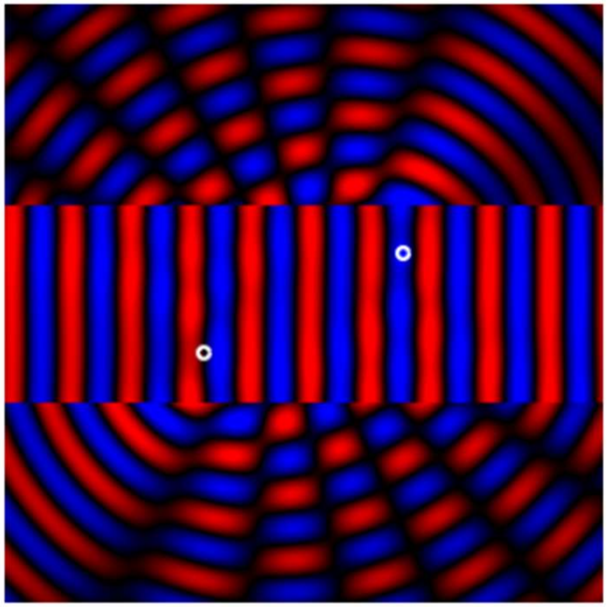
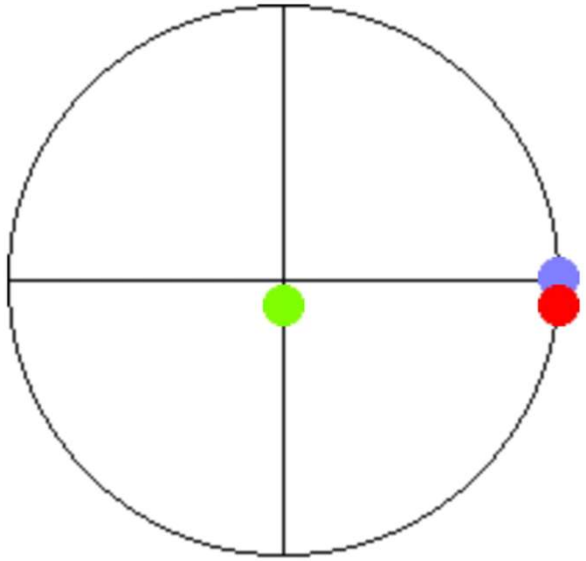
X-ray diffraction

Intensity of the scattered waves

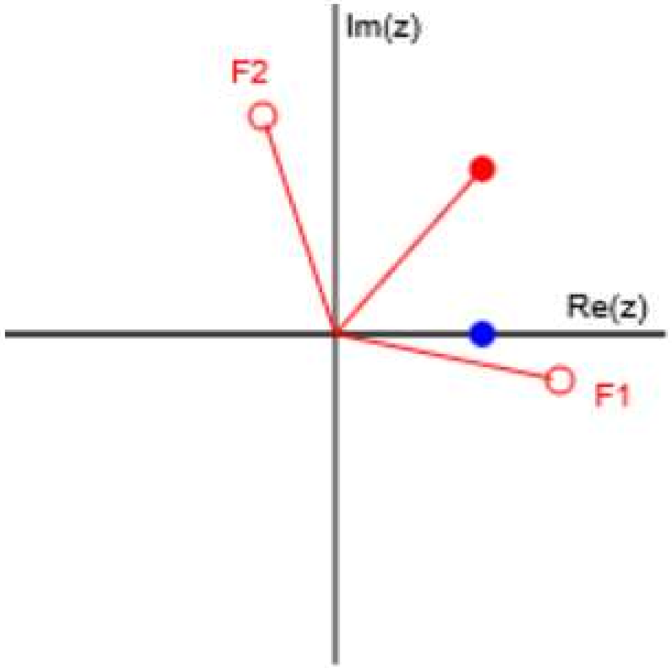


$$F(\vec{r}) = F_1 \frac{\cos\left(\vec{k}_1' \cdot (\vec{r} - \vec{r}_1) - \omega t + \vec{k} \cdot \vec{r}_1\right)}{|\vec{r} - \vec{r}_1|} + F_2 \frac{\cos\left(\vec{k}_2' \cdot (\vec{r} - \vec{r}_2) - \omega t + \vec{k} \cdot \vec{r}_2\right)}{|\vec{r} - \vec{r}_2|}$$

Using complex numbers to describe oscillations



$$e^{i\omega t} = \cos(\omega t) + i\sin(\omega t)$$



Intensity of the scattered waves

$$F(\vec{r}) = \frac{F_1}{R}\cos\left(\vec{k}'\cdot\vec{r} - \omega t + (\vec{k}-\vec{k}')\cdot\vec{r}_1\right) + \frac{F_2}{R}\cos\left(\vec{k}'\cdot\vec{r} - \omega t + (\vec{k}-\vec{k}')\cdot\vec{r}_2\right).$$

Write in terms of complex exponentials

$$F(\vec{r}) = \frac{F_1}{R}\exp\left(i\left(\vec{k}'\cdot\vec{r} - \omega t + (\vec{k}-\vec{k}')\cdot\vec{r}_1\right)\right) + \frac{F_2}{R}\exp\left(i\left(\vec{k}'\cdot\vec{r} - \omega t + (\vec{k}-\vec{k}')\cdot\vec{r}_2\right)\right)$$

Factor out $e^{-i\omega t}$

$$F(\vec{r}) = \left(\frac{F_1}{R}\exp\left(i\left((\vec{k}-\vec{k}')\cdot\vec{r}_1\right)\right) + \frac{F_2}{R}\exp\left(i\left((\vec{k}-\vec{k}')\cdot\vec{r}_2\right)\right)\right)e^{-i\omega t} = \mathcal{A}(\vec{r})e^{-i\omega t}.$$

