

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 5

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

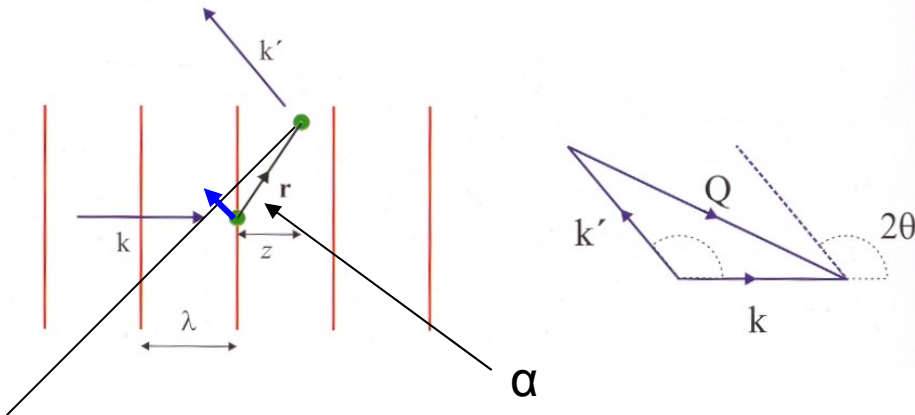
Kinematical Diffraction

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:

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

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

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

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

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:

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

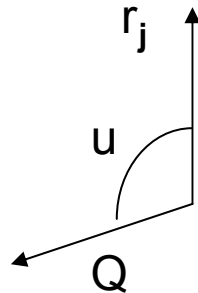
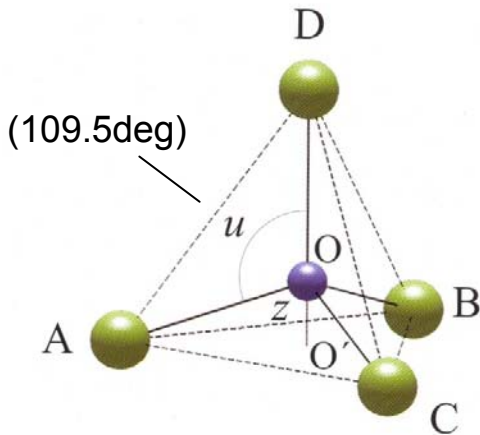
corrections f' and f'' arise from the fact that the electrons are bound in the atom

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

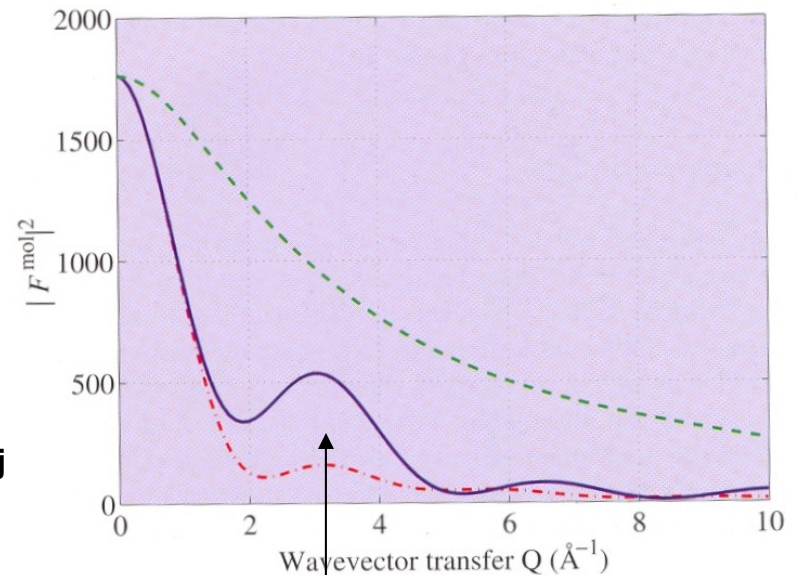


$$Qr_j = r_j \cos(u) = (1/3)Qr_j$$

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)



