Methoden moderner Röntgenphysik I+II: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2010/11 und SS 2011

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Location: SemRm 4, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 10.15 – 11.45

Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Hard X-Rays – Lecture 4

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Kinematical Diffraction

Kinematical Diffraction

One of the main applications of X-rays is the determination of structure(s) using diffraction.

Assume the scattering to be weak; multiple scattering effects are to be neglected: weak scattering limit $\equiv$ kinematical approximation.

Consider a 2 electron system:

α
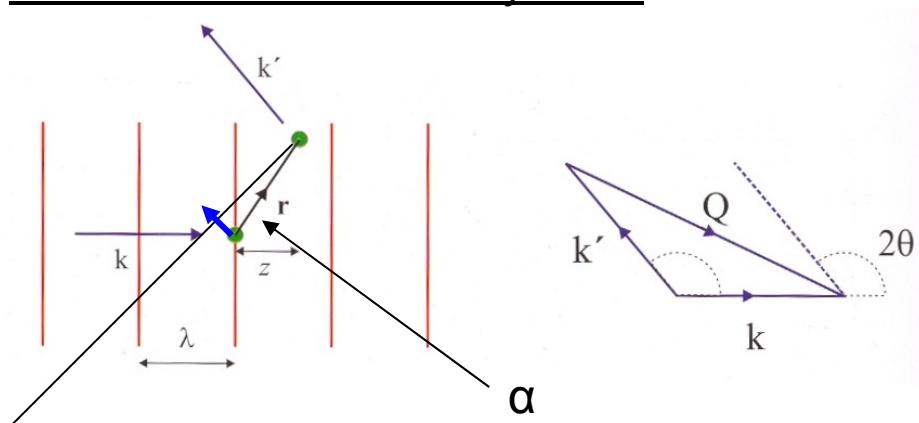
$z = r\cos\alpha;\ k\,z = k\,r\cos\alpha = \mathbf{k} \cdot \mathbf{r}$

$y = r\cos\beta;\ k'y = k'r\cos\beta = \mathbf{k'} \cdot \mathbf{r}$

path- or phase difference:

$\Delta\Phi = z\text{-}y = \mathbf{k}\cdot\mathbf{r} - \mathbf{k'}\cdot\mathbf{r} = \mathbf{Q}\cdot\mathbf{r}$

with

$Q = (4\pi/\lambda)\sin\theta$

scattering amplitude for 2 electrons:

$A(\mathbf{Q}) = -r_0\,[1 + \exp(i\mathbf{Q}\mathbf{r})]$

$I(\mathbf{Q}) = A(\mathbf{Q})\,A(\mathbf{Q})^*$

$\qquad = 2r_0^2\,[1+\cos(Qr)]$

see Fig. 4.2

for many electrons:

$A(\mathbf{Q}) = -r_0 \sum r_{j'}\ \exp(i\mathbf{Q}\mathbf{r}_{j'})$

Kinematical Diffraction

(a) Two electrons, $\mathbf{Q}$ parallel to $\mathbf{r}$

(b) Two electrons, orientational average

(c) Hydrogen like molecule, $\mathbf{Q}$ parallel to $\mathbf{r}$

Intensity (units of r_0^2)

Wavevector transfer Q (units of $2\pi/r$)
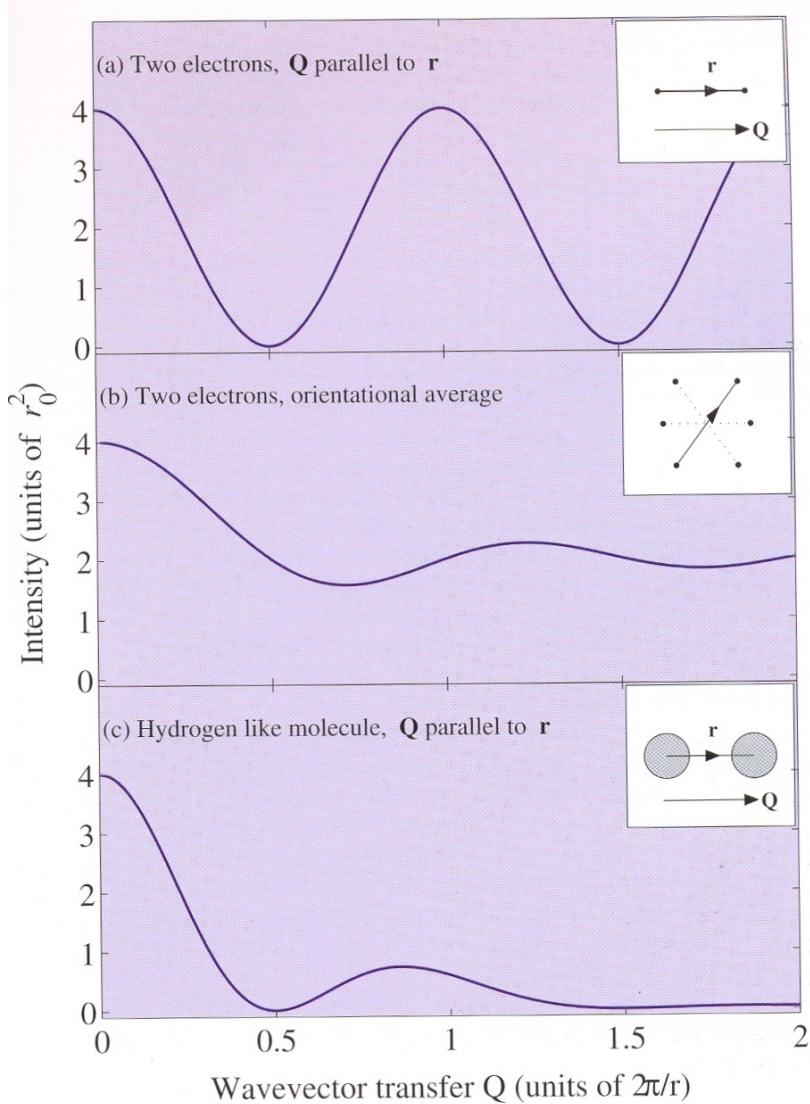
Two electron system:

$I(Q)= 2r_0^2 [1+\cos(Qr)]$

$Q \parallel r$

orientational average
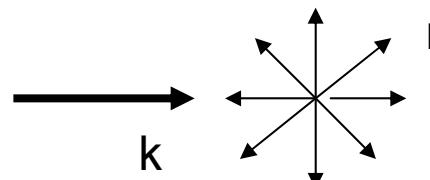
"smeared", no more "point-like" particles

for many systems, e.g. molecules the orientation of **r** will be random wrt **k**
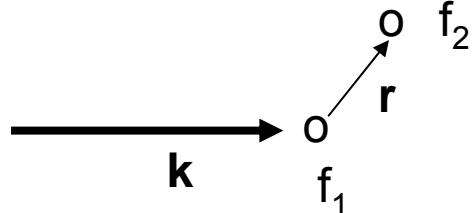
Orientational averaging: assume one electron at r=0, a second at r

$A(Q) = f1 + f_2 \exp(i\mathbf{Q}r)$

$I(Q) = f_1{}^2 + f_2{}^2 + f_1 f_2 \exp(iQr) + f_1 f_2 \exp(-iQr)$

orientational averaging: $\langle\exp(iQR)\rangle = \langle\exp(-iQr)\rangle$

$\langle I(Q)\rangle = f_1{}^2 + f_2{}^2 + 2 f_1 f_2 \langle\exp(iQr)\rangle$

$$\langle\exp(i\mathbf{Q}r)\rangle = \frac{\int \exp(iQr\cos\theta)\ \sin\theta\ d\theta d\Phi}{\int \sin\theta\ d\theta d\Phi} \longleftarrow 4\pi$$

$\int \exp(iQr\cos\theta)\ \sin\theta\ d\theta d\Phi$

$= 2\pi \int \exp(iQr\cos\theta)\ \sin\theta\ d\theta$

$= 2\pi\ (-1/iQr) \int_{iQr}{}^{-iQr}\ \exp(x)\ dx$

$= 4\pi \sin(Qr)/Qr$

$\langle I(Q)\rangle = f_1{}^2 + f_2{}^2 + 2 f_1 f_2 \sin(Qr)/Qr$

see figure 4.2 b

if the position of the electons distributed or smeared: see Figure 4.2c

Scattering from an atom:

scattering amplitude of an atom ≡ atomic form factor $f_0(Q)$ [in units of r_0]

$\rho(r)$: electronic number density ≡ charge density

$$f_0(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q}\mathbf{r}) \, d\mathbf{r}$$

$$= \begin{cases} Z & Q \to 0 \\ 0 & Q \to \infty \end{cases}$$

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508
F	3.5392	10.2825	2.6412	4.2944	1.5170	0.2615	1.0243	26.1476	0.2776
Si	6.2915	2.4386	3.0353	32.333	1.9891	0.6785	1.5410	81.6937	1.1407
Cu	13.338	3.5828	7.1676	0.2470	5.6158	11.3966	1.6735	64.820	1.5910
Ge	16.0816	2.8509	6.3747	0.2516	3.7068	11.4468	3.683	54.7625	2.1313
Mo	3.7025	0.2772	17.236	1.0958	12.8876	11.004	3.7429	61.6584	4.3875

table 4.1: J. Als-Nielsen & D. McMorrow

note: atomic form factor is FT of electronic charge distribution

$f_0(Q/4\pi)$ tabulated:

$$f_0(Q/4\pi) = \sum_{j=1}^{4} a_j \exp -b_j (Q/4\pi)^2 + c$$

note:

$$f = f_0(Q) + f' + f''$$

corrections f' and f'' arise from the fact that the electrons are bound in the atom

Scattering from a molecule:

