Methoden moderner Röntgenphysik II: Streuung und Abbildung

Lecture 6	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2017 G. Grübel, A. Philippi-Kobs, O. Seeck, T. Schneider, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	12:30 - 14:00	(starting 4.4.)
	Thursday	8:30 - 10:00	(until 13.7.)

DESY

Methoden moderner Röntgenphysik II: Streuung und Abbildung

Part I:
Basics of X-ray Physics
by Gerhard Grübel (GG)

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 from Interfaces
Snell's Law, Fresnel Equations

Kinematical Diffraction (I)
Diffraction from an Atom, a Molecule, from Liquids, Glasses, …

Kinematical Diffraction (II)
Diffraction from a Crystal, Reciprocal Lattice, Structure Factor, …

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Scattering from a Crystal

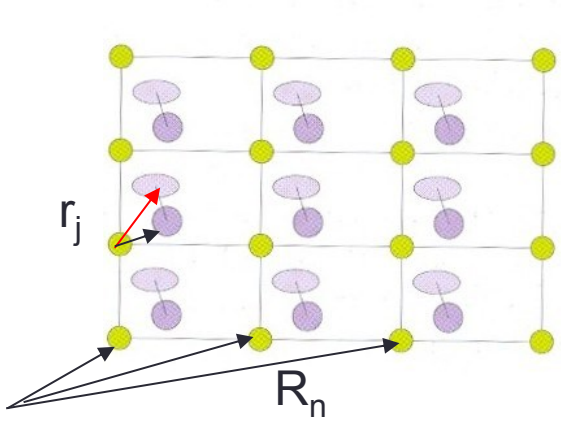
$$A(\mathbf{Q}) = -r_0 \sum_{r_j'} e^{i\mathbf{Q}\mathbf{r}_j'}$$

Crystallography:

Determine electron density within unit cell

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

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



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

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

Scattering from Atoms on a Crystal Lattice

Concept: build up crystal from **lattice** + **basis**

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

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

(primitive ≡ area or volume minimized)

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

There are: 5 distinct lattices in 2-D

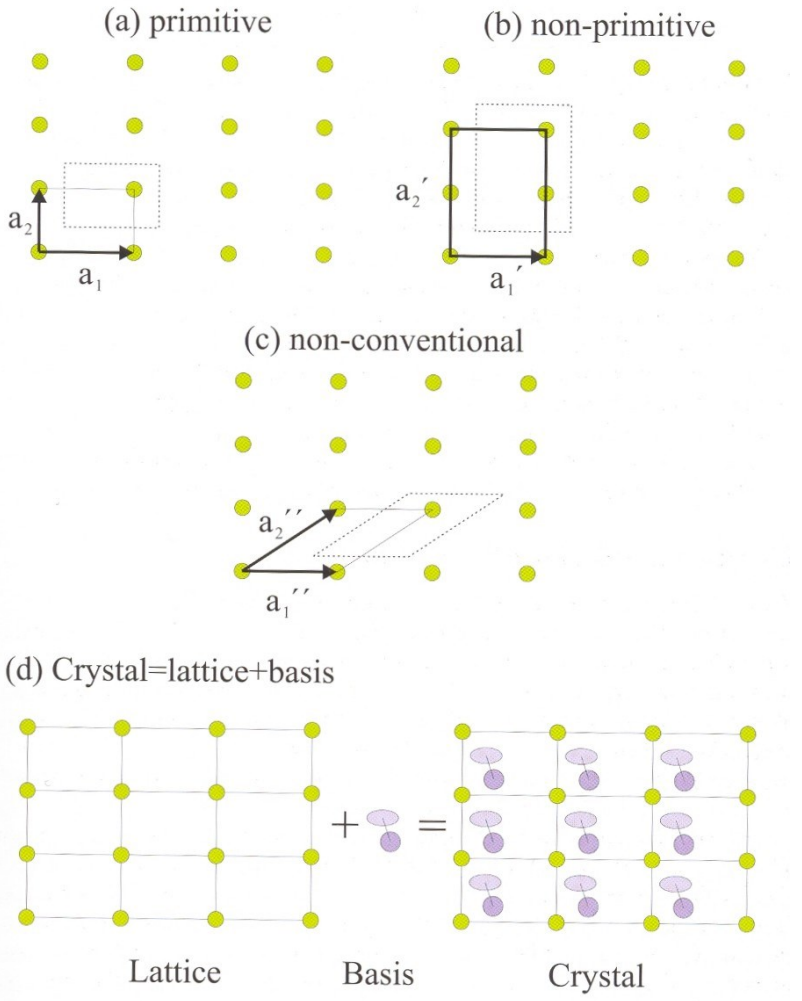
14 distinct lattices in 3-D

called the Bravais lattices

Add basis to yield:

32 possible point groups

230 possible symmetry groups



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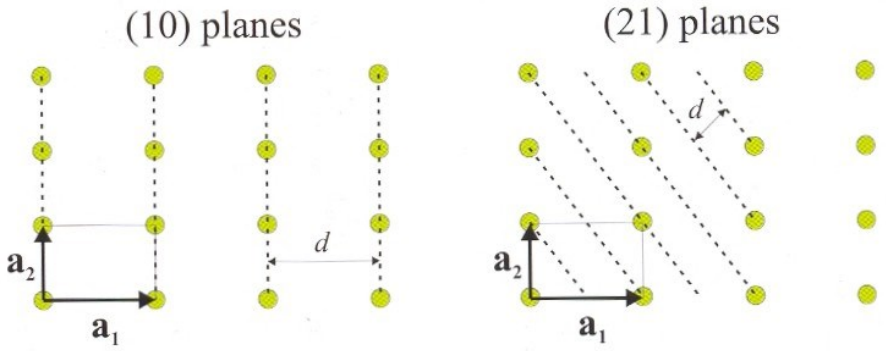
Lattice Planes and Miller Indices

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:

$$\mathbf{R_n} + \mathbf{r_j}$$

origin unit cell atom in cell

$$F^{crystal}(\mathbf{Q}) = \sum_{\mathbf{r_j}} F_j{}^{mol}(\mathbf{Q}) e^{i\mathbf{Q}\mathbf{r_j}} \bullet \sum_{\mathbf{R_n}} e^{i\mathbf{Q}\mathbf{R_n}}$$

unit cell structure factor lattice sum

Evaluation of the Lattice Sum:

$\sum_{\mathbf{R_n}} e^{i\mathbf{QR_n}}$ (i)

number of terms is enormous

(i) is of order unity (many $e^{i\phi}$ 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.

Concept: construct an artificial lattice with lattice vectors $\mathbf{a_1}^*$, $\mathbf{a_2}^*$ and $\mathbf{a_3}^*$ such that:

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

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

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

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

since

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

only if

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

so that the scattering amplitude will not vanish.

Thus: Q needs to be a reciprocal lattice vector.

Laue condition

Q = G

Wave vector transfer has 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:

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

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

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

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

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

$$\mathbf{a}_1 = \left(\frac{a}{2}\right)(\mathbf{y}' + \mathbf{z}'), \qquad \mathbf{a}_2 = \left(\frac{a}{2}\right)(\mathbf{z}' + \mathbf{x}'),$$

