

X-ray diffraction by crystalline materials

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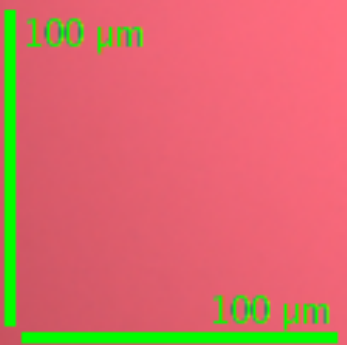
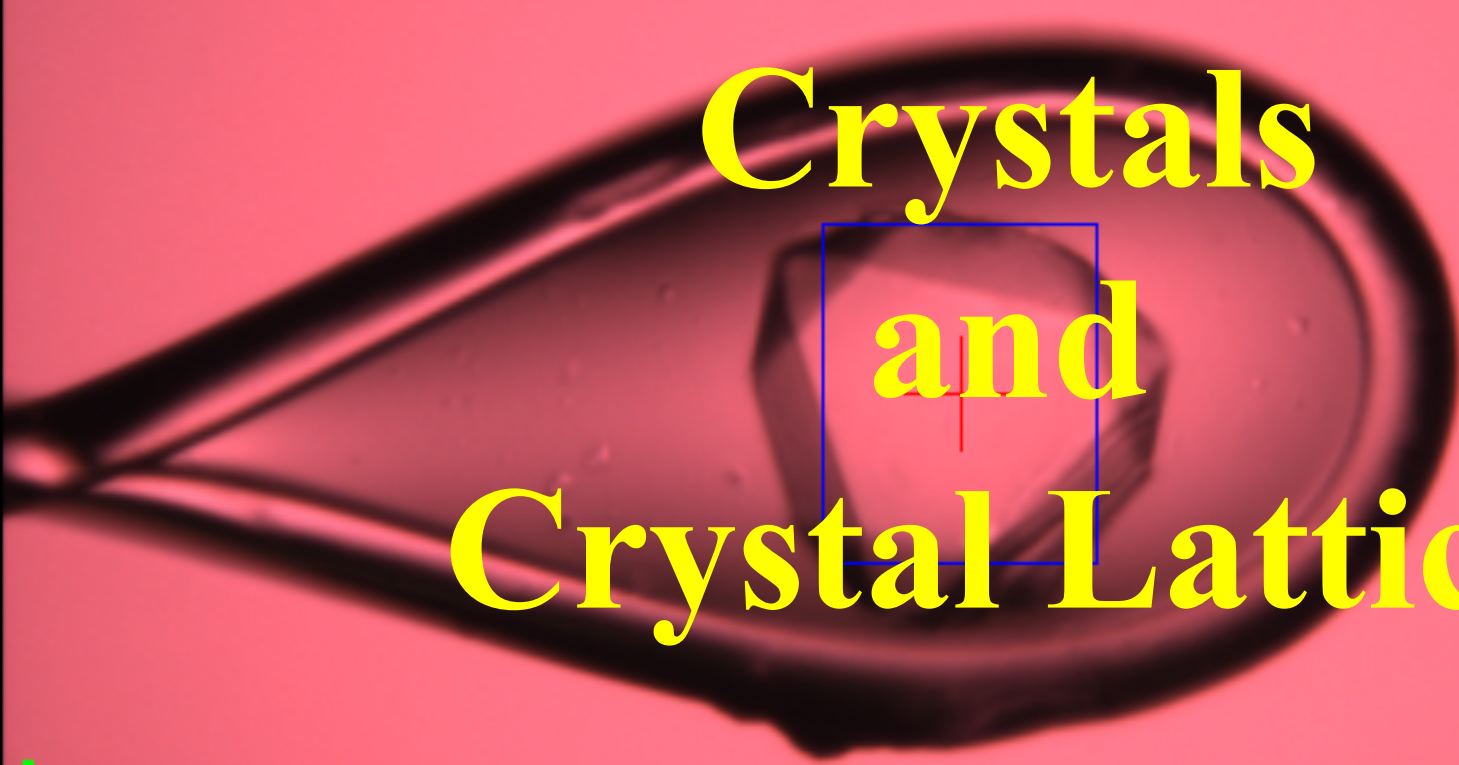
- Crystals and crystal lattice
- Some mathematics
- X-ray Diffraction by single crystal
- Additional concepts (to make things more confused)
- Powders diffraction
- Something different



