Advanced Topics in Condensed Matter (ATCOMA): Lecture 3

for physics students for VF (Vertiefungsfächer)

- “Bio/Medical Physics“
- “Nanostructures“
- “Condensed Matter”

for NanoScience students

Last week:

- Introduction and some general concepts
- Elementary scattering process

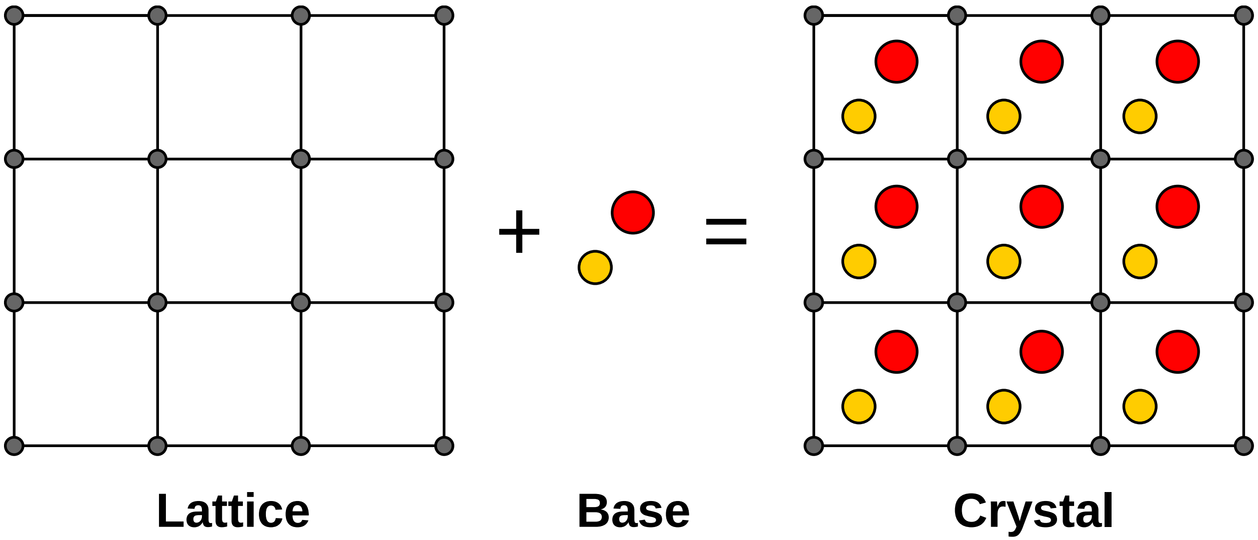
Today:

- Scattering from crystals

Later:

- Scattering from disordered systems / liquids
- Scattering from surfaces and interfaces
- General scattering theory: Correlations in space and time
- Miscellaneous topics, applications, and examples

3.1 Scattering from crystals

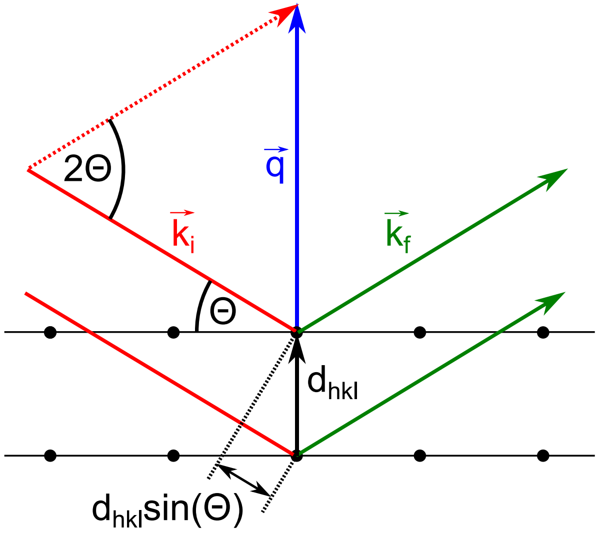


3.1 Scattering from crystals

Different ways to “discuss“ Bragg peaks

1) Bragg‘s law

$$\boxed{n\lambda = 2d_{hkl}\sin\theta}$$



hkl = Miller indices

2) Scattering phase

constructive interference

$$e^{iqd_{hkl}} = 1$$

$$qd_{hkl} = 2\pi n$$

$$\frac{4\pi}{\lambda}\sin\theta\, d_{hkl} = 2\pi n$$

$$n\lambda = 2d_{hkl}\sin\theta$$

3) Reciprocal space

positions of the diffraction maxima at reciprocal space vectors

$$\boxed{\vec{q} = \vec{G}_{hkl}}$$

3.1 Scattering from crystals

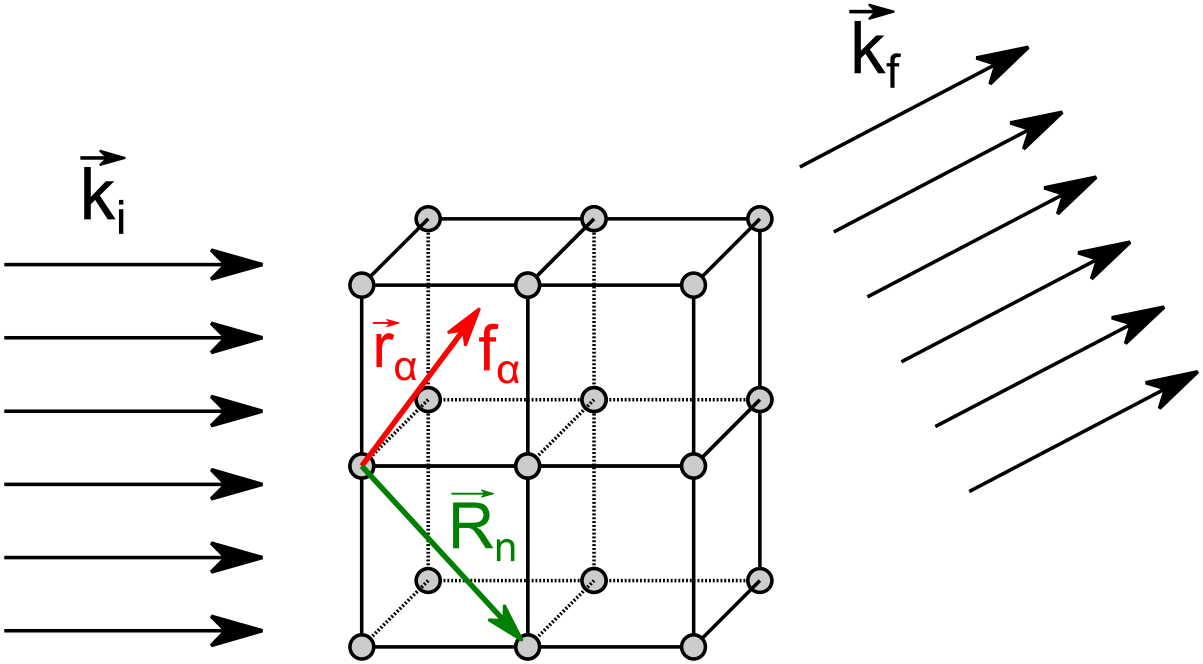
General approach

... consider scattering from atoms $f(q)$

... then sum over all atoms in unit cell at positions $\vec{r}_\alpha$

... then sum over all unit cells at positions $\vec{R}_n$

...