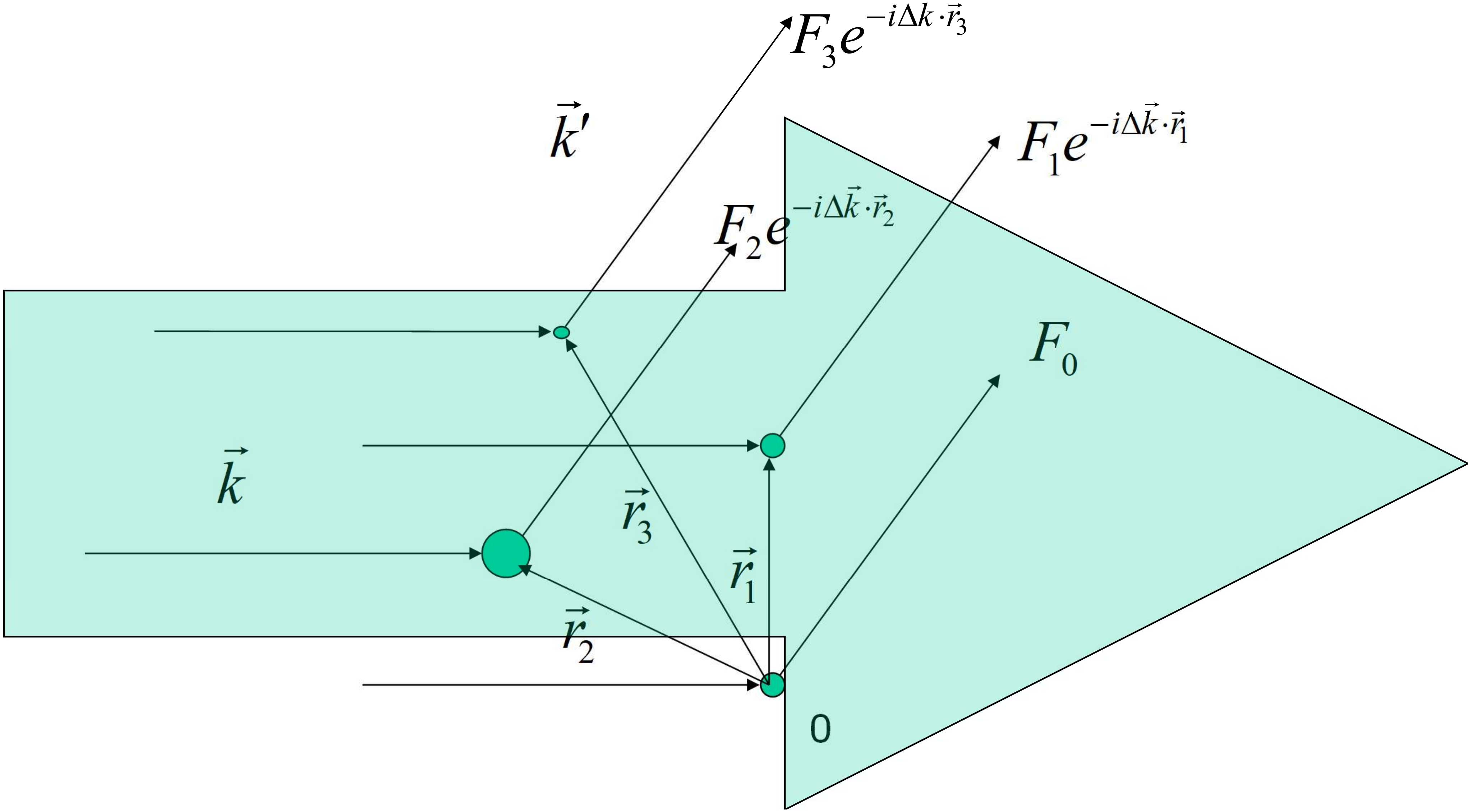
The intensity is the amplitude squared

$$I \propto \mathcal{A}^*\mathcal{A}.$$

For many scatterers:

$$\mathcal{A} = \sum_{i=j}^{N}\frac{F_j}{R}\exp\left(i\left((\vec{k}-\vec{k}')\cdot\vec{r}_j\right)\right)$$

Interference



Amplitude: $\mathcal{A} = \sum_{i=j}^{N} \frac{F_j}{R} \exp\left(i \left((\vec{k} - \vec{k}') \cdot \vec{r}_j \right) \right)$

Elastic x-ray scattering

In elastic x-ray scattering, the amplitude of the scattering from a specific point is proportional to the electron density. Since the electron density is a continuous function, the amplitude of the scattered waves is written as a volume integral over the crystal.

$$\mathcal{A} \propto \int n(\vec{r}')\exp\left(i\left((\vec{k}-\vec{k}')\cdot\vec{r}'\right)\right)d^3r'.$$

The electron density is a periodic function.

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

$$\mathcal{A} \propto \int \sum_{\vec{G}} n_{\vec{G}}\exp\left(i\left((\vec{G}+\vec{k}-\vec{k}')\cdot\vec{r}'\right)\right)d^3r'.$$

Diffraction condition

$$\mathcal{A} \propto \int \sum_{\vec{G}} n_{\vec{G}} \exp\left(i\left((\vec{G}+\vec{k}-\vec{k}')\cdot\vec{r}'\right)\right) d^3r'.$$

There will be destructive interference unless

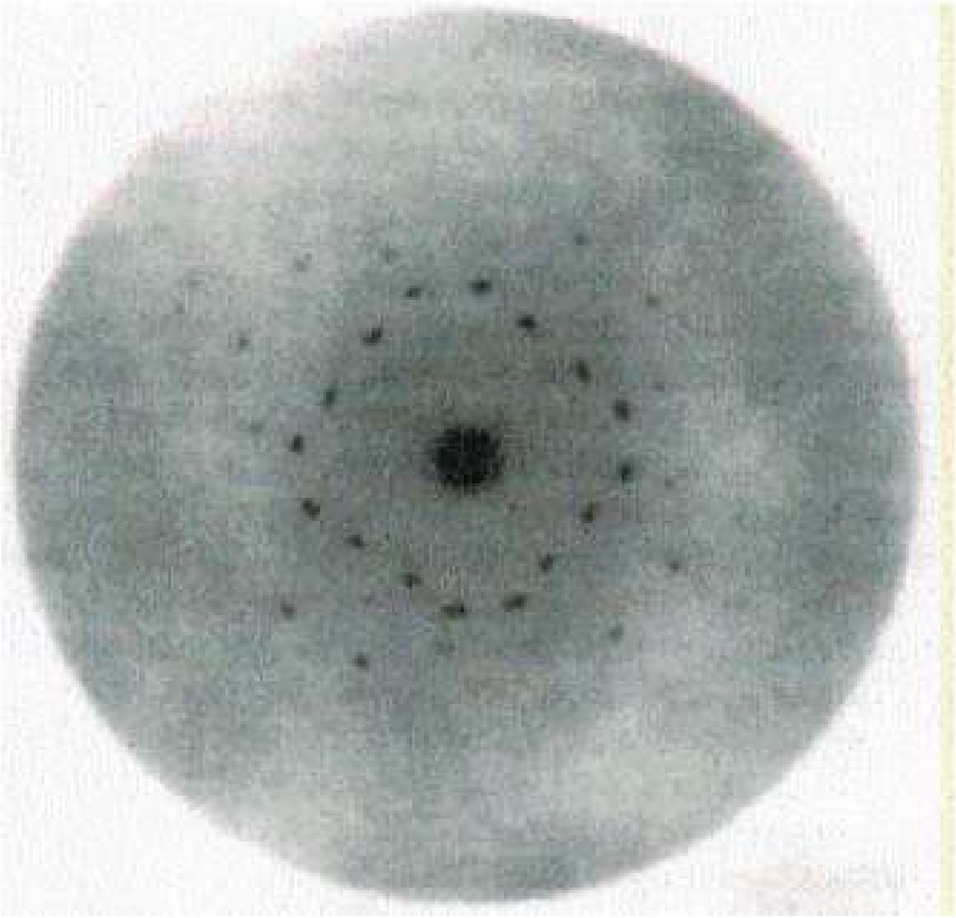
$$\vec{G}+\vec{k}-\vec{k}' = 0,$$

diffraction condition: $\boxed{\vec{G} = \vec{\Delta k}}$

The intensity of the peak at G is $|n_G|^2$

nobel prize 1914

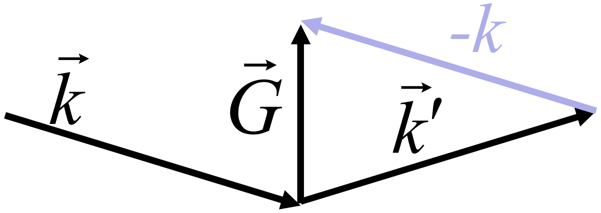
first diffraction experiment of Max von Laue 1912
ZnS single crystal, exposure time 30'
the 5th diffraction pattern