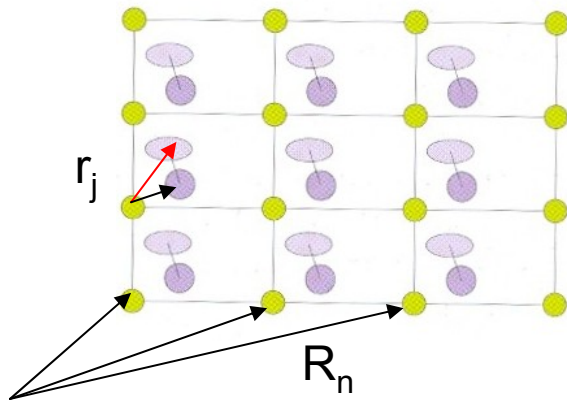
(F-F bond)

Scattering from a crystal

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

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

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



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

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

lattice sum

unit cell structure factor

Scattering from atoms on a crystal lattice

concept: build up crystal from lattice+basis

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

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

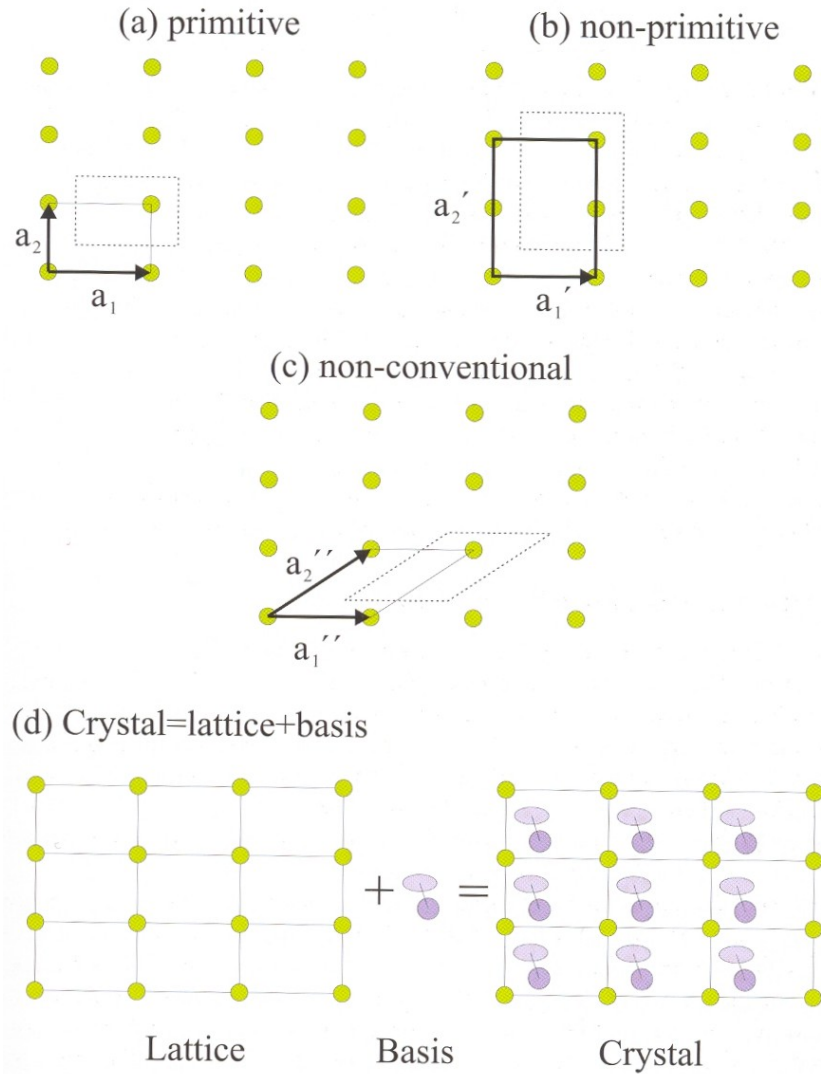
3-D lattice: $R_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

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



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 .