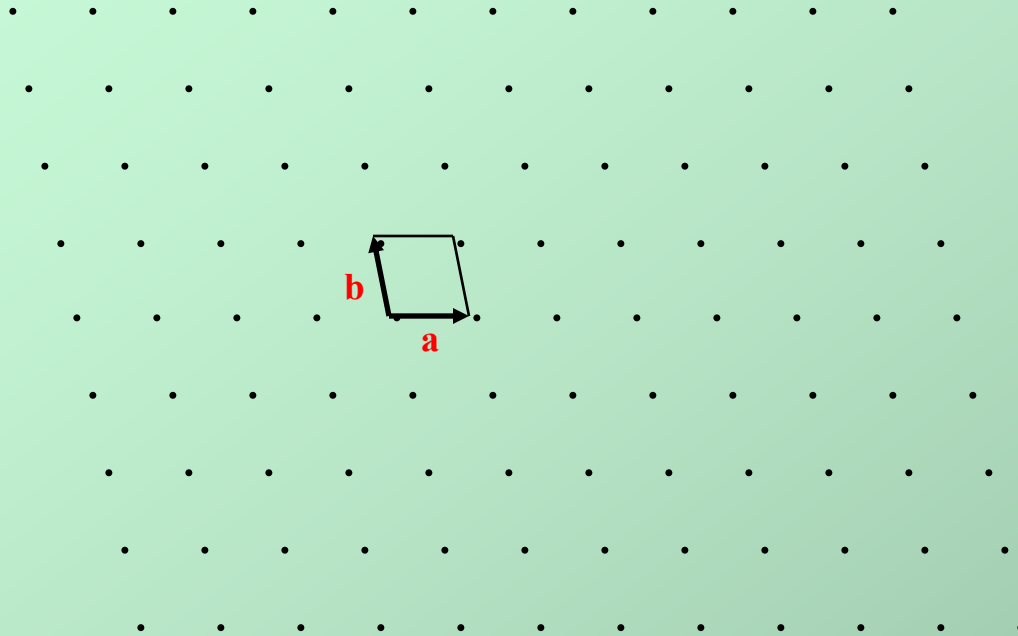
100 μm

100 μm

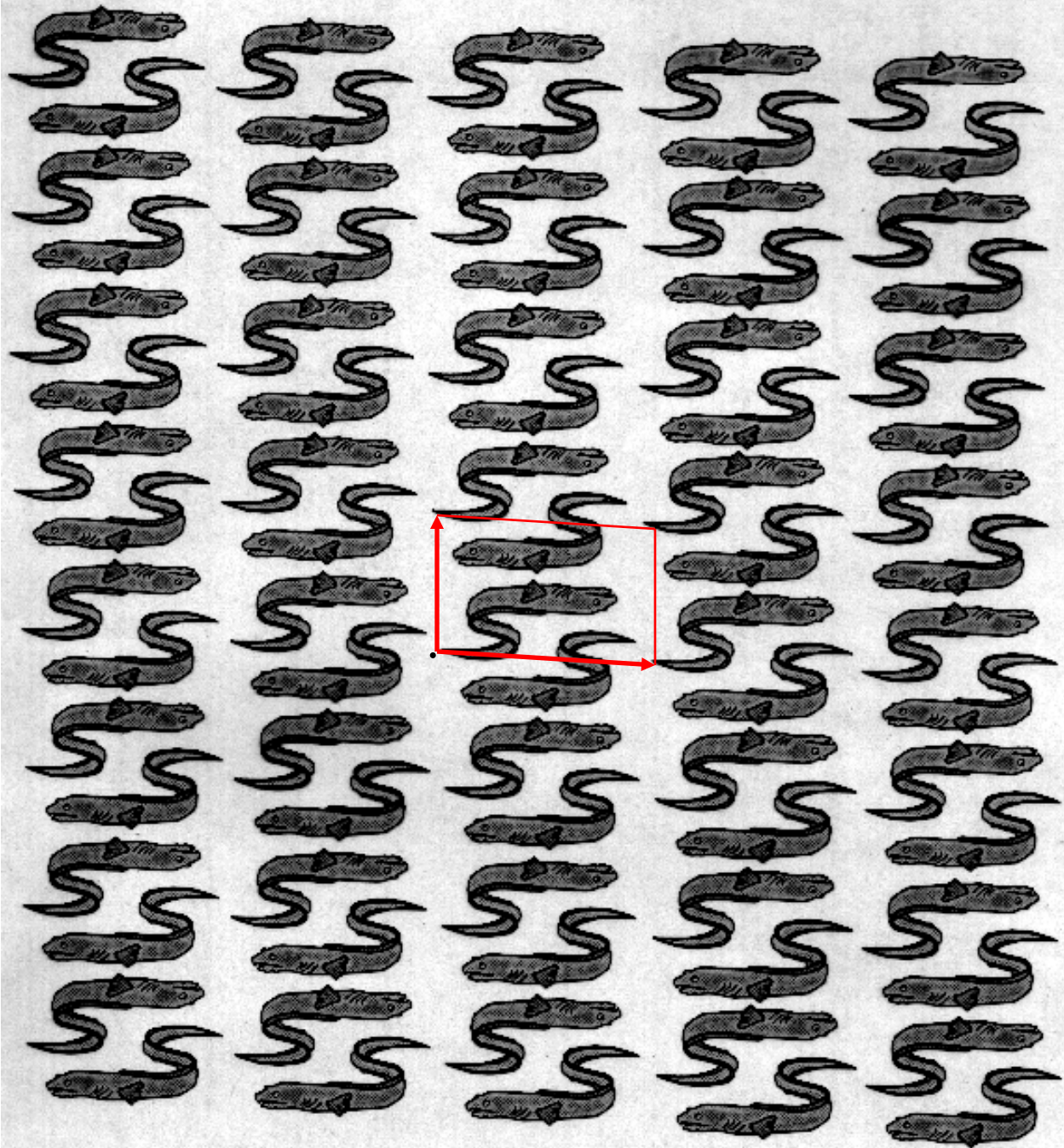
Crystals and Crystal Lattice



Crystal Lattice



$$\mathbf{r}_{u,v,w} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$



Symmetry elements in crystals

Rotation axes: 1, 2, 3, 4, 6

Screw axes: 2_1 , 3_1 , 3_2 , 4_1 , 4_2 , 4_3 , 6_1 , 6_2 , 6_3 , 6_4 , 6_5

Mirror plane: m

Inversion center: $\bar{1}$

Glide planes: a , b , c , n

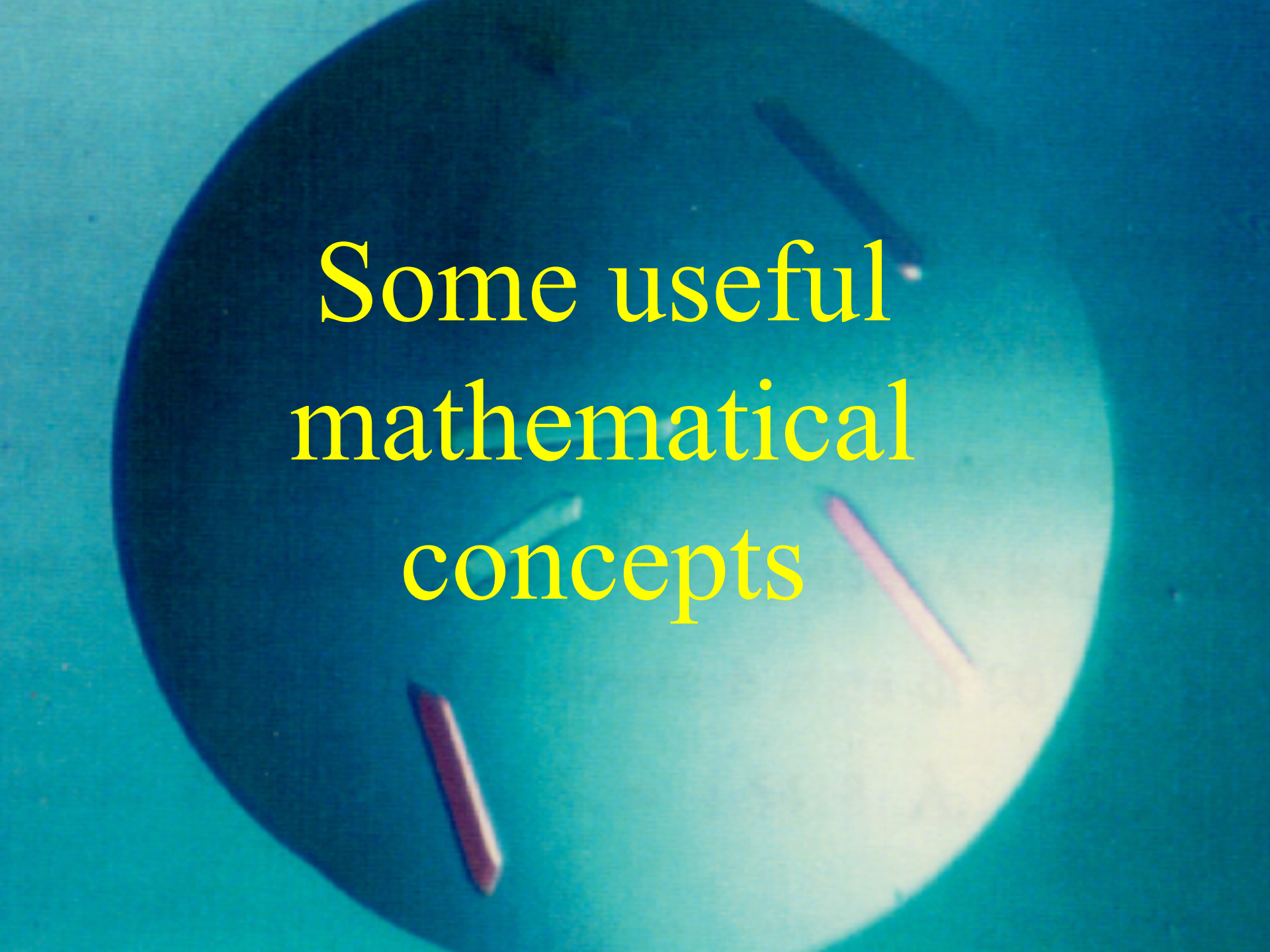
Inversion axes: $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$

32 point groups

14 Bravais lattices

230 space groups

International Tables for x-ray crystallography,
Vol A, Reidel, Dordrecht



Some useful
mathematical
concepts

Dirac δ function

In one dimension:

$$\begin{aligned}\delta(x-x_0) &= 0 \text{ for } x \neq x_0 \\ &= \infty \text{ for } x = x_0\end{aligned}$$

In three dimensions:

$$\delta(\mathbf{r}-\mathbf{r}_0) = \delta(x-x_0) \delta(y-y_0) \delta(z-z_0)$$

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

A three-dimensional lattice defined by vectors \mathbf{a} , \mathbf{b} and \mathbf{c} and $\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ can be represented by the function:

$$L(\mathbf{r}) = \sum_u \sum_v \sum_w \delta(\mathbf{r} - \mathbf{r}_{u,v,w})$$

Fourier transforms

$$g(\mathbf{S}) = \int_{-\infty}^{\infty} f(\mathbf{r}) e^{2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{r}$$

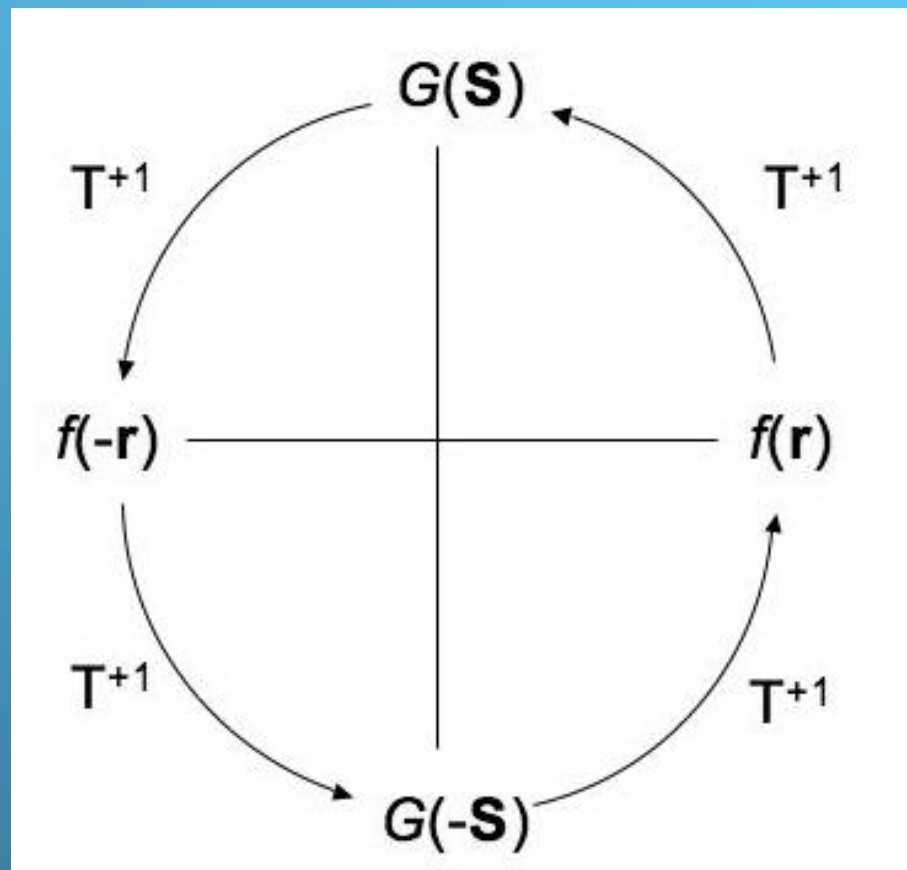
$$f(\mathbf{r}) = \int_{-\infty}^{\infty} g(\mathbf{S}) e^{-2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{S}$$