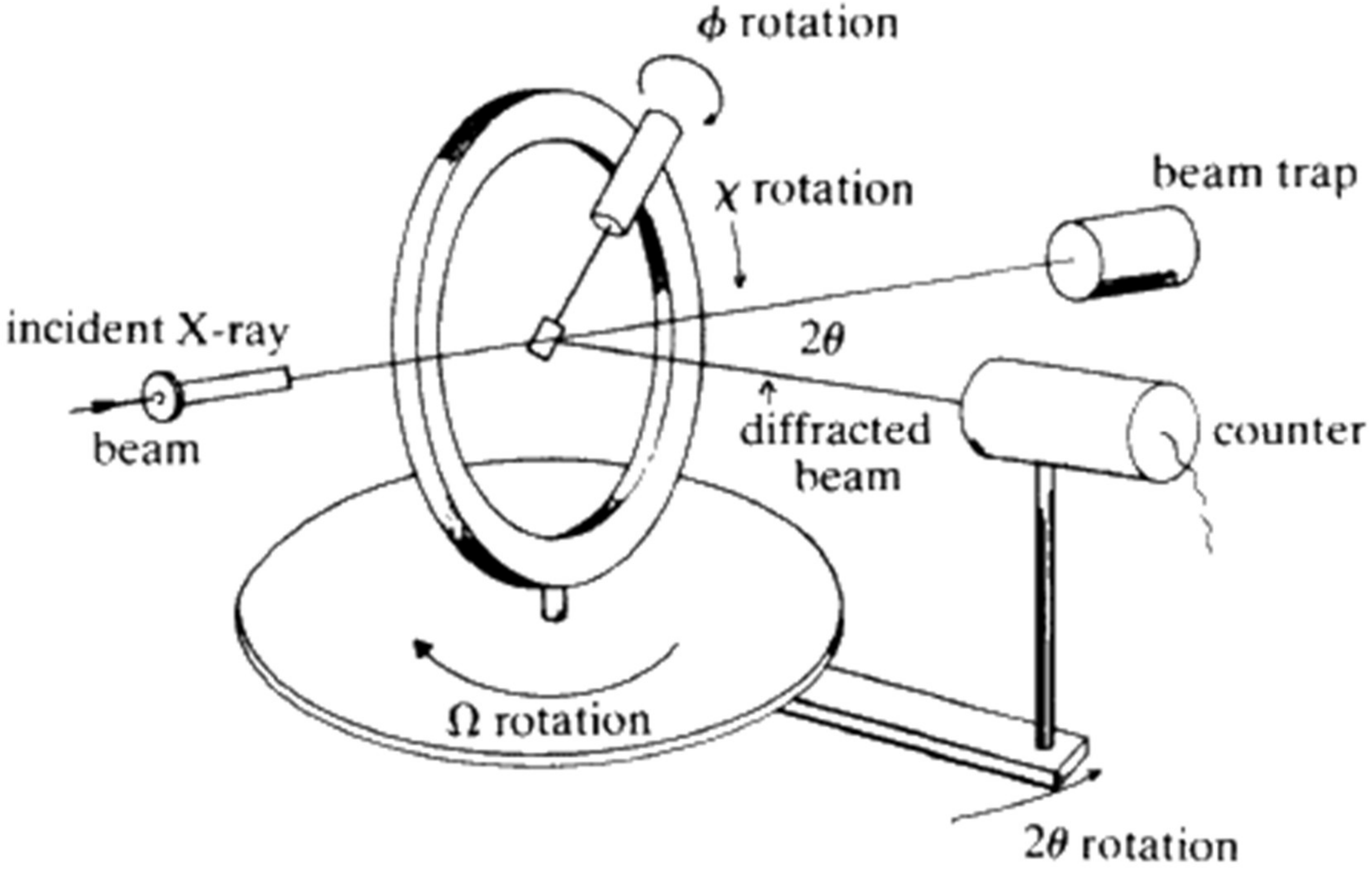
M. von Laue (1879-1960)

$$\vec{G} = \Delta\vec{k}$$

$$\vec{k}' - \vec{k} = \Delta\vec{k} = \vec{G}$$

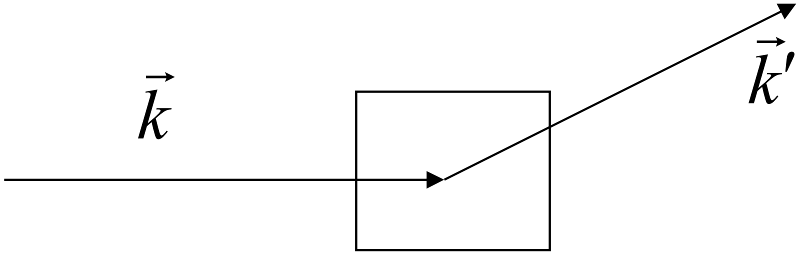


$$|\vec{k}| = |\vec{k}'| \text{ for elastic scattering}$$



http://serc.carleton.edu/research_education/geochemsheets/techniques/SXD.html

Single crystal diffraction



$$\vec{G} = \Delta\vec{k} = \vec{q}$$

Scattering wave vector

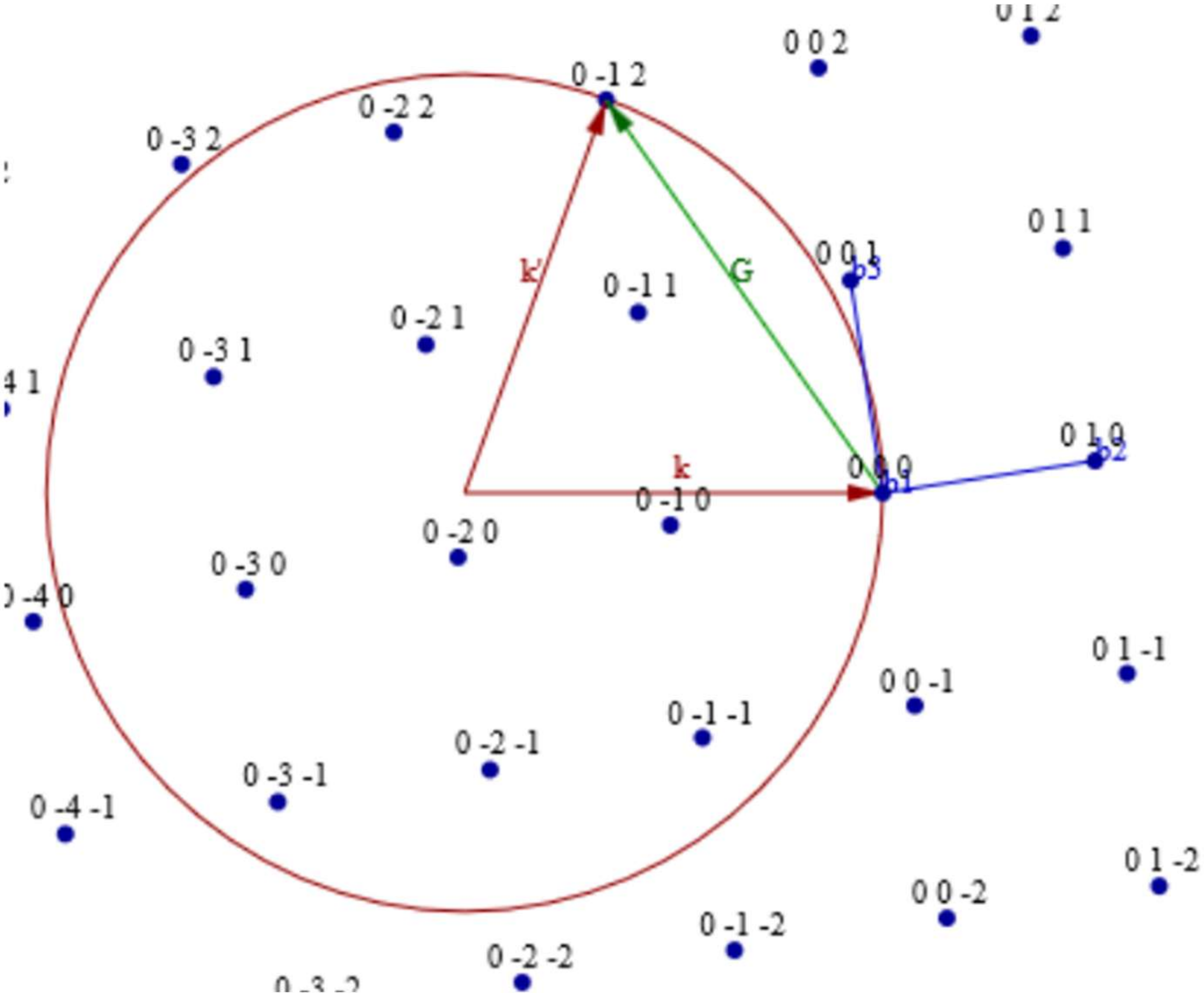
Every time a diffraction peak is observed, record *G*. When many *G* vectors are known, determine the reciprocal lattice.

