Methoden moderner Röntgenphysik II: Streuung und Abbildung

Lecture 6

Vorlesung zum Haupt/Masterstudiengang Physik

SS 2013

G. Grübel, M. Martins, E. Weckert

Location: Hörs AP, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 8:30 – 10.00

Methoden moderner Röntgenphysik II: Streuung und Abbildung

Introduction
Overview, Introduction to X-ray scattering

X-ray Scattering Primer
Elements of X-ray scattering

Sources of X-rays, Synchrotron Radiation
Laboratory sources, accelerator bases sources

Reflection and Refraction
Snell's law, Fresnel equations,

Kinematical Diffraction (I)
Diffraction from an atom, molecule, liquids, glasses,..

Kinematical Diffraction (II)
Diffraction from a crystal, reciprocal lattice, structure factor,..

Methoden moderner Röntgenphysik II: Streuung und Abbildung

Small Angle Scattering, and Soft Matter
Introduction, form factor, structure factor, applications, ..

Anomalous Diffraction
Introduction into anomalous scattering,..

Introduction into Coherence
Concept, First order coherence, ..

Coherent Scattering
Spatial coherence, second order coherence,..

Applications of coherent Scattering
Imaging and Correlation spectroscopy,..

Kinematical Diffraction

Scattering from an atom:

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

ρ(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:

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

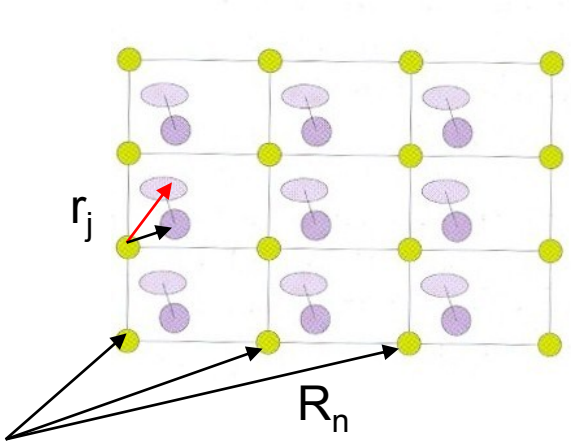
corrections f' and f'' arise from the fact that the electrons are bound in the atom

Scattering from a crystal

$A(\mathbf{Q}) = -r_0 \sum_{rj} \exp(i\, \mathbf{Q}\mathbf{r}_j')$

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

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



$A(\mathbf{Q}) = -r_0 \sum_{Rn} \exp(i\, \mathbf{Q}\mathbf{R}_n) \sum_{rj} \exp(i\, \mathbf{Q}\mathbf{r}_j)$

lattice sum — unit cell structure factor

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

Scattering from atoms on a crystal lattice

concept: build up crystal from lattice+basis

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

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

(primitive≡area or volume minimized)

