$$|\mathbf{k}| = |\mathbf{k}'| = \frac{1}{\lambda} \quad \text{or} \quad \hat{\mathbf{k}} = \lambda \mathbf{k}$$

$$\hat{\mathbf{k}} = \frac{\mathbf{k}}{|\mathbf{k}|} \quad - \text{ a unit vector in the } \mathbf{k} \text{ direction}$$

$$\hat{\mathbf{k}}' = \frac{\mathbf{k}'}{|\mathbf{k}'|} \quad - \text{ a unit vector in the } \mathbf{k}' \text{ direction}$$

$$\text{path length difference} = \mathbf{d} \cdot (\hat{\mathbf{k}} - \hat{\mathbf{k}}')$$

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Interference between scatterers

- Amplitude of scattered wave

$$\propto \quad f_1(2\theta) + f_2(2\theta) \cdot (phase\ shift\ factor)$$

- The phase shift factor depends on the path length difference =

$$\hat{\mathbf{k}} \cdot \mathbf{d} + (-\hat{\mathbf{k}}') \cdot \mathbf{d} = (\hat{\mathbf{k}} - \hat{\mathbf{k}}') \cdot \mathbf{d}$$

- For completely constructive interference, where n is some integer:

$$(\hat{\mathbf{k}} - \hat{\mathbf{k}}') \cdot \mathbf{d} = n\lambda \quad \text{or} \quad (\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} = n$$

- For completely destructive interference

Clegg, Sec. 1-6. $\quad (\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} = n + \frac{1}{2}$

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- For the general case the amplitude of the scattered wave:

$$A \propto f_1(2\theta) + f_2(2\theta) \cos\left[2\pi(\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} \right]$$

$$\cos\left[2\pi(\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} \right] = 1 \quad \text{when} \quad (\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} = n$$

$$\cos\left[2\pi(\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} \right] = -1 \quad \text{when} \quad (\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} = n + \frac{1}{2}$$

- In general we use a complex form:

$$A \propto f_1(2\theta) + f_2(2\theta) \exp\left\{ 2\pi i(\mathbf{k} - \mathbf{k}') \bullet \mathbf{d} \right\}$$

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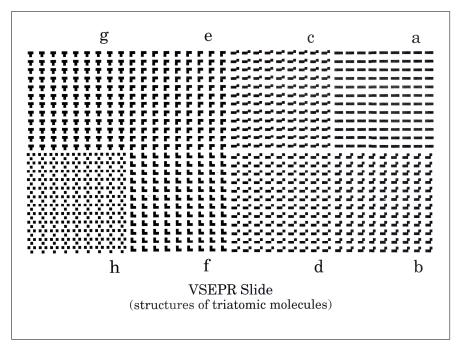
- In a crystal, all pairs of translationally equivalent atoms are separated by some direct Lattice Vector ($\mathbf{R}_i$).

∴ If all atoms in the crystal that are related by translational symmetry are to scatter X-rays to give constructive interference simultaneously, we must have the following:

$$\mathbf{R}_i \bullet (\mathbf{k} - \mathbf{k}') = n \quad \text{or} \quad e^{2\pi i(\mathbf{k} - \mathbf{k}') \bullet \mathbf{R}} = 1$$
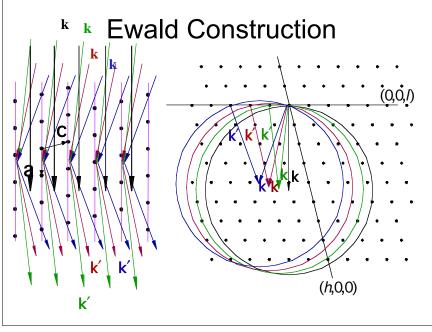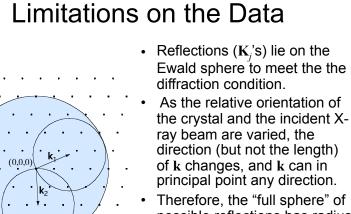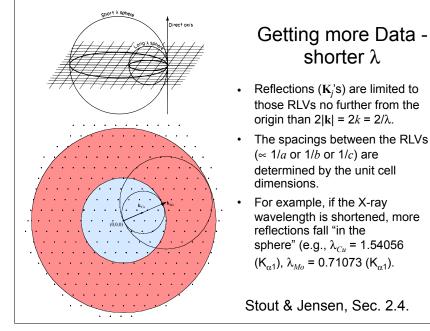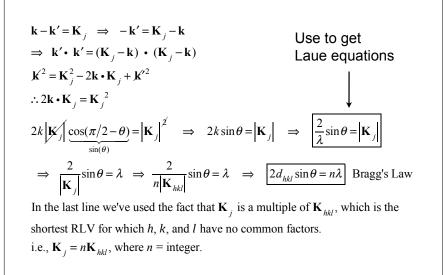
where $\mathbf{R}_i$ is any DLV.

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The beam is diffracted by a RLV!