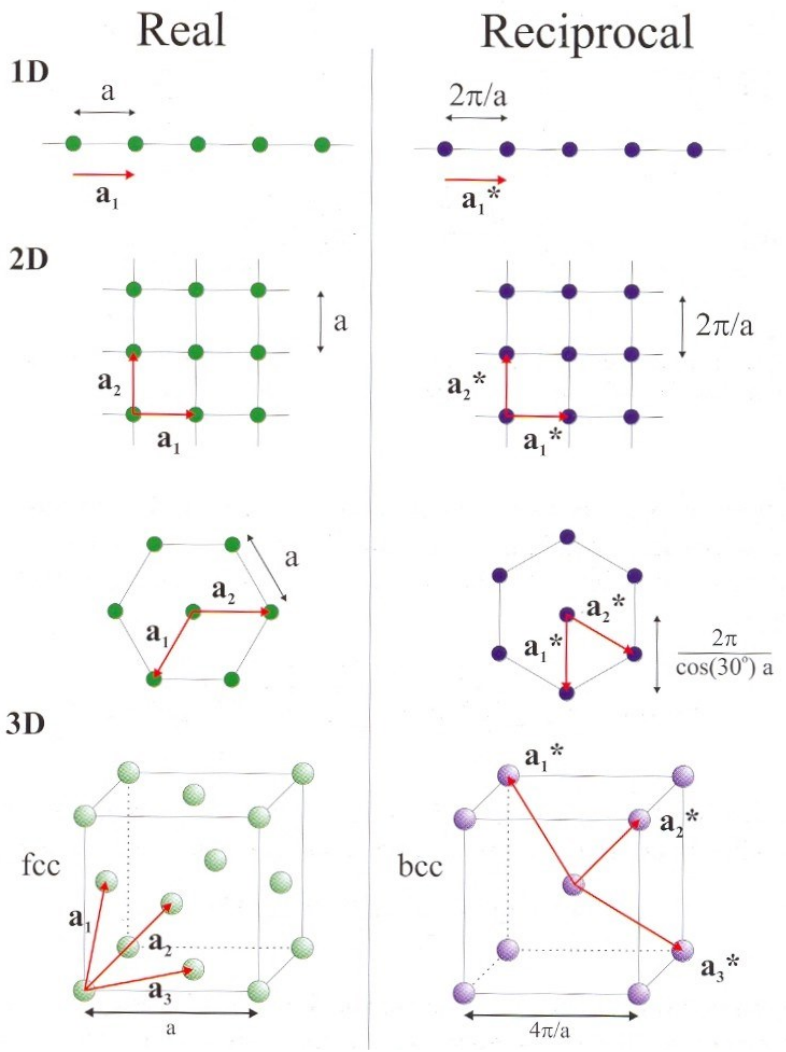
$$\mathbf{a}_3 = \left(\frac{a}{2}\right)(\mathbf{x}' + \mathbf{y}')$$

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

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

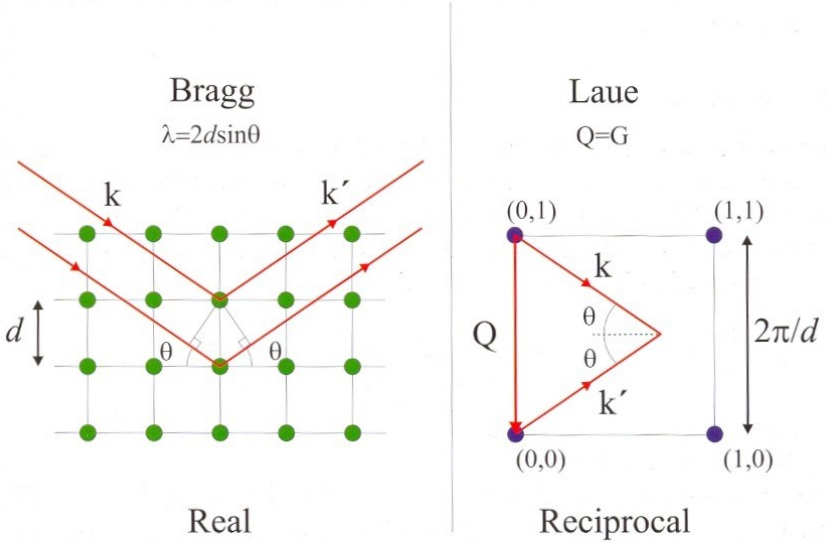
$$\mathbf{a}_3^* = \frac{4\pi}{a}\left(\frac{\mathbf{x}'}{2} + \frac{\mathbf{z}'}{2} - \frac{\mathbf{y}'}{2}\right)$$

(**x**', **y**', **z**' unit vectors)

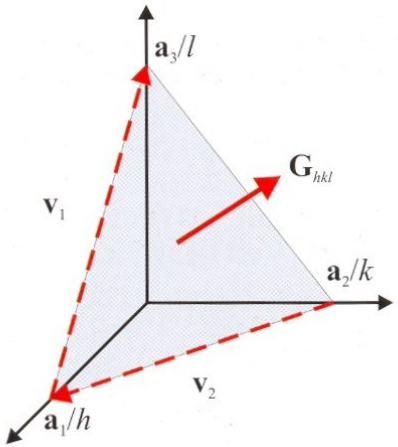


Equivalence of the Laue and the Bragg Conditions

(a) Equivalence of Bragg and Laue



(b) Miller indices and reciprocal lattice vectors



Bragg's law: $\sin\theta = \frac{\lambda}{2d}$

The Laue condition requires
$\mathbf{Q} = \mathbf{G}$

Example:

$$\mathbf{Q} = (0,1) = 0 \bullet \mathbf{a}_1^* + 1 \bullet \mathbf{a}_2^*$$

$$= \frac{2\pi}{d}\mathbf{x}_2'$$

$$\sin\theta = \frac{\left(\frac{Q}{2}\right)}{k} = \frac{Q\lambda}{4\pi}$$

$$\sin\theta = \frac{\frac{2\pi}{d}\lambda}{4\pi} = \frac{\lambda}{2d} \quad \text{q. e. d.}$$