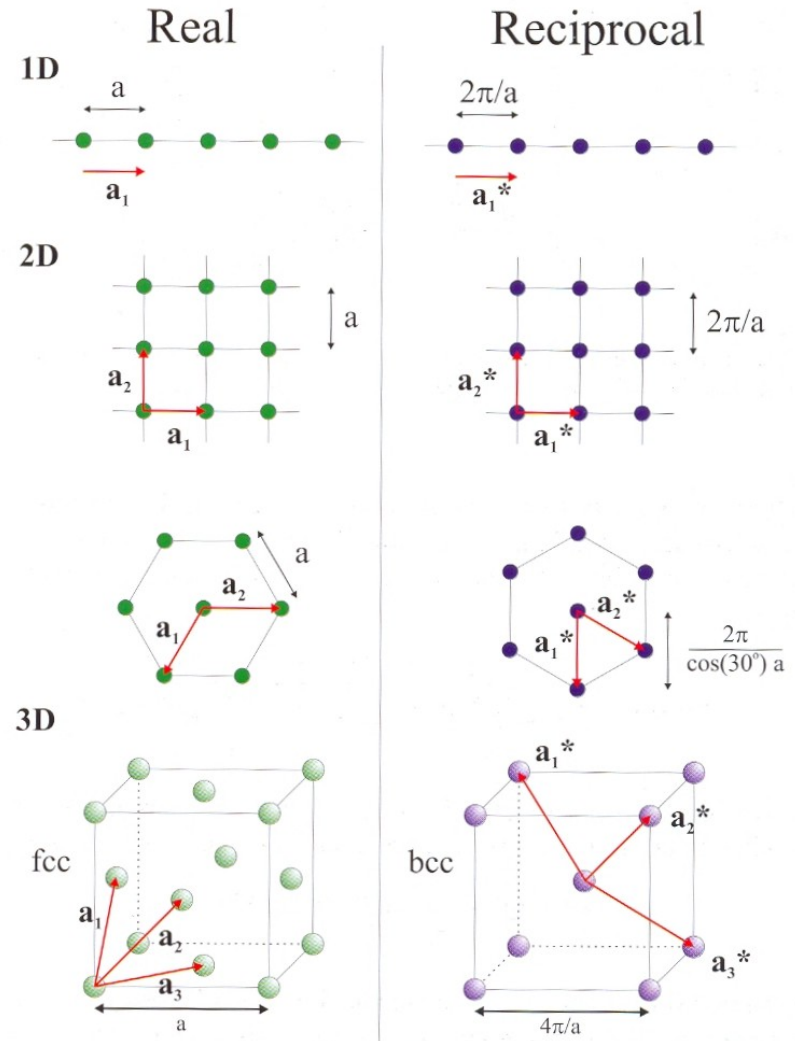
Example: fcc lattice

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

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

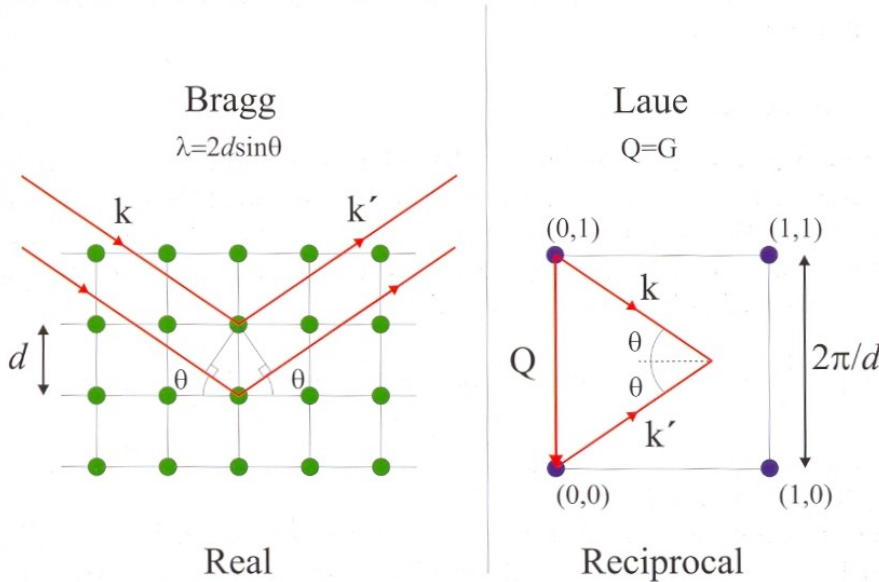
$$\mathbf{a}_2^* = (4\pi/a) (\mathbf{z}/2 + \mathbf{x}/2 - \mathbf{y}/2)$$