This places conditions on the possible vectors $\mathbf{k} - \mathbf{k}'$ that are exactly the same as the conditions used to define RLVs. We therefore obtain the Laue condition for diffraction:

$\mathbf{k} - \mathbf{k}' = \mathbf{K}_j$ where $\mathbf{K}_j$ is some RLV

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Bragg View

Path Differences between 1 and 2 = AB
Path Differences between 1' and 2' = BC

Clegg, Secs. 1.4-1.5.

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Bragg View

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Optical Transforms; Fraunhofer Diffraction

- The diffraction phenomenon can demonstrated with monochromatic visible light by use of optical transforms.
- The phenomenon relies on interference effects, like X-ray diffraction, though the scattering mechanism is different.
- The interference phenomenon occurs when the spacing between scatterers is on the same order of magnitude as the wavelength of the light used.

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X-Ray Diffraction / Optical Transforms

Fraunhofer diffraction

For constructive interference,
$$d \sin \phi = n\lambda$$

Bragg diffraction

For constructive interference,
$$2(d \sin \theta) = n\lambda$$

Discovery Slide

Unit Cell Slide

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g   e   c   a

h   f   d   b

VSEPR Slide
(structures of triatomic molecules)

Ewald Construction

$(0,0,0)$

$\mathbf{k}$

$\mathbf{k}'$

$\mathbf{K}_{hkl}$

$\mathbf{K}_{hkl} = \mathbf{k} - \mathbf{k}'$

- Start with reciprocal lattice and the incident wavevector, $\mathbf{k}$, originating at $(h,k,l) = (0,0,0)$.
- Draw a sphere with the tip of $\mathbf{k}$ at the center that contains the origin, $(0,0,0)$, on the sphere's surface.
- As the direction of $\mathbf{k}$ is changed, other RLVs ($\mathbf{K}_j$'s) move through the surface – which is the condition that a diffraction peak is observed.

Stout & Jensen, Sec. 2.4.

Ewald Construction

$\mathbf{c}$

$\mathbf{a}$

$\mathbf{k}$ $\mathbf{k}$

$\mathbf{k}$

$\mathbf{k}$

$\mathbf{k}'$ $\mathbf{k}'$ $\mathbf{k}'$

$\mathbf{k}'$ $\mathbf{k}'$

$\mathbf{k}'$

$(0,0,l)$

$(h,0,0)$

Limitations on the Data

$(0,0,0)$

$\mathbf{k}_1$

$\mathbf{k}_2$

- Reflections ($\mathbf{K}_j$'s) lie on the Ewald sphere to meet the the diffraction condition.
- As the relative orientation of the crystal and the incident X-ray beam are varied, the direction (but not the length) of $\mathbf{k}$ changes, and $\mathbf{k}$ can in principal point any direction.
- Therefore, the "full sphere" of possible reflections has radius $2|\mathbf{k}| = 2k = 2/\lambda$. The spacings between the RLVs (RL points) $\propto 1/a$ (or $1/b$ or $1/c$).

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Getting more Data - shorter λ

- Reflections ($\mathbf{K}_j$'s) are limited to those RLVs no further from the origin than $2|\mathbf{k}| = 2k = 2/\lambda$.

- The spacings between the RLVs ($\propto 1/a$ or $1/b$ or $1/c$) are determined by the unit cell dimensions.

- For example, if the X-ray wavelength is shortened, more reflections fall "in the sphere" (e.g., $\lambda_{Cu} = 1.54056$ ($K_{\alpha 1}$), $\lambda_{Mo} = 0.71073$ ($K_{\alpha 1}$).

Stout & Jensen, Sec. 2.4.

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$$\mathbf{k} - \mathbf{k}' = \mathbf{K}_j \quad \Rightarrow \quad -\mathbf{k}' = \mathbf{K}_j - \mathbf{k}$$

$$\Rightarrow \quad \mathbf{k}' \cdot \mathbf{k}' = (\mathbf{K}_j - \mathbf{k}) \cdot (\mathbf{K}_j - \mathbf{k})$$

$$k'^2 = \mathbf{K}_j^2 - 2\mathbf{k} \cdot \mathbf{K}_j + k'^2$$

$$\therefore 2\mathbf{k} \cdot \mathbf{K}_j = \mathbf{K}_j^2$$

Use to get Laue equations

$$2k |\mathbf{K}_j| \underbrace{\cos(\pi/2 - \theta)}_{\sin(\theta)} = |\mathbf{K}_j|^2 \quad \Rightarrow \quad 2k\sin\theta = |\mathbf{K}_j| \quad \Rightarrow \quad \boxed{\frac{2}{\lambda}\sin\theta = |\mathbf{K}_j|}$$

$$\Rightarrow \quad \frac{2}{|\mathbf{K}_j|}\sin\theta = \lambda \quad \Rightarrow \quad \frac{2}{n|\mathbf{K}_{hkl}|}\sin\theta = \lambda \quad \Rightarrow \quad \boxed{2d_{hkl}\sin\theta = n\lambda} \quad \text{Bragg's Law}$$

In the last line we've used the fact that $\mathbf{K}_j$ is a multiple of $\mathbf{K}_{hkl}$, which is the shortest RLV for which h, k, and l have no common factors.

i.e., $\mathbf{K}_j = n\mathbf{K}_{hkl}$, where n = integer.