3.1 Scattering from crystals

The scattering amplitude of a crystal is given by the summation of the scattered waves of all individual atoms

$$\boxed{E_1 = E_0 r_e \frac{e^{i(\vec{k}\cdot\vec{R}-\omega t)}}{R} \sum_{n,\alpha} f_\alpha e^{i\vec{q}\cdot\vec{R}_{n\alpha}}}$$

with the positions $\vec{R}_{n\alpha} = \vec{r}_\alpha + \vec{R}_n$

Position of the atom (α) within the unit cell (basis)

Position of the unit cell (n) within the crystal (lattice)

Thus

$$\boxed{E_1 = E_0 r_e \frac{e^{i(\vec{k}\cdot\vec{R}-\omega t)}}{R} \underbrace{\sum_{\alpha}^{UC} f_\alpha e^{i\vec{q}\cdot\vec{r}_\alpha}} \underbrace{\sum_{n_1}^{N_1} e^{i\vec{q}\cdot\vec{a}_1 n_1} \sum_{n_2}^{N_2} e^{i\vec{q}\cdot\vec{a}_2 n_2} \sum_{n_3}^{N_3} e^{i\vec{q}\cdot\vec{a}_3 n_3}}}$$

peak intensity
→ basis

Structure factor F
Gives information about position of atoms in the unit cell f_α at $\vec{r}_\alpha$

Geometric series $\sum x^n$
Gives information about the lattice parameters $\vec{a}_1, \vec{a}_2, \vec{a}_3, N_1, N_1, N_3$

peak position
→ lattice

3.1 Scattering from crystals

The total scattering intensity $I = E_1 E_2^*$ is given by

$$\boxed{I = I_0 \frac{r_e^2}{R^2} \quad |F(\vec{q})|^2 \quad L_{N_1}(\vec{q} \cdot \vec{a}_1) L_{N_2}(\vec{q} \cdot \vec{a}_2) L_{N_3}(\vec{q} \cdot \vec{a}_3)}$$

Which yields, after evaluation of the geometric series,
the interference functions

$$\boxed{L_N(qa) \coloneqq \left| \frac{e^{iqaN} - 1}{e^{iqa} - 1} \right|^2 = \frac{sin^2(qaN/2)}{sin^2(qa/2)}}$$

3.1 Scattering from crystals

Properties of interference function

$$L_{max} \sim N^2$$

$$\Delta L_N(qa) \sim N^{-1}$$

$$\int L_N(qa)dq \sim N$$

For $N \rightarrow \infty$, $L_N(qa)$ → δ-function with maxima at **(Laue equations)**

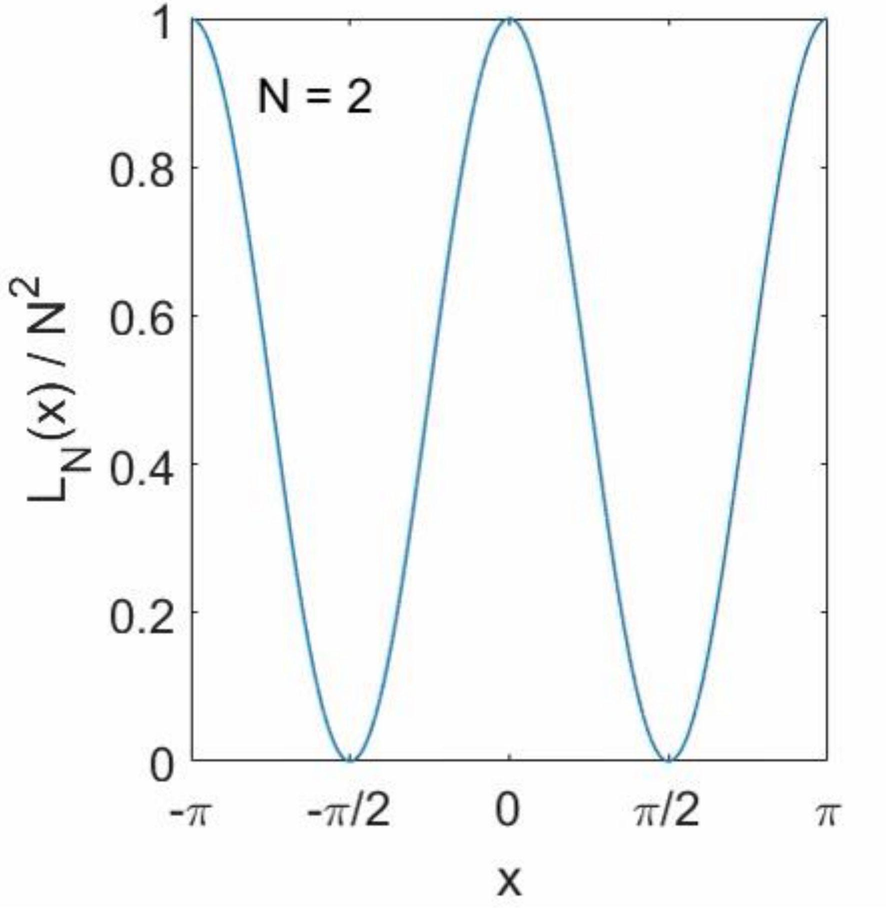
$$\vec{q} \cdot \vec{a}_1 = 2\pi h$$

$$\vec{q} \cdot \vec{a}_2 = 2\pi k$$

$$\vec{q} \cdot \vec{a}_3 = 2\pi l$$

i.e. $\vec{q} = \vec{G}_{hkl}$

$$\frac{L_N(x)}{N^2} = \frac{sin^2(Nx)}{N^2 sin^2(x)}$$



Question: Isn‘t $L_N(qa)$ → δ-function unphysical?

3.2 Practical examples and contrast considerations

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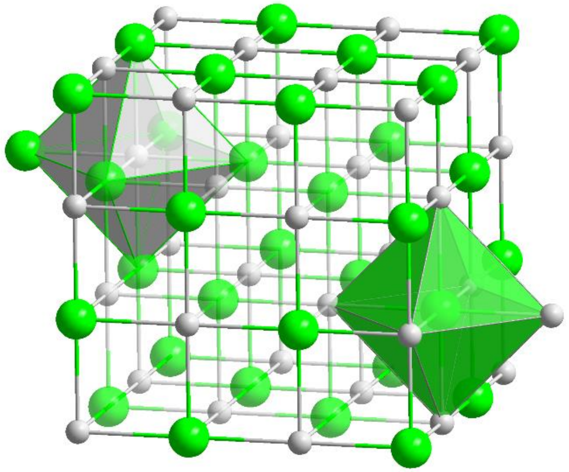
Example: sodium chloride



Source: https://de.wikipedia.org/wiki/Natriumchlorid

face-centered cubic (fcc) with 2-atom basis

$$\vec{r}_{Na} = (0{,}0{,}0) \times \tfrac{1}{2} a_0$$

$$\vec{r}_{Cl} = (1{,}0{,}0) \times \tfrac{1}{2} a_0$$

resulting structure factor

$$\begin{aligned} F_{NaCl} &= 4(f_{Na} + f_{Cl}) && \text{for } h,k,l \text{ even} \\ &= 4(f_{Na} - f_{Cl}) && \text{for } h,k,l \text{ odd} \\ &= 0 && \text{for } h,k,l \text{ mixed} \end{aligned}$$

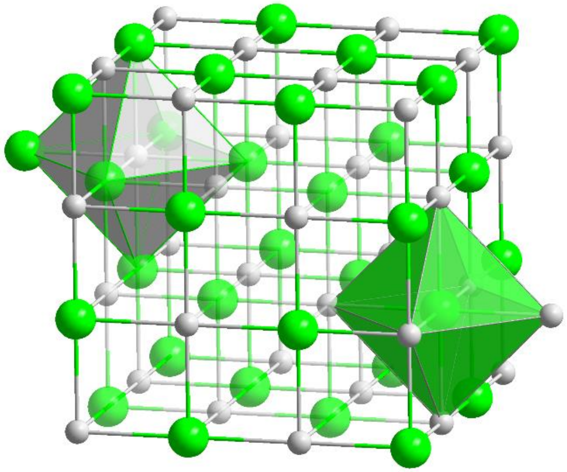
calculation of structure factor

$$F_{NaCl} = f_{Na}\left(1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right) + f_{Cl}\left(e^{i\pi(h+k+l)} + e^{i\pi l} + e^{i\pi k} + e^{i\pi h}\right)$$

$$= \underbrace{\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + + e^{i\pi(k+l)}\right]}_{\substack{\textbf{Structure factor fcc} \\ F\,=\,0 \text{ for mixed odd and even } h,k,l}} \times \underbrace{\left[f_{Na} + f_{Cl} e^{i\pi(h+k+l)}\right]}_{\substack{\textbf{Structure factor basis} \\ \text{Additional modulation}}}$$