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



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

$Q = G$

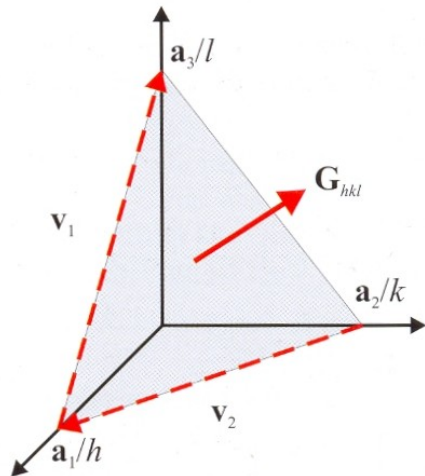
Example:

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

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

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

(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).

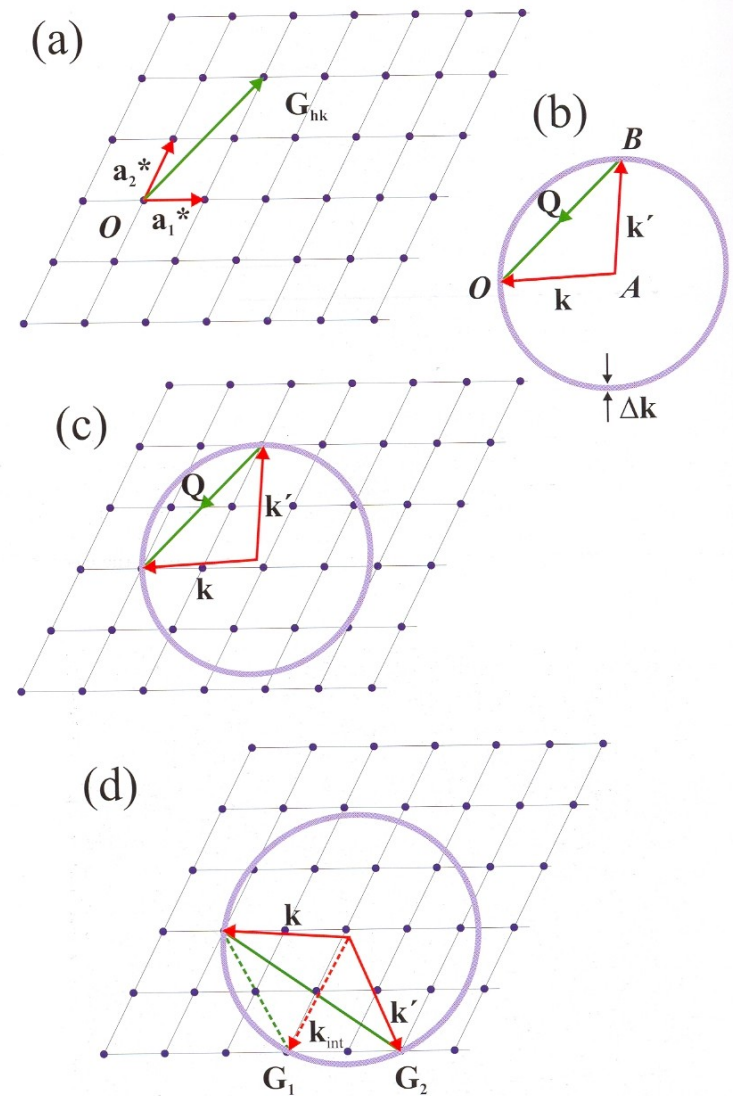
If any reciprocal lattice point falls on the circle then the Laue conditions is fulfilled (c).

