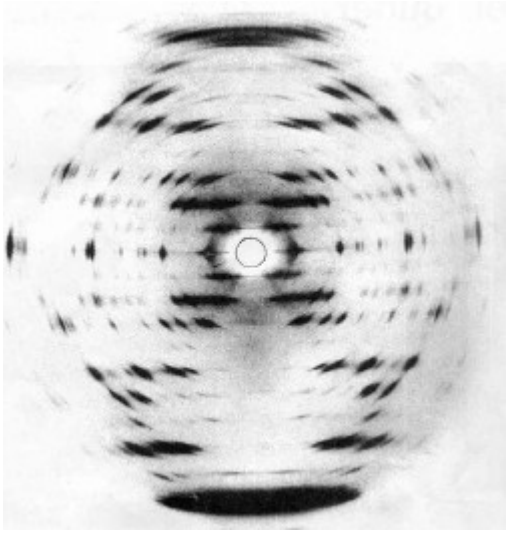
crystal structure solution



Measure reciprocal lattice vectors from $\Delta\vec{k} = \vec{G}$

Find the primitive reciprocal lattice vectors

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$$

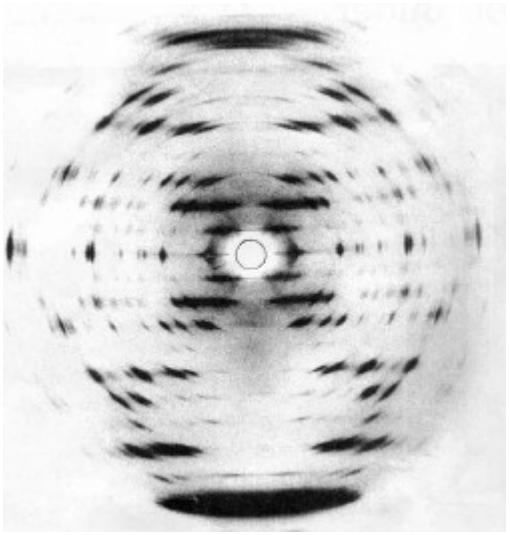
$$\vec{a}_1 = 2\pi \frac{\vec{b}_2 \times \vec{b}_3}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

Determine the Bravais lattice

$$\vec{a}_2 = 2\pi \frac{\vec{b}_3 \times \vec{b}_1}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

$$\vec{a}_3 = 2\pi \frac{\vec{b}_1 \times \vec{b}_2}{\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)}$$

crystal structure solution



"Guess" the crystal structure

Table 4.3.2.2 | pdf |
Elastic atomic scattering factors of electrons for neutral atoms and s up to 2.0 Å^{-1}

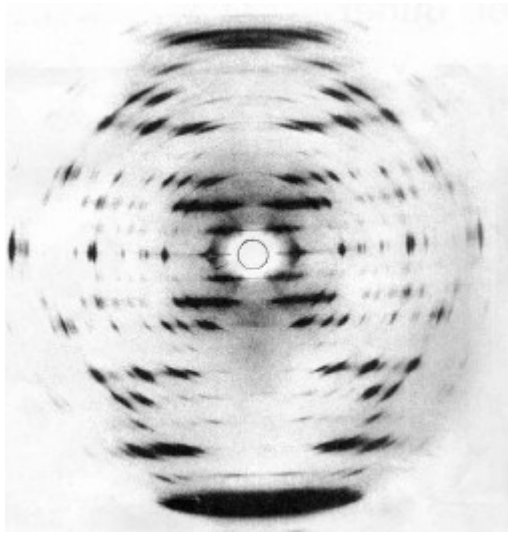
Element	Z	a_1	a_2	a_3	a_4	a_5	b_1	b_2	b_3
H	1	0.0349	0.1201	0.1970	0.0573	0.1195	0.5347	3.5867	12.3471
He	2	0.0317	0.0838	0.1526	0.1334	0.0164	0.2507	1.4751	4.4938
Li	3	0.0750	0.2249	0.5548	1.4954	0.9354	0.3864	2.9383	15.3829
Be	4	0.0780	0.2210	0.6740	1.3867	0.6925	0.3131	2.2381	10.1517
B	5	0.0909	0.2551	0.7738	1.2136	0.4606	0.2995	2.1155	8.3816
C	6	0.0893	0.2563	0.7570	1.0487	0.3575	0.2465	1.7100	6.4094
N	7	0.1022	0.3219	0.7982	0.8197	0.1715	0.2451	1.7481	6.1925
O	8	0.0974	0.2921	0.6910	0.6990	0.2039	0.2067	1.3815	4.6943
F	9	0.1083	0.3175	0.6487	0.5846	0.1421	0.2057	1.3439	4.2788
Ne	10	0.1269	0.3535	0.5582	0.4674	0.1460	0.2200	1.3779	4.0203
Na	11	0.2142	0.6853	0.7692	1.6589	1.4482	0.3334	2.3446	10.0830
Mg	12	0.2314	0.6866	0.9677	2.1882	1.1339	0.3278	2.2720	10.9241
Al	13	0.2390	0.6573	1.2011	2.5586	1.2312	0.3138	2.1063	10.4163
Si	14	0.2519	0.6372	1.3795	2.5082	1.0500	0.3075	2.0174	9.6746
P	15	0.2548	0.6106	1.4541	2.3204	0.8477	0.2908	1.8740	8.5176
S	16	0.2497	0.5628	1.3899	2.1865	0.7715	0.2681	1.6711	7.0267
Cl	17	0.2443	0.5397	1.3919	2.0197	0.6621	0.2468	1.5242	6.1537
Ar	18	0.2385	0.5017	1.3428	1.8899	0.6079	0.2289	1.3694	5.2561

From the atomic form factors, calculate the structure factors n_G.

Compare $|n_G|^2$ to the measurements

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$$

the δ-function approximation



"Guess" the crystal structure

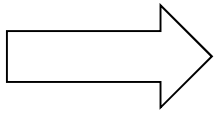


Table 4.3.2.2 | pdf |
Elastic atomic scattering factors of electrons for neutral atoms and s up to 2.0 Å^{-1}

Element	Z	a_1	a_2	a_3	a_4	a_5	b_1	b_2	b_3
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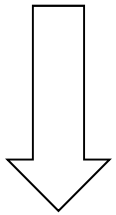
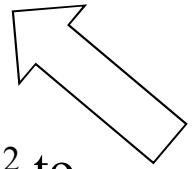
He	2	0.0317	0.0838	0.1526	0.1334	0.0164	0.2507	1.4751	4.4938
Li	3								9
Be	4								7
B	5								
C	6								
N	7								
O	8								
F	9	0.1083	0.3175	0.6487	0.5846	0.1421	0.2057	1.3439	4.2788
Ne	10	0.1269	0.3535	0.5582	0.4674	0.1460	0.2200	1.3779	4.0203
Na	11								0
Mg	12								1
Al	13								3
Si	14								
P	15								
S	16								
Cl	17	0.2443	0.5397	1.3919	2.0197	0.6621	0.2468	1.5242	6.1537
Ar	18	0.2385	0.5017	1.3428	1.8899	0.6079	0.2289	1.3694	5.2561

$$n_{u.c.}(\vec{r}) = \sum_j Z_j \delta(\vec{r} - \vec{r}_j)$$

$$n_{\vec{G}} = \sum_j Z_j \exp(-i\vec{G} \cdot \vec{r}_j)$$



From the atomic form factors, calculate the structure factors n_G.