3-D lattice: $R_n = n_1a_1 + n_2a_2 + n_3a_3$

There are: 5 distinct lattices in 2-D

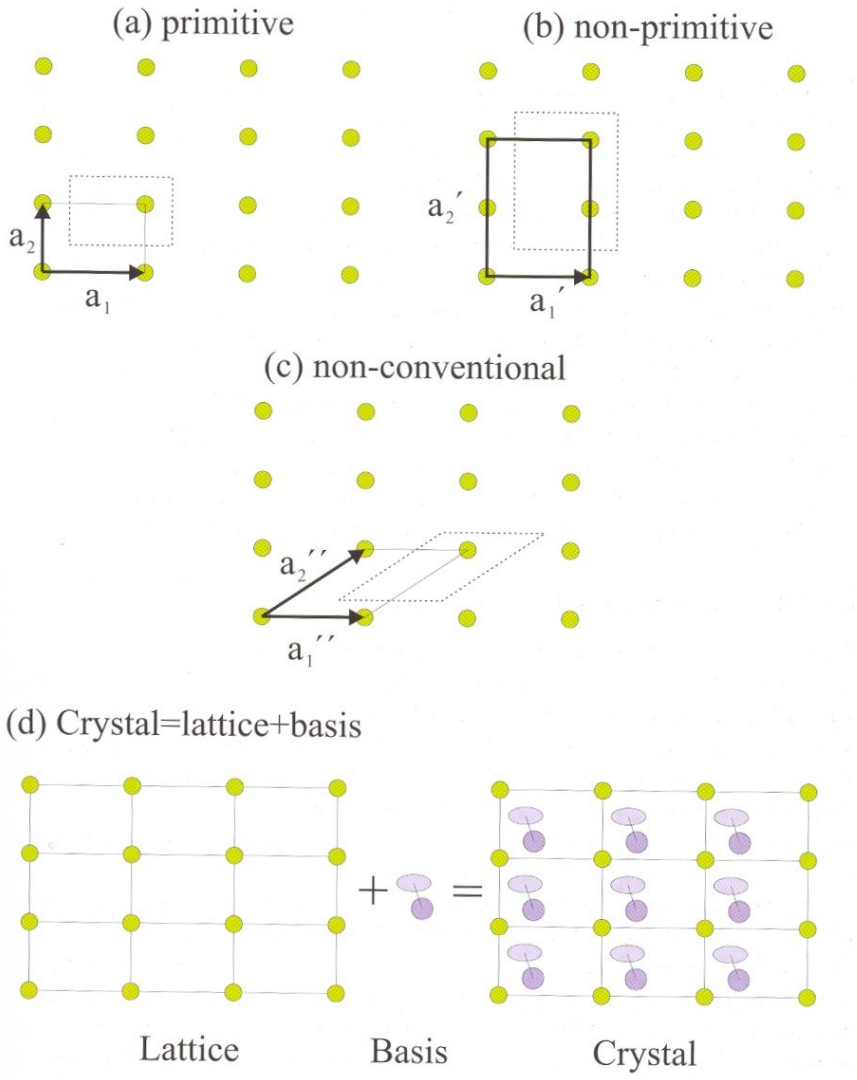
14 distinct lattices in 3-D

called the Bravais lattices

add basis to yield:

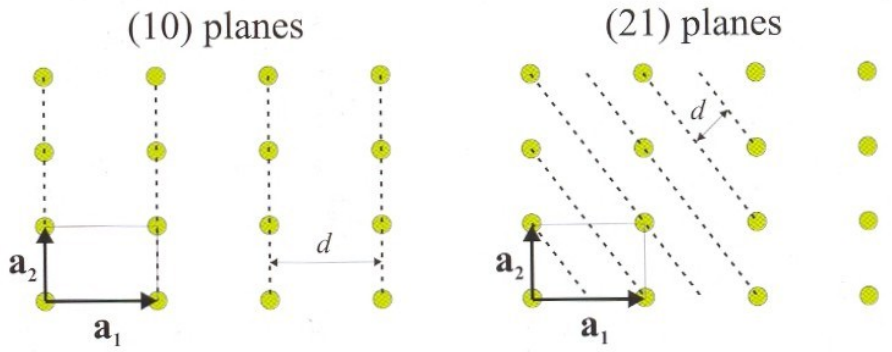
32 possible point groups

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

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

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

$$F^{crystal}(Q) = \sum_{rj} F_j^{mol}(Q) \exp(i\mathbf{Q}\mathbf{r}_j) \bullet \sum_{Rn} \exp(i\mathbf{Q}\mathbf{R}_n)$$

unit cell structure factor lattice sum

Evaluation of the lattice sum:

$$\sum_{Rn} \exp(i\,\mathbf{Q}\mathbf{R}_n) \qquad \text{(i)}$$

number of terms is enormous

(i) is of order unity (many exp(iΦ) 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.

Concept: 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) [$Q\bullet R_n$ 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.