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)

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

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

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

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

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

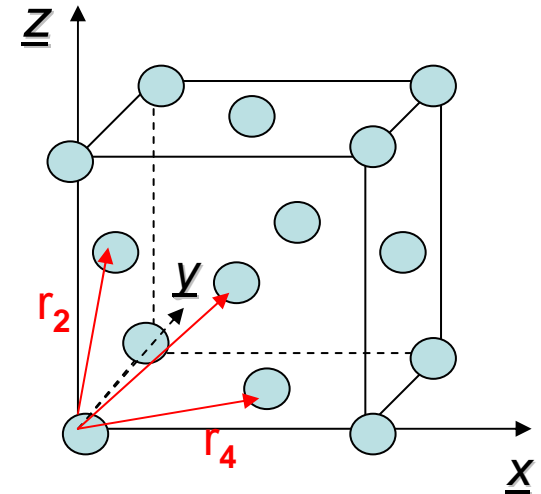
$$v_c = a_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

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

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

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

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



The unit cell structure factor for a fcc lattice

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

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

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

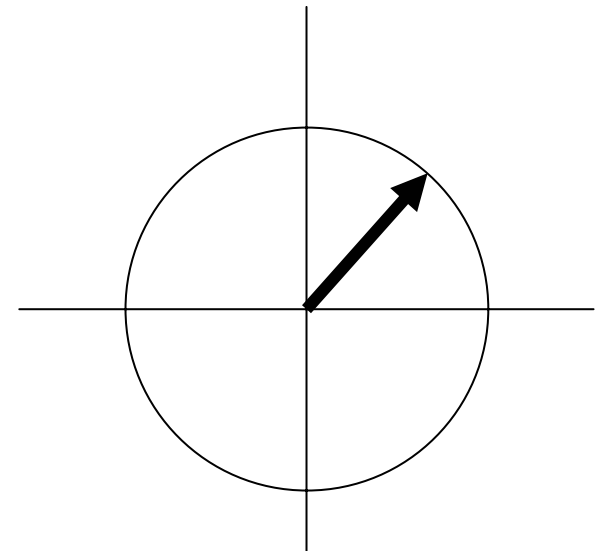
$$I_{hkl}^{\text{fcc}}(\mathbf{Q}) = F(\mathbf{Q}) \cdot F^*(\mathbf{Q})$$

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 N1, N2:

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

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

Lattice vibrations, Debye-Waller factor, TDS (1)

$$F_{\text{crystal}}(\mathbf{Q}) = \sum_n f(\mathbf{Q}) \exp(i \mathbf{Q} \cdot \mathbf{r}_n)$$

Elastic waves (phonons) excited at finite T.

Effect of vibrations: $\mathbf{r}_n = \mathbf{R}_n + \mathbf{u}_n$

↑ displacement
↑ time averaged position

$$\langle \mathbf{u}_n \rangle = 0 \quad \langle \rangle: \text{thermal average}$$

$$I = \left\langle \sum_n f(\mathbf{Q}) \exp[i\mathbf{Q}(\mathbf{R}_m + \mathbf{u}_m)] \times \sum_n f^*(\mathbf{Q}) \exp[-i\mathbf{Q}(\mathbf{R}_n + \mathbf{u}_n)] \right\rangle$$

$$= \sum_m \sum_n f(\mathbf{Q}) f^*(\mathbf{Q}) \exp[i\mathbf{Q}(\mathbf{R}_m + \mathbf{R}_n)] \times \langle \exp[i\mathbf{Q}(\mathbf{u}_m - \mathbf{u}_n)] \rangle$$

for $\mathbf{u}_m \parallel \mathbf{Q}$: u_{Qm}

$$\langle \exp[i\mathbf{Q}(\mathbf{u}_m - \mathbf{u}_n)] \rangle = \langle \exp[iQ(u_{Qm} - u_{Qn})] \rangle$$

Gaussian distribution of displacements:

$$\langle e^{ix} \rangle = \exp[-\langle x^2 \rangle]$$

$$\langle \exp[iQ(u_{Qm} - u_{Qn})] \rangle = \exp[-1/2 \langle Q^2 (u_{Qm} - u_{Qn})^2 \rangle]$$

$$= \exp[-1/2 Q^2 \langle (u_{Qm} - u_{Qn})^2 \rangle]$$

$$= \exp[-1/2 Q^2 \langle u_{Qm}^2 \rangle] \exp[-1/2 Q^2 \langle u_{Qn}^2 \rangle] \times \exp[Q^2 \langle u_{Qm} u_{Qn} \rangle]$$