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Laue Equations

$n\lambda = 2d_{hkl}\sin\theta;$

$K_{hkl}^2 = (4/\lambda^2)\sin^2\theta \quad$ where $\quad \mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad$ (***)

or $[1/d^2] = (4/\lambda^2)\sin^2\theta$, since $K_{hkl}^2 = [1/d^2]$

The "Laue Equations" for each crystal class can be derived from the form (***).

Cubic
$\sin^2\theta = A(h^2 + k^2 + l^2); \; A = \lambda^2/4a^2 \quad$ or $\quad [1/d^2] = (h^2 + k^2 + l^2)/a^2$
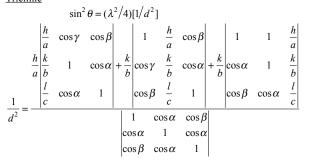
Tetragonal
$\sin^2\theta = A(h^2 + k^2) + Cl^2; \; A = \lambda^2/4a^2; \; C = \lambda^2/4c^2$
or $[1/d^2] = (h^2 + k^2)/a^2 + l^2/c^2$

Hexagonal
$\sin^2\theta = A(h^2 + hk + k^2) + Cl^2; \; A = \lambda^2/3a^2; \; C = \lambda^2/4c^2$
or $[1/d^2] = 4(h^2 + k^2)/3a^2 + l^2/c^2$

Orthorhombic
$\sin^2\theta = Ah^2 + Bk^2 + Cl^2; \; A = \lambda^2/4a^2; \; B = \lambda^2/4b^2; \; C = \lambda^2/4c^2$
or $[1/d^2] = h^2/a^2 + k^2/b^2 + l^2/c^2$

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Laue Equations, cont.

Monoclinic
$\sin^2\theta = Ah^2 + Bk^2 + Cl^2 - Dhl$
$A = \lambda^2/(4a^2\sin^2\beta); \; B = \lambda^2/4b^2;$
$C = \lambda^2/(4c^2\sin^2\beta); \; D = (\lambda^2\cos\beta)/(2ac\sin^2\beta)$
or $[1/d^2] = h^2/(a^2\sin^2\beta) + k^2/b^2 + l^2/(c^2\sin^2\beta) - 2hl\cos\beta/(ac\sin^2\beta)$

$K_{hkl}^2 = (4/\lambda^2)\sin^2\theta$

where $\quad \mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad$ (***)

Triclinic

$$\sin^2\theta = (\lambda^2/4)[1/d^2]$$

$$\frac{1}{d^2} = \frac{\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \frac{k}{b} & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} \frac{h}{a} + \begin{vmatrix} 1 & \frac{h}{a} & \cos\beta \\ \cos\gamma & \frac{k}{b} & \cos\alpha \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} \frac{k}{b} + \begin{vmatrix} 1 & 1 & \frac{h}{a} \\ \cos\alpha & 1 & \frac{k}{b} \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix} }{\begin{vmatrix} 1 & \cos\alpha & \cos\beta \\ \cos\alpha & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}$$

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Example

If a hexagonal crystal has a $(1\bar{1}0)$ reflection at $2\theta = 8.5°$, at what 2θ angle would you expect to observe the (110) reflection?

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Results

- The distances between lattice planes are on the order of lengths of unit cells (~10 Å)
- 50 Å ≥ d_{hkl} ≥ 0.5 Å for most "small molecule structures"
- Two most common sources:
  λ_{Cu} = 1.540562 Å ($K_{\alpha 1}$)
  λ_{Mo} = 0.71073 Å ($K_{\alpha 1}$)

Neutron Diffraction
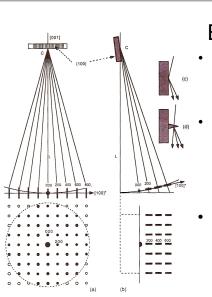
- In neutron diffraction, so-called *thermal* neutrons are usually used.
- Thermal neutrons have deBroglie wavelengths that are comparable to typical X-ray wavelengths:
  λ_{Cu} = 1.5418 Å,
  λ_{Mo} = 0.71069 Å,
  $\lambda_n = h/p_n = h[3m_n k_B T]^{-1/2} = 1.45$ Å
- A major advantage of neutron diffraction is in the very different form factors, which have magnitudes that do not scale with atomic number (good for many light atoms, especially deuterium).
- Neutron spin (magnetic moment) can be exploited to probe magnetic ordering.

