

Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2009/10

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Location: SemRm 4, Physik, Jungiusstrasse

Thursdays 10.15 – 11.45

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Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Hard X-Rays - Introduction into X-ray physics - Lecture 4

| | | |
|----------------|--|------|
| 22.10. | Introduction | (GG) |
| 29.10. | X-ray Scattering Primer, Sources of X-rays | (GG) |
| 5.11. | Refraction and Reflexion, Kinematical Scattering (I) | (GG) |
| 12.11. | Kinematical Scattering Theory (II) | (GG) |
| 19.11. | Applications of KST and “perfect” crystals | (GG) |
| 26.11. | Small Angle and Anomalous Scattering | (GG) |
| 3.12. - 7. 1. | Modern Crystallography | (AM) |
| 14. 1. - 4. 2. | Coherence base techniques | (CG) |

Coherence of light and matter I: from basic concepts to modern applications

Introduction into X-ray physics: 22.10.-26.11.

Introduction

Overview, Introduction to X-ray scattering

X-ray Scattering Primer and Sources of X-rays

Elements of X-ray scattering, sources of X-rays

Reflection and Refraction, Kinematical Diffraction (I)

Snell's law, Fresnel equations, diffraction from an atom, molecule, crystal,...

Kinematical Diffraction (II)

Reciprocal lattice, structure factor,...

Applications of Kinematical Diffraction and “perfect” crystals

Quasiperiodic lattices, crystal truncation rods, lattice vibrations, Debye-Waller factor, “perfect” crystal theory

SAXS, Anomalous Diffraction

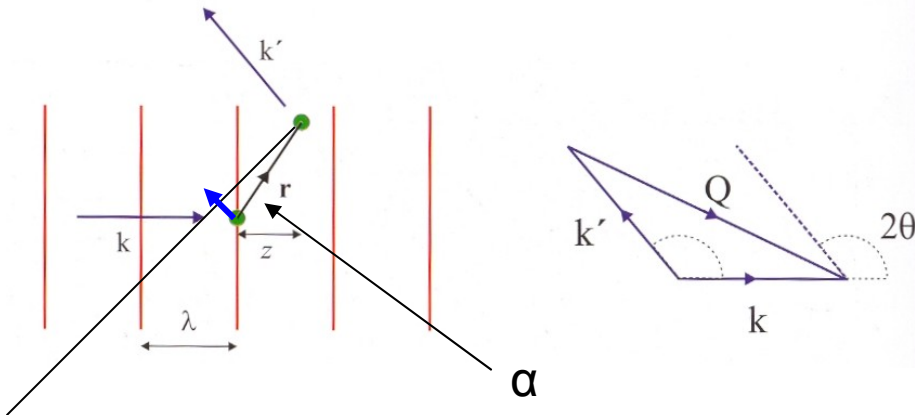
Introduction into small angle scattering and anomalous scattering

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 kinemtical approximation.

Consider a 2 electron system:



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

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

path- or phase difference:

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

with

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

scattering amplitude for 2 electrons:

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

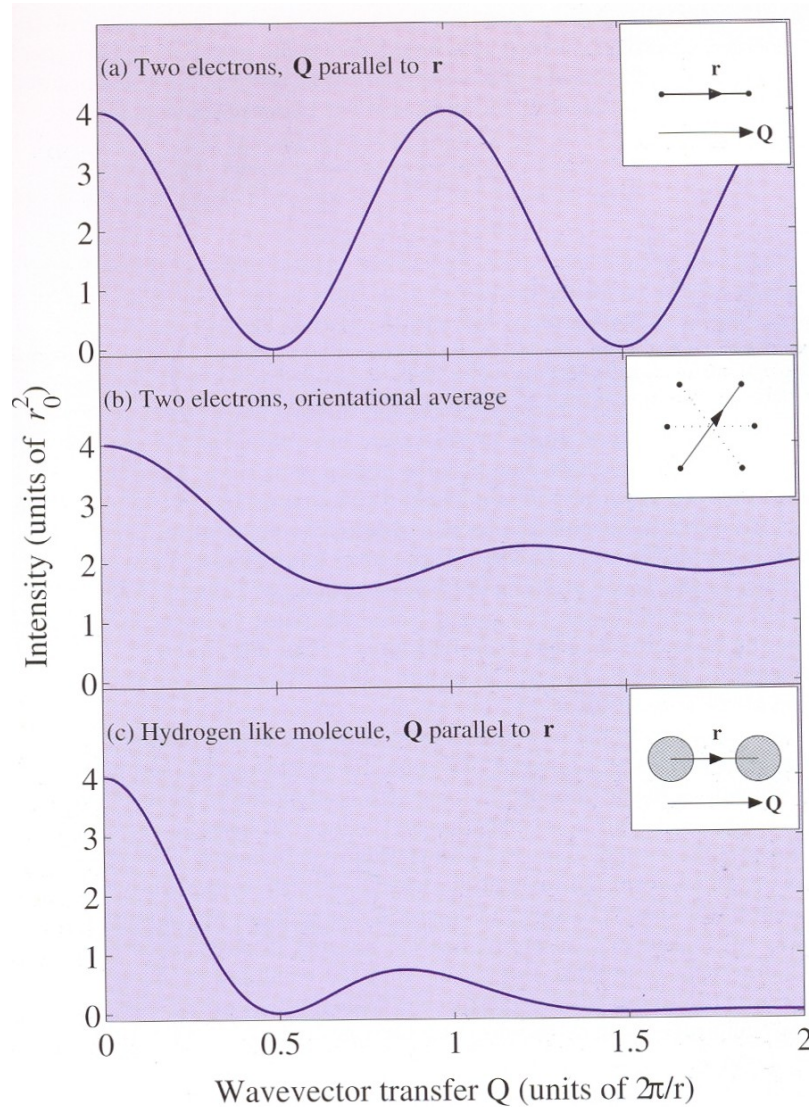
$$\begin{aligned} I(\mathbf{Q}) &= A(\mathbf{Q}) A(\mathbf{Q})^* \\ &= 2r_0^2 [1 + \cos(Qr)] \end{aligned}$$

see Fig. 4.2

for many electrons:

$$A(\mathbf{Q}) = -r_0 \sum_j \exp(i\mathbf{Q}\mathbf{r}_j)$$

Kinematical Diffraction

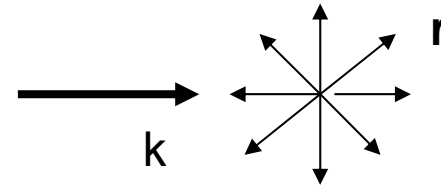


Two electron system:

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

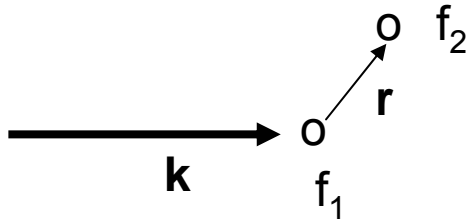
$$Q \parallel r$$

orientational average



“smeared”, no more “point-like” particles

for many systems, e.g. molecules the orientation of \mathbf{r} will be random wrt \mathbf{k}



Orientational averaging: assume one electron at $r=0$, a second at r

$$A(Q) = f_1 + f_2 \exp(i\mathbf{Q}\mathbf{r})$$

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

orientational averaging: $\langle \exp(i\mathbf{Q}\mathbf{r}) \rangle = \langle \exp(-i\mathbf{Q}\mathbf{r}) \rangle$

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

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

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

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

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

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

$$\langle I(Q) \rangle = f_1^2 + f_2^2 + 4\pi f_1 f_2 \sin(Qr)/Qr$$

see figure 4.2 b

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

Scattering from an atom:

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

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

$$f_0(Q) = \int \rho(r) \exp(iQr) dr$$

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

note: atomic form factor is FT of electronic charge distribution

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

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

| | 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:

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

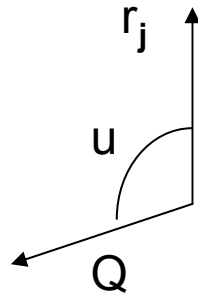
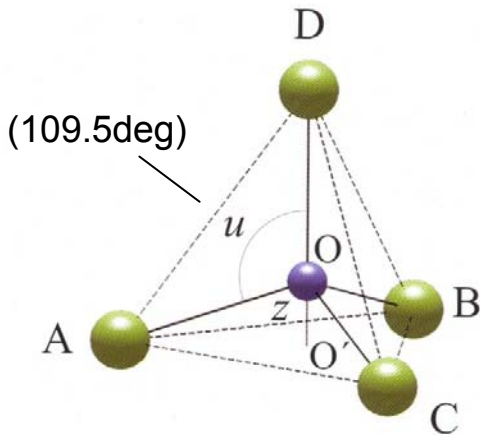
corrections f' and f'' arise from the fact that the electrons are bound in the atom