Lattice vibrations, Debye-Waller factor, TDS (2)

$$\exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] = 1 + \{ \exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] - 1 \}$$

$$I = \sum_m \sum_n f(Q) \exp[-1/2 Q^2 \langle u_{Qm}^2 \rangle] \exp[iQR_m] f^*(Q) \exp[-1/2 Q^2 \langle u_{Qn}^2 \rangle] \exp[iQR_n] + \\ \sum_m \sum_n f(Q) \exp[iQR_m] f^*(Q) \exp[-iQR_n] \{ \exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] - 1 \}$$

increasing with displacements: $\langle u_{Qm} u_{Qn} \rangle$

“Thermal Diffuse Scattering” (TDS)

$$f^{\text{atom}} = f(Q) \exp[-1/2 Q^2 \langle u^2 \rangle] = f(Q) \exp[-M]$$

with $\exp[-M]$: Debye-Waller factor

Thermal Diffuse Scattering (TDS)

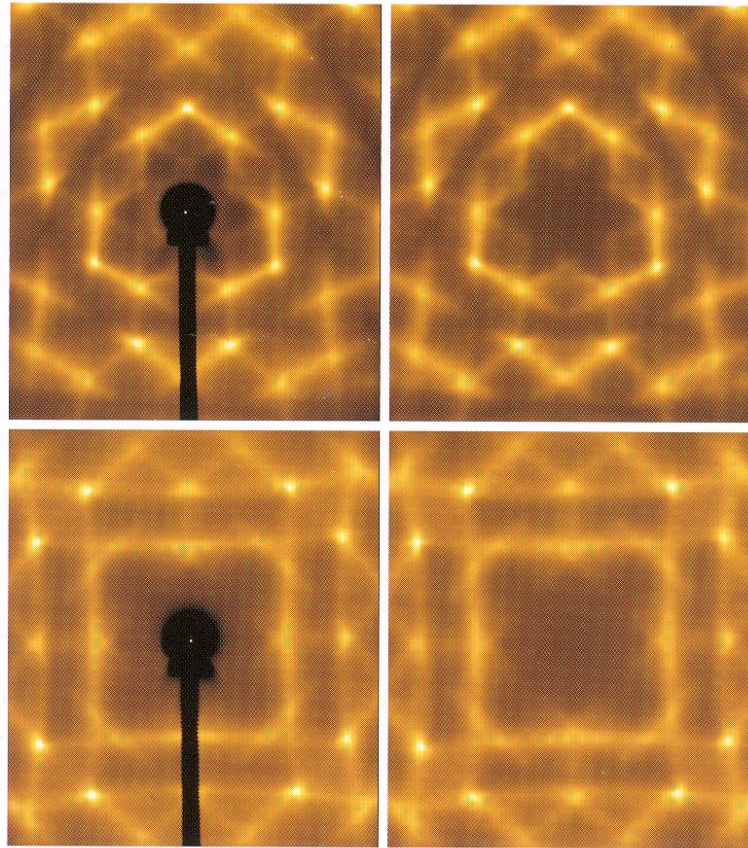


Figure 4.18: Thermal diffuse scattering (TDS) from Si. The data were collected in a transmission geometry (photon energy 28 keV) using an image plate detector. The data were collected on the UNI-CAT beamline at the Advanced Photon Source in an exposure time of ~ 10 s. The top and bottom left panels show the data taken with a (111) and a (100) axis parallel to the incident beam respectively. The data are plotted on a logarithmic scale. The brighter spots are not Bragg peaks, as the Laue condition is never exactly fulfilled, but are due to the build up of TDS close to the position of where the Bragg peaks would occur. The right panels show the corresponding calculated images based on a simultaneous pixel-by-pixel fit to the data [Holt et al., 1999].