$F^{mol}(Q) = \sum_{r_j} f_j(Q) \exp(iQr_j)$

——— CF_4

-.-.- CF_4 Q not || C-F

- - - - - molybdenum

example: CF_4:
assume OA=OB=OC=OD=1; z=OO'=cos(u) =1/3

(also 42 electrons)

(109.5deg)
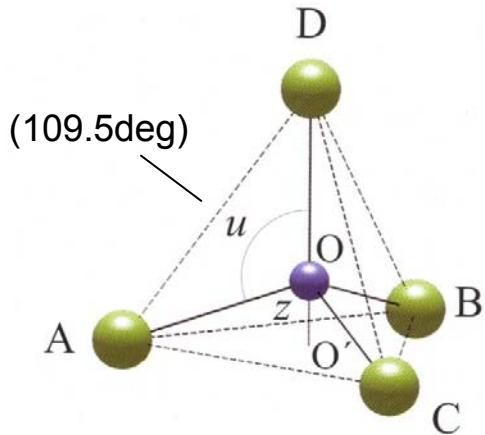
$Qr_j = Qr_j \cos(u) = (1/3)Qr_j$

Assume: Q || C-F bond

$F^{mol} = f^C(Q) + f^F(Q) [\exp(iQR) + 3\exp(iQr_j)\}$
$= f^C(Q) + f^F(Q) [3\exp(-/+iQR/3) + \exp(+/-iQR)]$

(F-F bond)
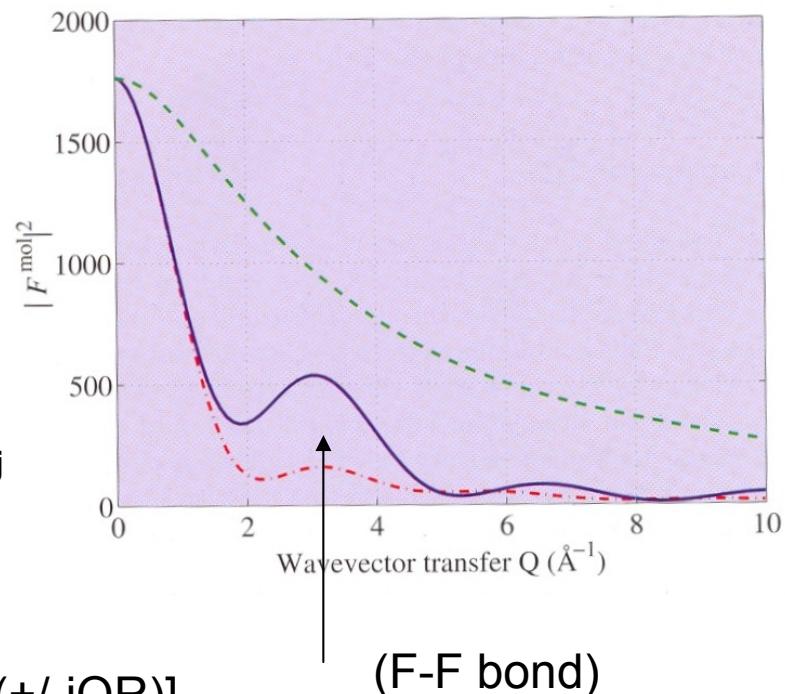
Scattering from a crystal

$A(\mathbf{Q}) = \sum_{\mathbf{r_j}} f_j(Q) \exp(i\, \mathbf{Q}\mathbf{r}_j')$

an extension to crystalline matter is simplified since there is translational symmetry.

crystalline matter: $\mathbf{r}_j' = \mathbf{R}_n + \mathbf{r}_j$

Crystallography:

determine electron density within unit cell

Note: one does measure
$I(Q) = A(Q)\, A^*(Q)$
and is thus not sensitive to phase shifts
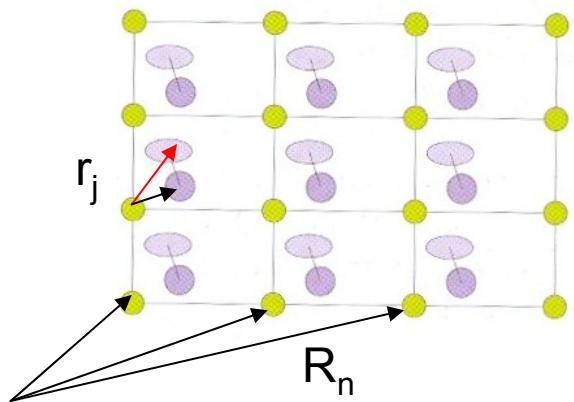
$A(\mathbf{Q}) = \sum_{\mathbf{Rn}} \exp(i\, \mathbf{Q}\mathbf{R_n}) \sum_{\mathbf{r_j}} f_j(Q) \exp(i\, \mathbf{Q}\mathbf{r_j})$

$\underbrace{\qquad\qquad\qquad}_{\text{lattice sum}}$ $\underbrace{\qquad\qquad}_{\text{unit cell structure factor}}$