Scattering from a molecule:

$$F^{\text{mol}}(\mathbf{Q}) = \sum_{r_j} f_j(\mathbf{Q}) \exp(i\mathbf{Q}r_j)$$

example: CF₄:

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

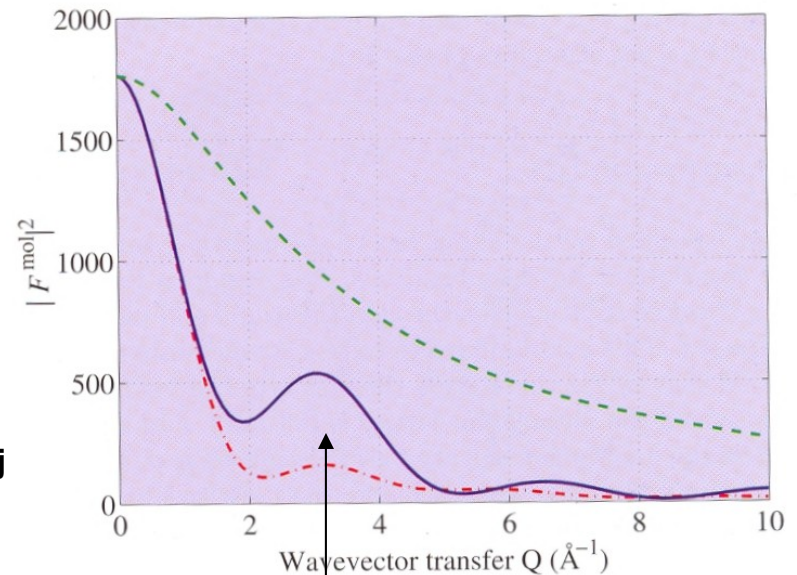


$$\mathbf{Q}r_j = Qr_j \cos(u) = (1/3)Qr_j$$

Assume: Q || C-F bond

$$\begin{aligned} F^{\text{mol}} &= f^{\text{C}}(\mathbf{Q}) + f^{\text{F}}(\mathbf{Q}) [\exp(i\mathbf{Q}R) + 3\exp(i\mathbf{Q}r_j)] \\ &= f^{\text{C}}(\mathbf{Q}) + f^{\text{F}}(\mathbf{Q}) [3\exp(-/+i\mathbf{Q}R/3) + \exp(+/-i\mathbf{Q}R)] \end{aligned}$$

- CF₄
- . - . - CF₄ Q not || C-F
- - - - molybdenum (also 42 electrons)



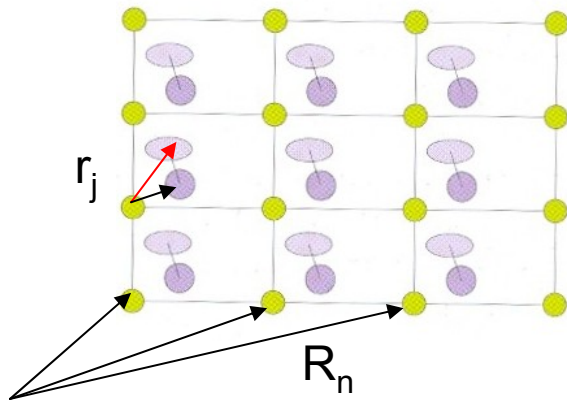
(F-F bond)

Scattering from a crystal

$$A(\mathbf{Q}) = -r_0 \sum_{r_j} \exp(i \mathbf{Q} r_j')$$

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

$$\text{crystalline matter: } r_j' = \mathbf{R}_n + r_j$$



$$A(\mathbf{Q}) = -r_0 \underbrace{\sum_{\mathbf{R}_n} \exp(i \mathbf{Q} \mathbf{R}_n)}_{\text{lattice sum}} \underbrace{\sum_{r_j} \exp(i \mathbf{Q} r_j)}_{\text{unit cell structure factor}}$$

lattice sum

unit cell structure factor

Crystallography:

determine electron density within unit cell

Note: one does measure $I(\mathbf{Q}) = A(\mathbf{Q}) A^*(\mathbf{Q})$ and is thus not sensitive to phase shifts

Scattering from atoms on a crystal lattice

concept: build up crystal from lattice+basis

2-D lattice: $R_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$

unit cell: primitive or (non-) primitive
(primitive=area or volume minimized)