The Ewald Sphere

Visualization of diffraction effects in reciprocal space (a).

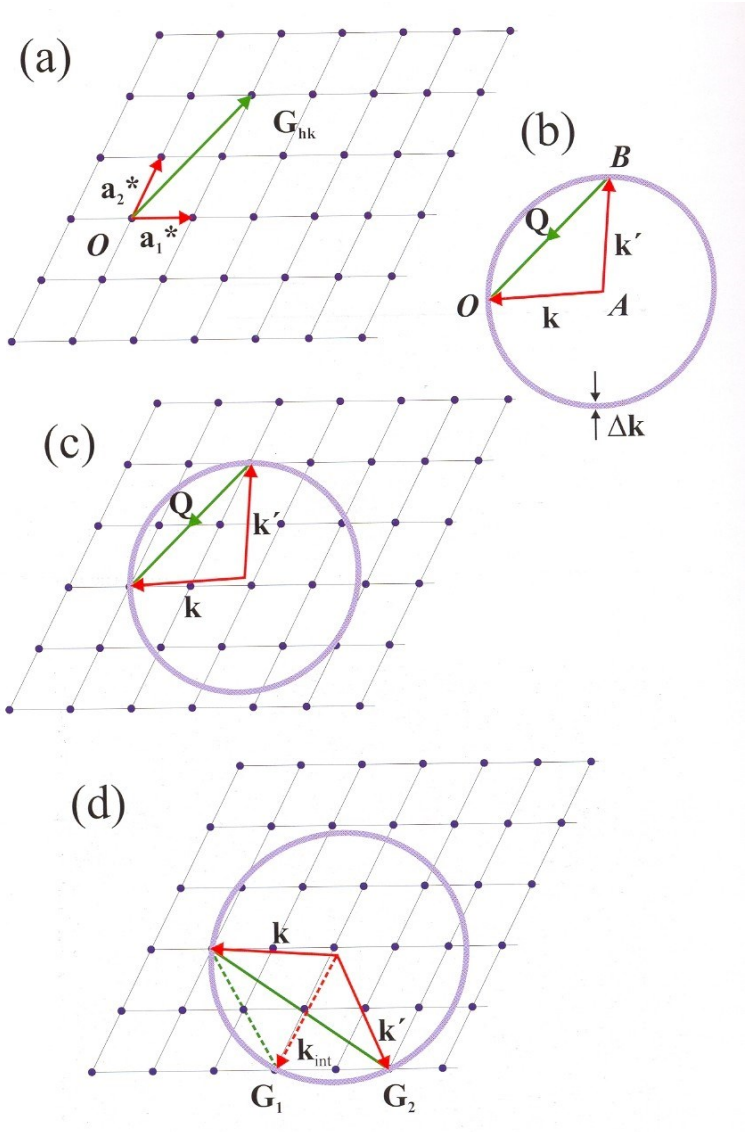
Laue condition requires $\mathbf{Q} = \mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^*$

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.

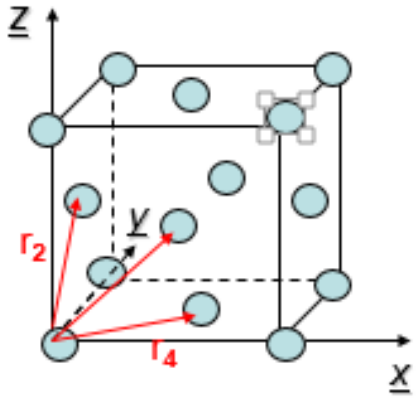


Note: More than one reciprocal lattice point can lie on the sphere ≡ multiple scattering.