Debye-Waller factor

unit cell structure factor including the DWf

$$F_{\text{unit cell}} = \sum_j f_j(Q) \exp[-M_j] \exp[i\mathbf{Q} \cdot \mathbf{r}_j]$$

$$M_j = 1/2 Q^2 \langle u^2_j \rangle = 1/2 (4\pi/\lambda)^2 \sin^2\theta \langle u^2_j \rangle \\ = B_j^T (\sin\theta/\lambda)^2$$

$$\text{with } B_j^T = 8\pi^2 \langle u^2_j \rangle$$

for isotropic vibrations:

$$\langle u^2 \rangle = \langle u_x^2 + u_y^2 + u_z^2 \rangle = 3 \langle u_C^2 \rangle$$

$$B_{T, \text{isotropic}} = 8\pi^2/3 \langle u^2 \rangle$$

within the Debye-model:

$$B_T = 6h^2/m_A k_B \Theta \left\{ \left[\Phi(\Theta/T) / \Theta/T \right] - 1/4 \right\}$$

with $\Phi(x) = (1/x) \int_0^x \xi / (\exp[\xi]-1) d\xi$

Θ : Debye temperature

m_A : atomic mass

$$B_T [\text{\AA}^2] = \left\{ 11492 T [\text{K}] / A \Theta^2 [\text{K}^2] \right\} \Phi(\Theta, T) \\ + 2873 / A \Theta [\text{K}]$$

Debye-Waller factor

$$B_T[\text{\AA}^2] = \{11492T[\text{K}]/A\Theta^2[\text{K}^2]\} \Phi(\Theta, T) + 2873 / A\Theta[\text{K}]$$

	A	Θ (K)	$B_{4.2}$	B_{77}	B_{293}
			(Å ²)		
Diamond	12	2230	0.11	0.11	0.12
Al	27	394	0.25	0.30	0.72
Si	28.1	645	0.17	0.18	0.33
Cu	63.5	343	0.13	0.17	0.47
Ge	72.6	374	0.11	0.13	0.35
Mo	96	450	0.06	0.08	0.18

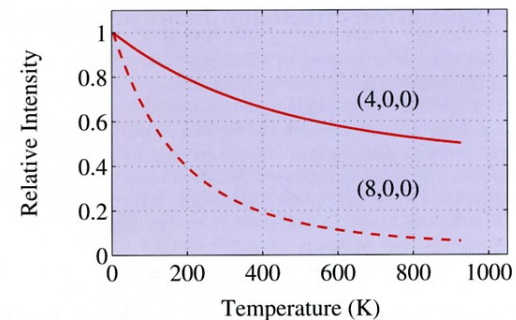
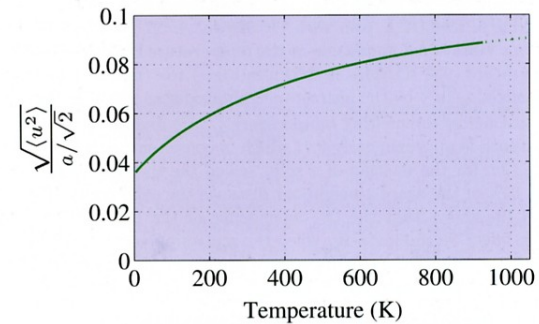
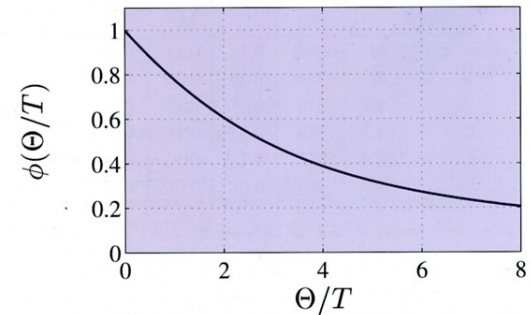


Figure 4.19: * Top: plot of the value of the integral $\phi(x)$ versus $x = \Theta/T$. Middle: temperature dependence of the rms fluctuation \mathbf{u} in units of $a/\sqrt{2}$ for Al. Bottom: the relative intensity of the scattered intensity from Al as a function of temperature. The curves were calculated for the (4,0,0) (solid line) and the (8,0,0) (dashed line) Bragg peaks respectively. The melting temperature of Al is 933 K.