Compare $|n_G|^2$ to the measurements

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$$

reciprocal lattice $\leftrightarrow$ real lattice

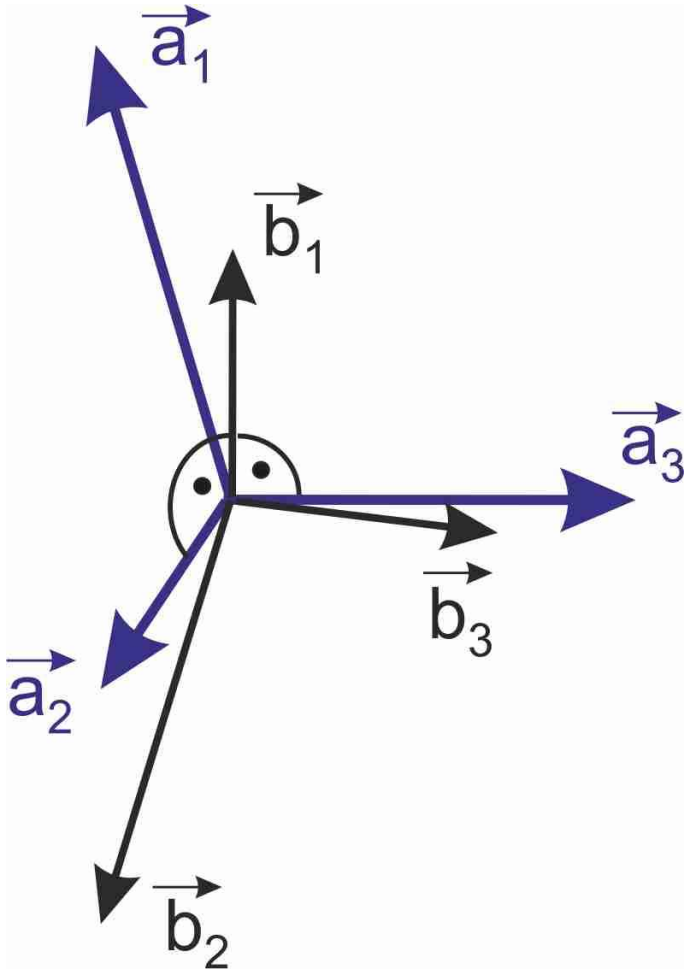
$$\vec{b}_1 \perp \vec{a}_2, \vec{a}_3$$

$$\vec{b}_2 \perp \vec{a}_1, \vec{a}_3$$

$$\vec{b}_3 \perp \vec{a}_1, \vec{a}_2$$

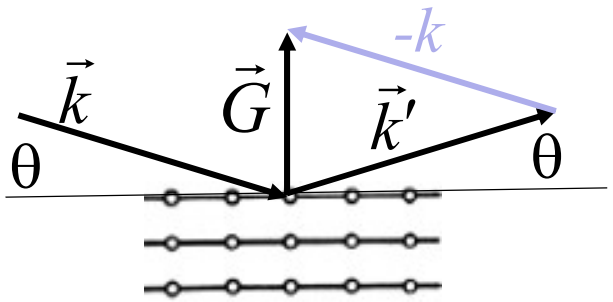
general:

$$\vec{G}_{hkl} \perp (hkl)$$



x-ray diffraction

$$\vec{G}_{hkl} \perp (hkl)$$



for $\theta = \pi/2$, $2|k| = |G|$

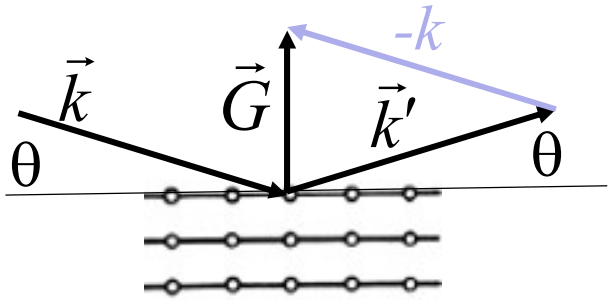
constructive interference takes place when $2d_{hkl} = \lambda$.

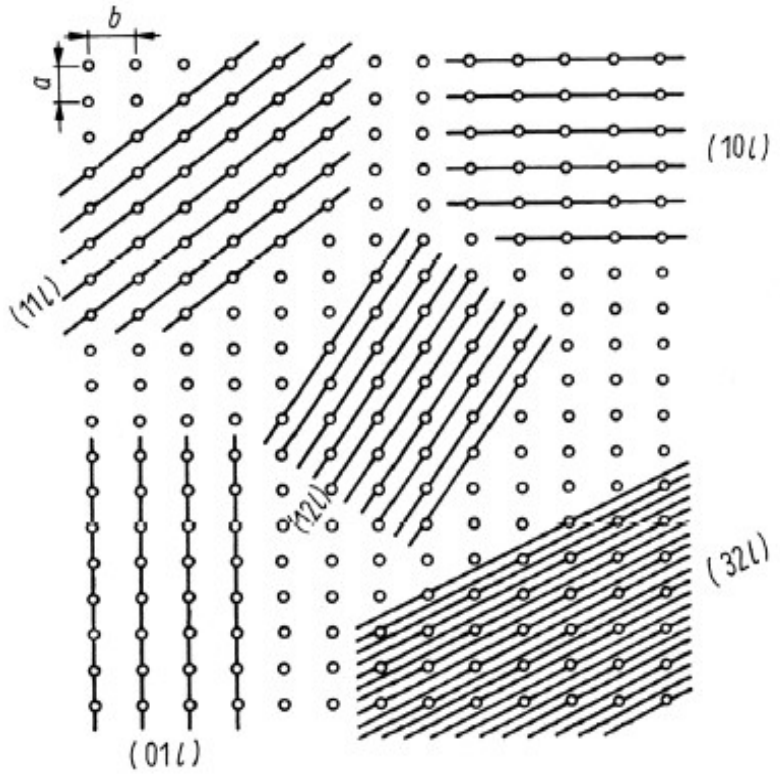
$$\frac{\left|\vec{G}_{hkl}\right|}{2} = \frac{2\pi}{2d_{hkl}} = \frac{2\pi}{\lambda} = \left|\vec{k}\right|$$

$$\left|\vec{G}_{hkl}\right| = \frac{2\pi}{d_{hkl}}$$

x-ray diffraction

$$\vec{G}_{hkl} \perp (hkl)$$





$$\left|\vec{G}_{hkl}\right| = \left|\Delta\vec{k}\right| = 2\left|\vec{k}\right|\sin\theta = \frac{2\pi}{d_{hkl}}$$

distance between the net planes

$$\left|\vec{G}_{hkl}\right| = \frac{2\pi}{d_{hkl}} \qquad \left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