The sample and the detector must be turned to find all of the diffraction peaks.

Gx	Gy	Gz	$\lvert n_G \rvert^2$
2.4E10	2.4E10	0	10341
2.4E10	0	2.4E10	9989

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

Ewald sphere $\Delta\vec{k} = \vec{G}$



Draw a vector representing the incoming radiation so that it ends at the origin. As the crystal is rotated around the origin, the condition for diffraction will be satisfied every time a reciprocal lattice point is on the sphere.

Determining real space primitive lattice vectors

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

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

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

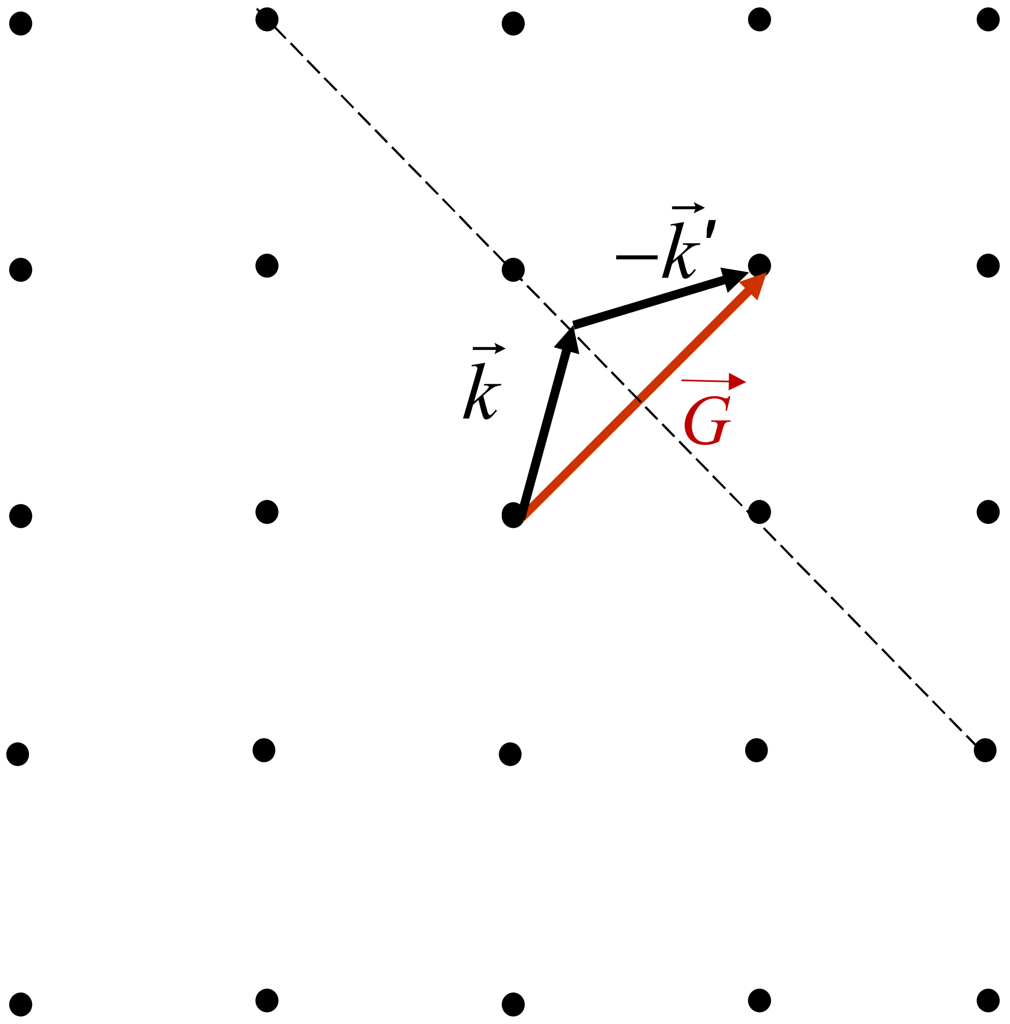
$\vec{b}_1, \vec{b}_2, \vec{b}_3$ determined from diffraction experiment

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

Volume of the primitive unit cell $\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)$

G vectors specify the Bravais lattice.

Diffraction condition



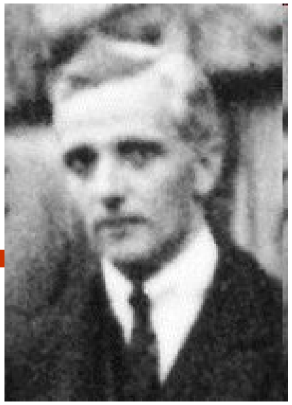
$$\vec{k}\,' - \vec{k} = \vec{G}$$

For every *G* there is a -*G* so the diffraction condition can also be written as

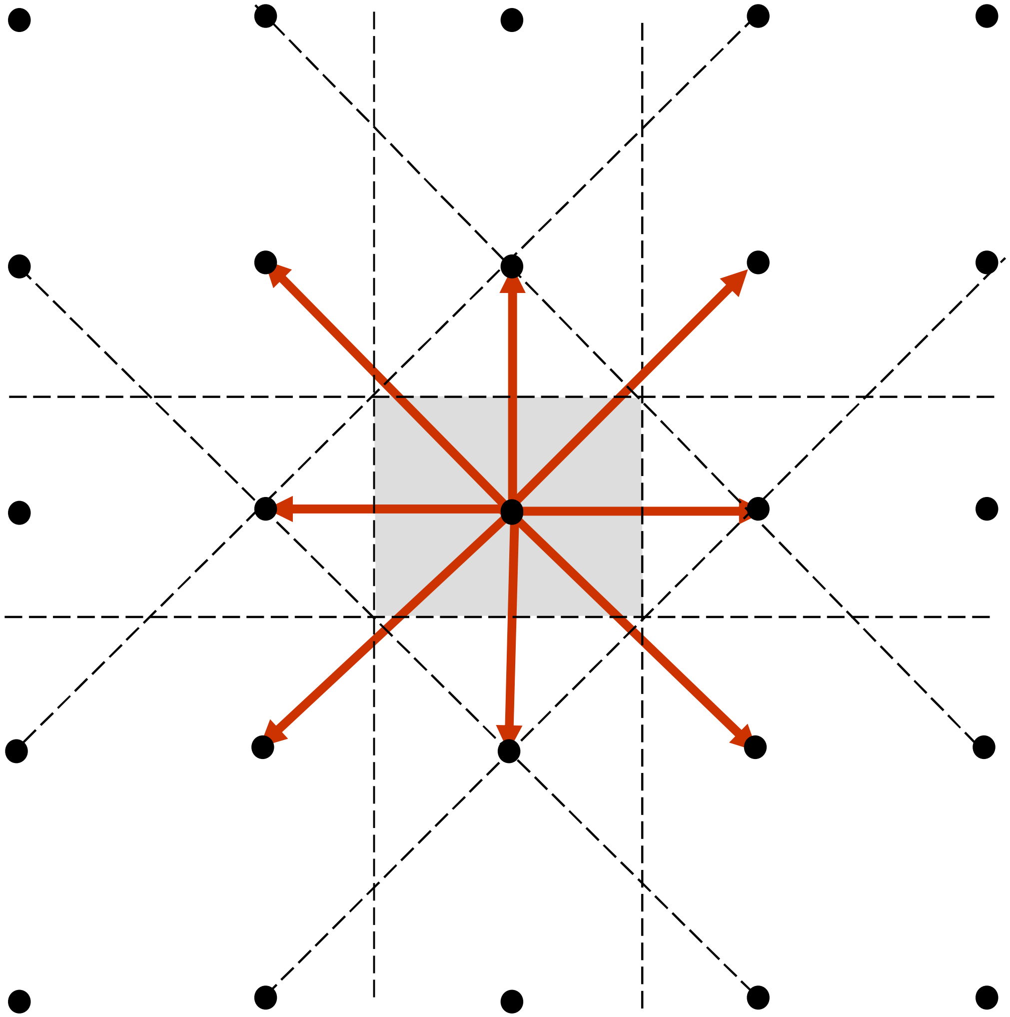
$$\vec{k} - \vec{k}\,' = \vec{G}$$

A wave will be diffracted if the wave vector ends on one of the planes. The wavelength changes when you change *k*.