$$g(\mathbf{S}) = T[f(\mathbf{r})] \quad f(\mathbf{r}) = T^{-1}[g(\mathbf{S})]$$

$$f(-\mathbf{r}) = T^{+1}[\mathbf{G}(\mathbf{S})] \quad (2B.1)$$

$$\mathbf{G}(-\mathbf{S}) = T^{+1}[f(-\mathbf{r})] \quad (2B.2)$$

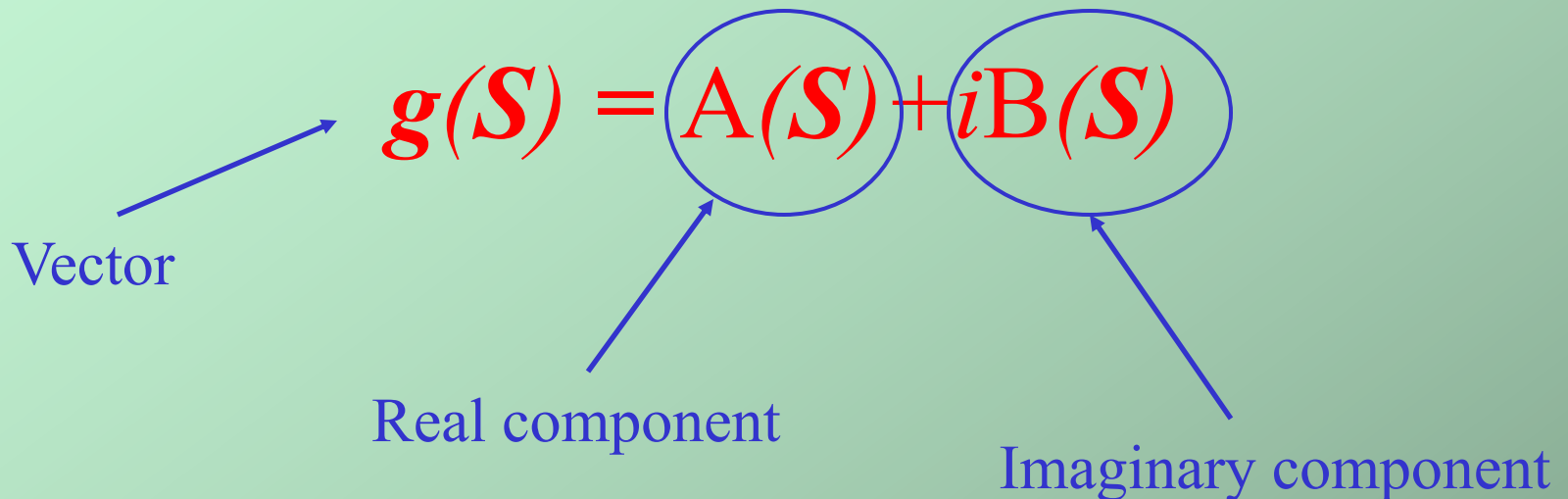
$$f(\mathbf{r}) = T^{+1}[\mathbf{G}(-\mathbf{S})] \quad (2B.3)$$



Fourier transforms

Euler formula: $\exp(i\alpha) = \cos(\alpha) + i\sin(\alpha)$

$$g(\mathbf{S}) = \int_{-\infty}^{\infty} f(\mathbf{r}) \{ \cos[2\pi(hx_j + ky_j + lz_j)] + i \sin[2\pi(hx_j + ky_j + lz_j)] \} d\mathbf{r}$$



$$G(S)=ab[\sin(\pi as)]/\pi as$$

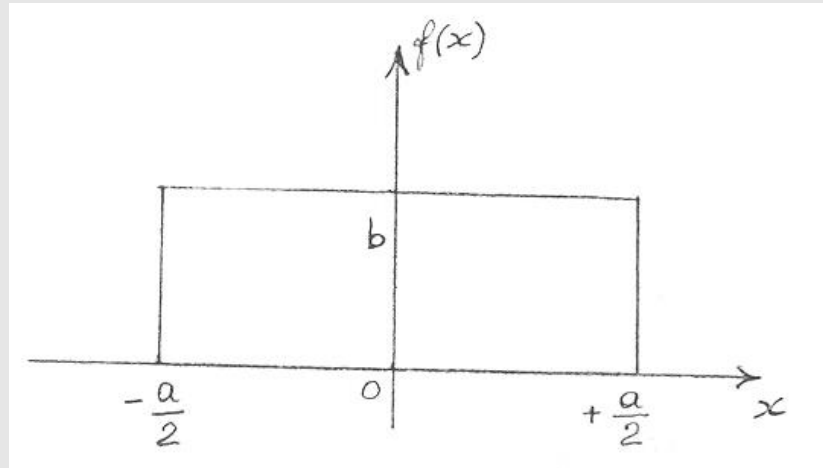
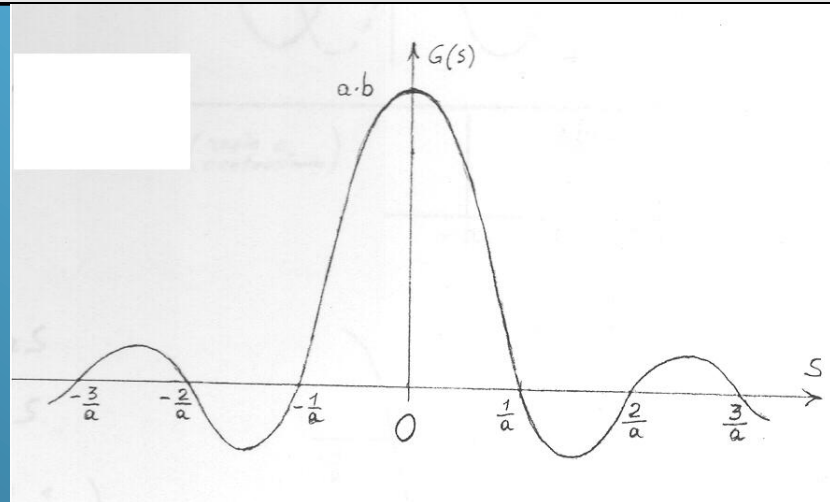


Fig. 2B.3A. Funzione gradino.



La funzione risultante vale ab nel punto 0, e 0 per tutti i valori di πas multipli di $\pm\pi$. I massimi e minimi della funzione sono in corrispondenza dei valori di $S = 0, \pm 3/(2a), \pm 5/(2a), \pm 7/(2a)$ etc.

Proprietà 2. Se $f(\mathbf{r})$ è reale, cioè $b(\mathbf{r}) = 0$, valgono le condizioni dette “di Friedel”:

$$\mathbf{G}(\mathbf{S}) = \mathbf{G}^*(-\mathbf{S}) \quad (2B.5)$$

e

$$\mathbf{G}(-\mathbf{S}) = \mathbf{G}^*(\mathbf{S}) \quad (2B.6).$$

Precisamente:

$$A(\mathbf{S}) = A(-\mathbf{S}) \quad (2B.7)$$

$$B(\mathbf{S}) = -B(-\mathbf{S}) \quad (2B.8)$$

e perciò:

$$|\mathbf{G}(\mathbf{S})| = |\mathbf{G}(-\mathbf{S})| \quad (2B.9)$$

$$\varphi(\mathbf{S}) = -\varphi(-\mathbf{S}) \quad (2B.10).$$

Proprietà 3. Se $f(\mathbf{r})$ è reale e centrosimmetrica, cioè $f(\mathbf{r}) = a(r) = a(-\mathbf{r})$, allora $\mathbf{G}(\mathbf{S})$ è reale. Per le proprietà 1 e 2 deve valere, infatti, che $\mathbf{G}(\mathbf{S}) = \mathbf{G}(-\mathbf{S}) = \mathbf{G}^*(-\mathbf{S}) = \mathbf{G}^*(\mathbf{S})$. Questo è possibile solo se:

$$\mathbf{G}(\mathbf{S}) = A(\mathbf{S}) \quad (2B.11)$$

$$A(\mathbf{S}) = A(-\mathbf{S}), B(\mathbf{S}) = 0 \quad (2B.12)$$

Vale infine la proprietà, che non dimostreremo, che se $\mathbf{f}(\mathbf{r})$ è complessa e centrosimmetrica, anche $\mathbf{G}(\mathbf{S})$ è complessa e centrosimmetrica.