3.2 Practical examples and contrast considerations

Example: sodium chloride



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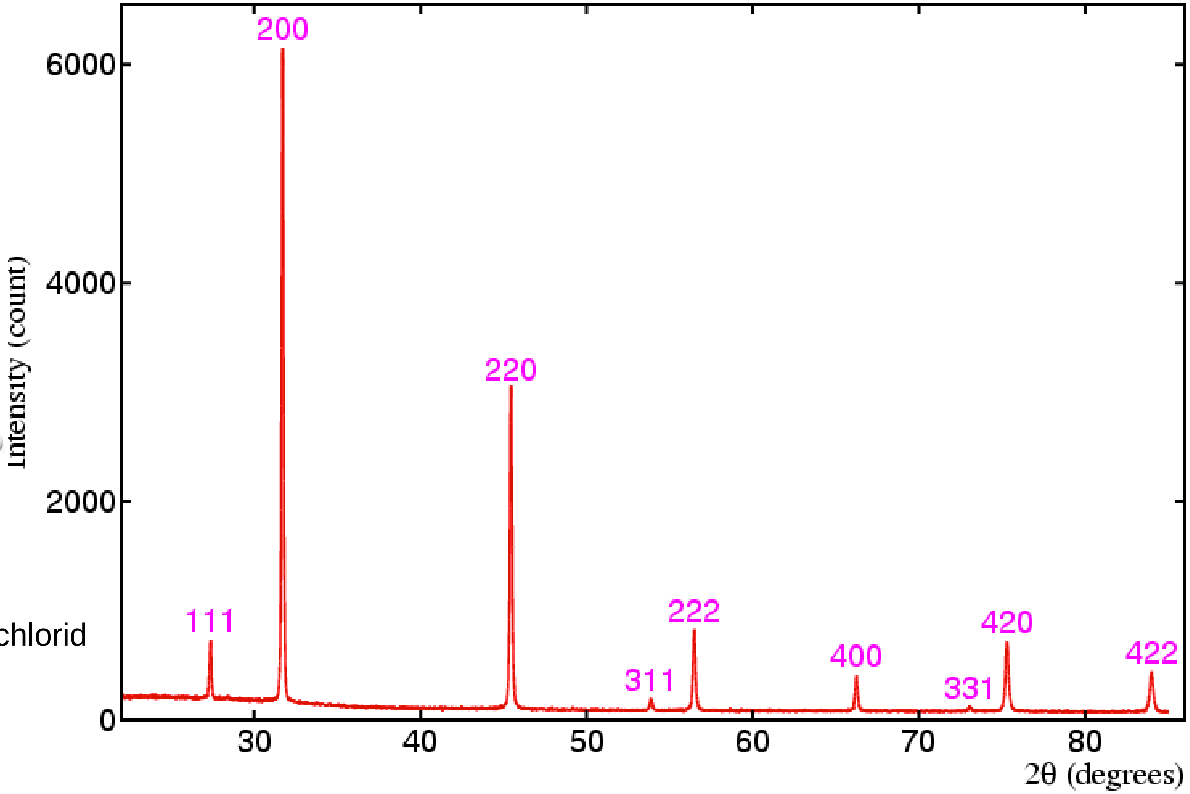


resulting structure factor

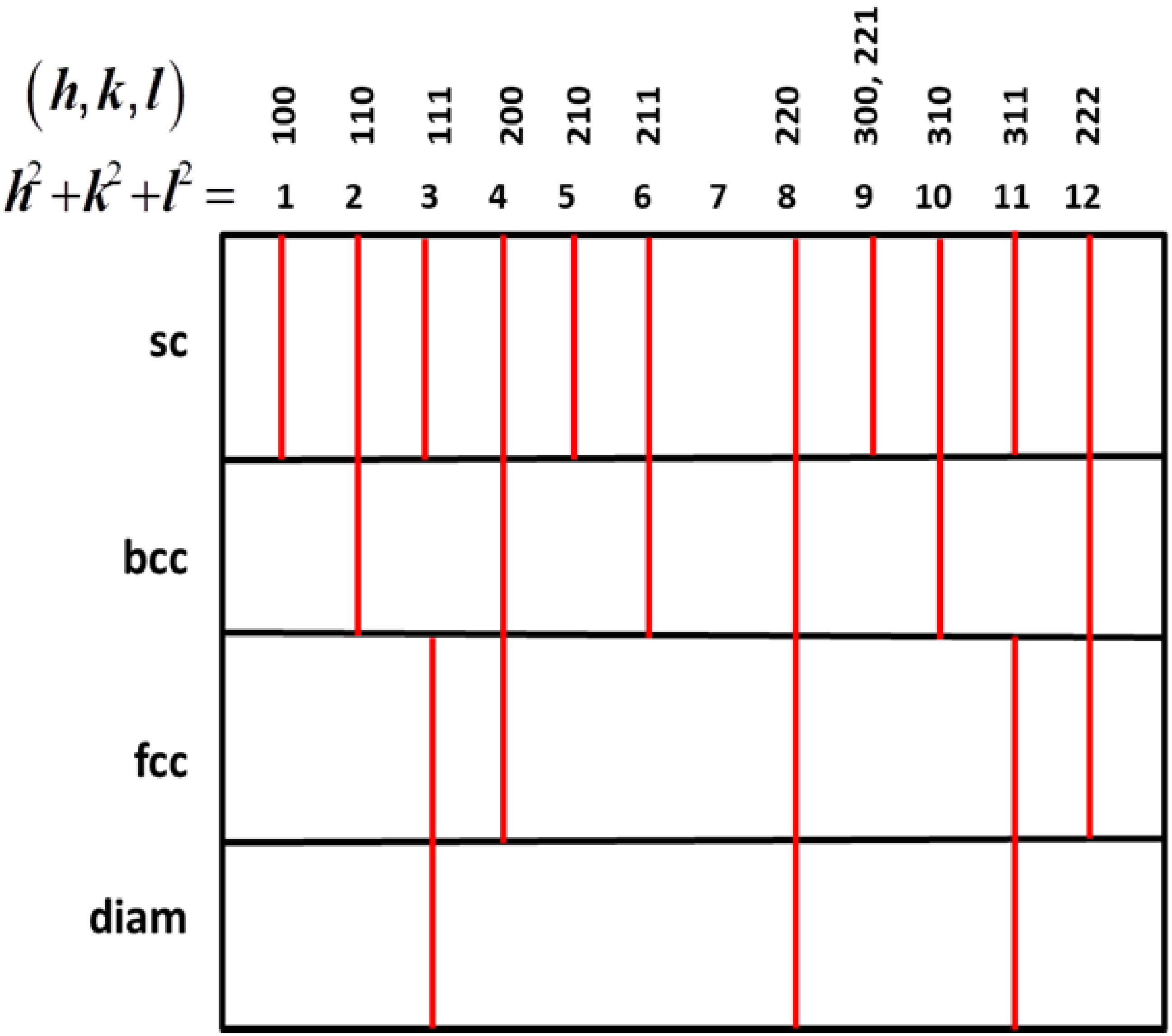
$$F_{NaCl} = 4(f_{Na} + f_{Cl}) \quad \text{for } h,k,l \text{ even}$$

$$= 4(f_{Na} - f_{Cl}) \quad \text{for } h,k,l \text{ odd}$$

$$= 0 \quad \text{for } h,k,l \text{ mixed}$$

3.2 Practical examples and contrast considerations

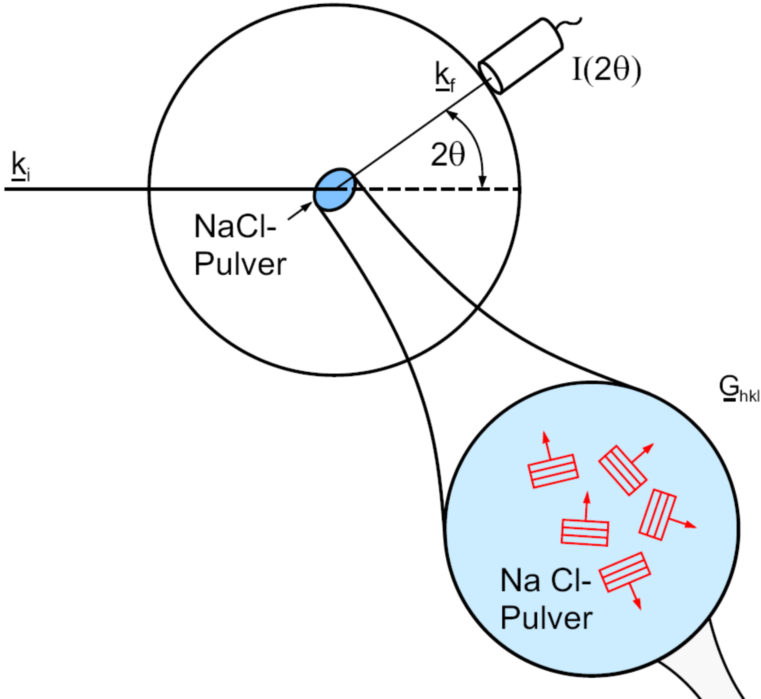
Example: allowed Bragg peaks for cubic symmetry: sc vs bcc vs fcc vs diamond