Brillouin zones

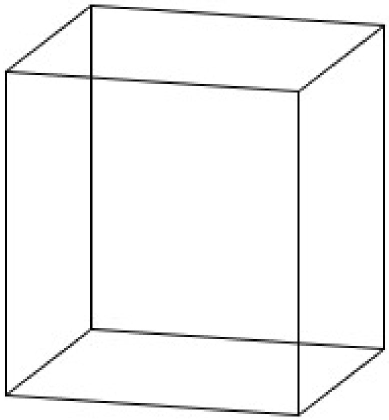


Leon Brillouin

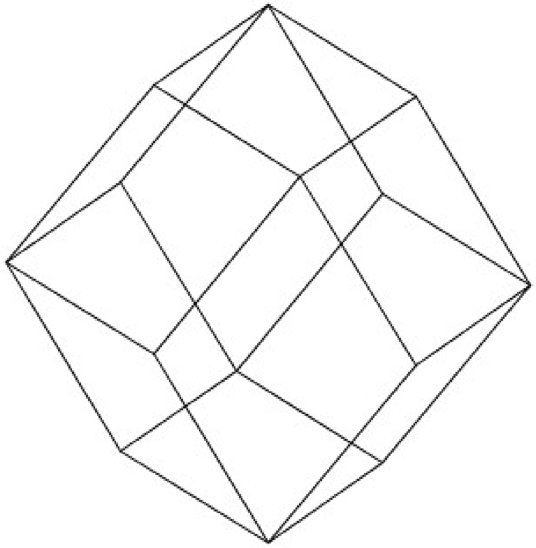


1st Brillouin zone consists of the *k*-states around the origin that can be reached without crossing a plane.

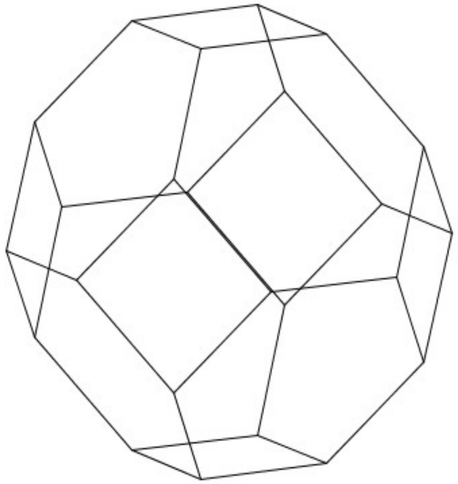
1st Brillouin zones



sc



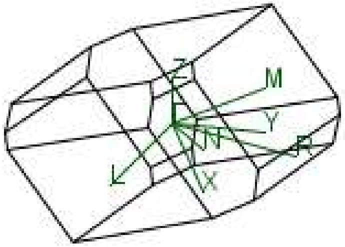
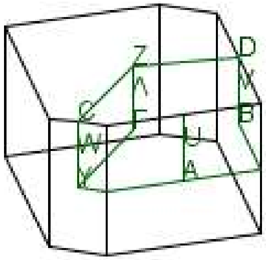
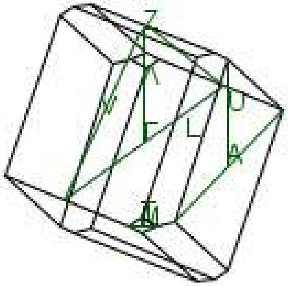
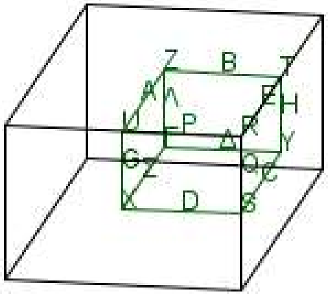
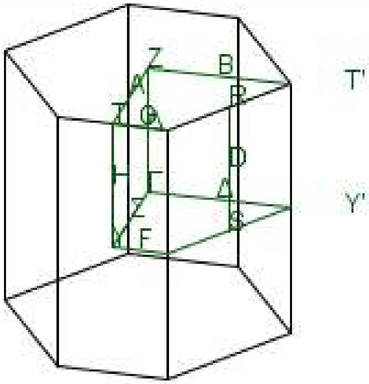
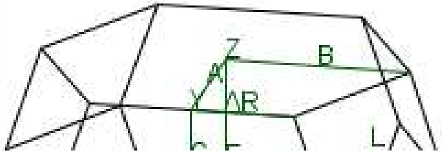
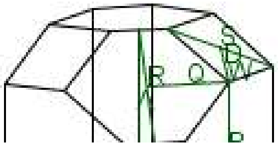
bcc



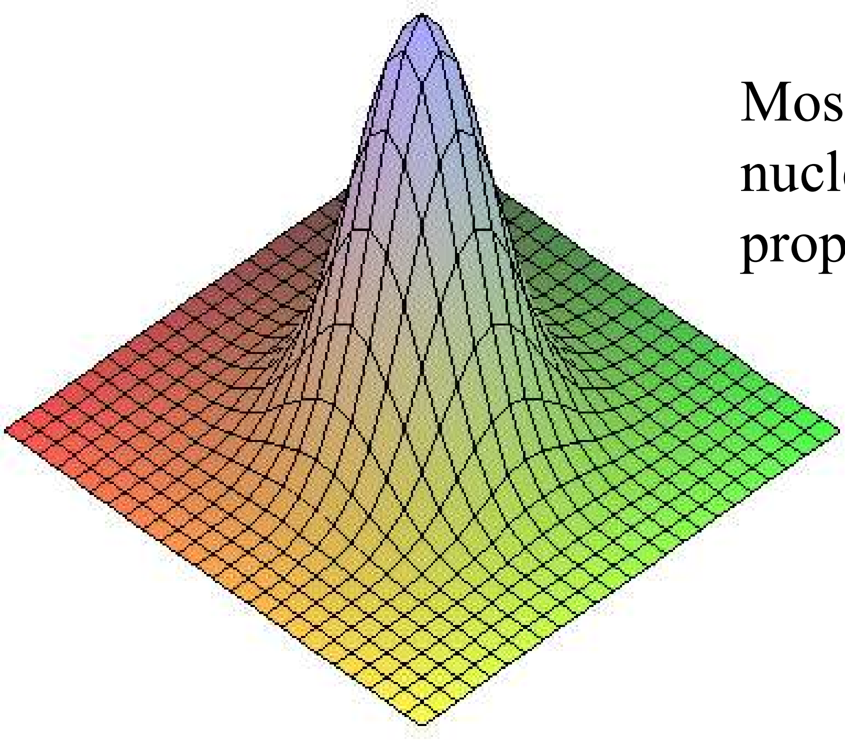
fcc

1st Brillouin is the Wigner-Seitz cell in reciprocal space.