Scattering from atoms on a crystal lattice

concept: build up crystal from lattice+basis

2-D lattice: $R_n = n_1 a_1 + n_2 a_2$

<u>unit cell:</u> primitive or (non-) primitive

           (primitive≡area or volume minimized)

3-D lattice: $R_n = n_1 a_1 + n_2 a_2 + n_3 a_3$

There are: 5 distinct lattices in 2-D

                14 distinct lattices in 3-D

called the Bravais lattices

add basis to yield:

       32   possible point groups
       230   possible symmetry groups

(a) primitive   (b) non-primitive

(c) non-conventional
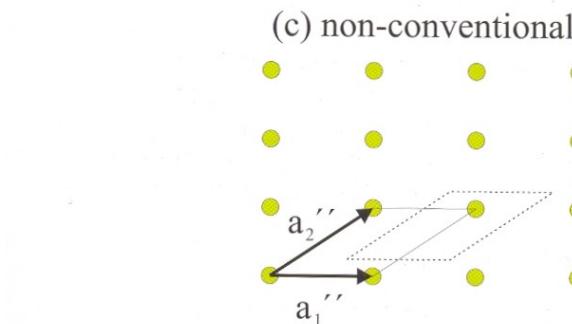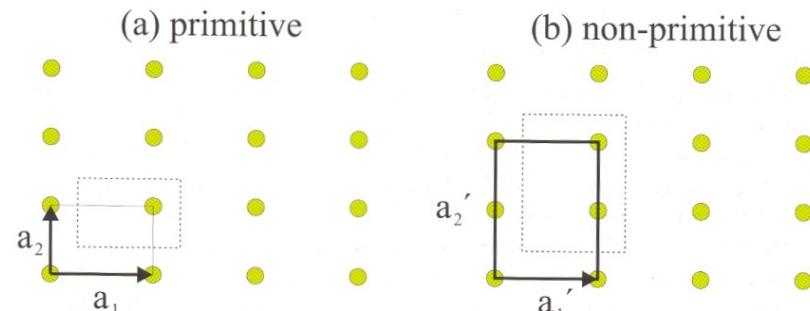
(d) Crystal=lattice+basis

Lattice   Basis   Crystal
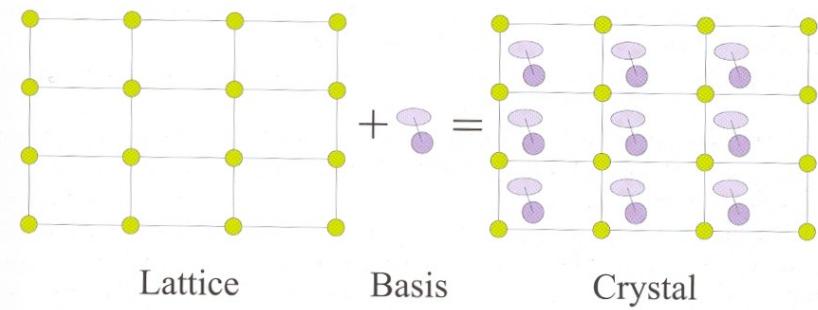
Lattice planes and Miller indices

The plane closest to the origin that has intercepts a_1/h, a_2/k, a_3/l is called the (h,k,l) plane
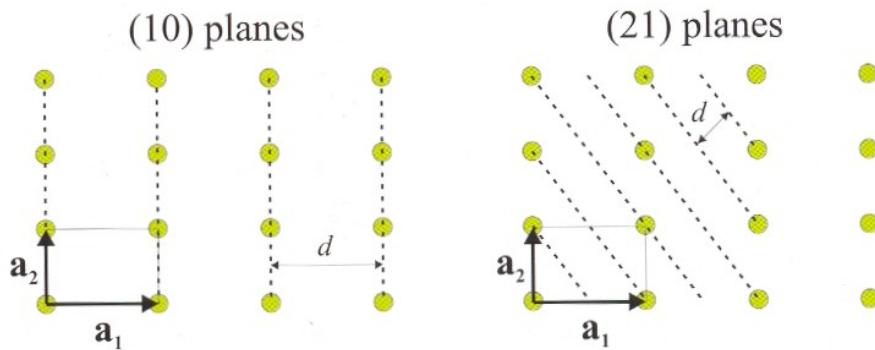
Rhombohedral, $a = b = c$, $\alpha = \beta = \gamma$:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + lh)(\cos^2\alpha - \cos\alpha)}{a^2(1 + 2\cos^3\alpha - 3\cos^2\alpha)}.$$

Hexagonal, $a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}.$$

Monoclinic, $\alpha = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right).$$

Orthorhombic, $\alpha = \beta = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.$$

Tetragonal, $a = b$, $\alpha = \beta = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.$$