Fourier transform of a lattice

For a finite one-dimensional lattice:

$$f(x) \equiv L(x) = \sum_n \delta(x-na) \quad g(S) = \sin(N\pi aS)/\sin(\pi aS)$$

For a finite three-dimensional lattice:

$$f(\mathbf{r}) = \sum_u \sum_v \sum_w \delta(\mathbf{r} - \mathbf{r}_{u,v,w})$$

$$G(\mathbf{S}) = [\sin(N\pi \mathbf{a} \cdot \mathbf{S})/\sin(\pi \mathbf{a} \cdot \mathbf{S})] \times [\sin(N\pi \mathbf{b} \cdot \mathbf{S})/\sin(\pi \mathbf{b} \cdot \mathbf{S})] \times [\sin(N\pi \mathbf{c} \cdot \mathbf{S})/\sin(\pi \mathbf{c} \cdot \mathbf{S})]$$

These transforms will have maxima when the following conditions are satisfied:

$$\mathbf{a} \cdot \mathbf{S} = h, \quad \mathbf{b} \cdot \mathbf{S} = k, \quad \mathbf{c} \cdot \mathbf{S} = l$$

with h , k and l integers.

The reciprocal lattice

$$\mathbf{a} \cdot \mathbf{S} = h, \quad \mathbf{b} \cdot \mathbf{S} = k, \quad \mathbf{c} \cdot \mathbf{S} = l$$

From each individual relationships, the shortest value of S in each direction is:

$$S = 1/a = a^* \quad S = 1/b = b^* \quad S = 1/c = c^*$$

$$\mathbf{a} \cdot \mathbf{a}^* = 1, \quad \mathbf{b} \cdot \mathbf{b}^* = 1, \quad \mathbf{c} \cdot \mathbf{c}^* = 1, \quad \mathbf{a} \cdot \mathbf{b}^* = 0, \text{ etc.}$$

The vector S can be defined in a way similar to \mathbf{r} , using three base vectors, that we have called \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* :

$$\mathbf{S}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

Conclusion: the Fourier transform of a mathematical lattice is a lattice whose periods are reciprocal with respect to the original ones.

Convolution

Siano $f(\mathbf{r})$ e $g(\mathbf{r})$ due funzioni definite nello spazio \mathbf{r} . Si definisce convoluzione delle due funzioni l'integrale del prodotto tra le funzioni stesse:

$$Q(\mathbf{r}) = \int_{-\infty}^{+\infty} f(\mathbf{r}')g(\mathbf{r} - \mathbf{r}')d\mathbf{r}' \quad (2B.19)$$

Si noti che \mathbf{r} ed \mathbf{r}' sono definiti nello stesso spazio. Per calcolare il valore della convoluzione in un punto \mathbf{r} , si trasla la funzione $g(\mathbf{r}')$ e si esegue il prodotto $f(\mathbf{r}')g(\mathbf{r} - \mathbf{r}')$ punto a punto, ottenendo una nuova funzione, la cui integrazione fornisce il valore $Q(\mathbf{r})$. La (2B.19) si definisce Q-convoluzione. La convoluzione viene anche scritta, in modo abbreviato, come:

$$Q(\mathbf{r}) = f(\mathbf{r}) * g(\mathbf{r}) \quad (2B.20).$$

La funzione:

$$P(\mathbf{r}) = \int_{-\infty}^{+\infty} f(\mathbf{r}')g(\mathbf{r}' - \mathbf{r})d\mathbf{r}' \quad (2B.21)$$

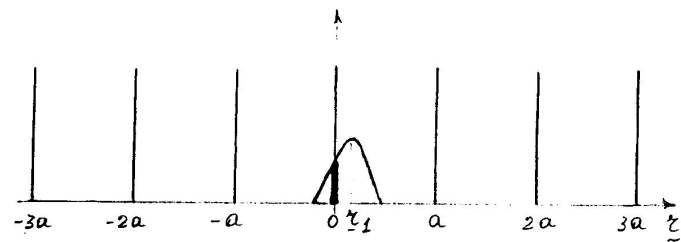
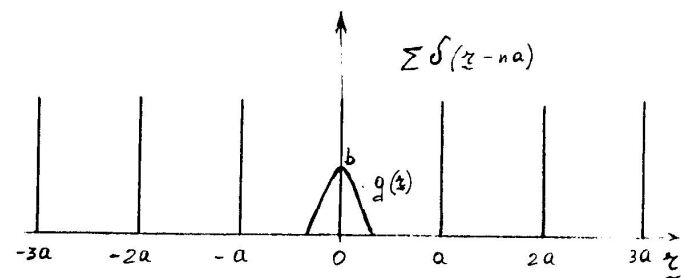
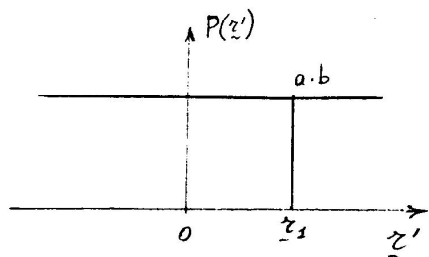
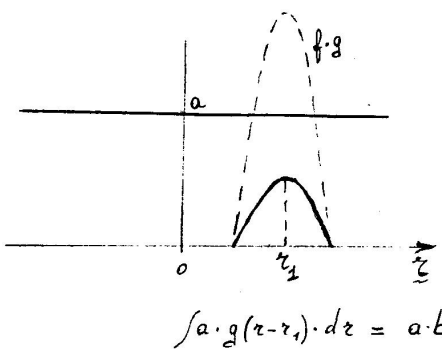
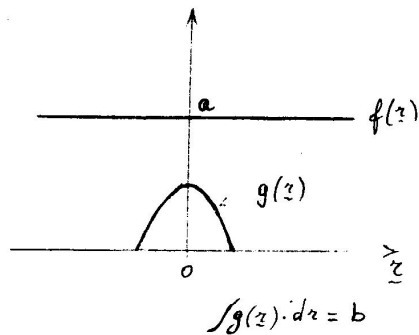
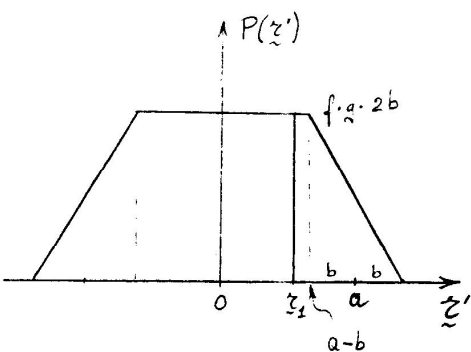
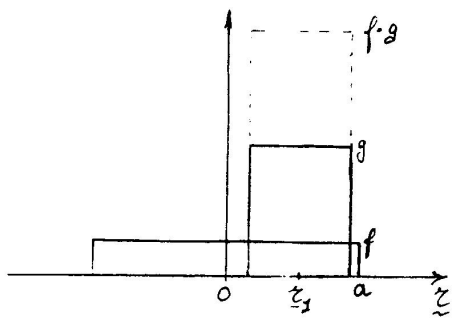
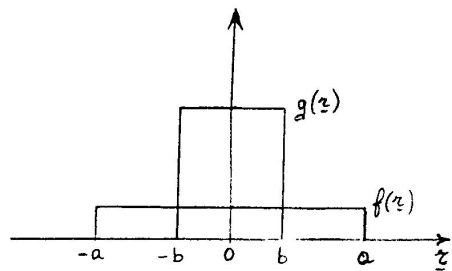
Viene invece definita P-convoluzione.

Convolution Theorem

Siano date due funzioni $f(\mathbf{r})$ e $g(\mathbf{r})$, e le loro trasformate di Fourier siano definite dalla (2.11). Il teorema fondamentale delle trasformate afferma che “la trasformata di Fourier della Q-convoluzione di due funzioni è uguale al prodotto delle trasformate delle due funzioni”. In simboli:

$$T^{+1}[Q(\mathbf{r})] = T^{+1}[f(\mathbf{r}) * g(\mathbf{r})] = T^{+1}[f(\mathbf{r})] \cdot T^{+1}[g(\mathbf{r})] \quad (2B.23)$$

Inversamente, per le proprietà delle trasformate, vale anche che “la trasformata di Fourier del prodotto di due funzioni è uguale alla Q-convoluzione delle trasformate delle due funzioni”.



$$\int \delta(z) \cdot g(z - z_1) \cdot dz = \int \delta(z) \cdot K \cdot dz = K$$

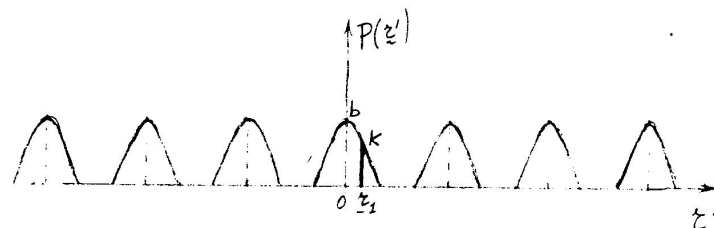


Fig. 2B.6. Esempi di Q-convoluzione di due funzioni. A sinistra, convoluzione tra due funzioni gradino. Al centro, convoluzione tra una funzione "picco" e una funzione costante. A destra, convoluzione tra una funzione "picco" e una funzione "griglia" monodimensionale. In tutti e tre i casi, i primi due disegni (in verticale) esemplificano due stadi della convoluzione, quello in basso il risultato finale.