Thus: 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:

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

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

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

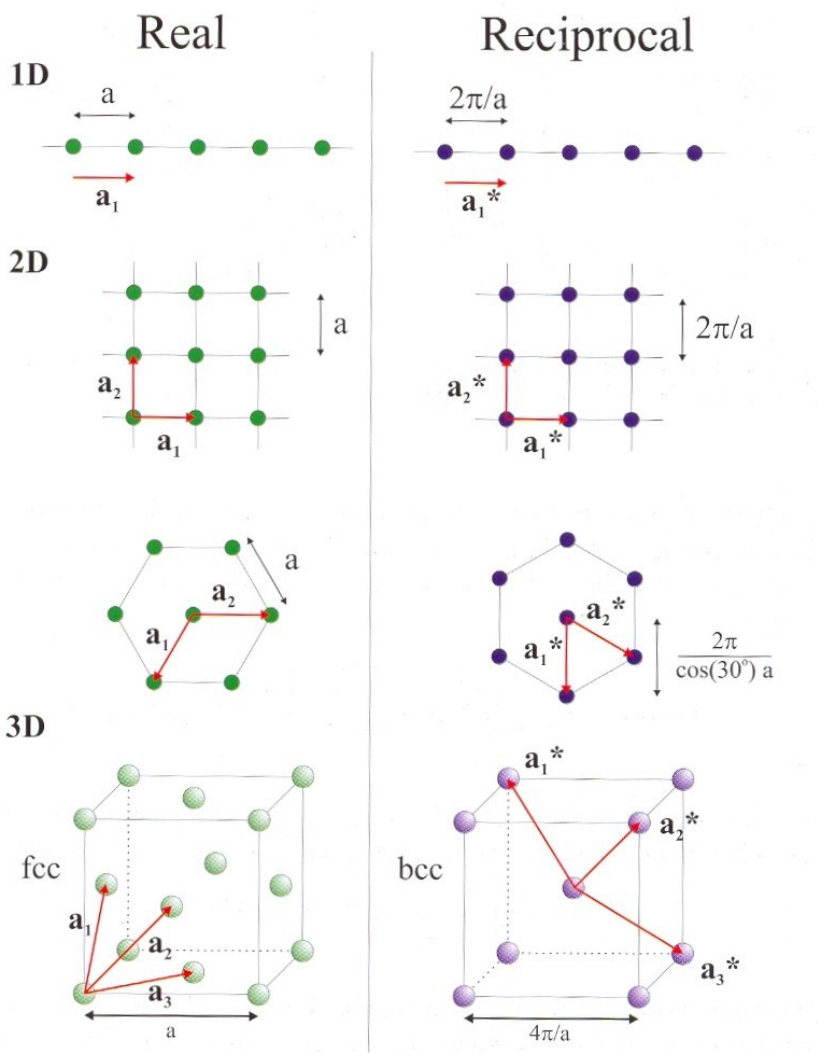
with $v_c = a_1 \bullet (a_2 \times a_3)$

<u>note:</u> 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.