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

$$F^{uc}(\mathbf{Q}) = \sum_{rj} F_j^{mol}(\mathbf{Q}) e^{i\mathbf{Q}\mathbf{r}_j}$$



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

$$\mathbf{r}_1 = \mathbf{0} \quad , \quad \mathbf{r}_2 = \frac{1}{2}a\left(\underline{\mathbf{y}} + \underline{\mathbf{z}}\right) \quad , \quad \mathbf{r}_3 = \frac{1}{2}a\left(\underline{\mathbf{z}} + \underline{\mathbf{x}}\right) \quad , \quad \mathbf{r}_4 = \frac{1}{2}a\left(\underline{\mathbf{x}} + \underline{\mathbf{y}}\right)$$

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

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

$$\mathbf{a}_2^* = \frac{2\pi}{v_c}(\mathbf{a}_2 \times \mathbf{a}_3) = \frac{2\pi}{a^3}\left[a\underline{\mathbf{z}} \times a\underline{\mathbf{x}}\right] = \frac{2\pi}{a}\left[\underline{\mathbf{z}} \times \underline{\mathbf{x}}\right] = \frac{2\pi}{a}\underline{\mathbf{y}}$$

$$\mathbf{a}_3^* = \frac{2\pi}{v_c}(\mathbf{a}_2 \times \mathbf{a}_3) = \frac{2\pi}{a^3}\left[a\underline{\mathbf{x}} \times a\underline{\mathbf{y}}\right] = \frac{2\pi}{a}\left[\underline{\mathbf{x}} \times \underline{\mathbf{y}}\right] = \frac{2\pi}{a}\underline{\mathbf{z}}$$

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

$$\mathbf{G}\bullet\mathbf{r}_1 = \frac{2\pi}{a}\left(h\underline{\mathbf{x}} + k\underline{\mathbf{y}} + l\underline{\mathbf{z}}\right) \bullet \mathbf{0} = 0$$

$$\mathbf{G}\bullet\mathbf{r}_2 = \frac{2\pi}{a}\left(h\underline{\mathbf{x}} + k\underline{\mathbf{y}} + l\underline{\mathbf{z}}\right) \bullet \frac{1}{2a}\left(\underline{\mathbf{y}} \times \underline{\mathbf{z}}\right) = \pi(k + l)$$

$$\mathbf{G}\bullet\mathbf{r}_3 = \frac{2\pi}{a}\left(h\underline{\mathbf{x}} + k\underline{\mathbf{y}} + l\underline{\mathbf{z}}\right) \bullet \frac{1}{2a}\left(\underline{\mathbf{z}} \times \underline{\mathbf{x}}\right) = \pi(h + l)$$

$$\mathbf{G}\bullet\mathbf{r}_4 = \frac{2\pi}{a}\left(h\underline{\mathbf{x}} + k\underline{\mathbf{y}} + l\underline{\mathbf{z}}\right) \bullet \frac{1}{2a}\left(\underline{\mathbf{x}} \times \underline{\mathbf{y}}\right) = \pi(h + k)$$

The Unit Cell Structure Factor for a fcc Lattice

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

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

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

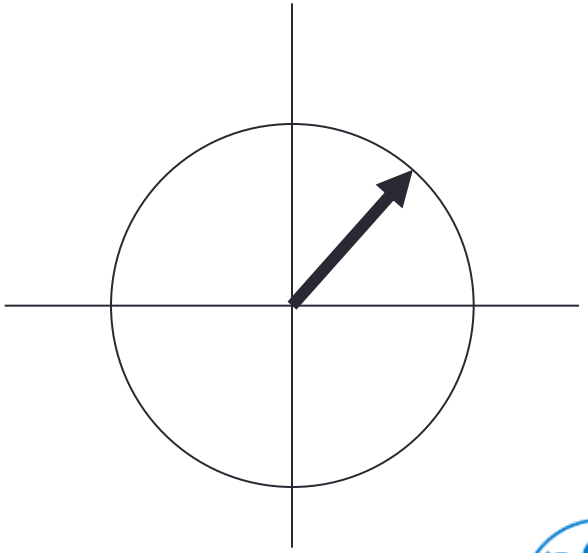
$$I_{hkl}^{fcc}(\mathbf{Q})(\mathbf{Q}) = F(\mathbf{Q}) \bullet F^{*}(\mathbf{Q})$$