Source: H. Zabel

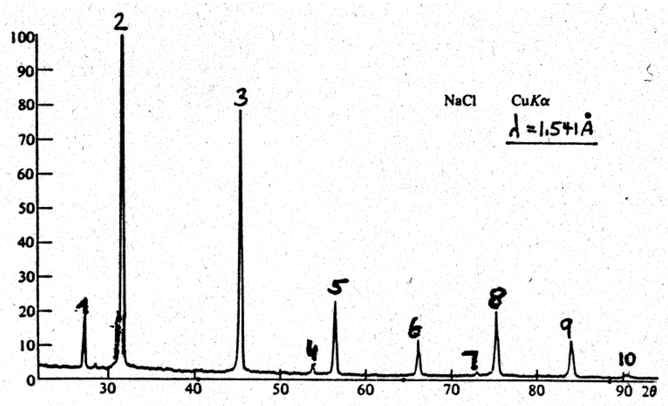
3.2 Practical examples and contrast considerations

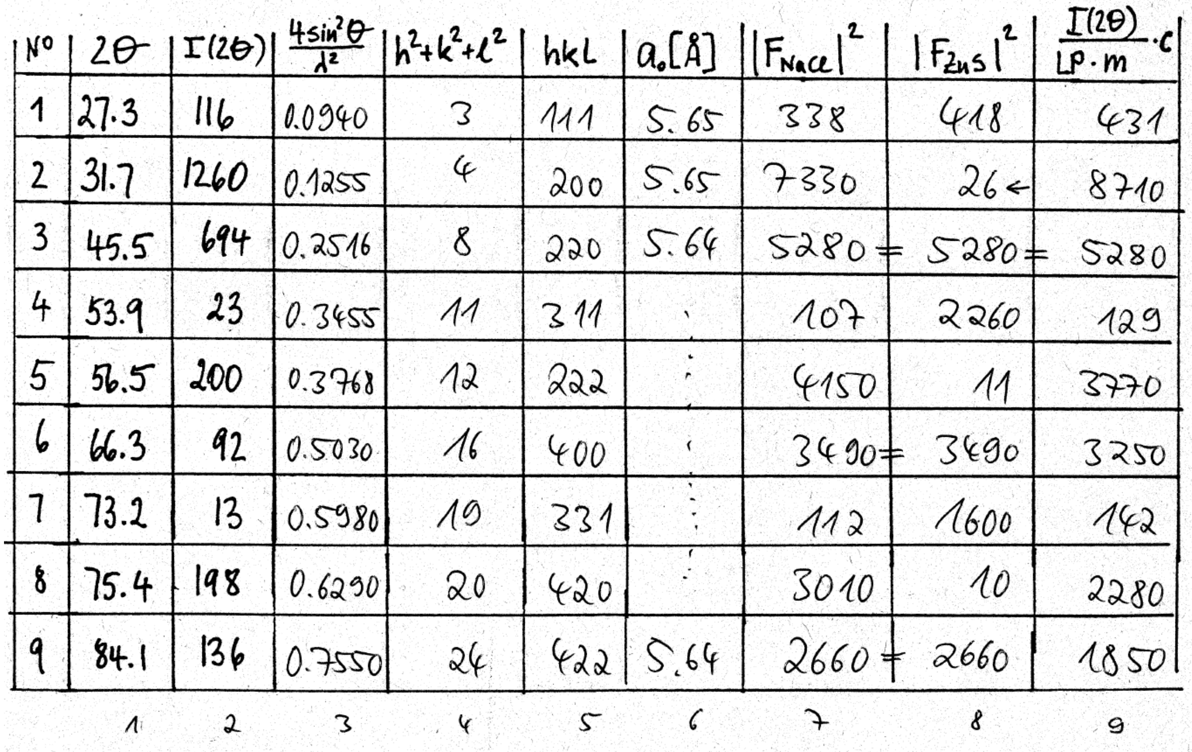
- Herstellung der Substanz und Auskristallisieren aus Lösung
- Chemische Analyse ergibt: $Na^{(+)}\ Cl^{(-)}$
  (d.h. Na und Cl in gleichen Anteilen)
- Bestimmung der Dichte: $\rho_{NaCl} = 2.196 g/cm^3$
- Präparation der Probe für die Beugungsmessungen
  - entweder Einkristall
  - oder Pulverprobe (hier gewählt)
- Messung möglichst vieler Beugungsreflexe (in Pulverspektren)



$\underline{G}_{hkl}$ verteilt in alle Raumrichtungen
(d.h. es gibt auch immer Körnchen, die in Reflexionsrichtung orientiert sind)

3.2 Practical examples and contrast considerations

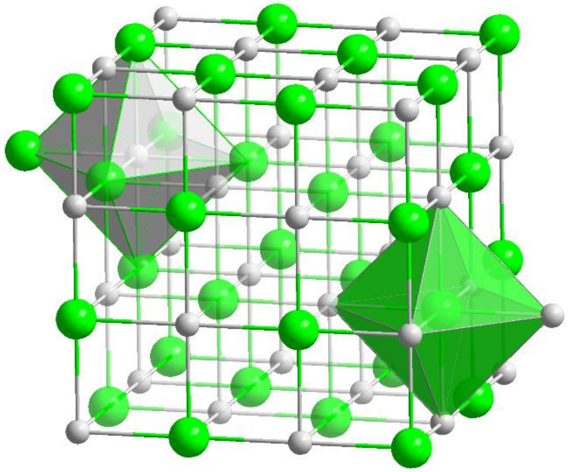




N°	2θ	$I(2\theta)$	$\frac{4\sin^2\theta}{\lambda^2}$	$h^2+k^2+l^2$	hkl	a_0 [Å]	$\lvert F_{NaCl}\rvert^2$	$\lvert F_{ZnS}\rvert^2$	$\frac{I(2\theta)}{LP\cdot m}\cdot C$
1	27.3	116	0.0940	3	111	5.65	338	418	431
2	31.7	1260	0.1255	4	200	5.65	7330	26 ←	8710
3	45.5	694	0.2516	8	220	5.64	5280 =	5280 =	5280
4	53.9	23	0.3455	11	311		107	2260	129
5	56.5	200	0.3768	12	222		4150	11	3770
6	66.3	92	0.5030	16	400		3490 =	3490	3250
7	73.2	13	0.5980	19	331		112	1600	142
8	75.4	198	0.6290	20	420		3010	10	2280
9	84.1	136	0.7550	24	422	5.64	2660 ≠	2660	1850
	1	2	3	4	5	6	7	8	9

3.2 Practical examples and contrast considerations

Example: sodium chloride



Source: https://de.wikipedia.org/wiki/Natriumchlorid

- Crystallography now established, of course
- Important and indispensable to date
- More and more complex structures,
  including macromolecular structures
- Several Nobel prizes
  in physics / chemistry / medicine