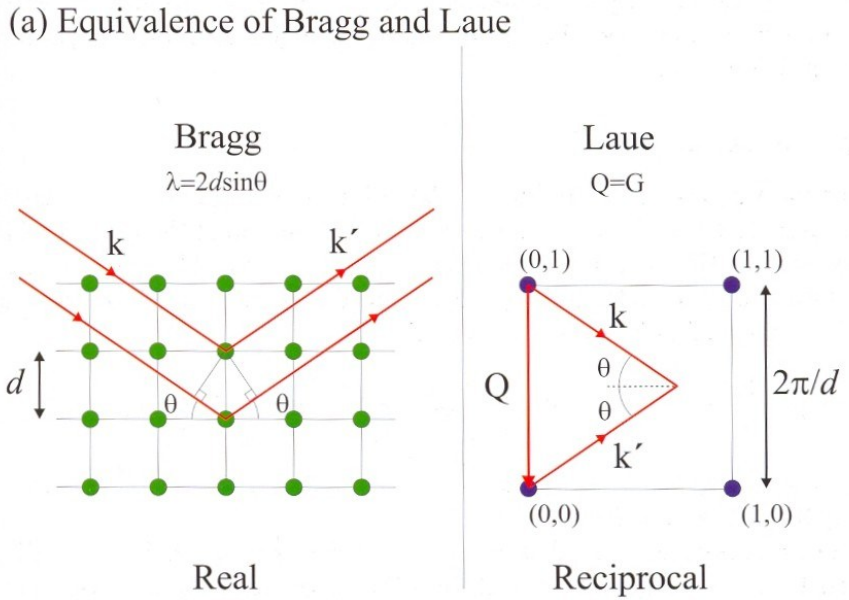
<u>Example:</u> fcc lattice

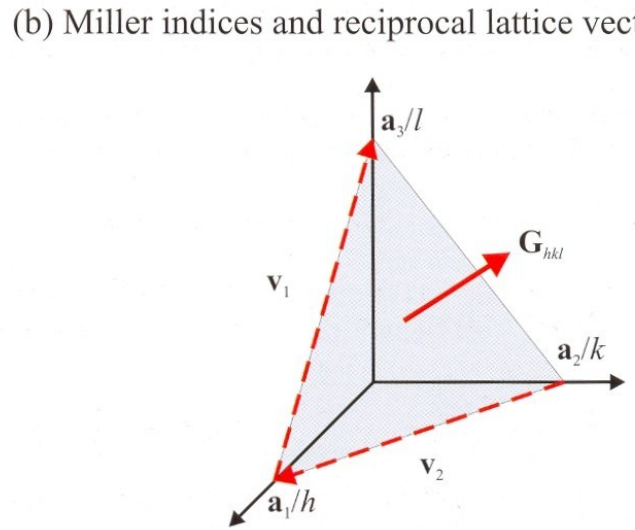
$a_1=(a/2)(y'+z')$, $a_2=(a/2)(z'+x')$, $a_3=(a/2)(x'+y')$

$$a_1^* = (4\pi/a)\,(y/2+z/2-x/2)$$
$$a_2^* = (4\pi/a)\,(z/2+x/2-y/2)$$
$$a_3^* = (4\pi/a)\,(x/2+z/2-y/2)$$



- Equivalence of the Laue and the Bragg conditions





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

The Laue condition requires

$Q = G$

Example:

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

$= (2\pi/d)\, \underline{x_2}'$

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

$\sin\theta = (2\pi/d)\lambda / 4\pi = \lambda/2d$ 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).

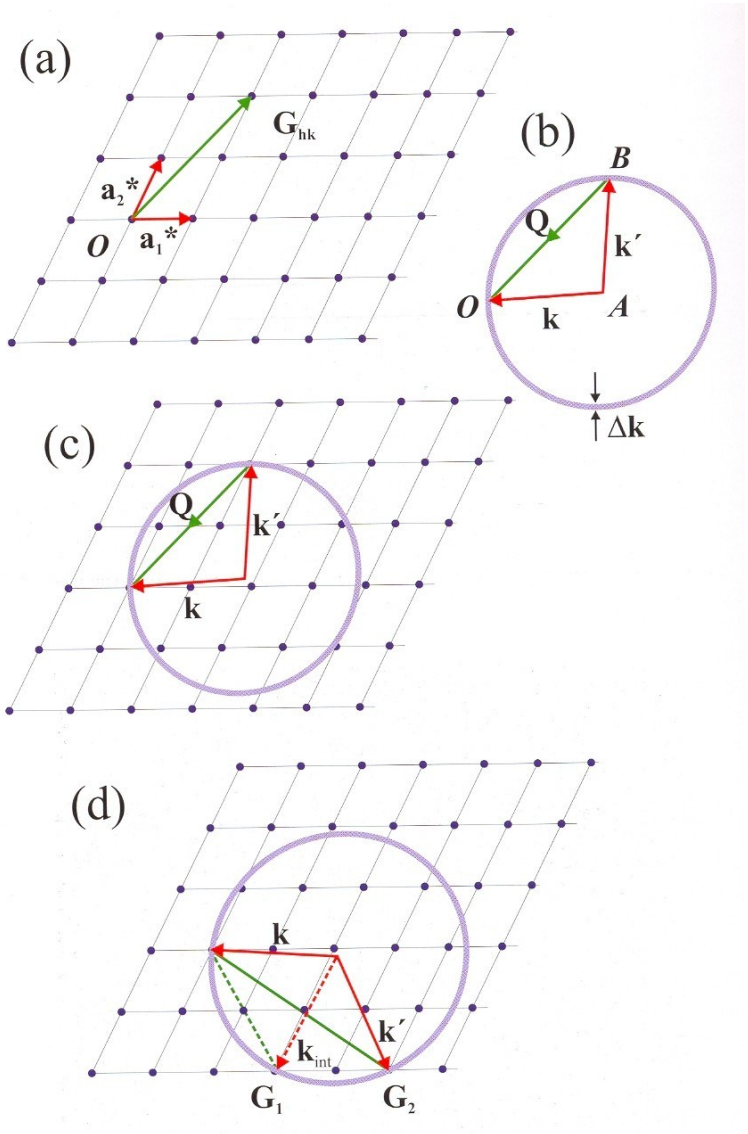
If any reciprocal lattice point falls on the circle then the Laue conditions is fulfilled (c).