Cubic, $a = b = c$, $\alpha = \beta = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}.$$

spacing formulae; B.E. Warren p.21

Laue conditions and reciprocal space

position of an atom in lattice and cell:

$$R_n + r_j$$

origin unit cell   atom in cell
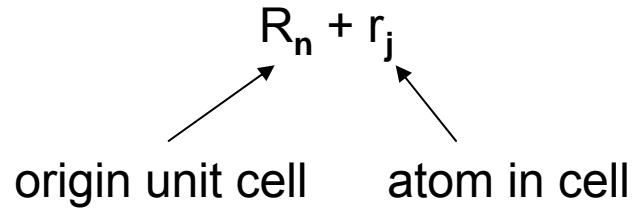
$$F^{\text{crystal}}(Q) = \sum_{r_j} F_j^{\text{mol}}(Q) \exp(i\mathbf{Q}r_j) \bullet \sum_{R_n} \exp(i\mathbf{Q}R_n)$$

unit cell structure factor   lattice sum

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<u>Evaluation of the lattice sum:</u>

$$\sum_{R_n} \exp(i\, \mathbf{Q}\mathbf{R_n}) \qquad \text{(i)}$$

number of terms is enormous

(i) is of order unity (many $\exp(i\Phi)$ terms)
except for:

$$\mathbf{Q}\bullet\mathbf{R_n} = 2\pi \times \text{integer} \qquad \text{(ii)}$$

in that case the lattice sum becomes big.

<u>Concept:</u> construct an artifical lattice with lattice vectors a_1^*, a_2^* and a_3^* such that:

$$a_i\bullet a_j^* = 2\pi\, \delta_{ij} \qquad \text{(iia)}$$

then any vector defined on the reciprocal lattice is of type:

$$G = h\mathbf{a_1}^* + k\mathbf{a_2}^* + l\mathbf{a_3}^* \qquad \text{(iii)}$$

(iii): G satisfies (ii) [$\mathbf{Q}\bullet\mathbf{R_n}$ x integer]

since

$$\mathbf{G}\bullet\mathbf{R_n} = 2\pi\, (hn_1 + kn_2 + ln_3)$$

only if

$$\boxed{Q = \mathbf{G}} \qquad \text{(Laue condition)}$$

so that the scattering amplitude will not vanish.

<u>Thus:</u>   Q need to be a reciprocal lattice vector.

Reciprocal Lattice

1-D: defined by (iia): $a_i \bullet a_j^* = 2\pi \, \delta_{ij}$

2-D and 3-D:

$$a_1^* = (2\pi/v_c) \, a_2 \times a_3$$

$$a_2^* = (2\pi/v_c) \, a_3 \times a_1$$

$$a_3^* = (2\pi/v_c) \, a_1 \times a_2$$

with $v_c = a_1 \bullet (a_2 \times a_3)$

note: in 2-D a_3 is chosen to be a unit vector normal to the 2-D plane spanned by a_1 and a_2.

Example: fcc lattice

$a_1 = (a/2)(y'+z')$, $a_2 = (a/2)(z'+x')$, $a_3 = (a/2)(x'+y')$

$$a_1^* = (4\pi/a)(y/2+z/2-x/2)$$
$$a_2^* = (4\pi/a)(z/2+x/2-y/2)$$
$$a_3^* = (4\pi/a)(x/2+z/2-y/2)$$
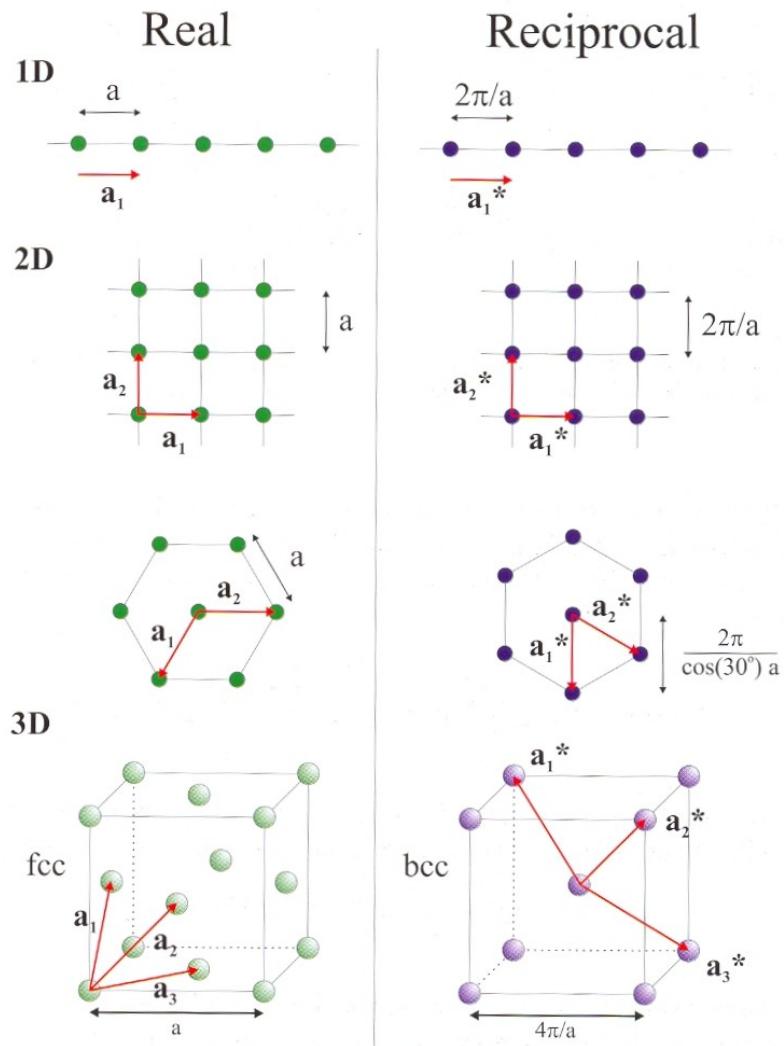
Equivalence of the Laue and the Bragg conditions