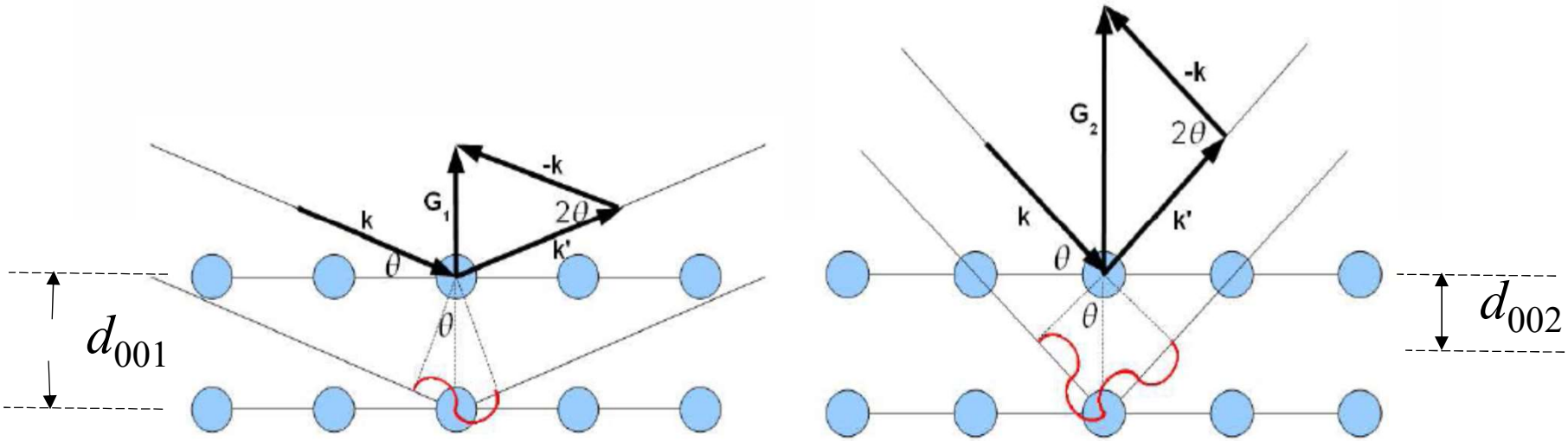
$$2d_{hkl}\sin\theta = \lambda$$

another formulation of the diffraction condition

Bragg and Laue conditions

Bragg condition: $2d\sin\theta = n\lambda$

Laue condition: $\Delta\vec{k} = \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ $\qquad 2d_{hkl}\sin\theta = \lambda$

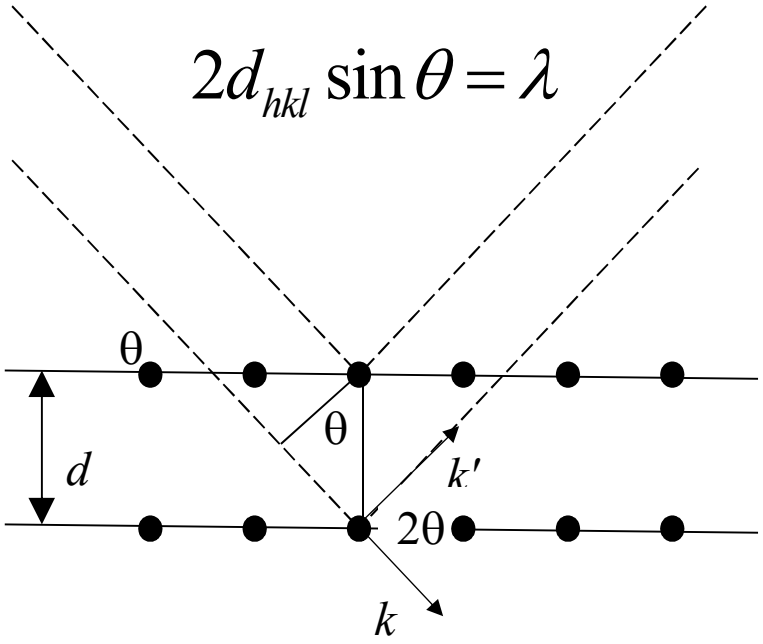


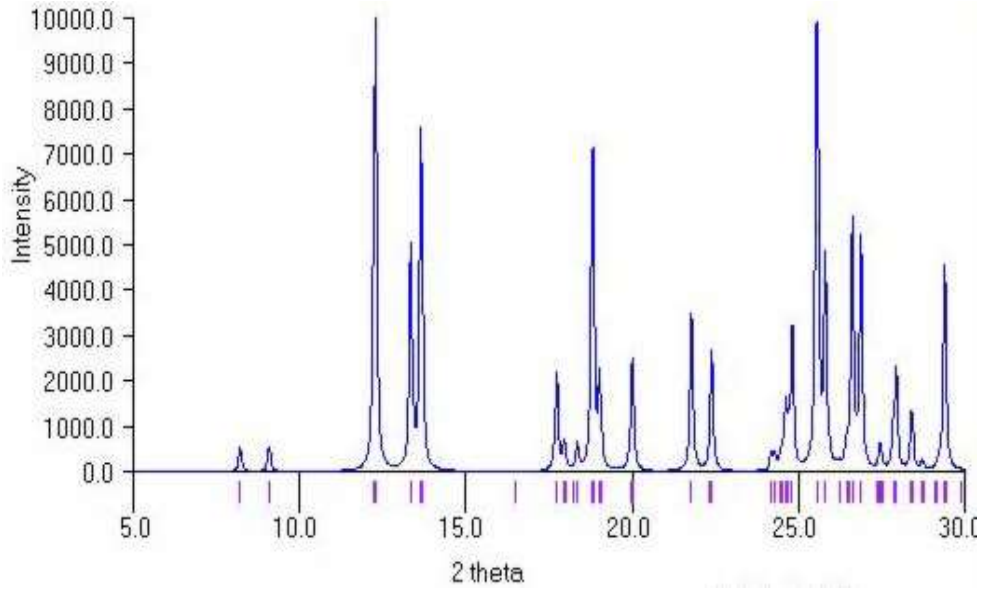
$n = 1 \Leftrightarrow 001$

$n = 2 \Leftrightarrow 002$

Powder diffraction

Powder diffraction is performed on a powder of many small crystals. Ideally, every possible crystalline orientation is represented equally in a powdered sample. The relative intensities of the diffraction peaks indicate which crystal structures are present.

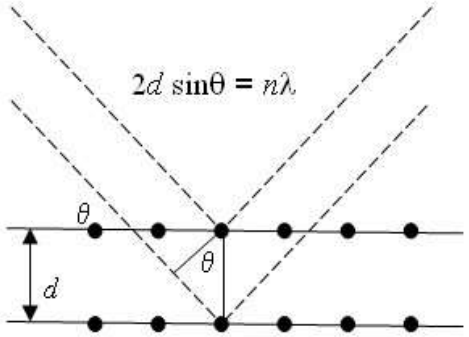




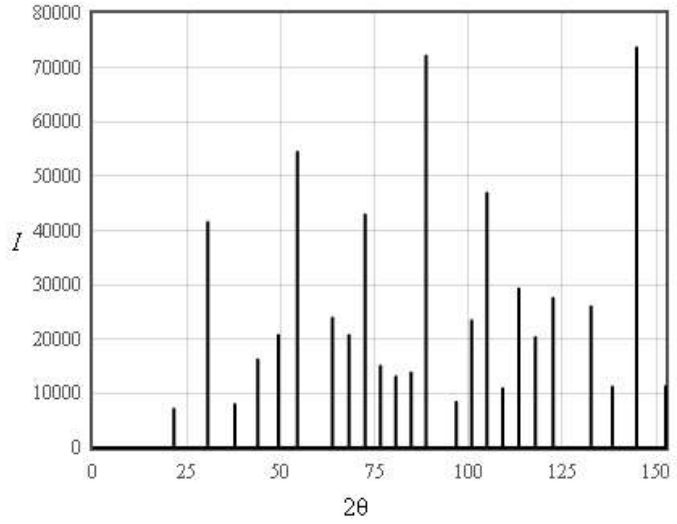
X-rays: Bragg diffraction

Powder diffraction

For powder diffraction, a crystal is ground into a fine powder so that there are many small crystals with random orientations. X-rays strike the surface of the sample at an angle θ and an x-ray detector is placed at an angle θ to the surface. Only planes parallel to the surface will diffract x-rays to the detector.