Brillouin zones

Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	 Triclinic	
Monoclinic $a \neq b \neq c$ $\alpha \neq 90°$ $\beta = \gamma = 90°$	 Monoclinic simple	 Monoclinic Base centered
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	 Orthorhombic simple	 Base centered
		

Electron density of an atom



Most of the electrons are concentrated around the nucleus. The integral over the electron density is proportional to the number of electrons.

$$n_j\left(\vec{r}\right) \propto \exp\left(-\frac{\left(\vec{r}-\vec{r}_j\right)^2}{r_0^2}\right)$$

Approximately a Gaussian centered at r_j

X-ray Fluorescence spectrometer

Tells you the atomic composition of a sample to a few %

Electron density

Write the electron density as a Fourier series

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = \sum_{\vec{T}} \sum_{j} n_j\left(\vec{r} - \vec{r}_j + \vec{T}\right),$$

Translation vector

position of atom *j* of the basis

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a unit cell.

$$\sum_{\vec{G}} \int_{\text{u.c.}} n_{\vec{G}} \underbrace{e^{i\vec{G}\cdot\vec{r}} e^{-i\vec{G}'\cdot\vec{r}}}_{1} \, d\vec{r} = \sum_{j} \int_{\text{u.c.}} n_j\left(\vec{r} - \vec{r}_j\right) e^{-i\vec{G}'\cdot\vec{r}} \, d\vec{r}.$$

Electron density

$$n_{\vec{G}} V = \sum_j \int n_j(\vec{r} - \vec{r}_j) e^{-i\vec{G}\cdot\vec{r}} d\vec{r}.$$

Make a substitution $\vec{r}' = \vec{r} - \vec{r}_j$.

$$n_{\vec{G}} = \frac{1}{V} \sum_j e^{-i\vec{G}\cdot\vec{r}_j} \underbrace{\int n_j\left(\vec{r}'\right) e^{-i\vec{G}\cdot\overrightarrow{r'}} d\vec{r}'}_{}.$$

Fourier transform of the electron density of atom *j*
= atomic form factor $f_j(|G|)$

Atomic form factor

$$f_j\left(\vec{G}\right) = \int n_j(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}}\, d\vec{r},$$

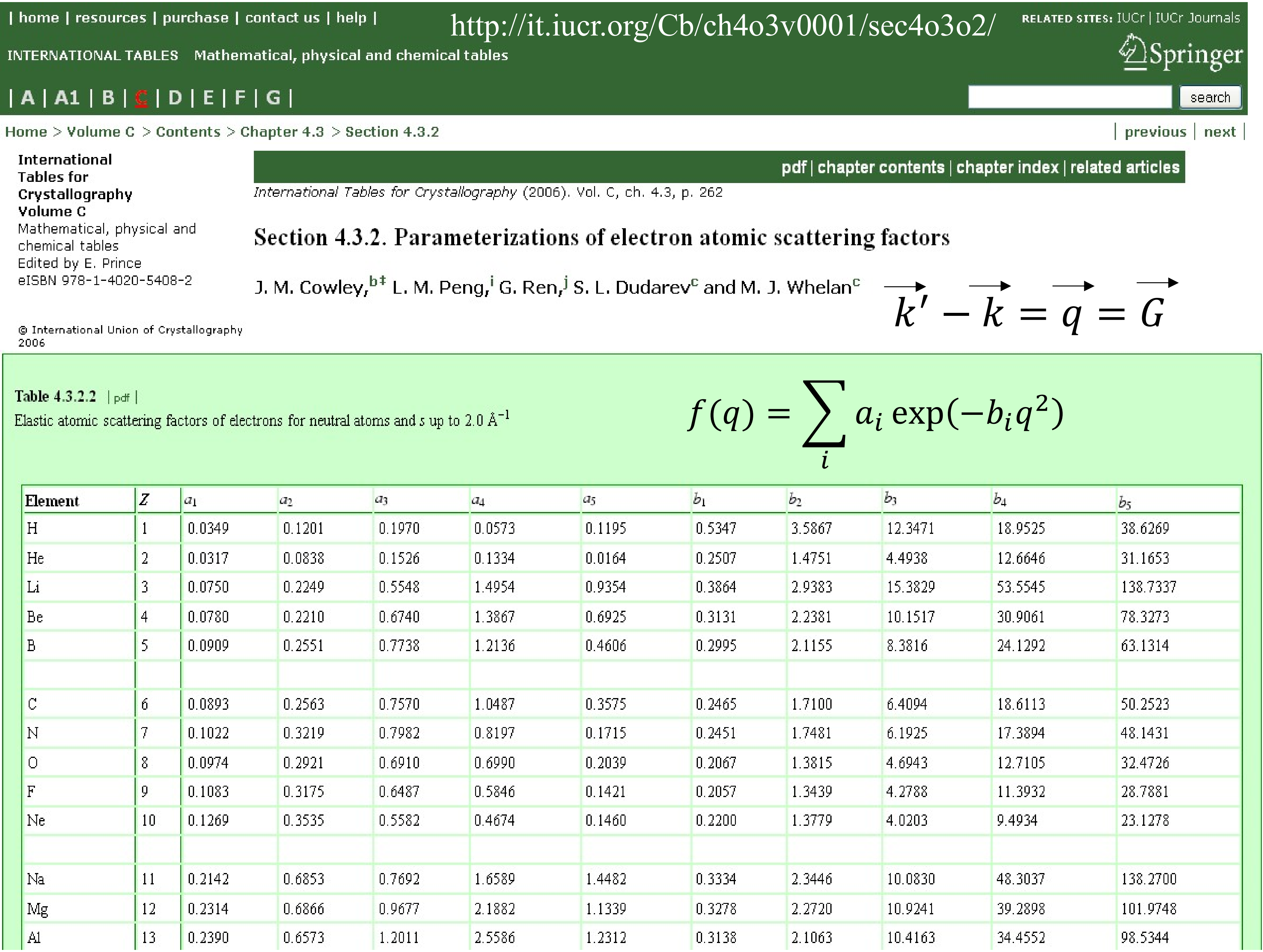
The atomic form factors can be looked up in a table.

The structure factors are given in terms of the atomic form factors.

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

sum over the basis

position of atom *j* of the basis



http://it.iucr.org/Cb/ch4o3v0001/sec4o3o2/

International Tables for Crystallography
Volume C
Mathematical, physical and chemical tables
Edited by E. Prince
eISBN 978-1-4020-5408-2