- Now some more examples

3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition

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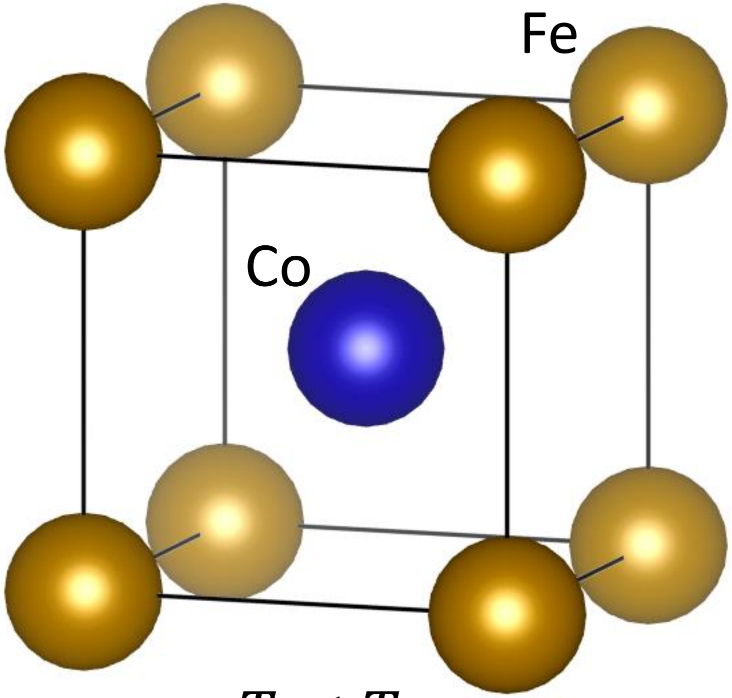
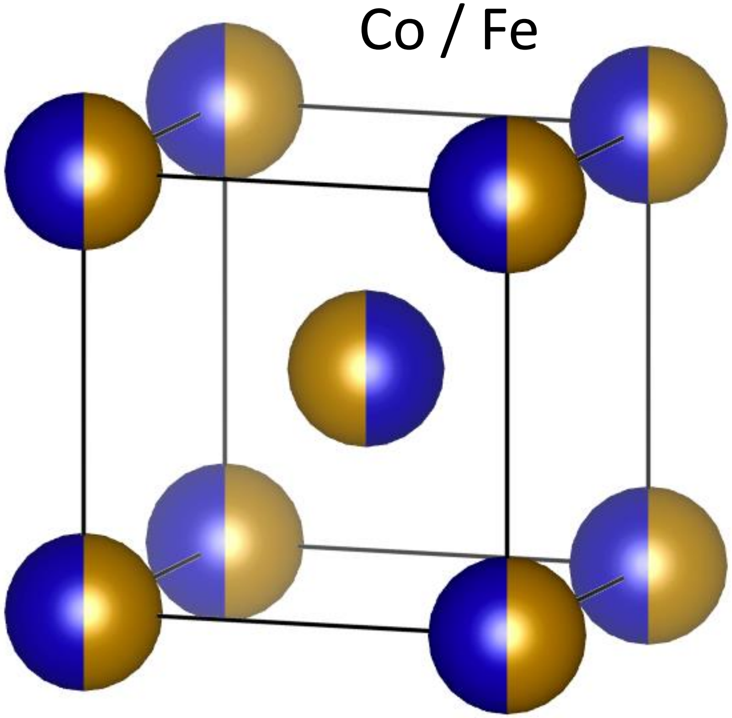
Example: FeCo alloy with order-disorder transition





$T < T_C$

$T_C \approx 900 - 1000\ ℃$

$T > T_C$

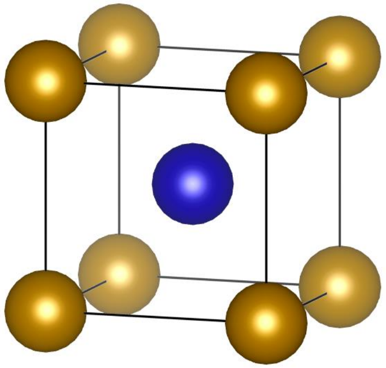
CsCl – structure, i.e. SC
with 2-atomic basis ($a \approx 2.84$ Å)

BCC with statistical occupation
of the 1-atomic basis ($a \approx 2.84$ Å)

3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition

Structure factor CsCl



$$\begin{array}{ccccccc} \vec{R}_{n\alpha} & = & \vec{R}_n^{(sc)} & + & \vec{r}_{Cs} & + & \vec{r}_{Cl} \\ & & \text{(sc)} & & (0,0,0) & & \frac{1}{2}(1,1,1)a_0 \end{array}$$

Bravais-Gitter: sc (simple cubic)
reziprokes Gitter: sc

$$\vec{G}_{hkl} = h\,\frac{2\pi}{a_0}\vec{e}_x + k\,\frac{2\pi}{a_0}\vec{e}_y + l\,\frac{2\pi}{a_0}\vec{e}_y$$

$$F_{CsCl} = f_{Cs}\,e^{i\vec{q}\cdot\vec{r}_{Cs}} + f_{Cl}\,e^{i\vec{q}\cdot\vec{r}_{Cl}} = f_{Cs} + f_{Cl}e^{i\pi(h+k+l)}$$

$$\boxed{\begin{array}{lllll} F_{CsCl} & = & ...f_{Cs}+f_{Cl} & \text{für } h+k+l \text{ gerade} & (110),\,(200),\,... \\ & & ...f_{Cs}-f_{Cl} & \text{für } h+k+l \text{ ungerade} & (100),\,(111),\,... \end{array}}$$

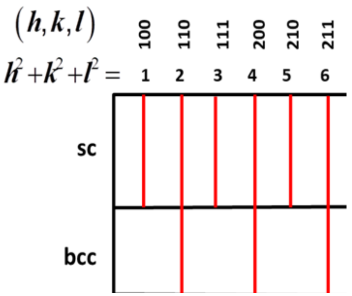
Bemerkung: $f_{Cs} = f_{Cl}$ ergibt das bcc-Gitter mit einatomiger Basis

$$\boxed{\begin{array}{lllll} F_{bcc} & = & ...2f & \text{für } h+k+l \text{ gerade} & (110),\,(200),\,... \\ & & ...0 & \text{für } h+k+l \text{ ungerade} & (100),\,(111),\,... \end{array}}$$

see BM KoMa

3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition



Structure factor

$$\begin{aligned} F_{CsCl} &= \ldots f_{Cs} + f_{Cl} && \text{für } h+k+l \text{ gerade} && (110),\ (200),\ \ldots \\ & \ldots f_{Cs} - f_{Cl} && \text{für } h+k+l \text{ ungerade} && (100),\ (111),\ \ldots \end{aligned}$$

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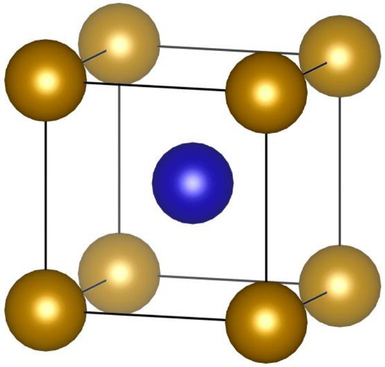
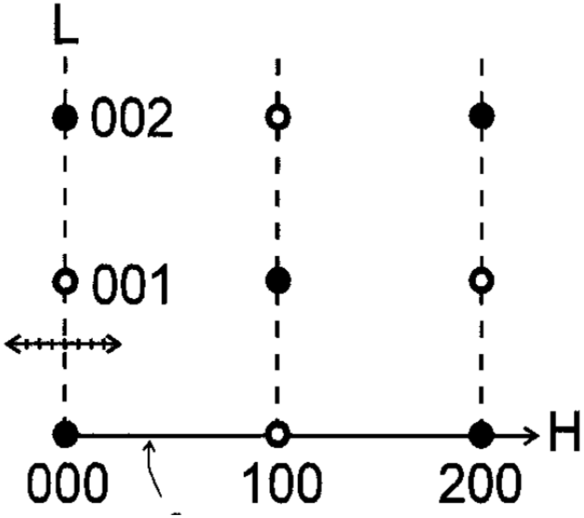
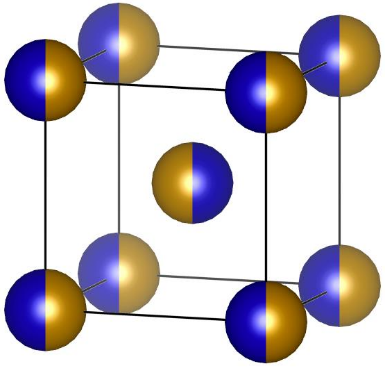






CsCl – structure, i.e. SC with 2-atomic basis ($a \approx 2.84$ Å)