Since there are many small crystals with random orientations in the sample, all possible crystal planes that can diffract the x-rays will contribute to the measured signal when θ satisifies the Bragg condition. The form below can calculate the powder diffraction pattern for any crystal with up to five atoms per primitive unit cell. Some buttons are provided that load the form with the data for certain crystals.



Primitive lattice vectors:

$\vec{a}_1$ = 4.12E-10 $\hat{x}$ + 0 $\hat{y}$ + 0 $\hat{z}$ [m]
$\vec{a}_2$ = 0 $\hat{x}$ + 4.12E-10 $\hat{y}$ + 0 $\hat{z}$ [m]
$\vec{a}_3$ = 0 $\hat{x}$ + 0 $\hat{y}$ + 4.12E-10 $\hat{z}$ [m]

Basis:

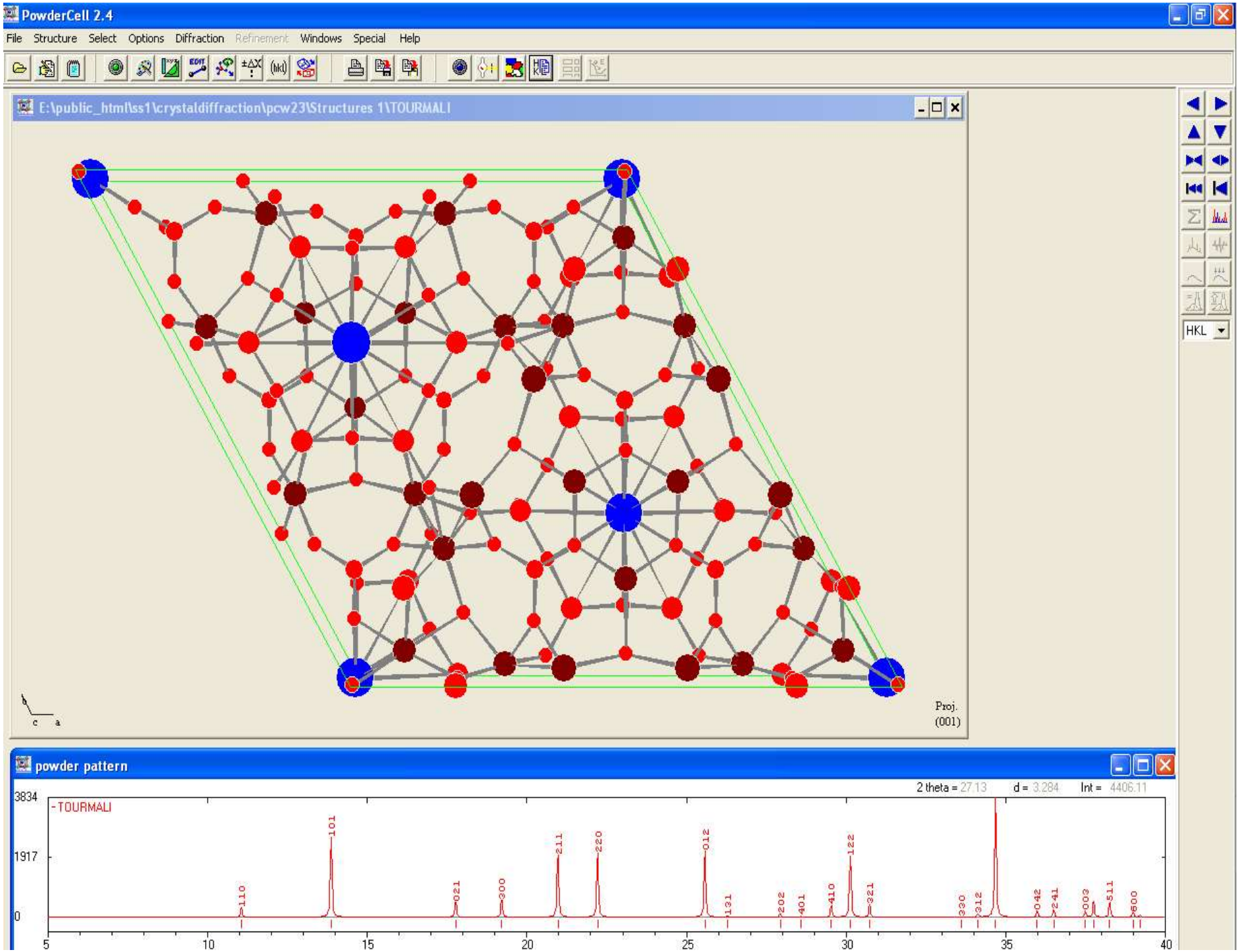
The positions of the atoms are given in fractional coodinates between -1 and 1.

Cs1+	0	$\vec{a}_1$ +	0	$\vec{a}_2$ +	0	$\vec{a}_3$
Cl1-	0.5	$\vec{a}_1$ +	0.5	$\vec{a}_2$ +	0.5	$\vec{a}_3$
		$\vec{a}_1$ +		$\vec{a}_2$ +		$\vec{a}_3$
		$\vec{a}_1$ +		$\vec{a}_2$ +		$\vec{a}_3$
		$\vec{a}_1$ +		$\vec{a}_2$ +		$\vec{a}_3$

X-ray wavelength λ [Å] = 1.540598 Cu Kα

submit

Al (fcc) | NaCl (fcc) | CsCl (sc) | SrTiO3 (perovskite, sc) | GaAs (Zincblend, fcc) | GaN (Wurtzite, hex)