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.

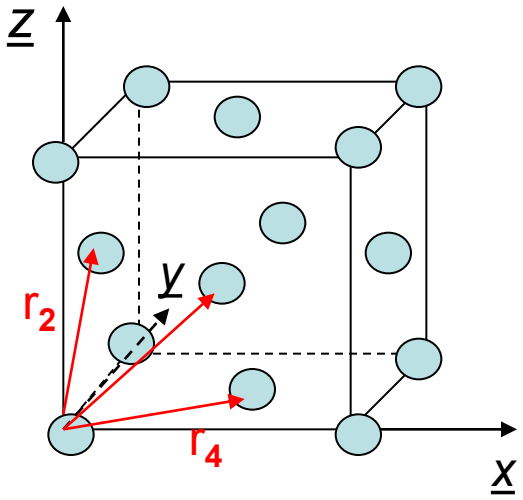
Note: More than one reciprocal lattice point can lie on the sphere ≡ multiple scattering.

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)*

$r_1 = 0$, $r_2 = ½\ a\ (\underline{y} + \underline{z})$, $r_3 = ½\ a\ (\underline{z} + \underline{x})$, $r_4 = ½\ a(\underline{x} + \underline{y})$

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

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

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

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

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

$$G \bullet r_1 = 2\pi/a\ (hx + ky + lz) \bullet 0 = 0$$
$$G \bullet r_2 = 2\pi/a\ (h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{y} + \underline{z}) = \pi\ (k+l)$$
$$G \bullet r_3 = 2\pi/a\ (h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{z} + \underline{x}) = \pi\ (h+l)$$
$$G \bullet r_4 = 2\pi/a\ (h\underline{x} + k\underline{y} + l\underline{z}) \bullet 1/2a(\underline{x} + \underline{y}) = \pi\ (h+k)$$

The unit cell structure factor for a fcc lattice

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

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

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

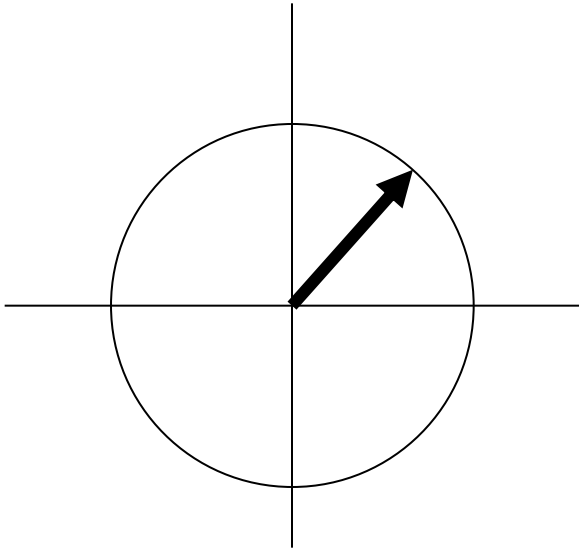
$$I_{hkl}^{fcc}(\mathbf{Q}) = F(\mathbf{Q}) \bullet F^*(\mathbf{Q})$$