(a) Equivalence of Bragg and Laue

Bragg — $\lambda = 2d\sin\theta$ — Real

Laue — $Q = G$ — Reciprocal

(b) Miller indices and reciprocal lattice vectors
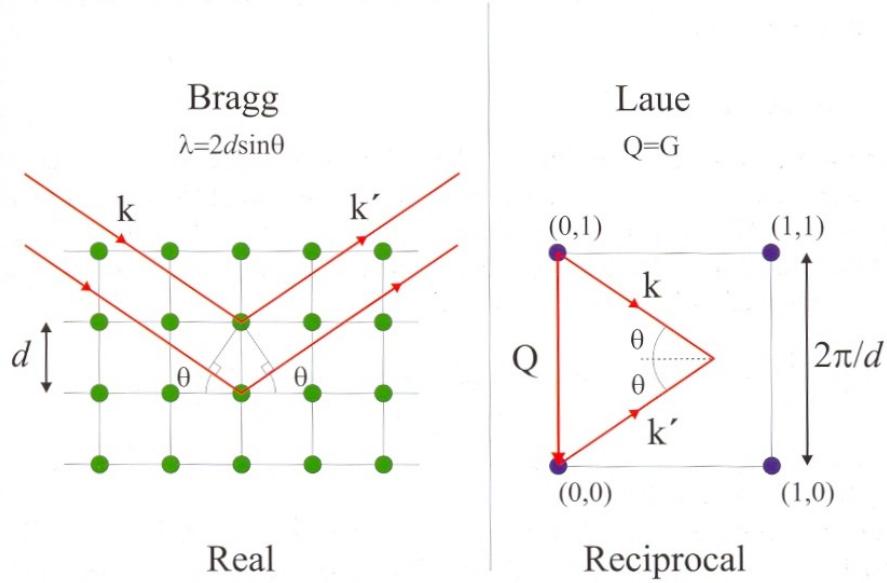
<u>Bragg's law:</u> $\sin\theta = \lambda/2d$

The Laue condition requires

$Q = G$

<u>Example:</u>

$Q = (0,1) = 0 \bullet a_1{}^* + 1 \bullet a_2{}^*$

$\qquad\qquad\qquad = (2\pi/d)\ \underline{x}_2{}'$

$\sin\theta = (Q/2)/k = Q\lambda/4\pi$

$\sin\theta = (2\pi/d)\lambda / 4\pi = \lambda/2d$ qed
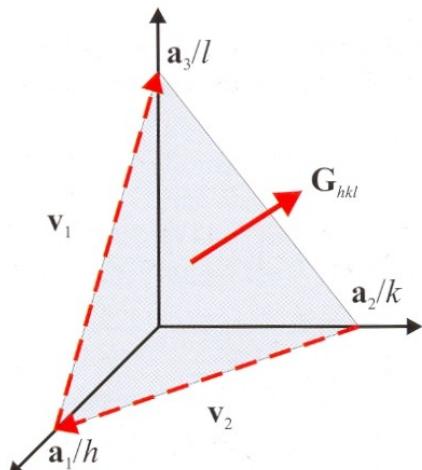
The Ewald shere

Visualisation of diffraction effects in reciprocal space (a).

Laue condition requires $Q = G = ha_1^* + ka_2^*$

Design sphere with radius k pointing to origin (b).

If any reciprocal lattice point falls on the circle then the Laue conditions is fulfilled (c).

Intensity is observed if the detector is placed in the direction of k' (c).

A rotation about O corresponds to a rotation of the crystal.

<u>Note:</u> More than one reciprocal lattice point can lie on the sphere ≡ multiple scattering.