PowderCell 2.4
File Structure Select Options Diffraction Refinement Windows Special Help
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HKL
Proj.
(001)
powder pattern
2 theta = 27.13
d = 3.284
Int = 4406.11
3834
1917
0
- TOURMALI
110
101
021
300
211
220
012
131
202
401
410
122
321
330
312
042
241
003
511
600
5
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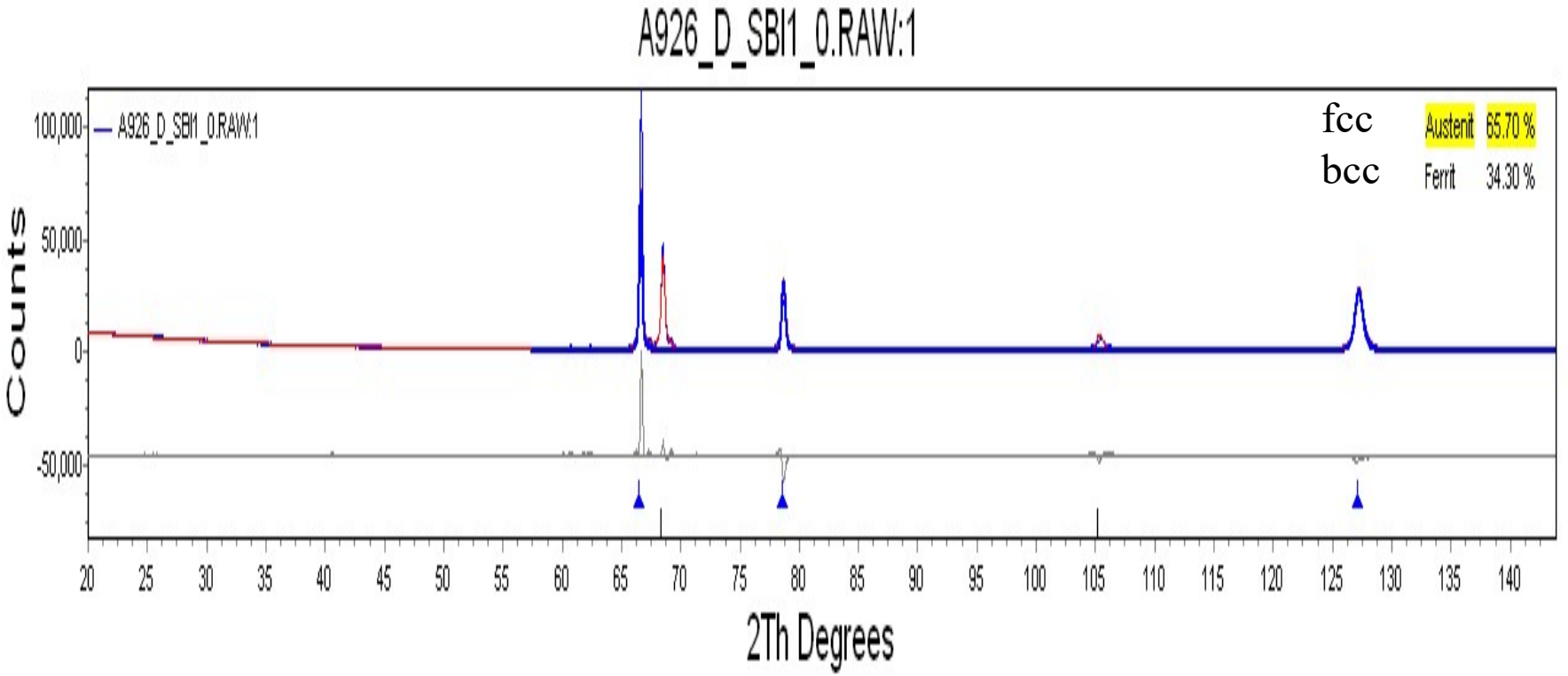
15
20
25
30
35
40


A926_D_SBI1_0.RAW:1
A926_D_SBI1_0.RAW:1
fcc
bcc
Austenit 65.70 %
Ferrit 34.30 %
Counts
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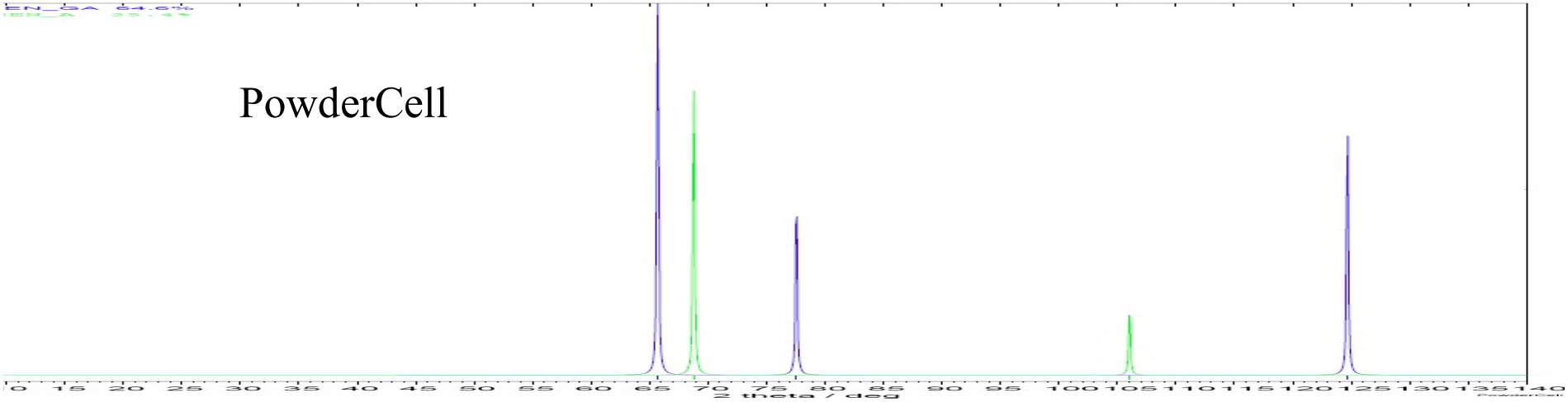
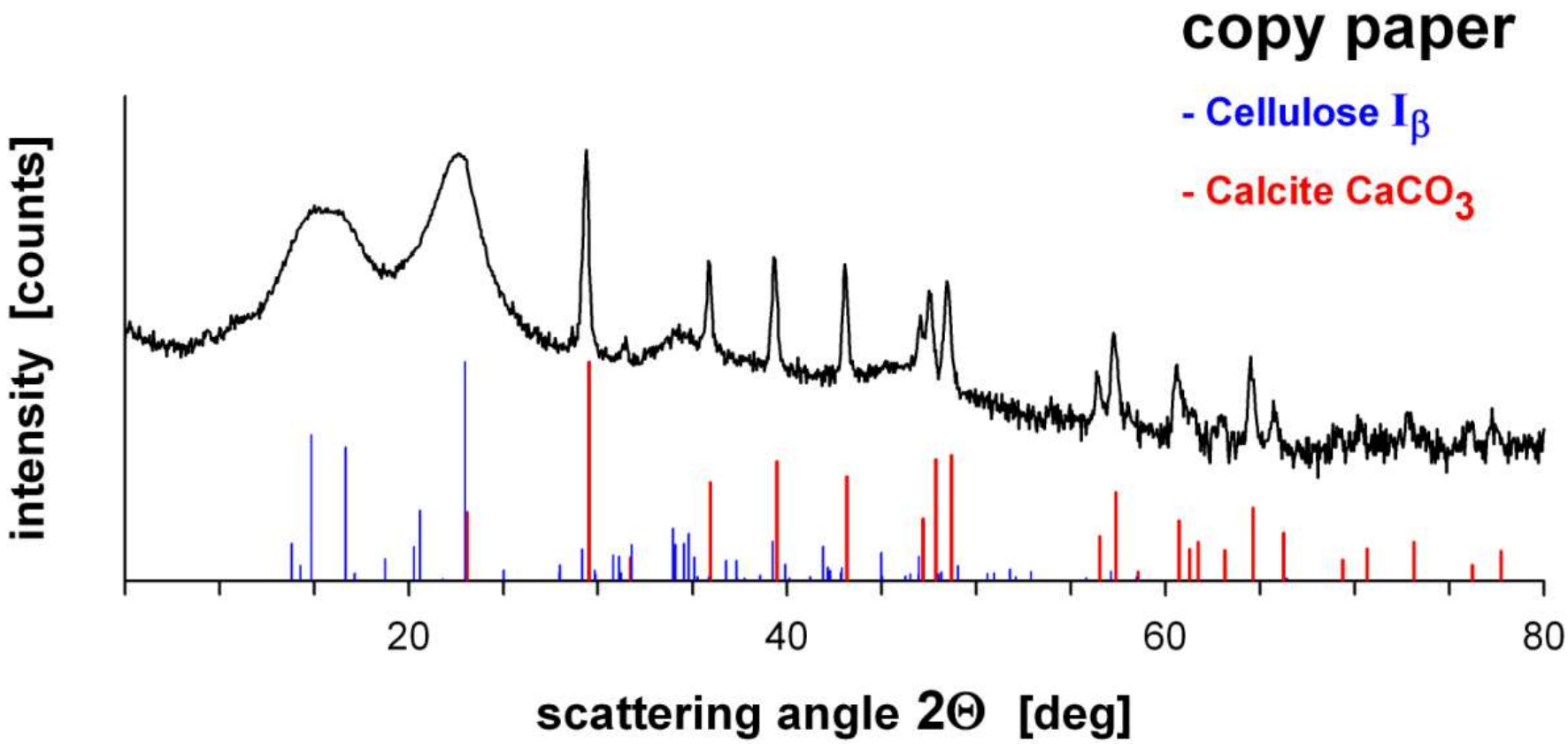
50,000
0
-50,000
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140
2Th Degrees