Electron Diffraction

- In high-energy electron diffraction, electrons with 100 keV kinetic energies are commonly used
- e⁻'s have short deBroglie wavelengths:
  λ_{Cu} = 1.5418 Å,
  λ_{Mo} = 0.71069 Å,
  $\lambda_{e,100keV} = h/p = h[2m_e E]^{-1/2} = 0.0039$ Å
- Ewald sphere is very large in comparison with reciprocal lattice spacings. Therefore, a large section of any plane tangent to the Ewald sphere is effectively "on the sphere" at the same time.
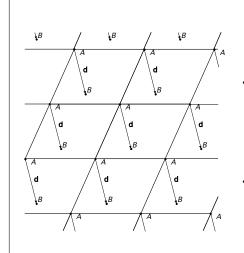
Summary

- The geometrical aspects of a crystal (cell dimensions, translational symmetry, etc.) determine the direct lattice.
- The direct lattice, in turn, determines the reciprocal lattice.
- There is a one-to-one correspondence between the RLVs and the vectors through which the incident radiation is diffracted.
- The *geometry* of the diffraction pattern is determined by the cell dimensions and symmetry - no specific structural details beyond symmetry and dimensions of the unit cell affect the "*positions*" of diffraction peaks.

Multiple Atom Structures

- Within translationally related sets of atoms, the conditions for constructive interference will be satisfied simultaneously. However, different sets of atoms will generally diffract the X-ray with different phases.
- Example: For the "crystal" shown here, when the set of A atoms all scatter the X-ray constructively with respect to each other, the set of B atoms will also scatter the X-ray constructively. But the the sets {A$_j$} and {B$_j$} will generally scatter with different phases.
- The resultant diffraction intensities will be determined by the sum of the diffraction amplitudes due to {A$_j$} and {B$_j$} - including the effect of different phases!

How do data determine "Structures" ?

- The <u>positions</u> of diffraction peaks tell us only about the lattice parameters.
- The <u>intensities</u> of the peaks tell us about the nature and positions of the atoms within the unit cell.
- The central problem of crystallography is in working backwards from the peak intensities to locations and identities of atoms in the unit cell.

Easier: How do "Structures" determine data?

Structure Factors

- With n atoms distributed throughout the unit cell, with fixed positions with respect to each other, scatter X-rays that produce interference patterns.

  Amplitude of scattered wave =

$$A \propto S_{\mathbf{K}} = \sum_{j=1}^{n} \underbrace{f_j'(\mathbf{K})}_{} \underbrace{\exp\left\{2\pi i \mathbf{K} \cdot \mathbf{d}_j\right\}}_{\text{geometric factor}}$$

  atomic form factor
  (determined by charge distribution of the jth atom)

The Structure Factor expression & Systematic Absences

- Symmetry operations place restrictions on how atoms in the cell must be distributed. (Physically, perhaps it is the other way around!)
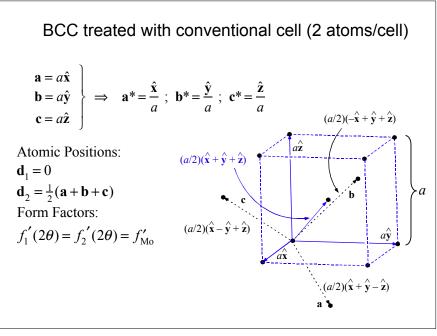
$$A \propto S_{\mathbf{K}} = \sum_{j=1}^{n} \underbrace{f_j'(2\theta)}_{\text{form factor}} \times \underbrace{\exp\left\{2\pi i \mathbf{K} \cdot \mathbf{d}_j\right\}}_{\text{geometric factor}}$$

- This means that there are symmetry relationships between the list of f_j's and $\mathbf{d}_j$'s.

Recall: BCC treated as Primitive

$$\mathbf{a} = \frac{a}{2}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}\right)$$

$$\mathbf{b} = \frac{a}{2}\left(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{c} = \frac{a}{2}\left(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

Use to find Recip. Lattice Basis:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}; \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}; \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V}$$
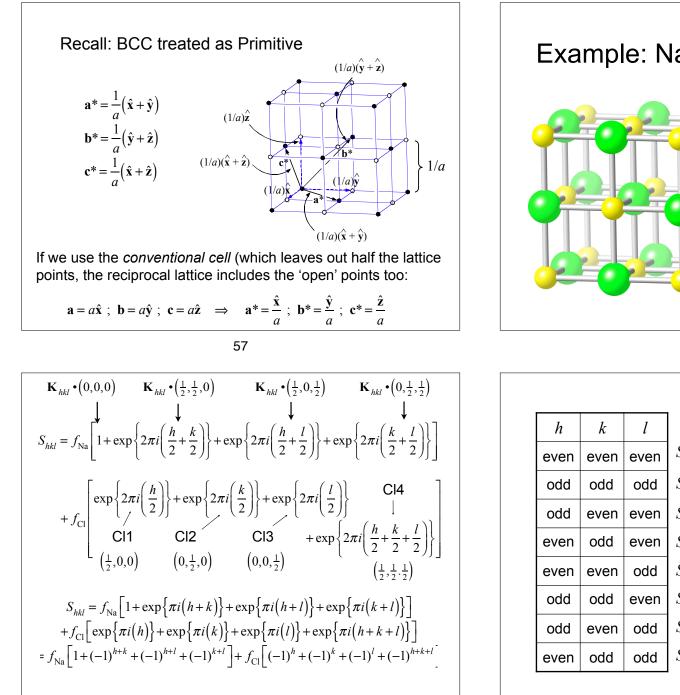
$$V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$$