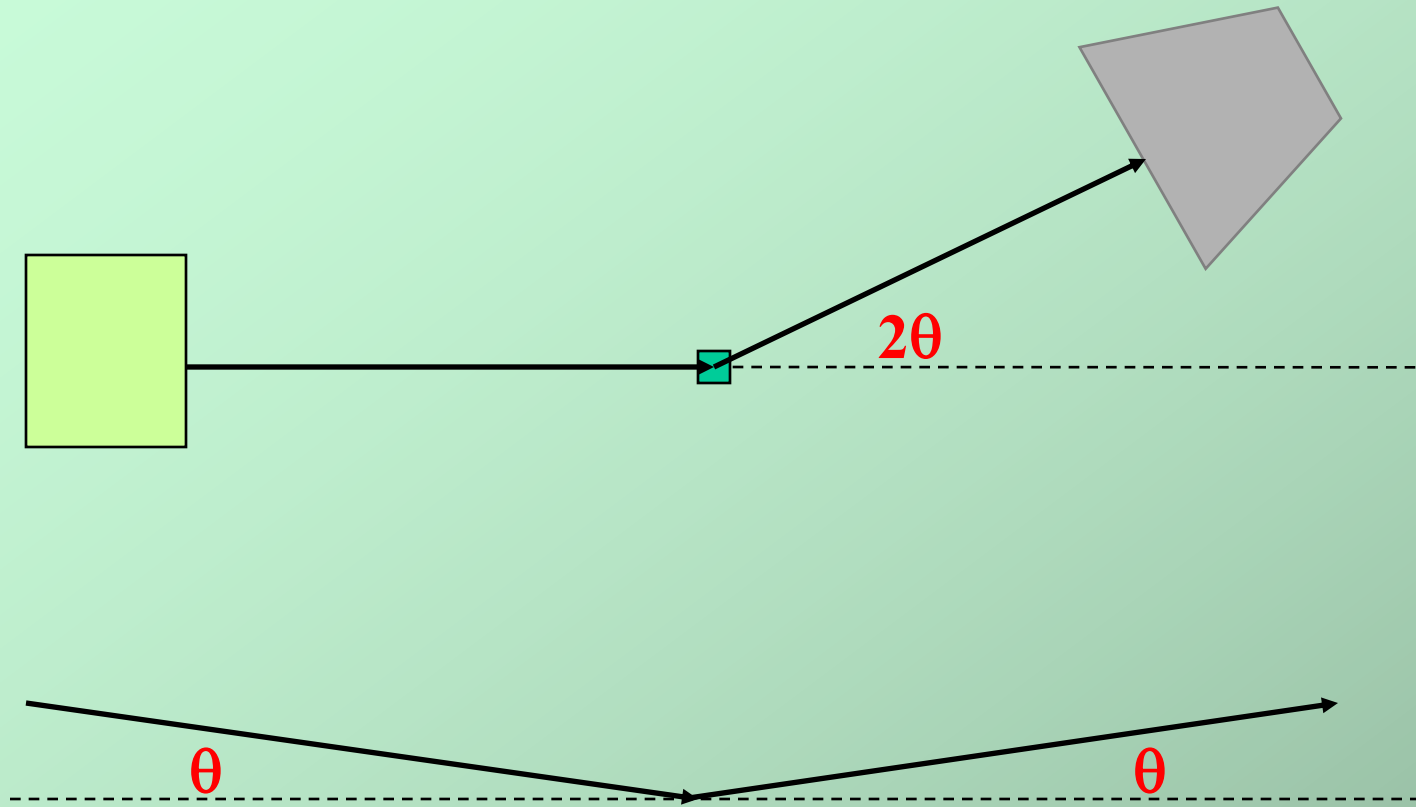
X-ray scattering



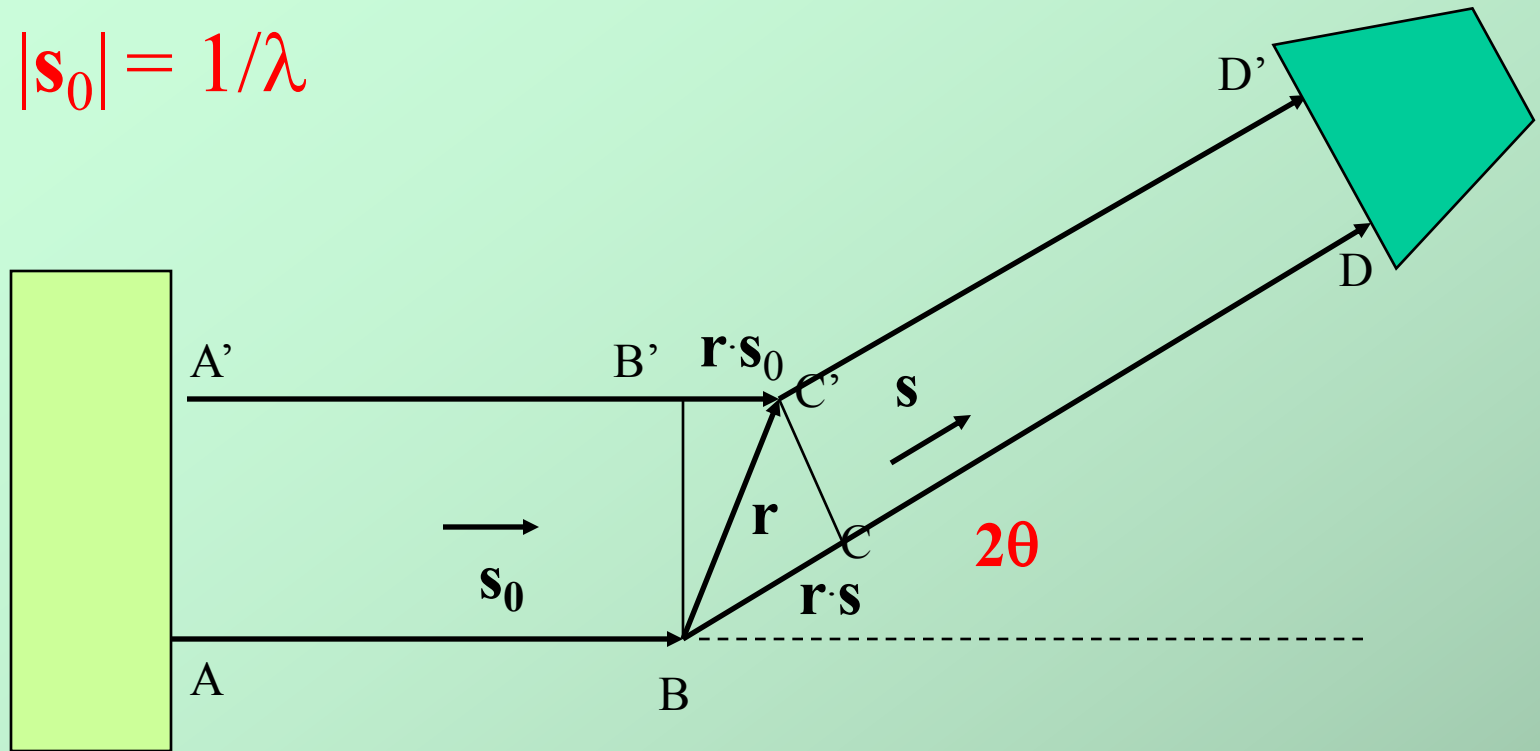
100 μm

100 μm

Elastic Scattering (Thomson)



$$|\mathbf{s}| = |\mathbf{s}_0| = 1/\lambda$$



$$\Delta = \text{phase difference} = \mathbf{r} \cdot \mathbf{s} - \mathbf{r} \cdot \mathbf{s}_0$$

$$\text{Let us define } \mathbf{S} = (\mathbf{s} - \mathbf{s}_0)$$

$$\Delta = \mathbf{r} \cdot \mathbf{S} \quad \text{where } |\mathbf{S}| = 2 \sin \theta / \lambda$$

If we call A_0 the amplitude of the wave scattered by the electron at the origin, then the amplitude of the wave scattered by an electron at point \mathbf{r} will be:

$$A_0 e^{2\pi i \mathbf{S} \cdot \mathbf{r}}$$

Indicating with A_{Th} the amplitude scattered by a free electron, we can define the scattering factor $f = A/A_{Th}$, corresponding to the number of electrons in the scattering point.