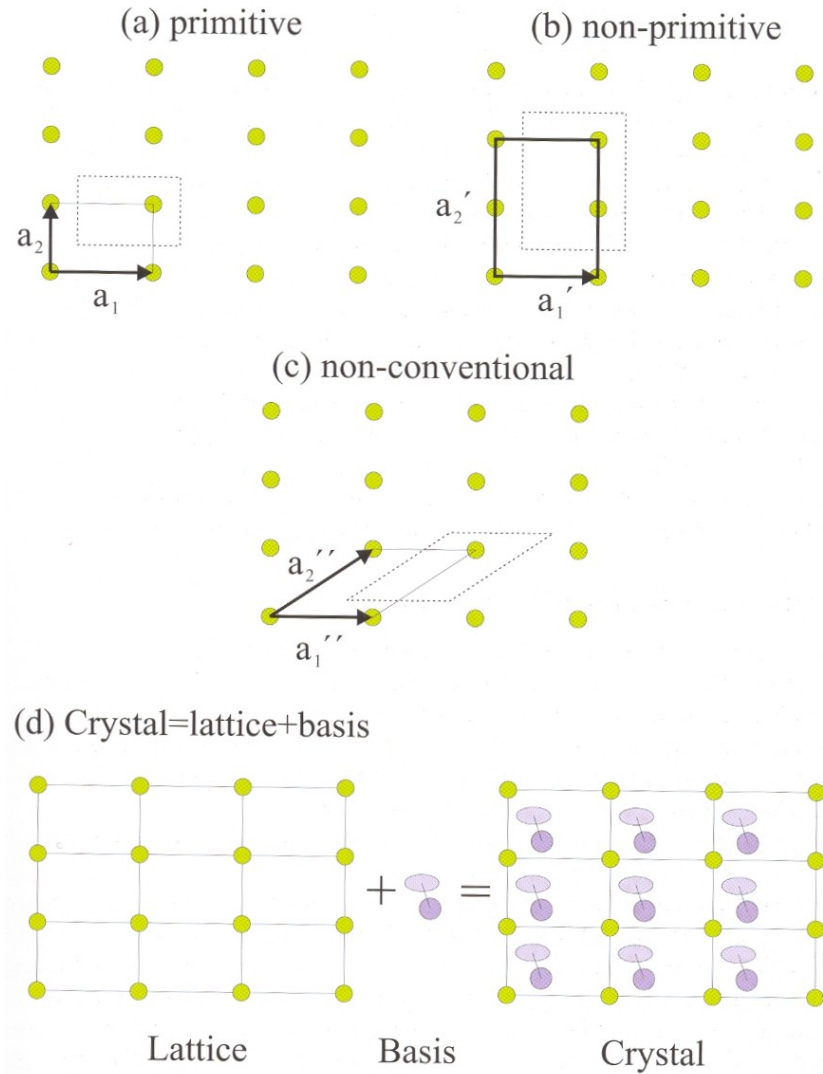
3-D lattice: $R_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

There are: 5 distinct lattices in 2-D
 14 distinct lattices in 3-D

called the Bravais lattices

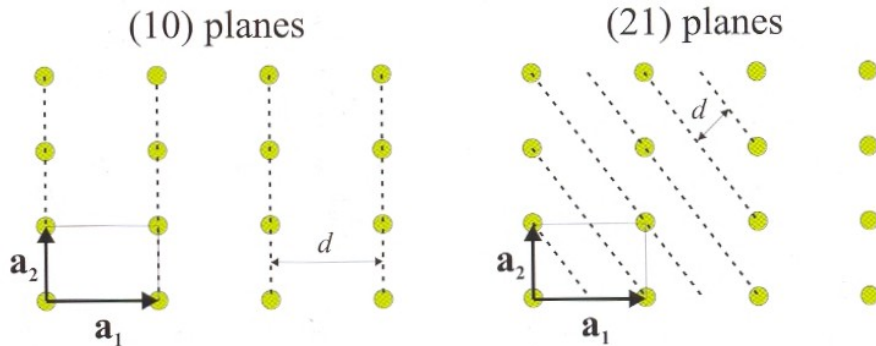
add basis to yield:

32 possible point groups
230 possible symmetry groups



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, $a = b$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$:

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

Monoclinic, $\alpha = \gamma = 90^\circ$:

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

Orthorhombic, $\alpha = \beta = \gamma = 90^\circ$:

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

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

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

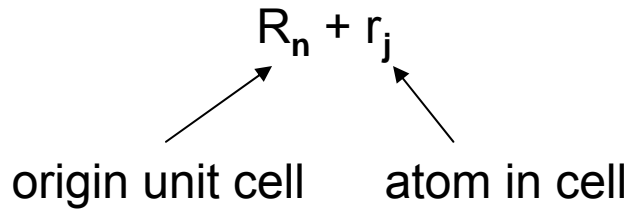
Cubic, $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$:

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

spacing formulae; B.E. Warren p.21

Laue conditions and reciprocal space

position of an atom in lattice and cell:



$$F_{\text{crystal}}(Q) = \underbrace{\sum_{r_j} F_j^{\text{mol}}(Q) \exp(i\mathbf{Q}r_j)}_{\text{unit cell structure factor}} \cdot \underbrace{\sum_{R_n} \exp(i\mathbf{Q}R_n)}_{\text{lattice sum}}$$

Evaluation of the lattice sum:

$$\sum_{\mathbf{R}_n} \exp(i \mathbf{Q} \cdot \mathbf{R}_n) \quad (\text{i})$$

number of terms is enormous

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

except for:

$$\mathbf{Q} \cdot \mathbf{R}_n = 2\pi \times \text{integer} \quad (\text{ii})$$

in that case the lattice sum becomes big.

Concept: construct an artificial lattice with lattice vectors \mathbf{a}_1^* , \mathbf{a}_2^* and \mathbf{a}_3^* such that:

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi \delta_{ij} \quad (\text{ia})$$

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

$$\mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* \quad (\text{iii})$$

(iii): \mathbf{G} satisfies (ii) [$\mathbf{Q} \cdot \mathbf{R}_n \times \text{integer}$]

since

$$\mathbf{G} \cdot \mathbf{R}_n = 2\pi (hn_1 + kn_2 + ln_3)$$

only if

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

so that the scattering amplitude will not vanish.

Thus: \mathbf{Q} need to be a reciprocal lattice vector.

Reciprocal Lattice

1-D: defined by (ia): $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi \delta_{ij}$

2-D and 3-D:

$$\mathbf{a}_1^* = (2\pi/v_c) \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{a}_2^* = (2\pi/v_c) \mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{a}_3^* = (2\pi/v_c) \mathbf{a}_1 \times \mathbf{a}_2$$

with $v_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$

note: in 2-D \mathbf{a}_3 is chosen to be a unit vector normal to the 2-D plane spanned by \mathbf{a}_1 and \mathbf{a}_2 .