BCC treated with conventional cell (2 atoms/cell)

$$\left.\begin{array}{l} \mathbf{a} = a\hat{\mathbf{x}} \\ \mathbf{b} = a\hat{\mathbf{y}} \\ \mathbf{c} = a\hat{\mathbf{z}} \end{array}\right\} \Rightarrow \mathbf{a}^* = \frac{\hat{\mathbf{x}}}{a}; \ \mathbf{b}^* = \frac{\hat{\mathbf{y}}}{a}; \ \mathbf{c}^* = \frac{\hat{\mathbf{z}}}{a}$$

Atomic Positions:

$$\mathbf{d}_1 = 0$$
$$\mathbf{d}_2 = \tfrac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$$

Form Factors:

$$f_1'(2\theta) = f_2'(2\theta) = f_{\text{Mo}}'$$

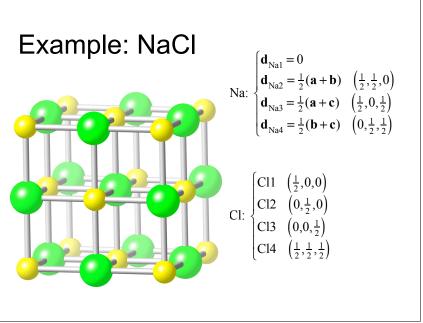- All recip. Lattice vectors are of the form

$$\mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$
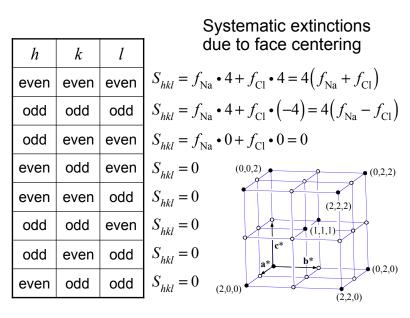
$$S_{hkl} = f_{\text{Mo}} \times \left[\exp\left\{2\pi i(h\cdot 0 + k\cdot 0 + l\cdot 0)\right\} + \exp\left\{2\pi i\left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)\right\} \right]$$
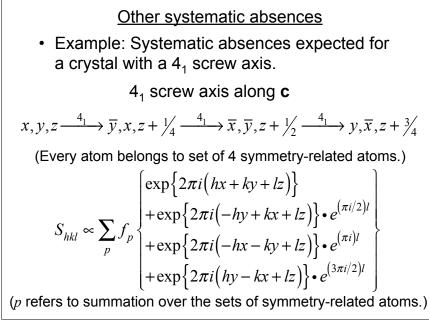
$$S_{hkl} = f_{\text{Mo}} \times \left[1 + \exp\left\{\pi i(h + k + l)\right\} \right]$$

If $h + k + l =$

even no. : $\exp\left\{i\pi(h+k+l)\right\} = 1 \ \Rightarrow \ S_{hkl} = 2f_{\text{Mo}}$

odd no. : $\exp\left\{i\pi(h+k+l)\right\} = -1 \ \Rightarrow \ S_{hkl} = 0$

$\therefore$ if $h + k + l =$ odd, reflection will not be observed.

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Recall: BCC treated as Primitive

$$\mathbf{a}^* = \frac{1}{a}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}}\right)$$

$$\mathbf{b}^* = \frac{1}{a}\left(\hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{c}^* = \frac{1}{a}\left(\hat{\mathbf{x}} + \hat{\mathbf{z}}\right)$$

$(1/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}})$
$(1/a)\hat{\mathbf{z}}$
$(1/a)(\hat{\mathbf{x}} + \hat{\mathbf{z}})$
$(1/a)\hat{\mathbf{x}}$
$(1/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}})$
$(1/a)\hat{\mathbf{y}}$
$\}\,1/a$

If we use the *conventional cell* (which leaves out half the lattice points, the reciprocal lattice includes the 'open' points too:

$$\mathbf{a} = a\hat{\mathbf{x}} \; ; \; \mathbf{b} = a\hat{\mathbf{y}} \; ; \; \mathbf{c} = a\hat{\mathbf{z}} \;\; \Rightarrow \;\; \mathbf{a}^* = \frac{\hat{\mathbf{x}}}{a} \; ; \; \mathbf{b}^* = \frac{\hat{\mathbf{y}}}{a} \; ; \; \mathbf{c}^* = \frac{\hat{\mathbf{z}}}{a}$$

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Example: NaCl

Na:
$$\begin{cases} \mathbf{d}_{Na1} = 0 \\ \mathbf{d}_{Na2} = \frac{1}{2}(\mathbf{a}+\mathbf{b}) & \left(\frac{1}{2},\frac{1}{2},0\right) \\ \mathbf{d}_{Na3} = \frac{1}{2}(\mathbf{a}+\mathbf{c}) & \left(\frac{1}{2},0,\frac{1}{2}\right) \\ \mathbf{d}_{Na4} = \frac{1}{2}(\mathbf{b}+\mathbf{c}) & \left(0,\frac{1}{2},\frac{1}{2}\right) \end{cases}$$