For N scattering points:

$$F(\mathbf{S}) = \sum_j f_j e^{2\pi i \mathbf{S} \cdot \mathbf{r}_j}$$

And the total scattered radiation for a continuous scatterer:

$$F(\mathbf{S}) = \int_{-\infty}^{\infty} \rho(\mathbf{r}) e^{2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{r}$$

$$F(\mathbf{S}) = \int_{-\infty}^{\infty} \rho(\mathbf{r}) e^{2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{r}$$

For the fundamental property of the Fourier transforms:

$$\rho(\mathbf{r}) = \int_{-\infty}^{\infty} F(\mathbf{S}) e^{-2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{S}$$

The atomic form factor

Electronic distribution of an atom (gaussian):

$$\rho(r) = z N e^{-kr^2}$$

Its Fourier-transform (gaussian):

$$f(s) = z e^{- (\pi^2/k)s^2}$$

Diffraction by a crystal

Let us first consider the scattering by the atoms present in the unit cell. If there are N atoms at positions defined by a set of vectors $\{\mathbf{r}_j\} (j=1, N)$, and neglecting bonding, the electron density at point \mathbf{r} in the cell can be expressed by $\rho_j(\mathbf{r}-\mathbf{r}_j)$ and so:

$$\rho_{Cell}(\mathbf{r}) = \sum_j \rho_j(\mathbf{r}-\mathbf{r}_j)$$

And consequently the resulting scattering amplitude will be:

$$\mathbf{F}_{Cell}(\mathbf{S}) = \sum_j f_j(\mathbf{S}) e^{2\pi i \mathbf{S} \cdot \mathbf{r}}$$

Diffraction by a crystal

An infinite crystal may be considered as the convolution of a crystal cell with a lattice:

$$\rho_{Cryst}(\mathbf{r}) = \rho_{Cell}(\mathbf{r}) * L(\mathbf{r})$$

Applying the convolution theorem:

$$\begin{aligned} \mathbf{F}_{Cryst}(\mathbf{S}) &= T[\rho_{Cell}(\mathbf{r})] \times T[L(\mathbf{r})] = \\ &= (1/V) \mathbf{F}_{Cell}(\mathbf{S}) \sum_{h,k,l} \delta(\mathbf{S} - \mathbf{S}_H) \end{aligned}$$

with:

$$\mathbf{S}_H = ha^* + kb^* + lc^*$$

The previous formula states that $F_{Cryst}(\mathbf{S}) \neq 0$ only at the nodes of the reciprocal Lattice, where the $F_{Cellt}(\mathbf{S})$ continuous function is sampled. The vector \mathbf{H} , which defines the sampling, is defined by the so-called **Laue diffraction conditions**:

$$\mathbf{S} \cdot \mathbf{a} = h \quad \mathbf{S} \cdot \mathbf{b} = k \quad \mathbf{S} \cdot \mathbf{c} = l$$

where h , k and l are integer numbers. \mathbf{S} defines the discrete values along which diffraction can occur. The previous relationships defines also the sizes of the reciprocal lattice:

$$\mathbf{a}^* = (\mathbf{b} \wedge \mathbf{c}) / (\mathbf{a} \cdot \mathbf{b} \wedge \mathbf{c})$$

$$\mathbf{b}^* = (\mathbf{c} \wedge \mathbf{a}) / (\mathbf{a} \cdot \mathbf{b} \wedge \mathbf{c})$$

$$\mathbf{c}^* = (\mathbf{a} \wedge \mathbf{b}) / (\mathbf{a} \cdot \mathbf{b} \wedge \mathbf{c})$$

or, in case axes are perpendicular:

$$\mathbf{a}^* = 1/a, \quad \mathbf{b}^* = 1/b, \quad \mathbf{c}^* = 1/c$$

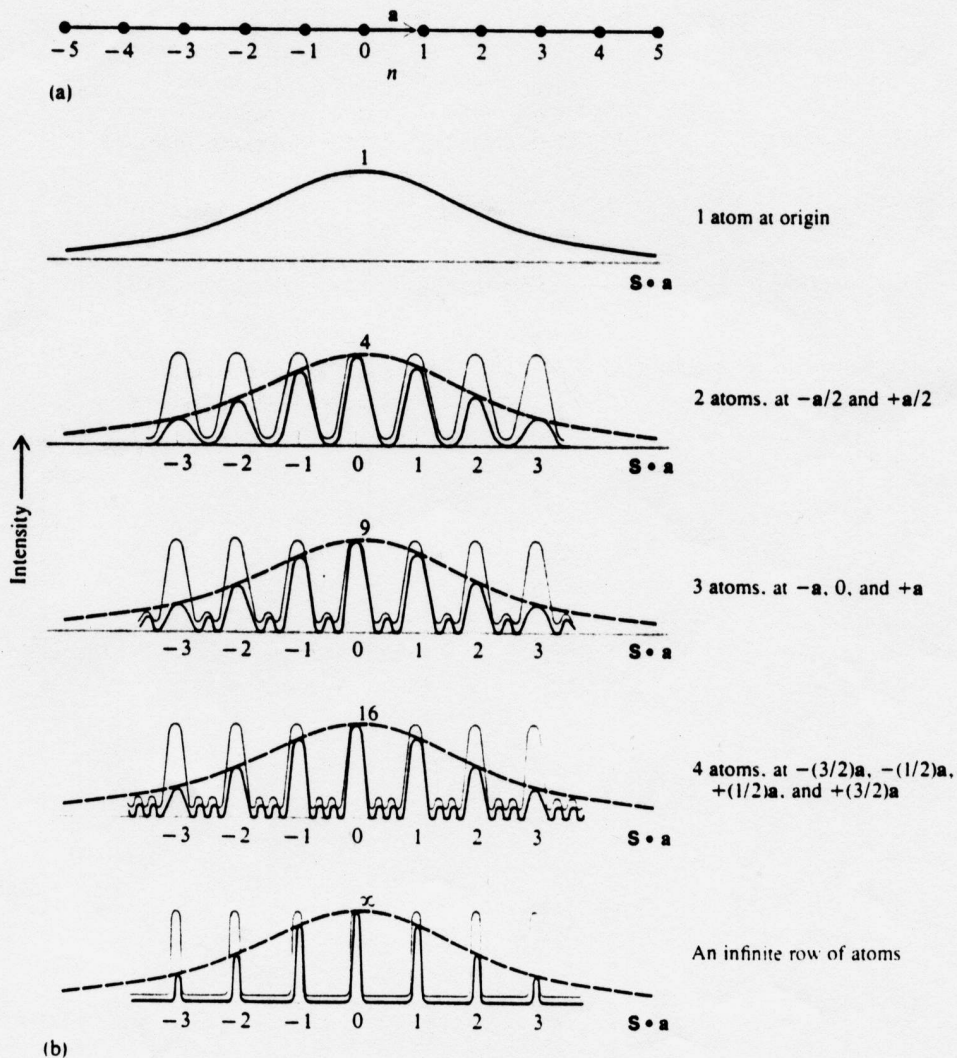


Figure 13-6

X-ray scattering from a one-dimensional array of atoms. (a) The array, as defined by the vector translation \mathbf{a} . (b) X-ray scattering intensity as a function of the number of atoms in the array. Shown are the actual observed scattering (black line), the scattering expected for a single atom (dashed line), and the fringe function produced by the array (colored line). The observed scattering is the product of the fringe function and the single-atom scattering. Note the changes in vertical scale as the number of atoms increases. The horizontal scale is in units of $S \cdot \mathbf{a}$ and is the same for all cases.

$$F_{\text{Cell}}(\mathbf{S}) = \sum_j f_j(\mathbf{S}) e^{2\pi i \mathbf{S} \cdot \mathbf{r}_j}$$

$$F_{\text{Cryst}}(\mathbf{S}) = (1/V) F_{\text{Cell}}(\mathbf{S}) \sum_{h,k,l} \delta(\mathbf{S} - \mathbf{S}_H)$$