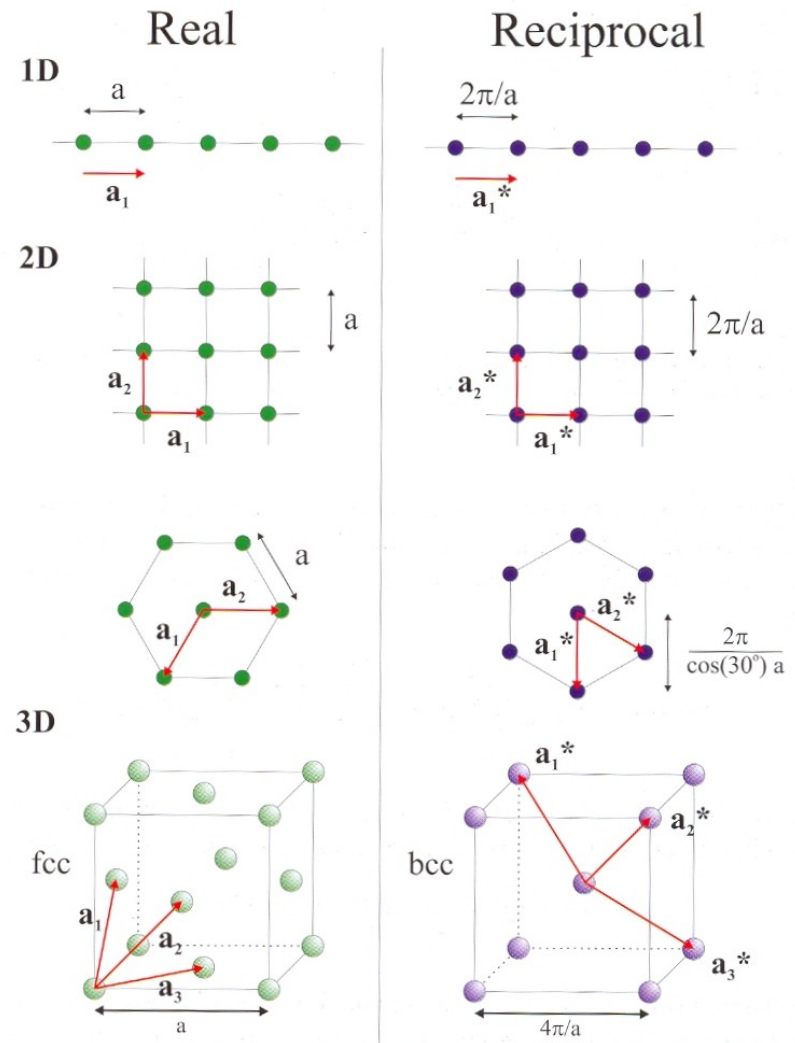
Example: fcc lattice

$$\mathbf{a}_1 = (a/2)(\mathbf{y}' + \mathbf{z}'), \quad \mathbf{a}_2 = (a/2)(\mathbf{z}' + \mathbf{x}'), \quad \mathbf{a}_3 = (a/2)(\mathbf{x}' + \mathbf{y}')$$

$$\mathbf{a}_1^* = (4\pi/a) (\mathbf{y}/2 + \mathbf{z}/2 - \mathbf{x}/2)$$

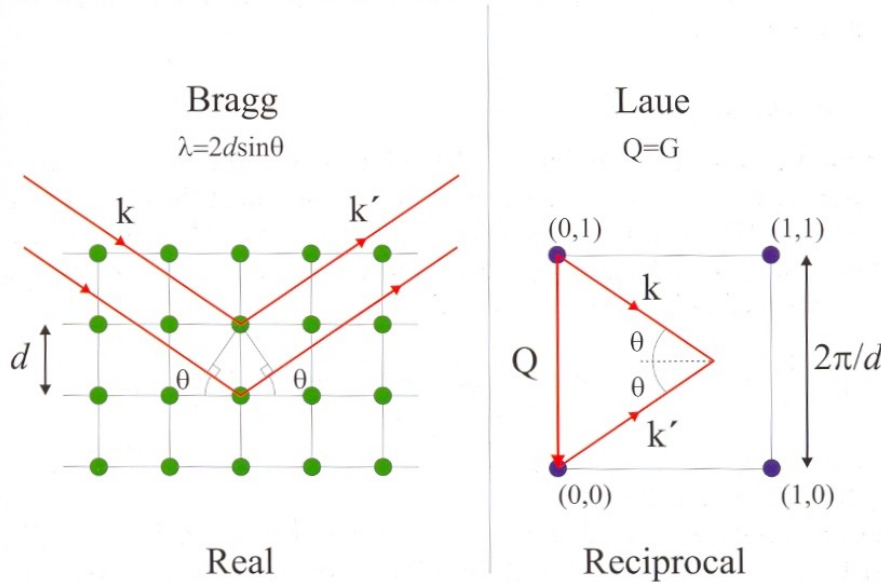
$$\mathbf{a}_2^* = (4\pi/a) (\mathbf{z}/2 + \mathbf{x}/2 - \mathbf{y}/2)$$

$$\mathbf{a}_3^* = (4\pi/a) (\mathbf{x}/2 + \mathbf{z}/2 - \mathbf{y}/2)$$



Equivalence of the Laue and the Bragg conditions

(a) Equivalence of Bragg and Laue



Bragg's law: $\sin\theta = \lambda/2d$

The Laue condition requires

$Q = G$

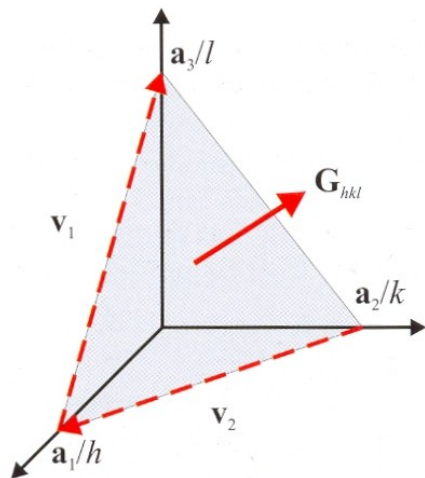
Example:

$$Q = (0,1) = 0 \cdot a_1^* + 1 \cdot a_2^* = (2\pi/d) \underline{x}_2'$$

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

$$\sin\theta = (2\pi/d)\lambda / 4\pi = \lambda/2d \quad \text{qed}$$

(b) Miller indices and reciprocal lattice vectors



The Ewald sphere

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).