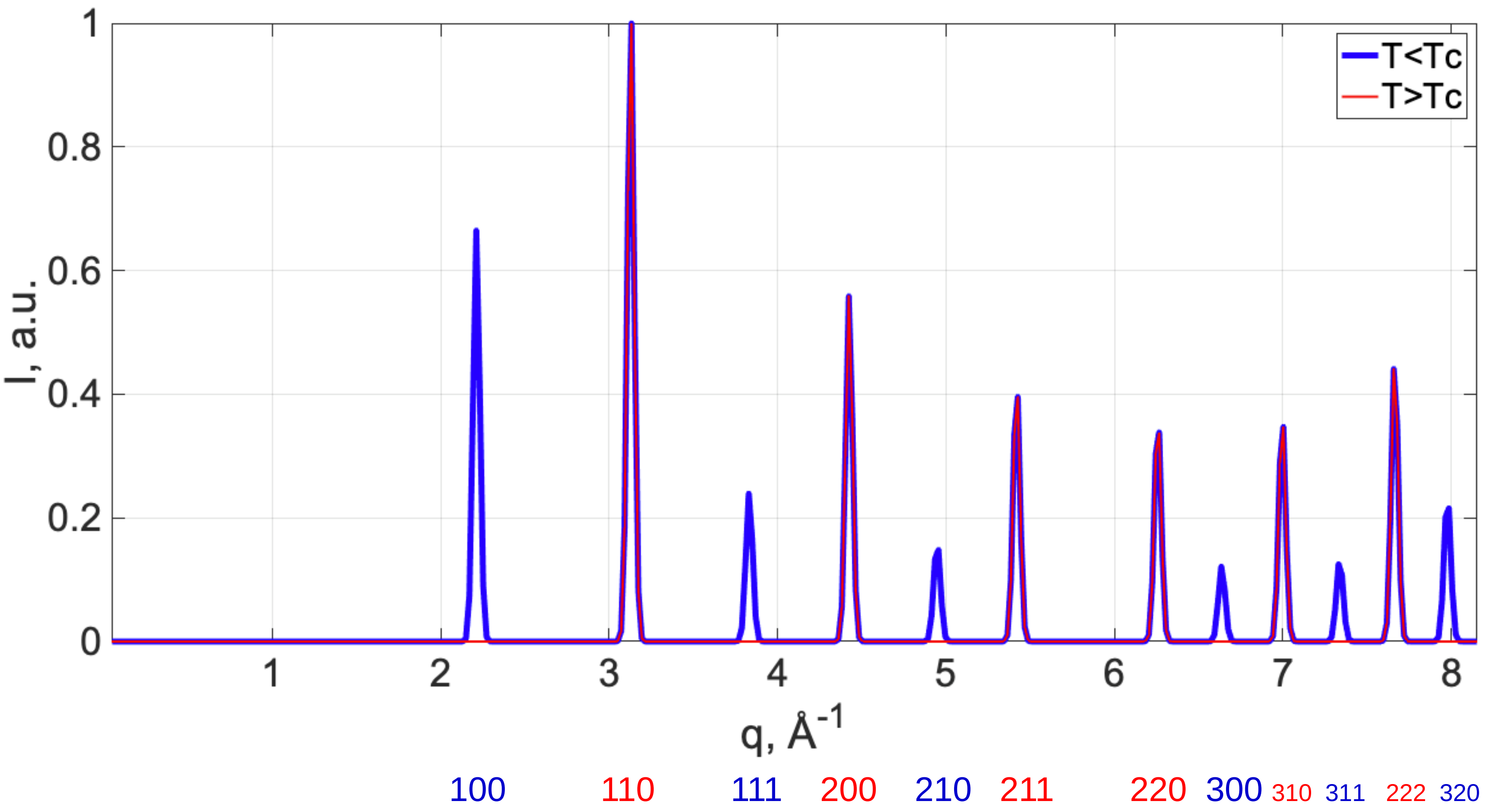
BCC with statistical occupation of the 1-atomic basis ($a \approx 2.84$ Å)

Krimmel et al., Phys. Rev. Lett. 78 (1997) 3880

3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition

Neutron scattering



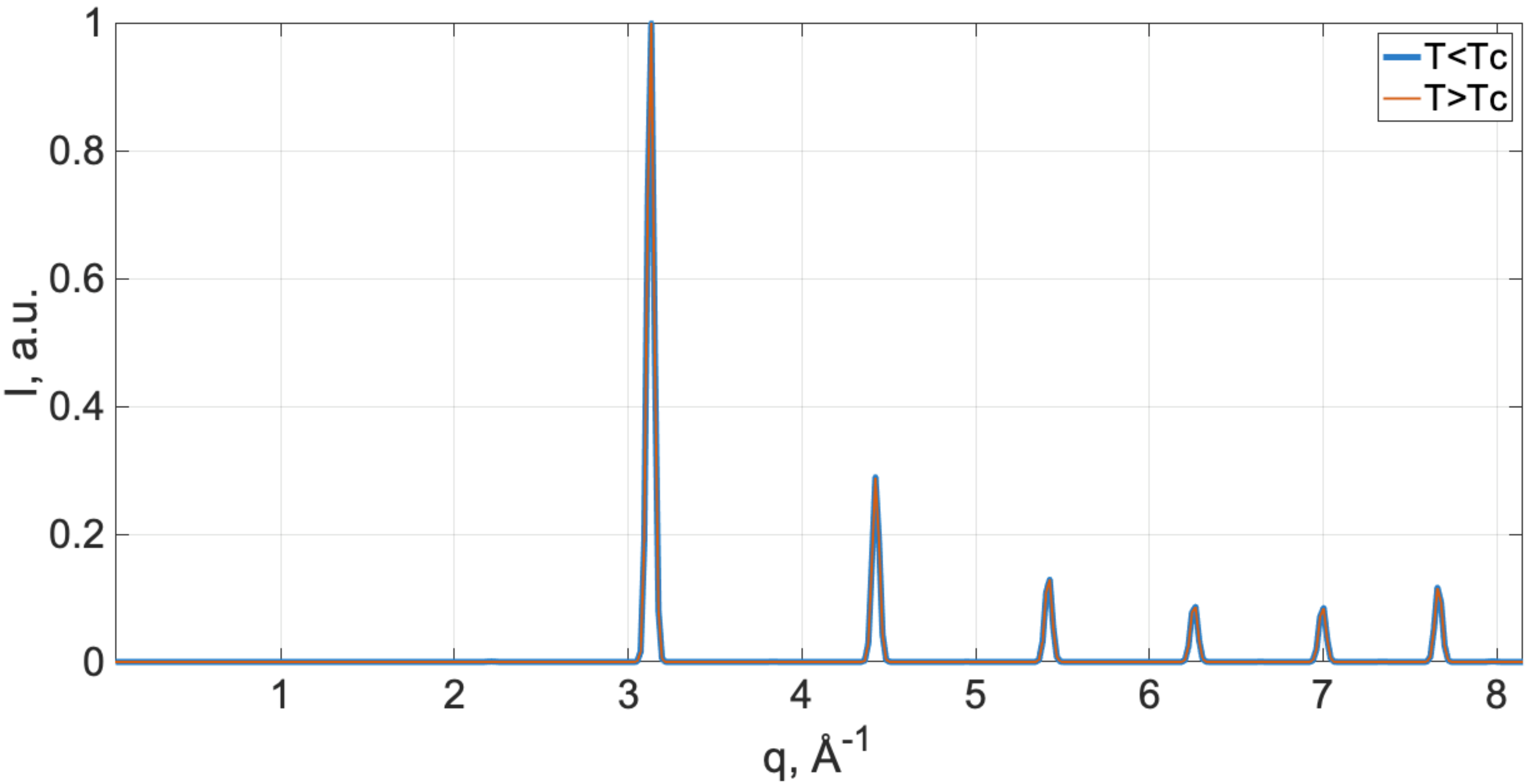
Note correction factors (not all considered)

- atomic form factor f(q) for X-rays
- multiplicity of the peaks
- polarization correction for X-ray (Lorentz factor)
- Debye-Waller factors

Source: Simulations by Ivan Zaluzhnyy

3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition X-ray scattering



100 110 111 200 210 211 220 300 310 311 222 320

Note

$(27 + 26)^2 = 2809$

$(27 - 26)^2 = 1$

Note correction factors (not all considered)