Cl:
$$\begin{cases} Cl1 & \left(\frac{1}{2},0,0\right) \\ Cl2 & \left(0,\frac{1}{2},0\right) \\ Cl3 & \left(0,0,\frac{1}{2}\right) \\ Cl4 & \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) \end{cases}$$

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$\mathbf{K}_{hkl}\cdot(0,0,0) \quad \mathbf{K}_{hkl}\cdot\left(\frac{1}{2},\frac{1}{2},0\right) \quad \mathbf{K}_{hkl}\cdot\left(\frac{1}{2},0,\frac{1}{2}\right) \quad \mathbf{K}_{hkl}\cdot\left(0,\frac{1}{2},\frac{1}{2}\right)$

$$S_{hkl} = f_{Na}\left[1 + \exp\left\{2\pi i\left(\frac{h}{2}+\frac{k}{2}\right)\right\} + \exp\left\{2\pi i\left(\frac{h}{2}+\frac{l}{2}\right)\right\} + \exp\left\{2\pi i\left(\frac{k}{2}+\frac{l}{2}\right)\right\}\right]$$

$$+ f_{Cl}\left[\exp\left\{2\pi i\left(\frac{h}{2}\right)\right\} + \exp\left\{2\pi i\left(\frac{k}{2}\right)\right\} + \exp\left\{2\pi i\left(\frac{l}{2}\right)\right\} + \exp\left\{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right\}\right]$$

Cl1 $\left(\frac{1}{2},0,0\right)$ Cl2 $\left(0,\frac{1}{2},0\right)$ Cl3 $\left(0,0,\frac{1}{2}\right)$ Cl4 $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

$$S_{hkl} = f_{Na}\left[1 + \exp\left\{\pi i(h+k)\right\} + \exp\left\{\pi i(h+l)\right\} + \exp\left\{\pi i(k+l)\right\}\right]$$

$$+ f_{Cl}\left[\exp\left\{\pi i(h)\right\} + \exp\left\{\pi i(k)\right\} + \exp\left\{\pi i(l)\right\} + \exp\left\{\pi i(h+k+l)\right\}\right]$$

$$= f_{Na}\left[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}\right] + f_{Cl}\left[(-1)^{h} + (-1)^{k} + (-1)^{l} + (-1)^{h+k+l}\right]$$

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Systematic extinctions due to face centering

h	k	l	
even	even	even	$S_{hkl} = f_{Na}\cdot 4 + f_{Cl}\cdot 4 = 4\left(f_{Na}+f_{Cl}\right)$
odd	odd	odd	$S_{hkl} = f_{Na}\cdot 4 + f_{Cl}\cdot(-4) = 4\left(f_{Na}-f_{Cl}\right)$
odd	even	even	$S_{hkl} = f_{Na}\cdot 0 + f_{Cl}\cdot 0 = 0$
even	odd	even	$S_{hkl} = 0$
even	even	odd	$S_{hkl} = 0$
odd	odd	even	$S_{hkl} = 0$
odd	even	odd	$S_{hkl} = 0$
even	odd	odd	$S_{hkl} = 0$

$(0,0,2)$ $(0,2,2)$ $(2,2,2)$ $(1,1,1)$ $\mathbf{c}^*$ $\mathbf{a}^*$ $\mathbf{b}^*$ $(0,2,0)$ $(2,0,0)$ $(2,2,0)$

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Other systematic absences

- Example: Systematic absences expected for a crystal with a 4_1 screw axis.

4_1 screw axis along **c**

$$x,y,z \xrightarrow{\;4_1\;} \bar{y},x,z+\tfrac{1}{4} \xrightarrow{\;4_1\;} \bar{x},\bar{y},z+\tfrac{1}{2} \xrightarrow{\;4_1\;} y,\bar{x},z+\tfrac{3}{4}$$

(Every atom belongs to set of 4 symmetry-related atoms.)

$$S_{hkl} \propto \sum_p f_p \begin{cases} \exp\{2\pi i(hx+ky+lz)\} \\ +\exp\{2\pi i(-hy+kx+lz)\}\cdot e^{(\pi i/2)l} \\ +\exp\{2\pi i(-hx-ky+lz)\}\cdot e^{(\pi i)l} \\ +\exp\{2\pi i(hy-kx+lz)\}\cdot e^{(3\pi i/2)l} \end{cases}$$

(*p* refers to summation over the sets of symmetry-related atoms.)

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Consider $h = k = 0$

… and l = odd

$$S_{hkl} \propto \left(\sum_p f_p\right)\{\exp(2\pi i lz)\}\cdot\left[1+e^{\pi i/2}+e^{\pi i}+e^{3\pi i/2}\right]=0$$

    ↑   ↑   ↑   ↑

1st   2nd   3rd   4th
term term term term

… and l = 2, 6, 10 …

$$S_{hkl} \propto \left(\sum_p f_p\right)\{\exp(2\pi i lz)\}\cdot\left[1+\underset{(-1)}{e^{\pi i}}+1+\underset{(-1)}{e^{\pi i}}\right]=0$$

… and l = 4, 8, 12 …

$$S_{hkl} \propto \; \sim\left[1+1+1+1\right] \quad \text{(non zero)}$$

For $h = k = 0$, only reflections with $l = 4, 8, 12$ … will be observed.