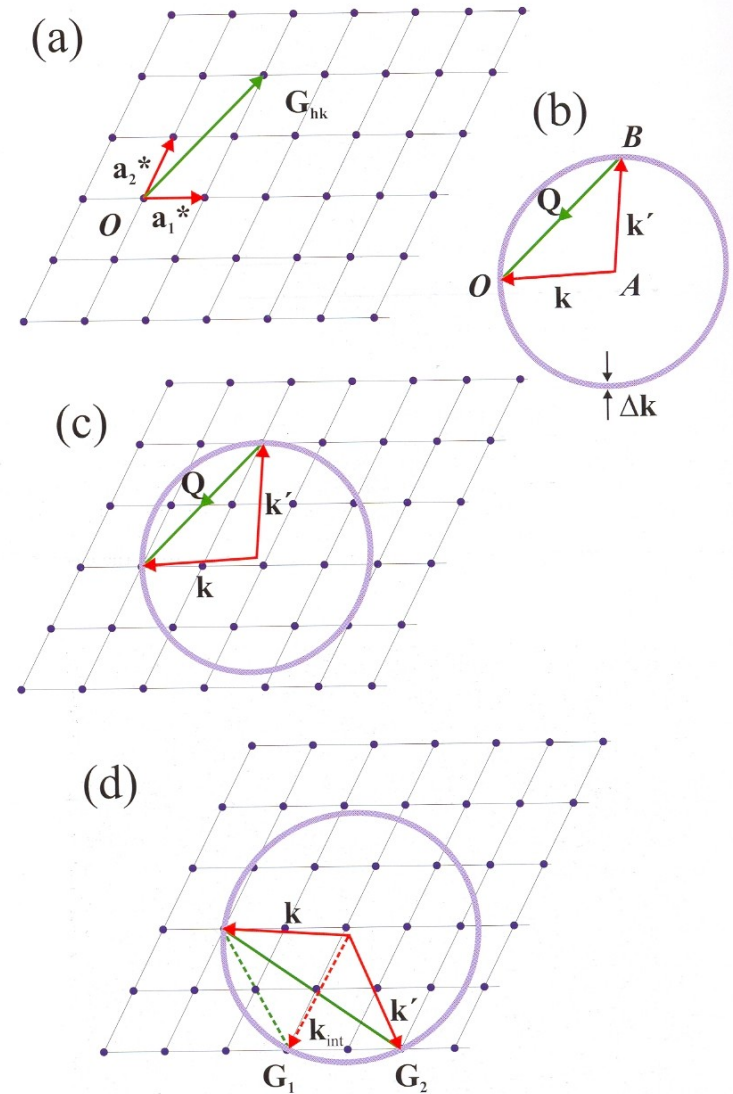
If any reciprocal lattice point falls on the circle then the Laue conditions is fulfilled (c).

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.

Note: More than one reciprocal lattice point can lie on the sphere \equiv 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

$$F^{\text{uc}}(\mathbf{Q}) = \sum_{r_j} F_j^{\text{mol}}(\mathbf{Q}) \exp(i\mathbf{Q}r_j)$$

example: fcc lattice (use conventional cubic unit cell)

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

$$\mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$$

$$\mathbf{a}_1^* = 2\pi/v_c (\mathbf{a}_2 \times \mathbf{a}_3) = 2\pi/a^3 [\underline{a}_y \times \underline{a}_z] = 2\pi/a [\underline{y} \times \underline{z}] = 2\pi/a \underline{x}$$

$$\mathbf{a}_2^* = 2\pi/v_c (\mathbf{a}_3 \times \mathbf{a}_1) = 2\pi/a^3 [\underline{a}_z \times \underline{a}_x] = 2\pi/a [\underline{z} \times \underline{x}] = 2\pi/a \underline{y}$$

$$\mathbf{a}_3^* = 2\pi/v_c (\mathbf{a}_1 \times \mathbf{a}_2) = 2\pi/a^3 [\underline{a}_x \times \underline{a}_y] = 2\pi/a [\underline{x} \times \underline{y}] = 2\pi/a \underline{z}$$