<u>Reflections:</u>

100 forbidden

111 allowed

200 allowed



Lattice sums

$S_N(\mathbf{Q}) = \sum_{RN} \exp(i\mathbf{Q}\mathbf{R_N})$

1-D: $R_N = na$

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

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

Als-Nielsen&McMorrow p.51

Laue condition almost fullfilled:

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

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

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

width:

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

FWHM ~ 1/N

N large:

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

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

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

Lattice sums (2D & 3D)

$$S_N(Q) = \sum_{RN} \exp(iQR_N)$$

2-D:

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

for large N1, N2:

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

A* area of unit cell in reciprocal space

3-D:

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

with $\mathbf{G}=h\mathbf{a1}^*+k\mathbf{a}_2^*+l\mathbf{a}_3^*$, N: number of unit cells, v^*_c volume unit cell in reciprocal space

Further topics

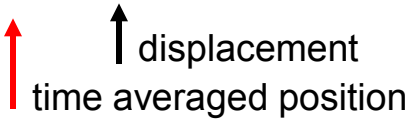
- Quasiperiodic lattices
- Crystal truncation rods
- Lattice vibrations, Debye-Waller factor, TDS
- Lorentz factor
- Diffraction from a fiber
- 2-D crystallography

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

$F^{crystal}(\mathbf{Q}) = \sum_n f(Q) \exp(i\, \mathbf{Q}\bullet\mathbf{r}_n)$

Elastic waves (phonons) excited at finite T.

Effect of vibrations: $r_n = R_n + u_n$



$<u_n> = 0$ $< >$: thermal average

$$I = <\sum_n f(Q)\exp[iQ(R_m+u_m)\, x \sum_n f^*(Q) \exp[-iQ(R_n+u_m)>$$

$$= \sum_m \sum_n f(Q)\, f^*(Q)\exp[iQ(R_m+R_n)\, x <\exp[iQ(u_m-u_n)>$$

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

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

Gaussian distribution of displacements:

$< e[ix] > = \exp [-<x^2>]$

$<\exp[iQ\{u_{Qm}-u_{Qn})]> =$

$\exp[-1/2 <Q^2(u_{Qm}-u_{Qn})^2>$

$= \exp [-1/2\, Q^2 <(u_{Qm}-u_{Qn})^2>$

$= \exp[-1/2Q^2<u^2_{Qm}>\exp[-1/2\, Q^2<u^2_{Qn}>$

$\times \exp[Q^2<u_{Qm}u_{Qn}>$

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

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

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

$\sum_m \sum_n f(Q)\exp[iQR_m]\, f^*(Q)\, \exp[-iQR_n] \{\exp[Q^2(u_{Qm}u_{Qn}) - 1\}$

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

"Thermal Diffuse Scattering" (TDS)

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

with exp [-M] : Debye-Waller factor

Thermal Diffuse Scattering (TDS)