International Tables for Crystallography (2006). Vol. C, ch. 4.3, p. 262

Section 4.3.2. Parameterizations of electron atomic scattering factors

J. M. Cowley,[b‡] L. M. Peng,[i] G. Ren,[j] S. L. Dudarev[c] and M. J. Whelan[c]

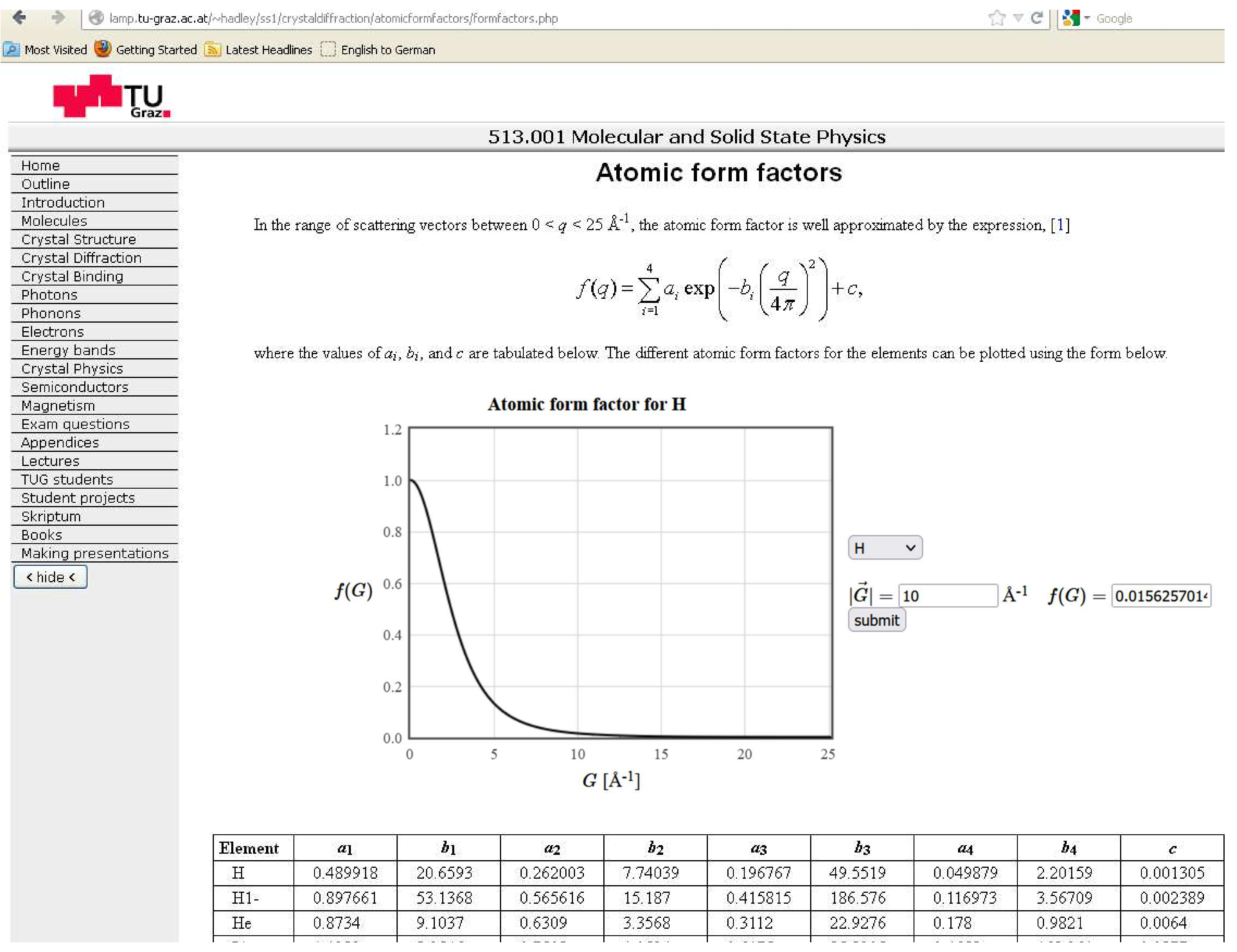
$$\overrightarrow{k'} - \overrightarrow{k} = \overrightarrow{q} = \overrightarrow{G}$$

Table 4.3.2.2

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

$$f(q) = \sum_i a_i \exp(-b_i q^2)$$

Element	Z	a_1	a_2	a_3	a_4	a_5	b_1	b_2	b_3	b_4	b_5
H	1	0.0349	0.1201	0.1970	0.0573	0.1195	0.5347	3.5867	12.3471	18.9525	38.6269
He	2	0.0317	0.0838	0.1526	0.1334	0.0164	0.2507	1.4751	4.4938	12.6646	31.1653
Li	3	0.0750	0.2249	0.5548	1.4954	0.9354	0.3864	2.9383	15.3829	53.5545	138.7337
Be	4	0.0780	0.2210	0.6740	1.3867	0.6925	0.3131	2.2381	10.1517	30.9061	78.3273
B	5	0.0909	0.2551	0.7738	1.2136	0.4606	0.2995	2.1155	8.3816	24.1292	63.1314
C	6	0.0893	0.2563	0.7570	1.0487	0.3575	0.2465	1.7100	6.4094	18.6113	50.2523
N	7	0.1022	0.3219	0.7982	0.8197	0.1715	0.2451	1.7481	6.1925	17.3894	48.1431
O	8	0.0974	0.2921	0.6910	0.6990	0.2039	0.2067	1.3815	4.6943	12.7105	32.4726
F	9	0.1083	0.3175	0.6487	0.5846	0.1421	0.2057	1.3439	4.2788	11.3932	28.7881
Ne	10	0.1269	0.3535	0.5582	0.4674	0.1460	0.2200	1.3779	4.0203	9.4934	23.1278
Na	11	0.2142	0.6853	0.7692	1.6589	1.4482	0.3334	2.3446	10.0830	48.3037	138.2700
Mg	12	0.2314	0.6866	0.9677	2.1882	1.1339	0.3278	2.2720	10.9241	39.2898	101.9748
Al	13	0.2390	0.6573	1.2011	2.5586	1.2312	0.3138	2.1063	10.4163	34.4552	98.5344



513.001 Molecular and Solid State Physics

Atomic form factors

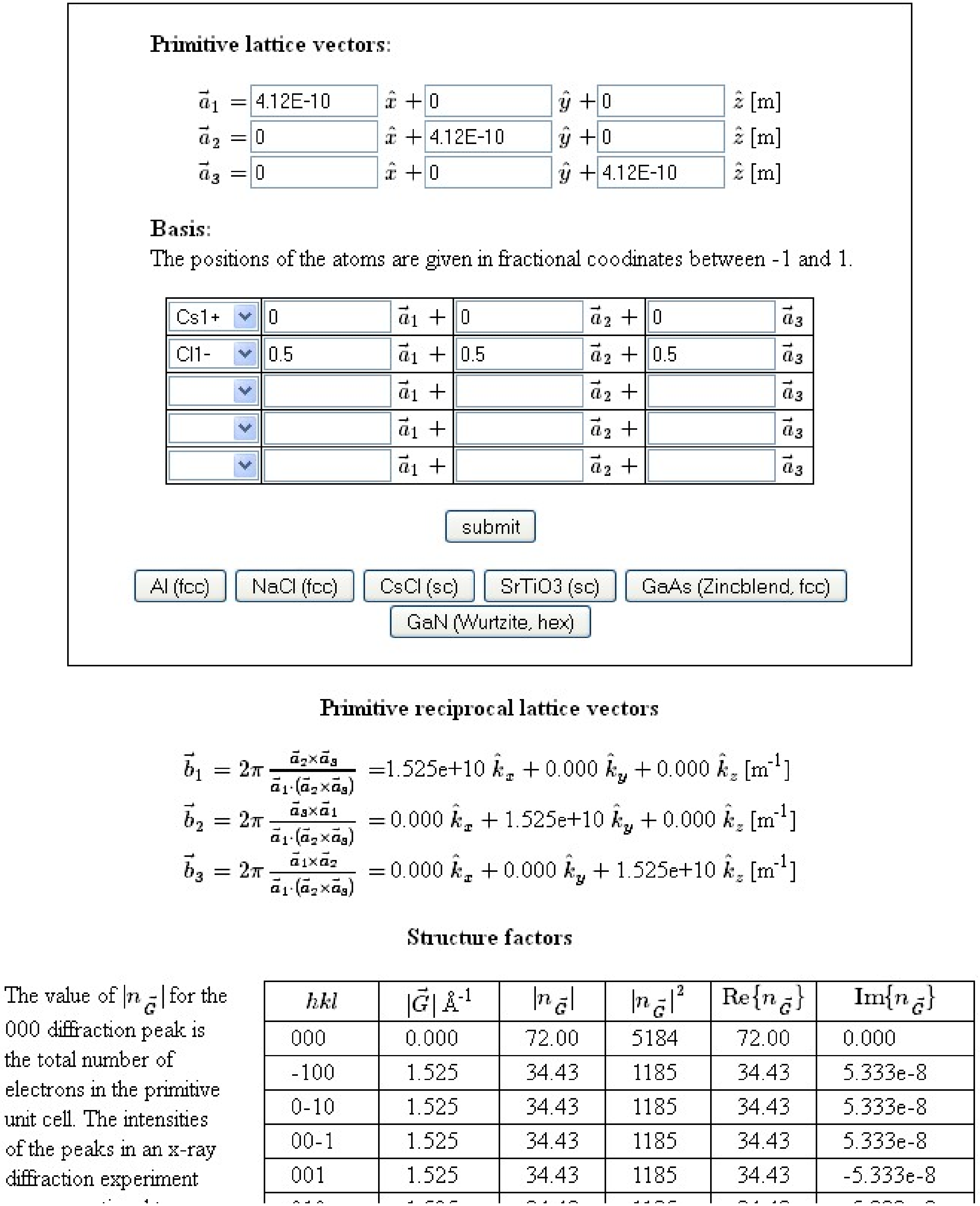
In the range of scattering vectors between $0 < q < 25$ Å^{-1}, the atomic form factor is well approximated by the expression, [1]

$$f(q)=\sum_{i=1}^{4} a_i \exp\left(-b_i\left(\frac{q}{4\pi}\right)^2\right)+c,$$

where the values of a_i, b_i, and c are tabulated below. The different atomic form factors for the elements can be plotted using the form below.