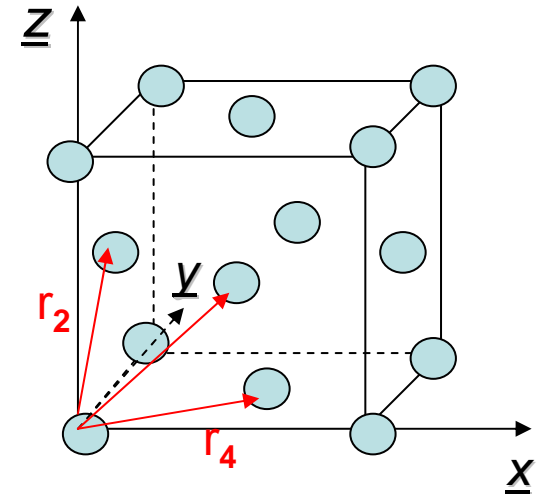
$$v_c = a_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

$$\mathbf{G} \cdot r_1 = 2\pi/a (hx + ky + lz) \cdot 0 = 0$$

$$\mathbf{G} \cdot r_2 = 2\pi/a (h\underline{x} + k\underline{y} + l\underline{z}) \cdot 1/2a(\underline{y} + \underline{z}) = \pi (k+l)$$

$$\mathbf{G} \cdot r_3 = 2\pi/a (h\underline{x} + k\underline{y} + l\underline{z}) \cdot 1/2a(\underline{z} + \underline{x}) = \pi (h+l)$$

$$\mathbf{G} \cdot r_4 = 2\pi/a (h\underline{x} + k\underline{y} + l\underline{z}) \cdot 1/2a(\underline{x} + \underline{y}) = \pi (h+k)$$



The unit cell structure factor for a fcc lattice

$$F_{hkl}^{\text{fcc}}(\mathbf{Q}) = \sum_{j=1-4} f(\mathbf{Q}) \exp(i\mathbf{Q}\mathbf{r}_j) = f(\mathbf{Q}) [\exp(i\mathbf{G}\mathbf{r}_1) + \dots \exp(i\mathbf{G}\mathbf{r}_4)]$$

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

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

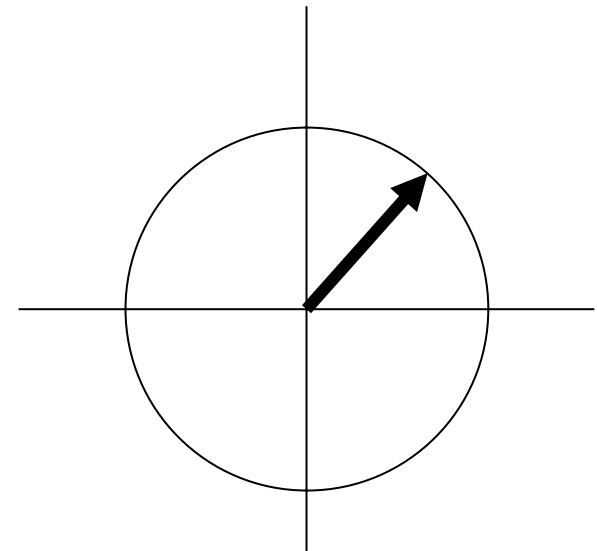
$$I_{hkl}^{\text{fcc}}(\mathbf{Q}) = F(\mathbf{Q}) \cdot F^*(\mathbf{Q})$$

Reflections:

100 forbidden

111 allowed

200 allowed



Lattice sums

$$S_N(\mathbf{Q}) = \sum_{\mathbf{R}_N} \exp(i\mathbf{Q}\mathbf{R}_N)$$

width:

$$|S_N(\xi=1/2N)| \approx (2/\pi)N \\ \approx 1/2 \text{ (peak height)}$$

1-D: $R_N = na$

$$\text{FWHM} \sim 1/N$$

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

N large:

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

Als-Nielsen&McMorrow p.51

$$|S_N(\xi)| \longrightarrow \delta(\xi)$$

Laue condition almost fulfilled:

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

$$|S_N(Q)| \longrightarrow a^* \delta(Q-G_h)$$

$$S_N(\xi) = \exp(i \pi \xi (N-1)) \bullet \\ [\sin(N\pi \xi) / \sin(\pi \xi)]$$

$$|S_N(Q)|^2 \longrightarrow N a^* \delta(Q-G_h)$$

$$|S_N(\xi)| = \xrightarrow{N \text{ large, } \xi \rightarrow 0} N$$

Lattice sums (2D & 3D)

$$S_N(\mathbf{Q}) = \sum_{\mathbf{R}_N} \exp(i\mathbf{Q}\mathbf{R}_N)$$

2-D:

$$|S_N(\xi_1, \xi_2)| \longrightarrow N_1 N_2 \delta(\xi_1) \delta(\xi_2)$$

for large N_1, N_2 :

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

A^* area of unit cell in reciprocal space

3-D:

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

with $\mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$, 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