- atomic form factor f(q) for X-rays
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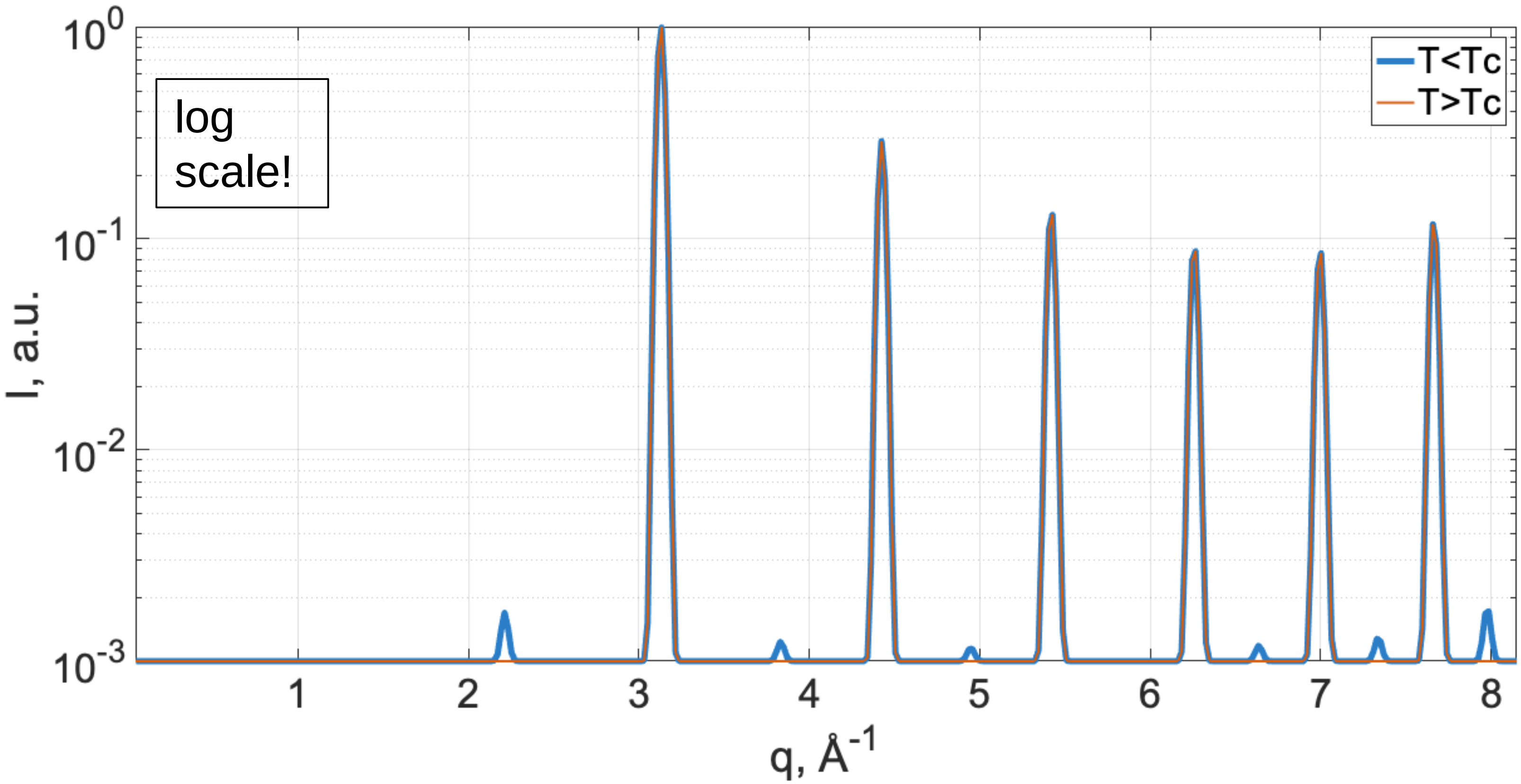
3.2 Practical examples and contrast considerations

Example: FeCo alloy with order-disorder transition

X-ray scattering



100 110 111 200 210 211 220 300 310 311 222 320

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Source: Simulations by Ivan Zaluzhnyy

3.3 Outlook: Some more advanced topics

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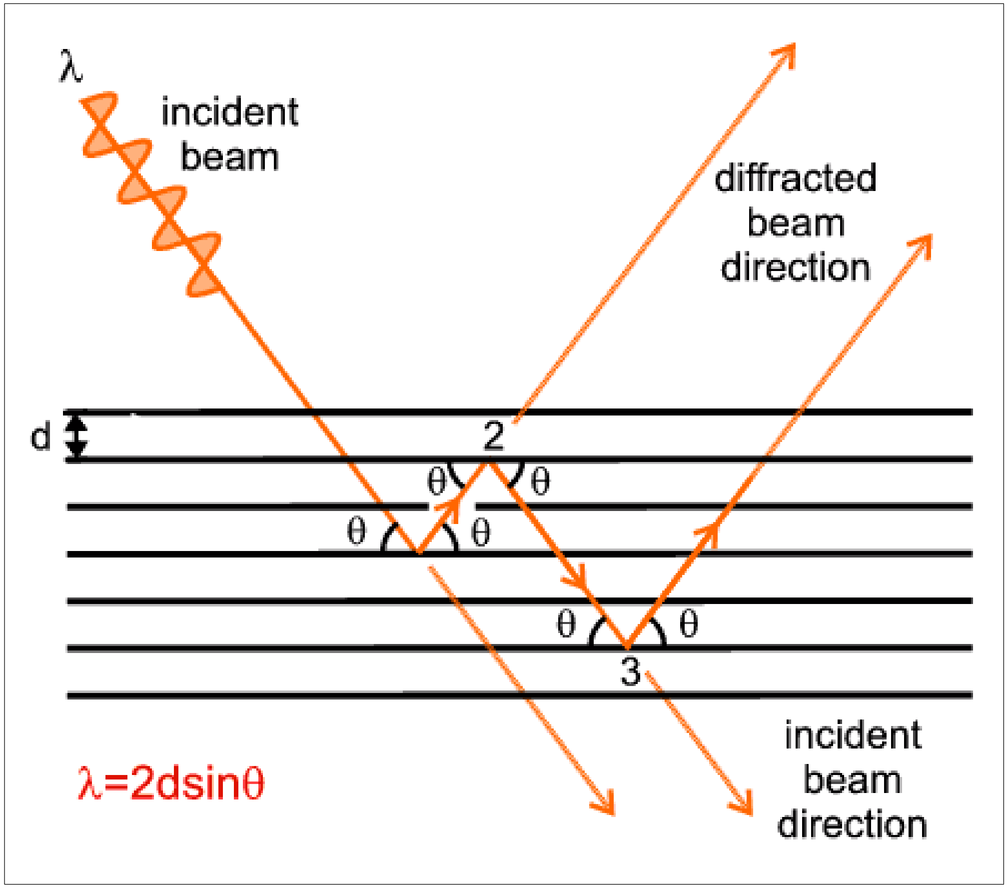
Remarks on the “limits of simple Fourier transforms“

The “equivalence“
of the scattering signal
with a Fourier transform (FT)
is based on the assumption that
each photon or neutron
is scattered at most once
(“kinematic approximation“).

If multiple scattering
has to be taken into account
(so-called “dynamical theory“),
e.g., for “perfect“ crystals,
the signal is no longer a direct FT.



Authier A. Dynamical Theory of X-ray Diffraction (IUCr Crystallographic Symposia)
Kovalchuk & Kohn X-ray standing waves - a new method of studying the structure of crystals, Sov. Phys. Usp. (1986)
Vartanyants & Kovalchuk Theory and applications of X-Ray standing waves in real crystals , Rep. Prog. Phys. (2001)

3.3 Outlook: Some more advanced topics

Remarks on the “phase problem“ in structure determination

What is the phase problem ?
We measure only intensities, not amplitudes and phases,
so the phase information is lost and no direct Fourier backtransform
of the data is possible to solve the structure directly.