PowderCell


copy paper
- Cellulose I_β
- Calcite $CaCO_3$
intensity [counts]
20
40
60
80
scattering angle 2Θ [deg]

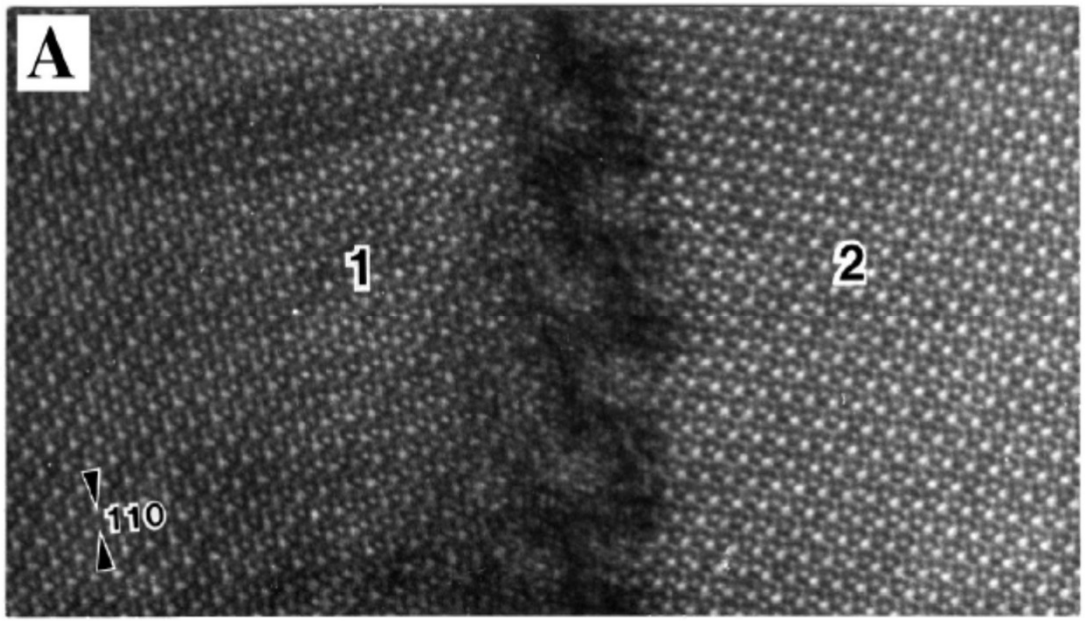
Powder diffraction

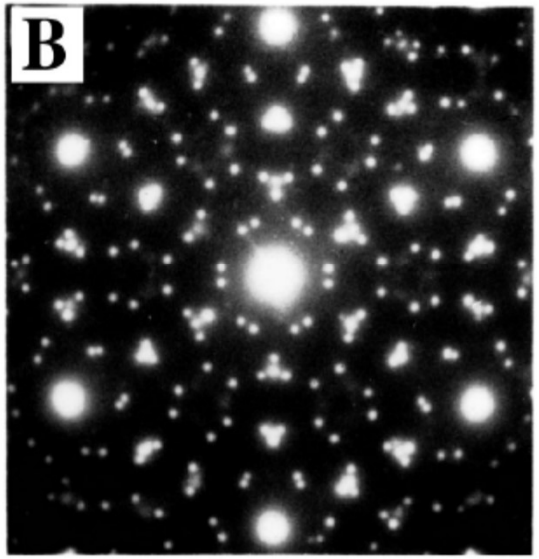
Phase identification
Every crystal has a specific "fingerprint" given by the positions and intensities of the diffraction peaks. The composition of a multi-phase specimen can be determined by fitting its diffraction pattern to the diffraction patterns of pure crystals which can be looked up in a database.

International Centre for Diffraction Data www.icdd.com
550,000 reference materials

Phase transitions, thermal expansion, piezoelectricity, piezomagnetism, bulk modulus, compliance tensor can be measured.

Electron diffraction in a TEM





The wavelength of the electrons is typically much smaller than the lattice spacing. The diffraction peaks in the plane perpendicular to k are observed.

Electron diffraction

In electron diffraction, the intensity of a diffraction peak at reciprocal lattice vector $\vec{G}$ is the square of the structure factor, $n_{\vec{G}}$.

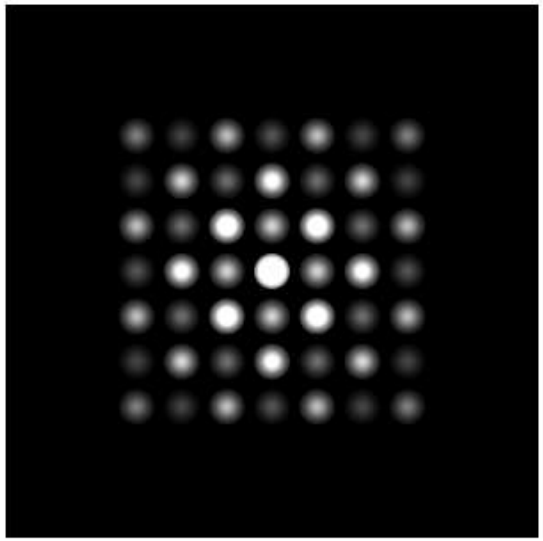
$$n_{\vec{G}} = \frac{1}{V}\sum_j f_j\left(\vec{G}\right)e^{-i\vec{G}\cdot\vec{r}_j} = \frac{1}{V}\sum_j f_j\left(\vec{G}\right)\left(\cos\left(\vec{G}\cdot\vec{r}_j\right) - i\sin\left(\vec{G}\cdot\vec{r}_j\right)\right)$$

Here V is the volume of the primitive unit cell, j sums over the atoms in the basis, $\vec{r}_j$ are the positions of the atoms in the basis, and $f_j\left(\vec{G}\right)$ are the electron atomic form factors evaluated at $\vec{G}$.