Remembering the definitions of \mathbf{r}_j and \mathbf{S} :

$$\mathbf{r}_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$$

$$\mathbf{S}_H = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

$$\mathbf{r}_j \cdot \mathbf{S} = hx_j + ky_j + lz_j$$

and the final formula of the structure factor of the crystal becomes:

$$F_{\text{Cryst}}(\mathbf{S}) \equiv F(hkl) = (1/V) \sum_j f_j(\mathbf{S}) e^{2\pi i (hx_j + ky_j + lz_j)}$$

$$F(hkl) = (1/V) \sum_j f_j(\mathbf{S}) e^{2\pi i(hx_j + ky_j + lz_j)}$$

$$F(hkl) = |F(hkl)| e^{i\phi}$$

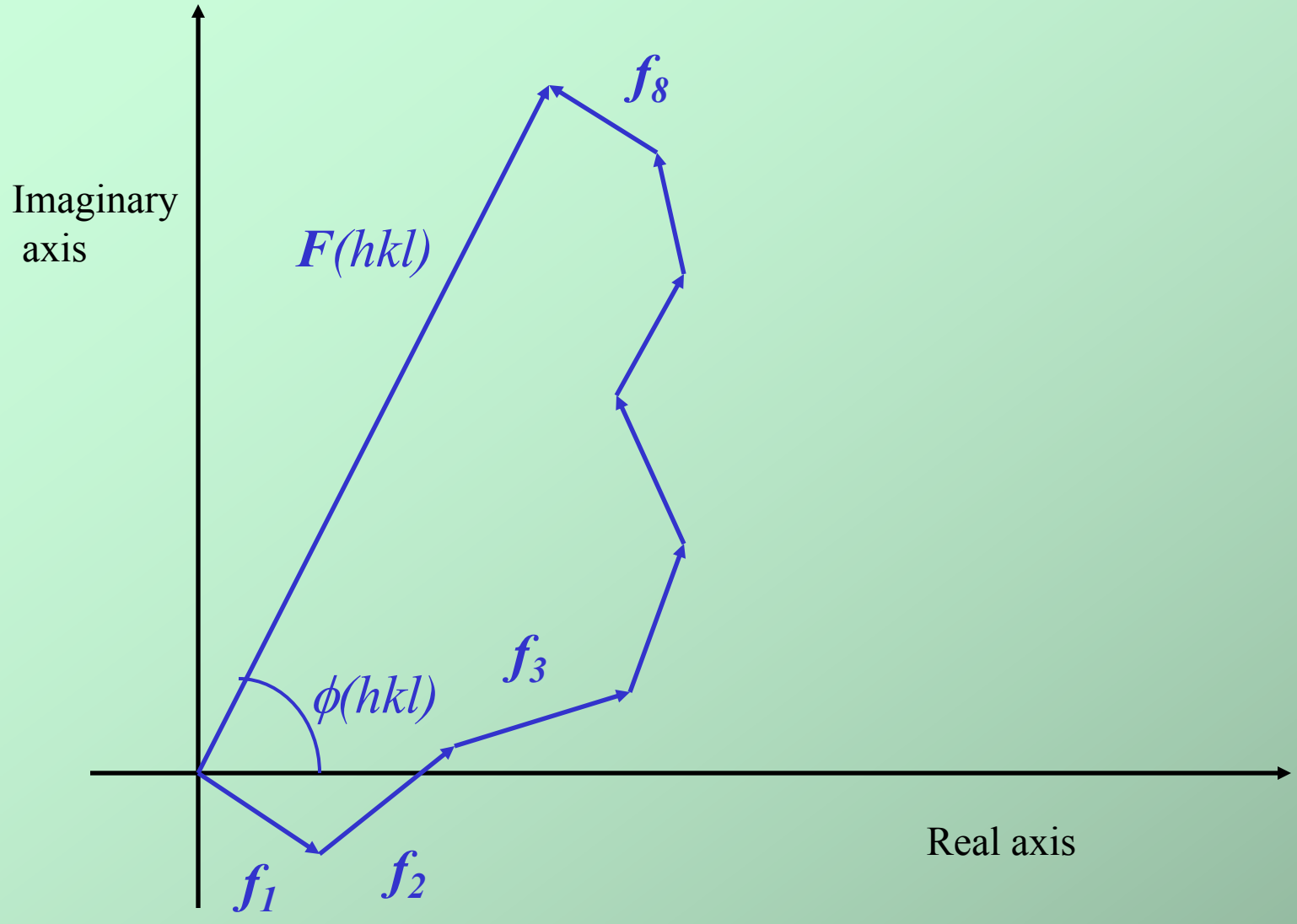
$F(hkl)$ is called the structure factor and it is a complex quantity. For calculation purposes, we can better express it as its real and imaginary parts:

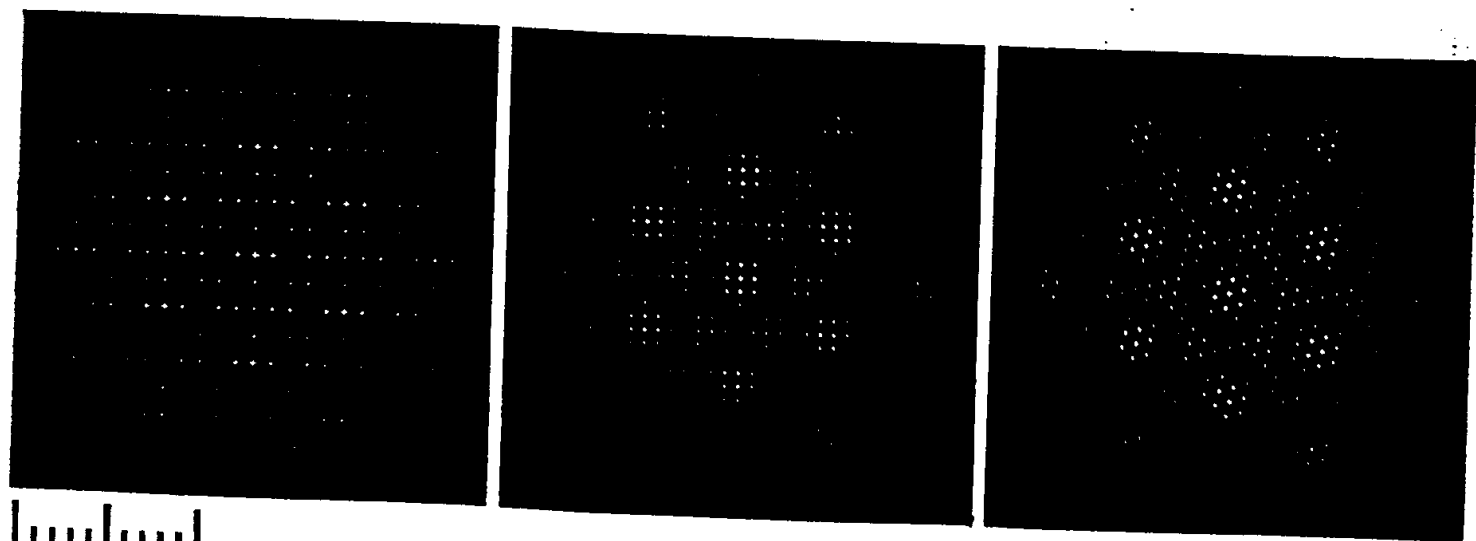
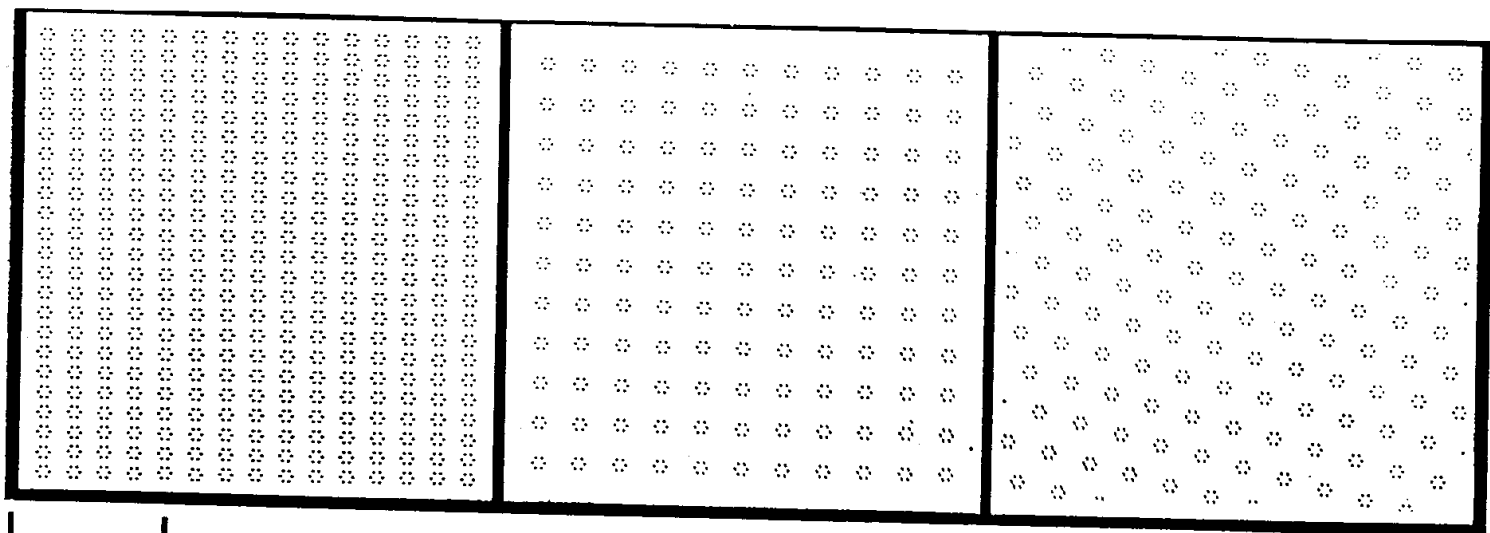
$$A(hkl) = \sum_j f_j(\mathbf{S}) \cos[2\pi i(hx_j + ky_j + lz_j)]$$