If the beam is not monochromatic the sphere adopts the corresponding width. In the white beam case all spots are ultimately detected.
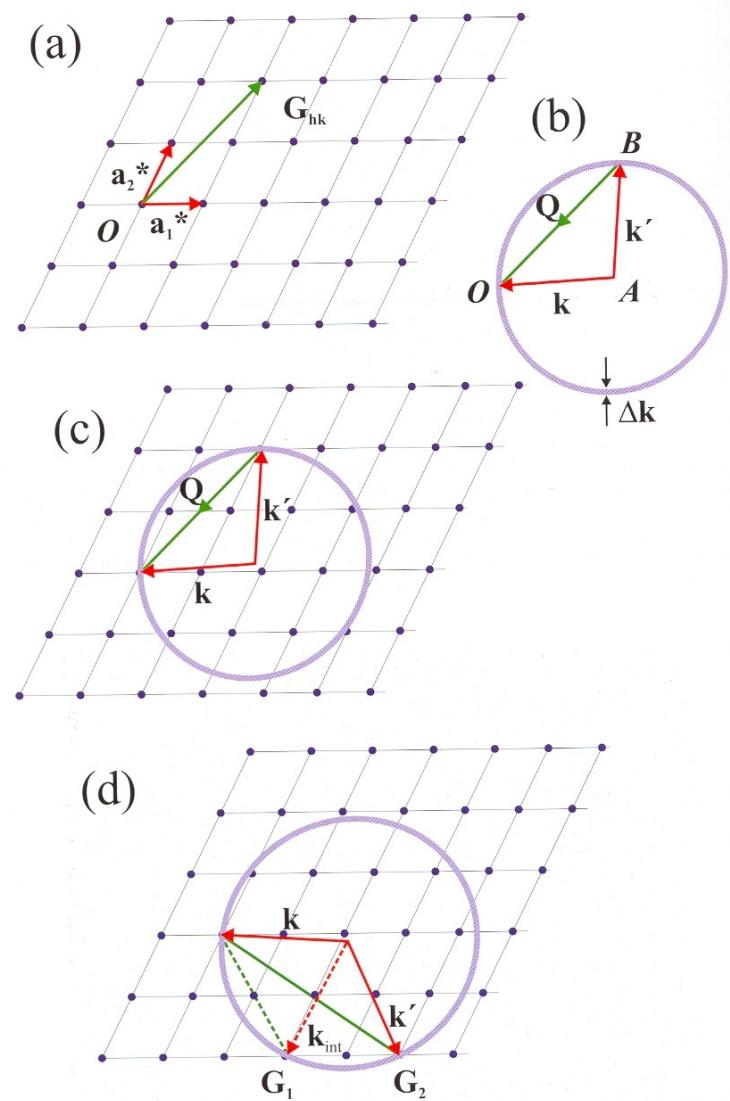
The unit cell structure factor

$$F^{uc}(Q) = \sum_{rj} F_j^{mol}(Q) \exp(iQr_j)$$

example: fcc lattice *(use conventional cubic unit cell)*

$r_1 = 0$, $r_2 = \frac{1}{2}$ a ($\underline{y} + \underline{z}$), $r_3 = \frac{1}{2}$ a ($\underline{z} + \underline{x}$), $r_4 = \frac{1}{2}$ a($\underline{x} + \underline{y}$)

$G = ha_1{}^* + ka_2{}^* + la_3{}^*$

$a_1{}^* = 2\pi/v_c\ (a_2 x a_3) = 2\pi/a^3\ [a\underline{y} \times a\underline{z}] = 2\pi/a\ [\underline{y} \times \underline{z}] = 2\pi/a\ \underline{x}$

$a_2{}^* = 2\pi/v_c\ (a_2 x a_3) = 2\pi/a^3\ [a\underline{z} \times a\underline{x}] = 2\pi/a\ [\underline{z} \times \underline{x}] = 2\pi/a\ \underline{y}$

$a_3{}^* = 2\pi/v_c\ (a_2 x a_3) = 2\pi/a^3\ [a\underline{x} \times a\underline{y}] = 2\pi/a\ [\underline{x} \times \underline{y}] = 2\pi/a\ \underline{z}$

$v_c = a1 \bullet (a_2 \times a_3)$

$G \bullet r_1 = 2\pi/a\ (\ hx + ky + lz) \bullet 0$　　　　　　　$= 0$
$G \bullet r_2 = 2\pi/a\ (\ h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{y} + \underline{z})$　　$= \pi\ (k+l)$
$G \bullet r_3 = 2\pi/a\ (\ h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{z} + \underline{x})$　　$= \pi\ (h+l)$
$G \bullet r_4 = 2\pi/a\ (\ h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{x} + \underline{y})$　　$= \pi\ (h+k)$
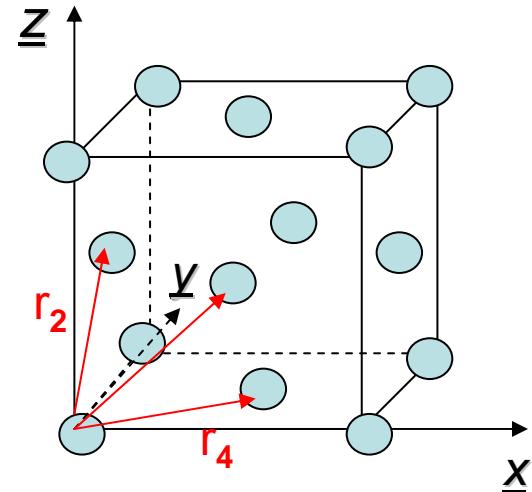
The unit cell structure factor for a fcc lattice