<u>Reflections:</u>

100 forbidden

111 allowed

200 allowed



Lattice Sums

$$S_N(Q) = \sum_{R_N} e^{iQR_N}$$

1D: $R_N = na$

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

$$|Sn(Q)| = \frac{\sin(NQa/2)}{\sin(Qa/2)}$$ Als-Nielsen&McMorrow p.51

Laue condition almost fulfilled:

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

$$|S_N(\xi)| = \frac{\sin(N\pi\xi)}{\sin(\pi\xi)}$$

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

Width:

$$\left|S_N\left(\xi = \frac{1}{2N}\right)\right| \approx \left(\frac{2}{\pi}\right) N \approx \frac{1}{2} N$$

FWHM ~ 1/N

N large:

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

$$|S_{N(Q)}| \longrightarrow a^* \Sigma_{Gh}\, \delta(Q - G_h)$$

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

Lattice Sums (2D & 3D)

$$S_N(Q) = \sum_{R_N} e^{iQR_N}$$

2D:

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

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

3D:

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

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

Quasi-periodic 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)

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

Elastic waves (phonons) excited at finite T.

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

displacement

time averaged position

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

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

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

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

$$\langle e^{i\mathbf{Q}(\mathbf{u}_m-\mathbf{u}_n)} \rangle = \langle e^{i\mathbf{Q}(u_{Qm}-u_{Qn})} \rangle$$

Gaussian distribution of displacements:

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

$$\langle e^{iQ(u_{Qm}-u_{Qn})} \rangle = e^{-\frac{1}{2}\langle Q^2(u_{Qm}-u_{Qn})^2 \rangle}$$

$$= e^{-\frac{1}{2}Q^2\langle(u_{Qm}-u_{Qn})^2\rangle}$$

$$= e^{-\frac{1}{2}Q^2\langle u_{Qm}^2\rangle} e^{-\frac{1}{2}Q^2\langle u_{Qn}^2\rangle} \times e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

Lattice Vibrations, Debye-Waller Factor, TDS (2)

$$e^{Q^2<u_{Qm}u_{Qn}>} = 1 + \left\{e^{Q^2<u_{Qm}u_{Qn}>} - 1\right\}$$

$$\Rightarrow I(\boldsymbol{Q}) = \sum_m \sum_n f(\mathbf{Q}) e^{-\frac{1}{2}Q^2<u_{Qm}^2>} e^{i\mathbf{Q}\mathbf{R}_m} f^*(\mathbf{Q})\, e^{-\frac{1}{2}Q^2<u_{Qn}^2>} e^{-i\mathbf{Q}\mathbf{R}_n} +$$

$$\sum_m \sum_n f(\mathbf{Q})\, e^{i\mathbf{Q}\mathbf{R}_m} f^*(\mathbf{Q}) e^{-i\mathbf{Q}\mathbf{R}_n} \left\{e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right\}$$

increasing with displacements: $<u_{Qm}u_{Qn}>$

"Thermal Diffuse Scattering" (TDS)

$$f^{atom} = f(Q)e^{-\frac{1}{2}Q^2<u^2>} = f(Q)e^{-M}$$

with e^{-M} : Debye-Waller factor

Thermal Diffuse Scattering (TDS)