The form below calculates the electron structure factors based on this formula. The crystal structure is specified by providing the primitive lattice vectors and the positions of the atoms in the basis. A basis of up to five atoms can be calculated. The script first calculates the primitive reciprocal lattice vectors and from them calculates the reciprocal lattice vectors $\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$.

On this page, the direction of the incoming electrons is given in terms of the primitive lattice vectors in reciprocal space, $H\vec{b}_1 + K\vec{b}_2 + L\vec{b}_3$. Usually the direction of the incoming electrons are given in terms of the conventional lattice vectors. Be aware that the [100] is a (usually) different direction if primitive lattice vectors are used than if conventional lattice vectors are used.

H: 1 K: 0 L: 0



[010] →

Primitive lattice vectors:

$\vec{a}_1 =$	4.12E-10	$\hat{x} +$	0	$\hat{y} +$	0	$\hat{z}$ [m]
$\vec{a}_2 =$	0	$\hat{x} +$	4.12E-10	$\hat{y} +$	0	$\hat{z}$ [m]
$\vec{a}_3 =$	0	$\hat{x} +$	0	$\hat{y} +$	4.12E-10	$\hat{z}$ [m]

Basis:

The positions of the atoms are given in fractional coodinates between -1 and 1.

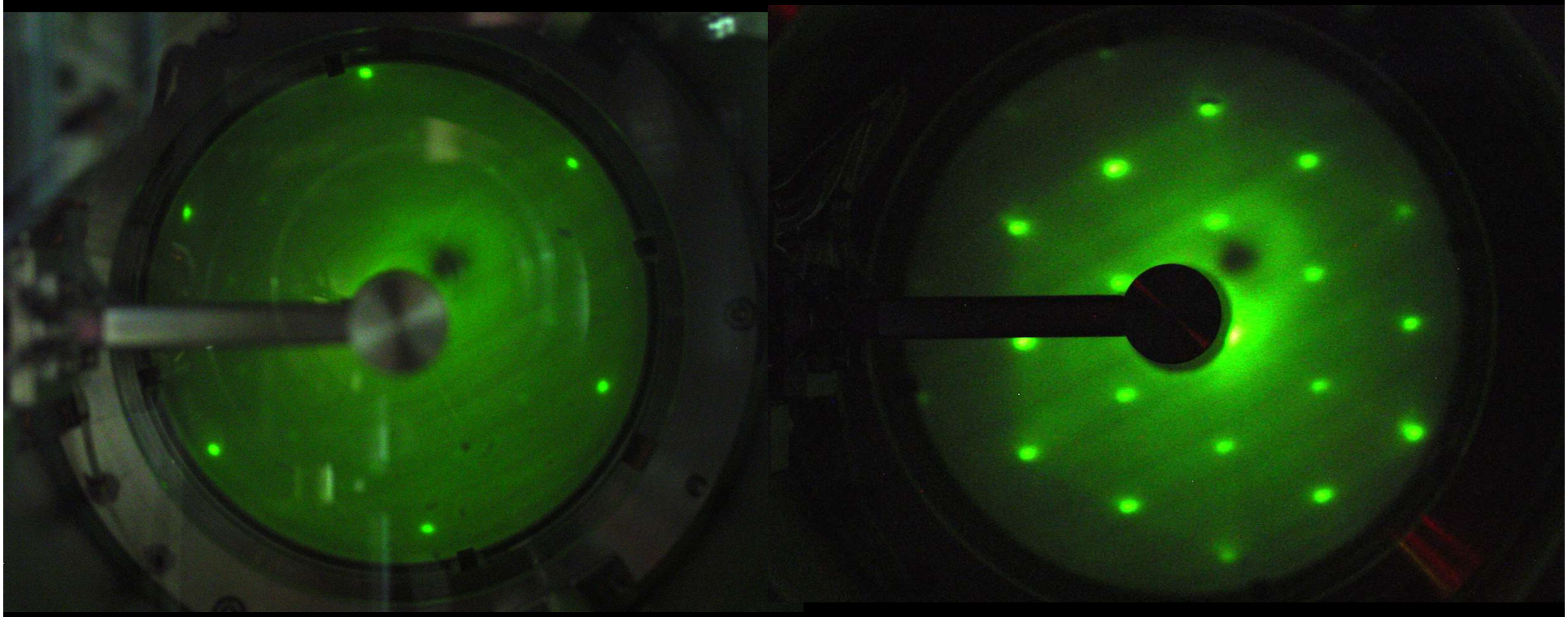
Cs	0	$\vec{a}_1 +$	0	$\vec{a}_2 +$	0	$\vec{a}_3$
Cl	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0.5	$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$

submit

LEED

Low Energy Electron Diffraction

$100\ \text{V} \rightarrow k \sim 5 \times 10^{10}\ \text{m}^{-1}$



Clean Pd (111)

Pd (111) + 0.3 ML VO_x

LEED is surface sensitive

LEED

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/atomicformfactors/LEED.php

Energy of the electron beam: 100 [eV]

Primitive lattice vectors:

$\vec{a}_1 =$ 4.12E-10 $\hat{x} +$ 0 $\hat{y}$ [m]

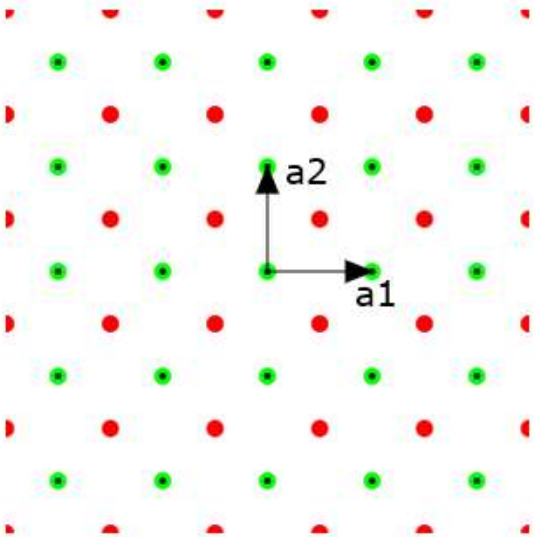
$\vec{a}_2 =$ 0 $\hat{x} +$ 4.12E-10 $\hat{y}$ [m]

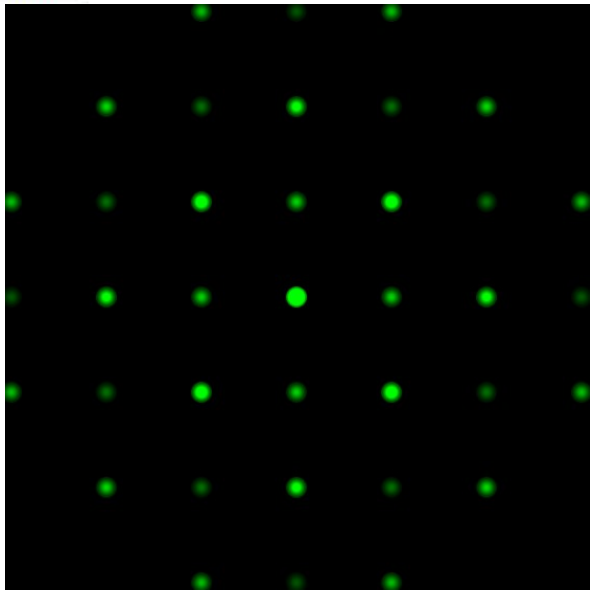
Basis:

The positions of the atoms are given in fractional coodinates between -1 and 1.