Possible strategies to solve the “phase problem“
(apart from “guessing“, which works fairly well)
- anomalous scattering (X-rays)
- isotopic substitution (neutrons)
- Patterson map
- ...

$$F_{hkl} = \sum_{\alpha} f_\alpha \, e^{i\vec{G}_{hkl}\cdot\vec{r}_\alpha}$$

$$P(\vec{r}) = \sum_{hkl} |F_{hkl}|^2 \, e^{i\vec{G}_{hkl}\cdot\vec{r}_\alpha}$$

3.3 Outlook: Some more advanced topics

Preparatory exercise (see also https://en.wikipedia.org/wiki/Structure_factor):

Calculation of the structure factor of diamond;

This is an fcc lattice with a 2-atomic basis

$$F_{hk\ell}(\mathrm{basis}) = \mathrm{f}\sum_{\mathrm{j}=1}^{2} \mathrm{e}^{[-2\pi\mathrm{i}(\mathrm{hx_j}+\mathrm{ky_j}+\ell\mathrm{z_j})]} = \mathrm{f}\left[1+\mathrm{e}^{[-\mathrm{i}\pi/2(\mathrm{h}+\mathrm{k}+\ell)]}\right] = \mathrm{f}\left[1+(-\mathrm{i})^{\mathrm{h}+\mathrm{k}+\ell}\right]$$

And then the structure factor for the diamond cubic structure is the product of this and the structure factor for FCC above, (only including the atomic form factor once)

$$F_{hk\ell} = f\left[1+(-1)^{h+k}+(-1)^{k+\ell}+(-1)^{h+\ell}\right] \times \left[1+(-i)^{h+k+\ell}\right]$$

with the result

- If h, k, ℓ are of mixed parity (odd and even values combined) the first (FCC) term is zero, so $|F_{hk\ell}|^2 = 0$
- If h, k, ℓ are all even or all odd then the first (FCC) term is 4
  - if h+k+ℓ is odd then $F_{hk\ell} = 4f(1 \pm i), |F_{hk\ell}|^2 = 32f^2$
  - if h+k+ℓ is even and exactly divisible by 4 ($h+k+\ell = 4n$) then $F_{hk\ell} = 4f \times 2, |F_{hk\ell}|^2 = 64f^2$
  - if h+k+ℓ is even but not exactly divisible by 4 ($h+k+\ell \neq 4n$) the second term is zero and $|F_{hk\ell}|^2 = 0$

These points are encapsulated by the following equations:

$$F_{hk\ell} = \begin{cases} 8f, & h+k+\ell = 4N \\ 4(1\pm i)f, & h+k+\ell = 2N+1 \\ 0, & h+k+\ell = 4N+2 \end{cases}$$

$$\Rightarrow |F_{hk\ell}|^2 = \begin{cases} 64f^2, & h+k+\ell = 4N \\ 32f^2, & h+k+\ell = 2N+1 \\ 0, & h+k+\ell = 4N+2 \end{cases}$$

where N is an integer.

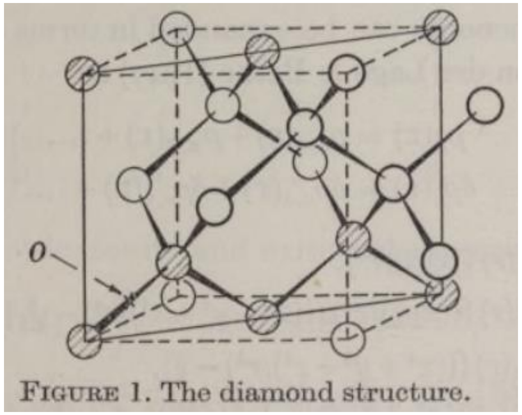


FIGURE 1. The diamond structure.

3.3 Outlook: Some more advanced topics

Question:

Why are some forbidden peaks not completely absent in X-ray diffraction ?

e.g. in diamond, the (222) is supposed to be forbidden, but is not strictly 0 !

A possible answer:

Non-spherical symmetry of C (in particular in tetragonal environment);

Using X-ray diffraction, this can actually be used to determine the non-spherical contributions to the charge density distribution around the C atoms

(expressed via “Kubic Harmonics” (KH) by von der Lage & Bethe 1947)

Note that the 2 inequivalent atoms A and B with different relative orientation of the orbitals (bonds)

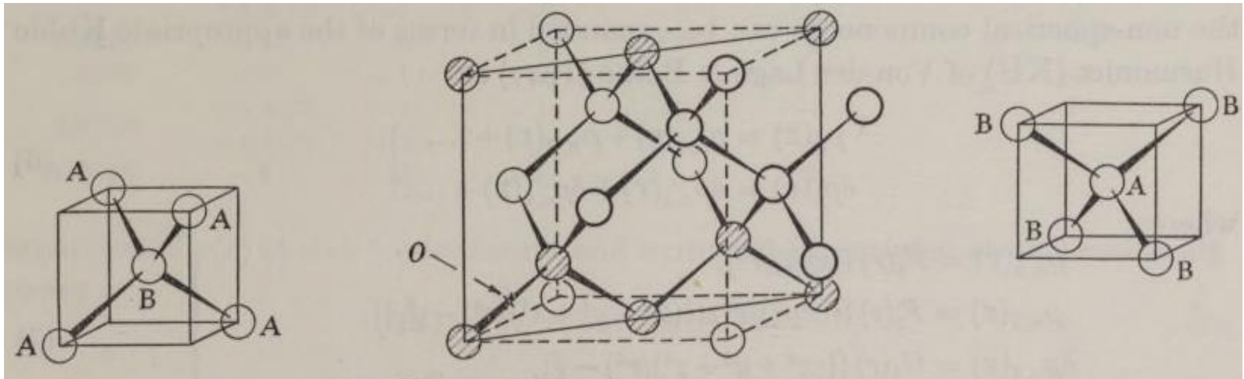


FIGURE 1. The diamond structure.

Dawson, B. 1967 Proc. Roy. Soc. A 298, 264, The covalent bond in diamond

3.3 Outlook: Some more advanced topics

Question:

Why are some forbidden peaks not completely absent in neutron diffraction ?

e.g. the (666) in Si is supposed to be forbidden, but is not strictly 0 !

A possible answer:

Non-spherical symmetry of Si (in particular in tetragonal environment) leads to an anharmonic potential for the vibration of the atoms;

this anharmonicity, in particular at high T and higher order reflections, e.g. (666), leads to the “imperfect cancellation of scattering amplitudes” from the two inequivalent atoms, since their relative distance may no longer be ¼ (111), i.e. ¼ along the main diagonal of the cubic unit cell. Note that in the diamond structure, there are 8 “holes” towards which the atoms can “swing” more easily.

Thus, “forbidden reflections” may be observed.

Note that for neutron diffraction, this has nothing to do with scattering from the (anisotropy of the) electron cloud, since the neutrons scatter from “delta-like” nuclei, so it is the positions of the nuclei, which matters (and at high T these are not in the symmetrical positions for an anharmonic potential).

Thus, the forbidden reflections can actually be used to determine the (non-spherical) contributions to the anharmonicity of the atomic potentials.

Dawson, B., and Willis, B.T.M., 1967 Proc. Roy. Soc. A 298, 307, Anharmonic vibration and forbidden reflexions in Si and Ge

3.3 Outlook: Some more advanced topics

Question:

Why are some forbidden peaks not completely absent ?

More literature on this subject:

Dawson, B. 1967 Proc. Roy. Soc.A 298, 264,
The covalent bond in diamond

Dawson, B., and Willis, B.T.M., 1967 Proc. Roy. Soc. A 298, 307,
Anharmonic vibration and forbidden reflexions in Silicon and Germanium

Dawson, B., Hurley, A.C., Maslen, V.W. 1967 Proc. Roy. Soc. A 298, 289,
Anharmonic vibration in fluorite structures

Dawson, B. 1967 Proc. Roy. Soc.A 298, 255,
A general structure factor formalism for interpreting accurate x-ray and neutron diffraction data

High-resolution characterization of the forbidden Si 200 and Si 222 reflections
Peter Zaumseil J. Appl. Cryst. (2015) 48, 528

Klaus Eichhorn, Armin H. Kirfel and Karl F. Fischer, Z. Naturforsch. 43a, 391 (1988)
Anisotropic Anomalous Dispersion in Cuprite, Cu_20

David H. Templeton and Lieselotte K. Templeton, Acta Cryst. (1986). A42, 478
X-ray Birefringence and Forbidden Reflections in Sodium Bromate