$$F_{hkl}^{fcc}(\mathbf{Q}) = \sum_{j=1-4} f(Q) \exp(i\mathbf{Q}r_j) = f(Q) [\exp(i\mathbf{G}r_1) + \ldots \exp(i\mathbf{G}r_4)]$$

$$F_{hkl}^{fcc}(Q) = f(Q) [1 + \exp(i\pi(k+l)) + \exp(i\pi(h+l)) + \exp(i\pi(h+k))]$$

$$= \begin{cases} 4 & \text{if h,k,l are all even or odd} \\ \\ 0 & \text{otherwise} \end{cases}$$

$$I_{hkl}^{fcc}(\mathbf{Q}) = F(\mathbf{Q}) \bullet F^*(\mathbf{Q})$$

Reflections:

100 forbidden

111 allowed

200 allowed
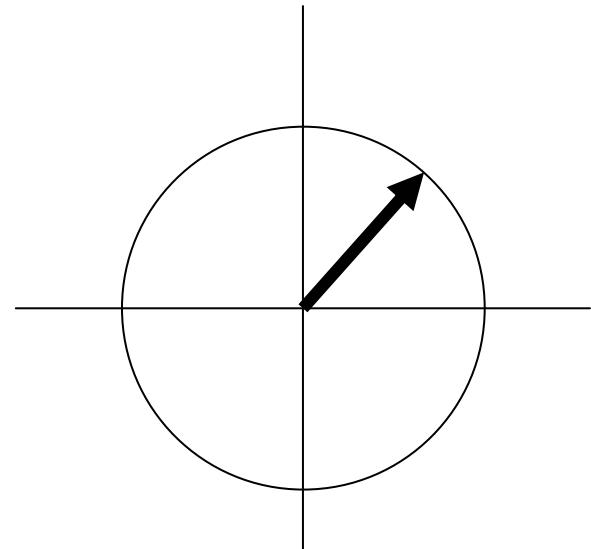
Lattice sums

$S_{\mathbf{N}}(\mathbf{Q}) = \sum_{\mathbf{R}N} \exp(i\mathbf{QR_N})$

<u>1-D:</u> $R_{\mathbf{N}} = na$

$S_{\mathbf{N}}(Q) = \sum_{n=0}^{N-1} \exp(iQna)$

$|Sn(Q)| = \sin(N\pi Q)/\sin(\pi Q)$

Als-Nielsen&McMorrow p.51

<u>Laue condition almost fullfilled:</u>

$Q = (h+\xi) a^*$

$S_{\mathbf{N}}(\xi) = \exp(i \pi\xi(N-1)) \bullet$
$\qquad\qquad [\sin(N\pi\xi) / \sin(\pi\xi)]$

$|S_{\mathbf{N}}(\xi)| = \xrightarrow{\text{N large, } \xi\to 0} N$

<u>width:</u>

$|S_{\mathbf{N}}(\xi=1/2N)| \approx (2/\pi)N$
$\qquad\qquad\qquad \approx \tfrac{1}{2} \text{ (peak height)}$

$FWHM \sim 1/N$

<u>N large:</u>

$|S_{\mathbf{N}}(\xi)| \xrightarrow{\qquad} \delta(\xi)$

$|S_{\mathbf{N}}(Q)| \xrightarrow{\qquad} a^* \delta (Q-G_{\mathbf{h}})$

$|S_{\mathbf{N}}(Q)|^2 \xrightarrow{\qquad} N a^* \delta (Q-G_{\mathbf{h}})$

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Lattice sums (2D & 3D)

$$S_{\mathbf{N}}(Q) = \sum_{\mathbf{R}N} \exp(iQR_{\mathbf{N}})$$

2-D:

$$|S_{\mathbf{N}}(\xi_1, \xi_2)| \longrightarrow N_1 N_2 \delta(\xi_1) \delta(\xi_2)$$

for large N1, N2:

$$|S_{\mathbf{N}}(Q)|^2 \longrightarrow (N_1 a_1{}^*)(N_2 a_2{}^*) \delta(\mathbf{Q}-\mathbf{G}) = NA^*\delta(\mathbf{Q}-\mathbf{G})$$

A* area of unit cell in reciprocal space

3-D:

$$|S_{\mathbf{N}}(Q)|^2 \longrightarrow N v_c{}^*\delta(\mathbf{Q}-\mathbf{G})$$

with **G=ha1*+ka$_2$*+la$_3$*,** N: number of unit cells, v*$_c$ volume unit cell in reciprocal space

Further topics

Quasiperiodic lattices

Crystal truncation rods

Lattice vibrations, Debye-Waller factor, TDS

Lorentz factor

Diffraction from a fiber

2-D crystallography