62

Other systematic absences

- Example: crystal with an *a*-glide $\perp$ to a 4_1 axis.

  (4_1 screw axis along **c**, $\therefore$ *a* glide || to the *ab*-plane)

  $$x,y,z \xrightarrow{\;a-glide\;} x+\tfrac{1}{2},y,\bar{z} \xrightarrow{\;a-glide\;} x+1,y,z$$

  $$S_{hkl} \propto \sum_p f_p \begin{cases} \exp\{2\pi i(hx+ky+lz)\} \\ +\exp\{2\pi i(h(x+1/2)+ky-lz)\} \end{cases}$$

This will be zero when the term in brackets is zero:

$$\exp\{2\pi i(hx+ky+lz)\} = -\exp\{2\pi i(h(x+1/2)+ky-lz)\}$$
$$\exp\{2\pi i(lz)\} = -\exp\{2\pi i(h/2-lz)\} = -e^{\pi i h}\exp\{2\pi i(-lz)\}$$
$$\exp\{2\pi i lz\} = -(-1)^h \exp\{-2\pi i lz\}$$

If $l = 0$, then absences occur where h = odd.

For *b*-glide $\perp$ to **c**-axis, find absences where k = odd ($l = 0$).

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Symmetry of the Diffraction Pattern; Equivalent Reflections - Laue Symmetry

The pattern of single crystal diffraction "spots" is often referred to as the *intensity-weighted reciprocal space*. Including the intensities, what symmetries should the intensity-weighted reciprocal space exhibit?

- In the absence of absorption and/or "anomalous scattering", reflections related to each other by inversion in reciprocal space, (*h,k,l*) and (*-h,-k,-l*), should be of equal intensity. This is called *Friedel's Law* and it applies *even for noncentrosymmetric space groups* (no inversion center).

The *Patterson symmetry* adds an inversion center if the space group is acentric. Therefore, in centrosymmetric cases, the Patterson symmetry is the same as the symmetry of the diffraction pattern.

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Symmetry of the Diffraction Pattern; Equivalent Reflections - Laue Symmetry

Translation of a crystal leaves reciprocal space unaffected. Therefore, the translational parts of symmetry operations can be ignored in finding reflections that are expected to be equivalent.
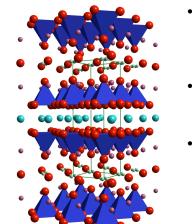
- Screw operations have same symmetry effect as simple rotational point group operations
- Glide operations have the same symmetry effect as simple mirror planes

See: Table 11.4, p. 382 in *Cotton*.

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$Tl_{(1+x)}BaSrCa_{(1-x)}Cu_2O_{(7-\delta)}$ Superconductor
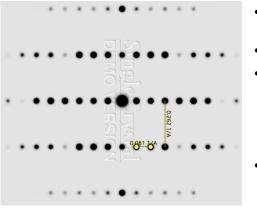
- Within the disorder model ($x = 0.22$), the space group is symmorphic: P4/mmm.
- The reciprocal lattice intensities reflect each symmetry operation
- No systematic absences

$a = 3.8234$ Å; $c = 12.384$ Å

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$Tl_{(1+x)}BaSrCa_{(1-x)}Cu_2O_{(7-\delta)}$ Superconductor

0.262 1/A

- Simulated electron diffraction
- 001 plane.
- The reciprocal lattice intensities reflect each symmetry operation
- No systematic absences

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$Tl_{(1+x)}BaSrCa_{(1-x)}Cu_2O_{(7-\delta)}$ Superconductor

0.262 1/A
0.081 1/A

- Simulated electron diffraction pattern
- 100 plane.
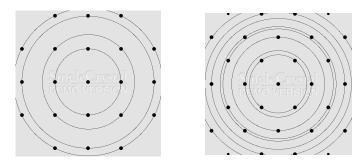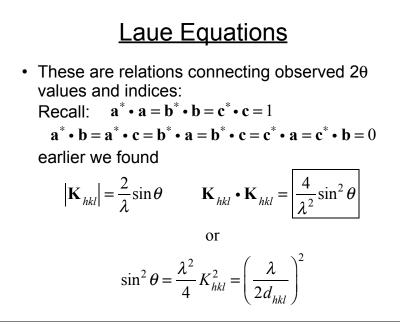- The reciprocal lattice intensities reflect each symmetry operation
- No systematic absences

$Tl_{(1+x)}BaSrCa_{(1-x)}Cu_2O_{(7-\delta)}$ Superconductor

- Simulated electron diffraction pattern
- 110 plane.
- The reciprocal lattice intensities reflect each symmetry operation
- No systematic absences

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Cs-Leucite, low symmetry (298K)

- At high temp (473K), Cs-leucite ($CsAlSi_2O_6$) adopts a cubic structure (space group: $Ia\bar{3}d$), a = 13.7062Å.