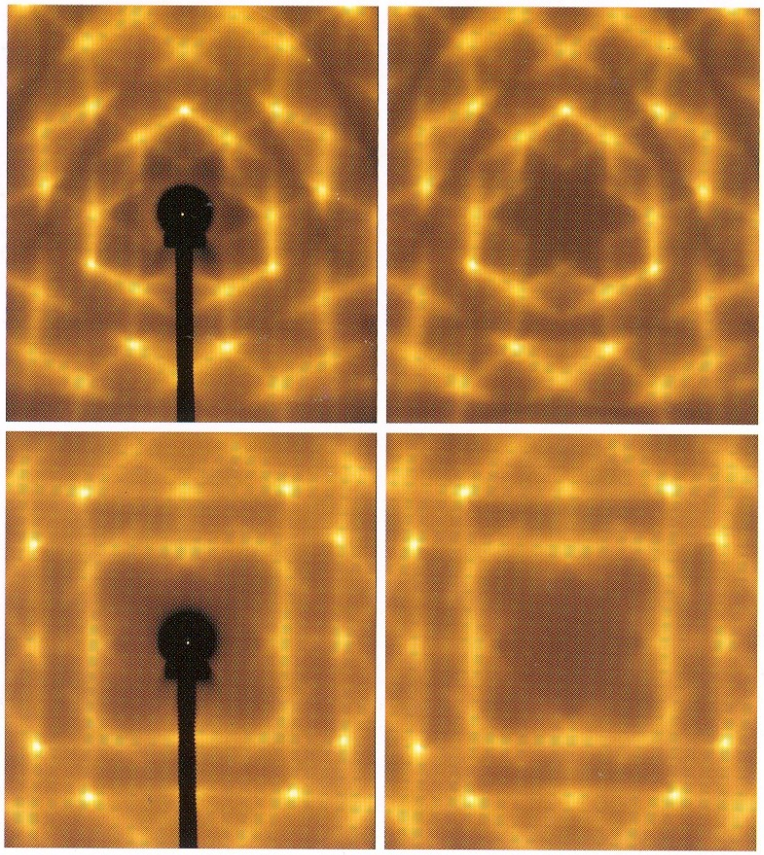


Figure 4.18: Thermal diffuse scattering (TDS) from Si. The data were collected in a transmission geometry (photon energy 28 keV) using an image plate detector. The data were collected on the UNI-CAT beamline at the Advanced Photon Source in an exposure time of ∼10 s. The top and bottom left panels show 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

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

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

$$= B_j^T (\sin\theta/\lambda)^2$$

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

for isotropic vibrations:

$$\langle u^2 \rangle = \langle u^2_x + u^2_y + u^2_z \rangle = 3 \langle u^2_C \rangle$$

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

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 $\Phi(x)\ (1/x) \int \xi \,/\, (\exp[\xi]-1)\, d\xi$

Θ: Debye temperature

m_A: atomic mass

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

Debye-Waller factor

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

	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

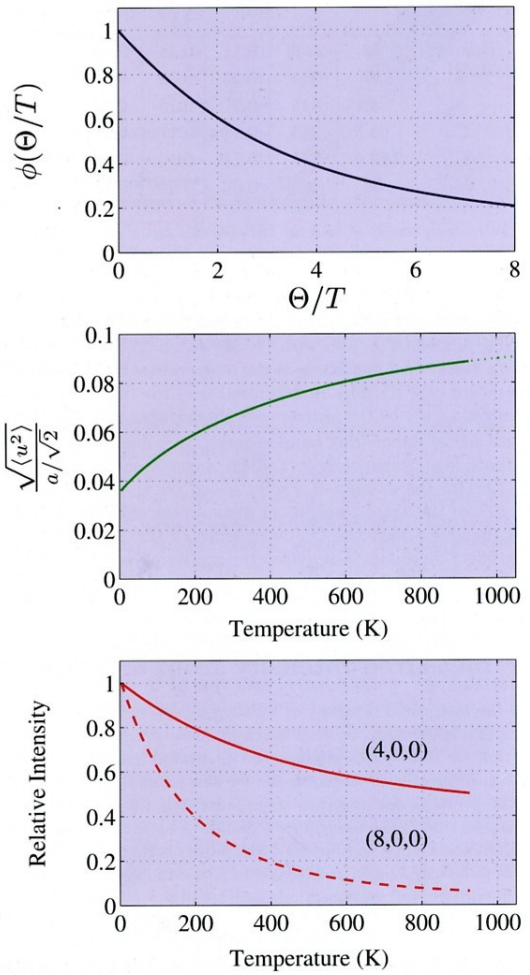


Figure 4.19: ⋆ Top: plot of the value of the integral $\phi(x)$ versus $x = \Theta/T$. Middle: temperature dependence of the rms fluctuation **u** in units of $a/\sqrt{2}$ for Al. Bottom: the relative intensity of the scattered intensity from Al as a function of temperature. The curves were calculated 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.