$|\vec{G}| =$ 10 Å^{-1} $f(G) =$ 0.015625701

Element	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
H	0.489918	20.6593	0.262003	7.74039	0.196767	49.5519	0.049879	2.20159	0.001305
H1-	0.897661	53.1368	0.565616	15.187	0.415815	186.576	0.116973	3.56709	0.002389
He	0.8734	9.1037	0.6309	3.3568	0.3112	22.9276	0.178	0.9821	0.0064



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	$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$

Primitive reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 1.525\text{e+}10\ \hat{k}_x + 0.000\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{m}^{-1}]$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000\ \hat{k}_x + 1.525\text{e+}10\ \hat{k}_y + 0.000\ \hat{k}_z\ [\text{m}^{-1}]$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000\ \hat{k}_x + 0.000\ \hat{k}_y + 1.525\text{e+}10\ \hat{k}_z\ [\text{m}^{-1}]$$

Structure factors

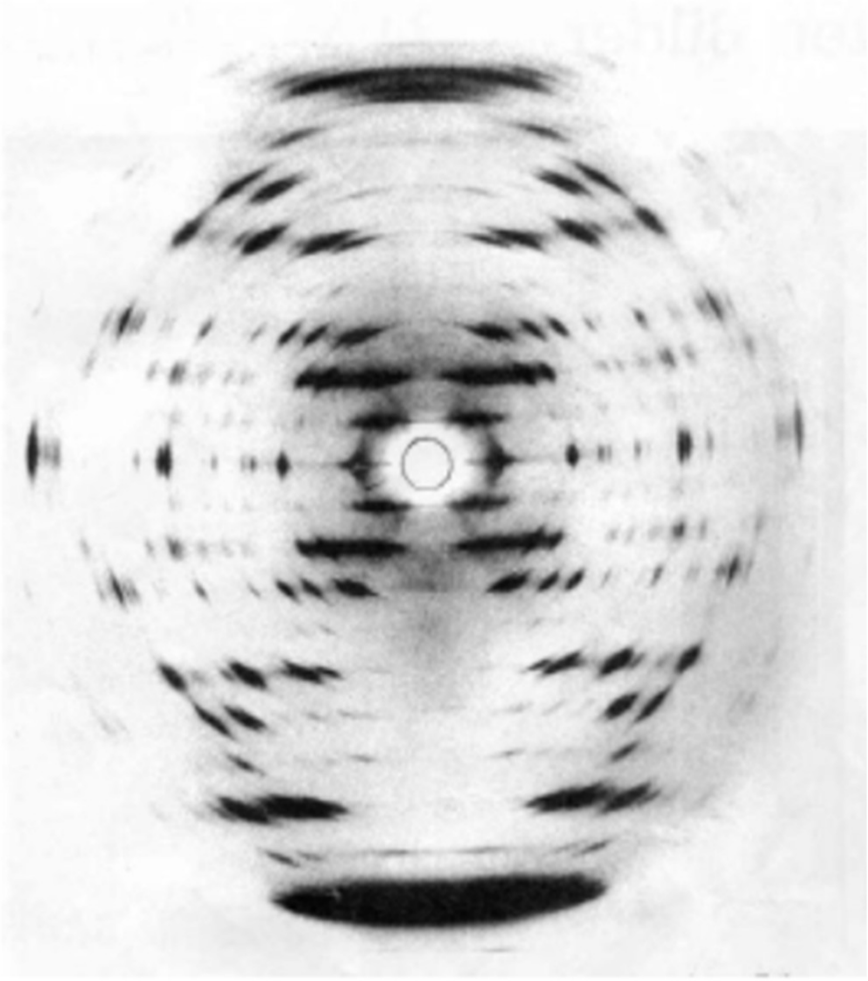
The value of $|n_{\vec{G}}|$ for the 000 diffraction peak is the total number of electrons in the primitive unit cell. The intensities of the peaks in an x-ray diffraction experiment

hkl	$\lvert\vec{G}\rvert$ Å^{-1}	$\lvert n_{\vec{G}}\rvert$	$\lvert n_{\vec{G}}\rvert^2$	$\text{Re}\{n_{\vec{G}}\}$	$\text{Im}\{n_{\vec{G}}\}$
000	0.000	72.00	5184	72.00	0.000
-100	1.525	34.43	1185	34.43	5.333e-8
0-10	1.525	34.43	1185	34.43	5.333e-8
00-1	1.525	34.43	1185	34.43	5.333e-8
001	1.525	34.43	1185	34.43	-5.333e-8

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

crystal structure solution

structural solution of the DNA
F.Crick, J.Watson, M.Wilkins
nobel laureate 1962 for medicine



Rosalind Franklin

crystal structure solution

"Guess" the crystal structure

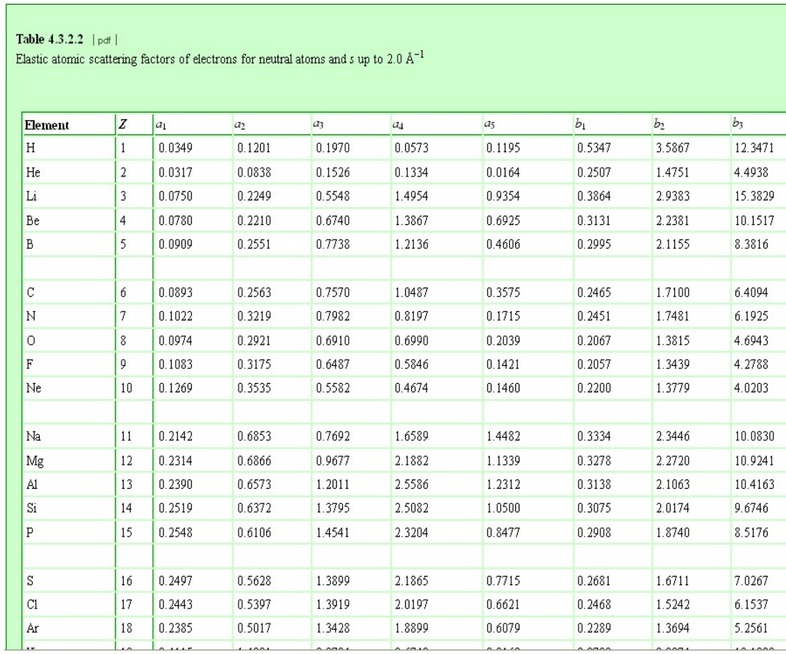


Table 4.3.2.2 | pdf |

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.

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

Compare $|n_G|^2$ to the measurements

x-ray diffraction

The shape and the dimensions of the unit cell can be deduced from the positions of the Bragg reflections; the content of the unit cell, on the other hand, must be determined from the intensities of the reflections.

Solid State Physics, Ibach and Lüth

Diffraction condition: $\Delta\vec{k} = \vec{G}$

The intensity of the peaks is proportional to the squared Fourier coefficients of the electron density.

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