- At room temperature, the symmetry is lower
- What is it?

$$I\frac{4_1}{a}\bar{3}\frac{2}{d}$$

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Leucite (298K), l = 0 plane

- Simulated electron diffraction pattern
- What symmetries are possible?

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Leucite (298K), h = 0 plane

- What symmetries are suggested?

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Leucite (298K), $l = 0$ plane

- Adjacent spots have a separation of 0.153 Å^{-1}.

- $^1/_{(0.153 \text{ Å}^{-1})}$ = 6.536 Å. What does this number mean?

0.153 1/A

Leucite (298K), $l = 0$ plane

- Intense peaks are indexed. (How was this done?)

Powder Diffraction

- In principle, powder diffraction is nothing more than a 'spatially averaged' version of single-crystal diffraction.

- Much of the rich spatial information one gathers in single-crystal data is lost in powder diffraction, only the 2θ information remains.

- However, once (if) the cell can be *inferred*, powder diffraction data is still quite powerful.

NaCl: $h = 0$ and $h = k$ planes

- The circles correspond to reflections on the same "cone", i.e., with the same 2θ values.

Laue Equations

- These are relations connecting observed 2θ values and indices:
Recall: $\quad \mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1$

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

earlier we found

$$\left| \mathbf{K}_{hkl} \right| = \frac{2}{\lambda} \sin\theta \qquad \mathbf{K}_{hkl} \cdot \mathbf{K}_{hkl} = \boxed{\frac{4}{\lambda^2} \sin^2\theta}$$

or

$$\sin^2\theta = \frac{\lambda^2}{4} K_{hkl}^2 = \left(\frac{\lambda}{2 d_{hkl}} \right)^2$$

- Any RLV is written as $\qquad \mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

$$\mathbf{K}_{hkl} \cdot \mathbf{K}_{hkl} = h^2 \mathbf{a}^* \cdot \mathbf{a}^* + k^2 \mathbf{b}^* \cdot \mathbf{b}^* + l^2 \mathbf{c}^* \cdot \mathbf{c}^*$$

$$+ 2hk\mathbf{a}^* \cdot \mathbf{b}^* + 2hl\mathbf{a}^* \cdot \mathbf{c}^* + 2kl\mathbf{b}^* \cdot \mathbf{c}^* = \frac{4}{\lambda^2} \sin^2\theta$$

- Special cases:
Orthorhombic

$$\mathbf{a}^* = \frac{1}{a}\hat{\mathbf{x}} \quad ; \quad \mathbf{b}^* = \frac{1}{b}\hat{\mathbf{y}} \quad ; \quad \mathbf{c}^* = \frac{1}{c}\hat{\mathbf{z}}$$

$$K^2 = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \Rightarrow \quad \sin^2\theta = \left(\frac{\lambda}{2} \right)^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

- <u>Cubic and Tetragonal - special cases of orthorhombic:</u>

$$\boxed{\begin{array}{l} \sin^2\theta = \left(\dfrac{\lambda}{2a} \right)^2 (h^2 + k^2 + l^2) \quad \text{cubic} \\[2mm] \sin^2\theta = \lambda^2 \left(\dfrac{h^2 + k^2}{4a^2} + \dfrac{l^2}{4c^2} \right) \quad \text{tetragonal} \end{array}}$$

- <u>Hexagonal</u>

$$\alpha = \beta = 90° \quad \gamma = 120°$$

$\qquad\qquad\qquad$ **c** out of plane of paper

$$\mathbf{a} = a\left(\frac{\sqrt{3}}{2}\hat{\mathbf{x}} - \frac{1}{2}\hat{\mathbf{y}} \right)$$

$$\mathbf{b} = a\hat{\mathbf{y}}$$

$$\mathbf{c} = c\hat{\mathbf{z}}$$

$$V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \frac{\sqrt{3}}{2} a^2 c$$

- <u>Reciprocal lattice</u>

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V} = \frac{ac\hat{\mathbf{x}}}{\left(\sqrt{3}/2 \right) a^2 c} = \frac{2}{\sqrt{3}a}\hat{\mathbf{x}}$$

$$\mathbf{b}^* = \frac{1}{a}\left(\frac{\hat{\mathbf{x}}}{\sqrt{3}} + \hat{\mathbf{y}} \right) \quad ; \quad \mathbf{c}^* = \frac{1}{c}\hat{\mathbf{z}}$$

- <u>Laue equation</u>

$$\sin^2\theta = \frac{\lambda^2}{4}\mathbf{K} \cdot \mathbf{K} = \frac{\lambda^2}{4}\left[h^2\left| \mathbf{a}^* \right|^2 + k^2\left| \mathbf{b}^* \right|^2 + l^2\left| \mathbf{c}^* \right|^2 + 2hk\mathbf{a}^* \cdot \mathbf{b}^* \right]$$

$$\sin^2\theta = \boxed{\frac{\lambda^2}{3a^2}\left(h^2 + k^2 + hk \right) + \frac{\lambda^2}{4c^2}l^2}$$