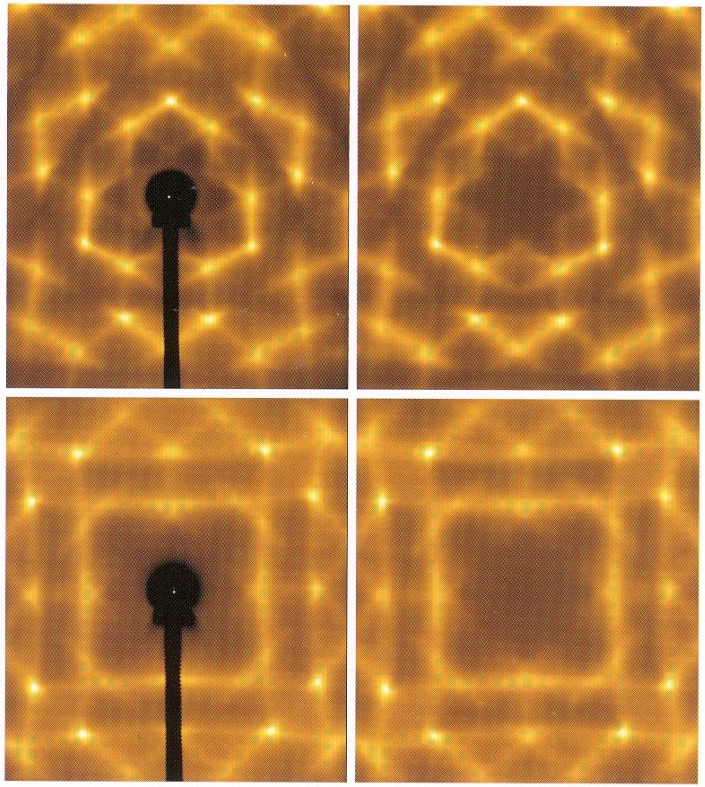


Figure 4.18: Thermal diffuse scattering (TDS) from Si. The data were collected in a transmission geometry (photon energy 28 keV) using an image plate detector. The data were collected on the UNI-CAT beamline at the Advanced Photon Source in an exposure time of ∼10 s. The top and bottom left panels show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

Unit cell structure factor including the DWF

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

$$M_j = \frac{1}{2} Q^2 < u_j^2 > = \frac{1}{2}\left(\frac{4\pi}{\lambda}\right)^2 (\sin\theta)^2 < u_j^2 >$$

$$= B_j^T \left(\frac{\sin\theta}{\lambda}\right)^2$$

with $B_j^T = 8\pi^2 < u_j^2 >$

For isotropic vibrations:

$$< u^2 > = < u_x^2 + u_y^2 + u_z^2 > = \ 3 \ < u_c^2 >$$

$$B_{T,\ \text{isotropic}} = \frac{8\pi^2}{3} < u_j^2 >$$

Within the Debye-model:

$$B_T = \frac{6h^2}{m_A k_B \Theta} \left\{ \left(\frac{\phi(\Theta/T)}{\Theta/T} \right) + \frac{1}{4} \right\}$$

With $\phi(x) \equiv \left(\frac{1}{x}\right) \int_0^x \frac{\xi}{(e^{\xi}-1)}\, d\xi$

Θ: Debye temperature

m_A: atomic mass

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

Debye-Waller Factor

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

	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

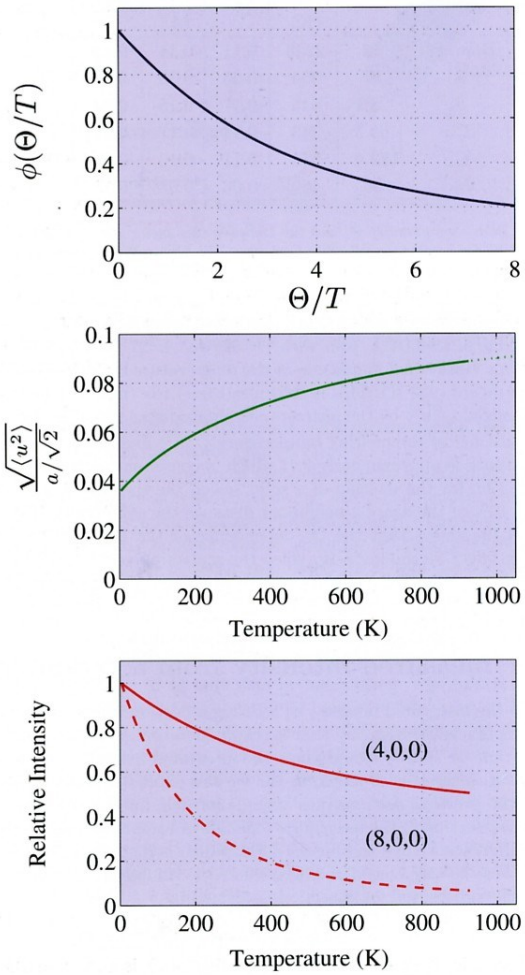


Figure 4.19: ⋆ Top: plot of the value of the integral $\phi(x)$ versus $x = \Theta/T$. Middle: temperature dependence of the rms fluctuation **u** in units of $a/\sqrt{2}$ for Al. Bottom: the relative intensity of the scattered intensity from Al as a function of temperature. The curves were calculated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