Cs	0	$\vec{a}_1 +$	0	$\vec{a}_2$
Cl	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2$
		$\vec{a}_1 +$		$\vec{a}_2$
		$\vec{a}_1 +$		$\vec{a}_2$
		$\vec{a}_1 +$		$\vec{a}_2$

submit





Forbidden reflections

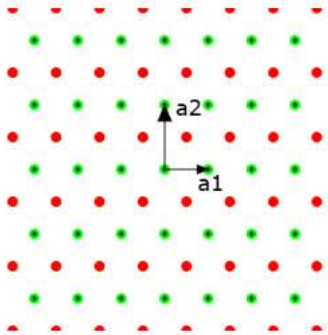
Primitive lattice vectors:

$\vec{a}_1 =$ 4.12E-10 $\hat{x} +$ 0 $\hat{y}$ [m]
$\vec{a}_2 =$ 0 $\hat{x} +$ 6.12E-10 $\hat{y}$ [m]

Basis:
The positions of the atoms are given in fractional coodinates between -1 and 1.

C	0	$\vec{a}_1 +$	0	$\vec{a}_2$	
C	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2$	
	0.2	$\vec{a}_1 +$	0.3	$\vec{a}_2$	
		$\vec{a}_1 +$		$\vec{a}_2$	
		$\vec{a}_1 +$		$\vec{a}_2$	

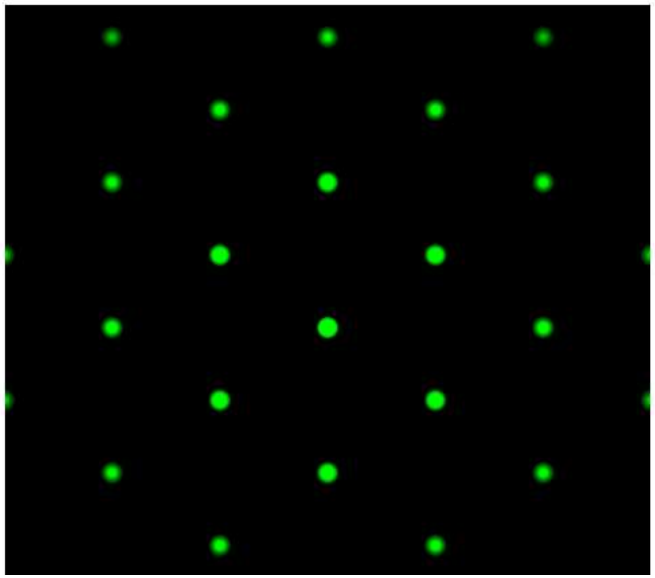
submit



Primitive reciprocal lattice vectors

$\vec{b}_1 = 2\pi \frac{R\,\vec{a}_2}{\vec{a}_1 \cdot R\,\vec{a}_2} =$1.525e+10 $\hat{k}_x +$ 0.000 $\hat{k}_y$ [m^{-1}]
$\vec{b}_2 = 2\pi \frac{R\,\vec{a}_1}{\vec{a}_1 \cdot R\,\vec{a}_2} =$ 0.000 $\hat{k}_x +$ -1.027e+10 $\hat{k}_y$ [m^{-1}]
with $R = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$

Low Energy
Electron Diffraction



Forbidden reflections

$$n_{u.c.}(\vec{r}) = \sum_j Z_j \delta(\vec{r} - \vec{r}_j)$$

Primitive reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 3.939\ \hat{k}_x + -2.275\text{e+}10\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{m}^{-1}]$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 3.939\ \hat{k}_x + 2.275\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{m}^{-1}]$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000\ \hat{k}_x + 0.000\ \hat{k}_y + 1.212\text{e+}10\ \hat{k}_z\ [\text{m}^{-1}]$$

$$n_{\vec{G}} = \sum_j Z_j \exp(-i\vec{G} \cdot \vec{r}_j)$$

Structure factors

The value of $|n_{\vec{G}}|$ for the 000 diffraction peak is the total number of electrons in the primitive unit cell. The intensities of the peaks in an x-ray diffraction experiment are proportional to $|n_{\vec{G}}|^2$. Note that elements with more electrons produce stronger diffraction intensities.

hkl	$\|\vec{G}\|$ Å^{-1}	$\|n_{\vec{G}}\|$	$\|n_{\vec{G}}\|^2$	$\text{Re}\{n_{\vec{G}}\}$	$\text{Im}\{n_{\vec{G}}\}$
000	0.000	75.94	5767	75.94	0.000
0-10	4.549e-10	37.87	1434	-37.87	0.02201
010	4.549e-10	37.87	1434	-37.87	-0.02201
0-20	9.098e-10	38.17	1457	-38.17	0.04379
020	9.098e-10	38.17	1457	-38.17	-0.04379
0-30	1.365e-9	75.94	5767	75.94	-0.1318
030	1.365e-9	75.94	5767	75.94	0.1318
0-3-1	1.212	0.3909	0.1528	0.02780	0.3899
0-31	1.212	0.3914	0.1532	-0.02727	0.3904
0-2-1	1.212	42.85	1836	-7.648	42.16
0-21	1.212	42.74	1827	7.551	42.07
0-1-1	1.212	43.01	1850	7.610	-42.33
0-11	1.212	42.96	1845	-7.561	-42.29
00-1	1.212	8.896e-8	7.914e-15	-1.573e-8	8.756e-8
001	1.212	8.896e-8	7.914e-15	-1.573e-8	-8.756e-8
01-1	1.212	42.96	1845	-7.561	42.29
011	1.212	43.01	1850	7.610	42.33
02-1	1.212	42.74	1827	7.551	-42.07
021	1.212	42.85	1836	-7.648	-42.16
03-1	1.212	0.3914	0.1532	-0.02727	-0.3904

Neutron diffraction

Typically a nuclear reactor is used as the neutron source

There are different atomic form factors for neutrons than for x-rays.

Determine the positions of H in biological samples.

Can for example distinguish between Fe and Co which have similar atomic form factors for x-rays.

Atomic beams

Hydrogen and Helium are used for diffraction studies

$$E = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

Low energies can be used for delicate samples.
Measure the surface like LEED.

Student projects

Use the electron diffraction or LEED programs to reproduce results from the scientific literature. (To test the programs.)

Write a program that calculates the neutron diffraction or the helium scattering structure factors.

The quantization of the electromagnetic field

Wave nature and the particle nature of light

Unification of the laws for electricity and magnetism (described by Maxwell's equations) and light

Quantization of the harmonic oscillator

Planck's radiation law

Serves as a template for the quantization of phonons, magnons, plasmons, electrons, spinons, holons and other quantum particles that inhabit solids.