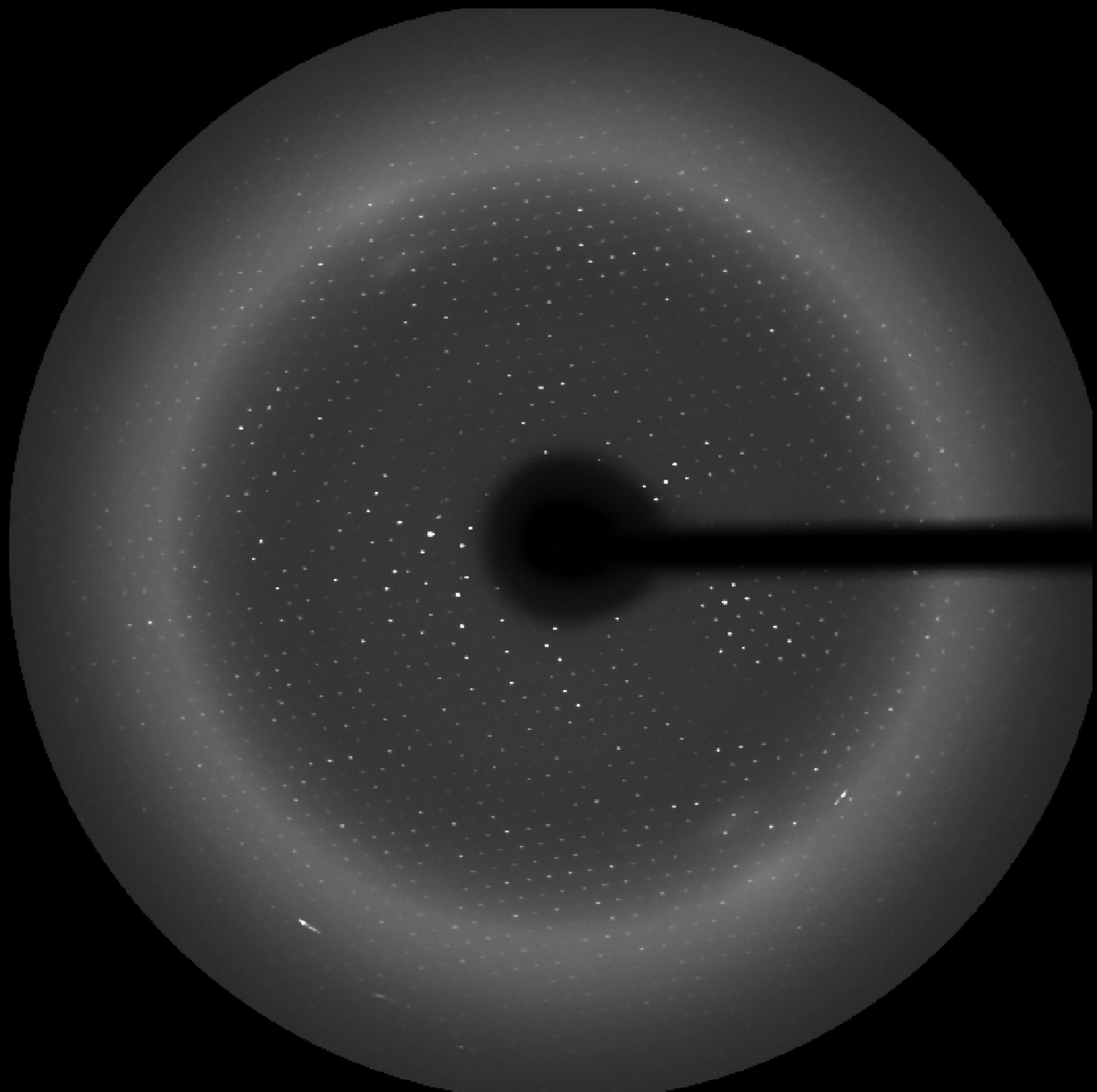
$$B(hkl) = \sum_j f_j(\mathbf{S}) \sin[2\pi i(hx_j + ky_j + lz_j)]$$

$$|F(hkl)| = (A(hkl)^2 + B(hkl)^2)^{1/2}$$

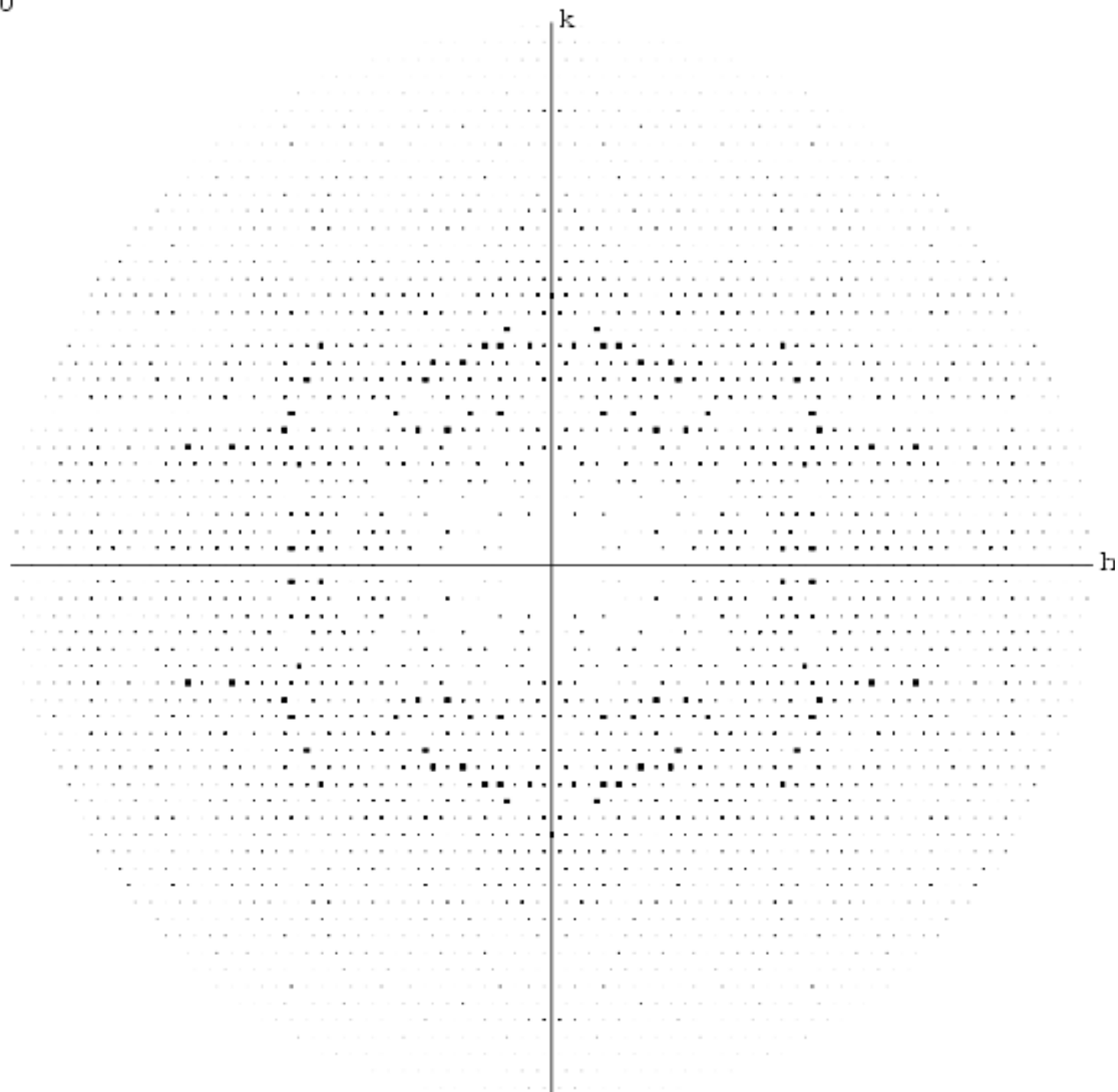
$$\phi(hkl) = \tan^{-1}[B(hkl)/A(hkl)]$$







=0



The electron density

$$\rho(\mathbf{r}) = \int_{-\infty}^{\infty} \mathbf{F}(\mathbf{S}) e^{-2\pi i \mathbf{S} \cdot \mathbf{r}} d\mathbf{S}$$

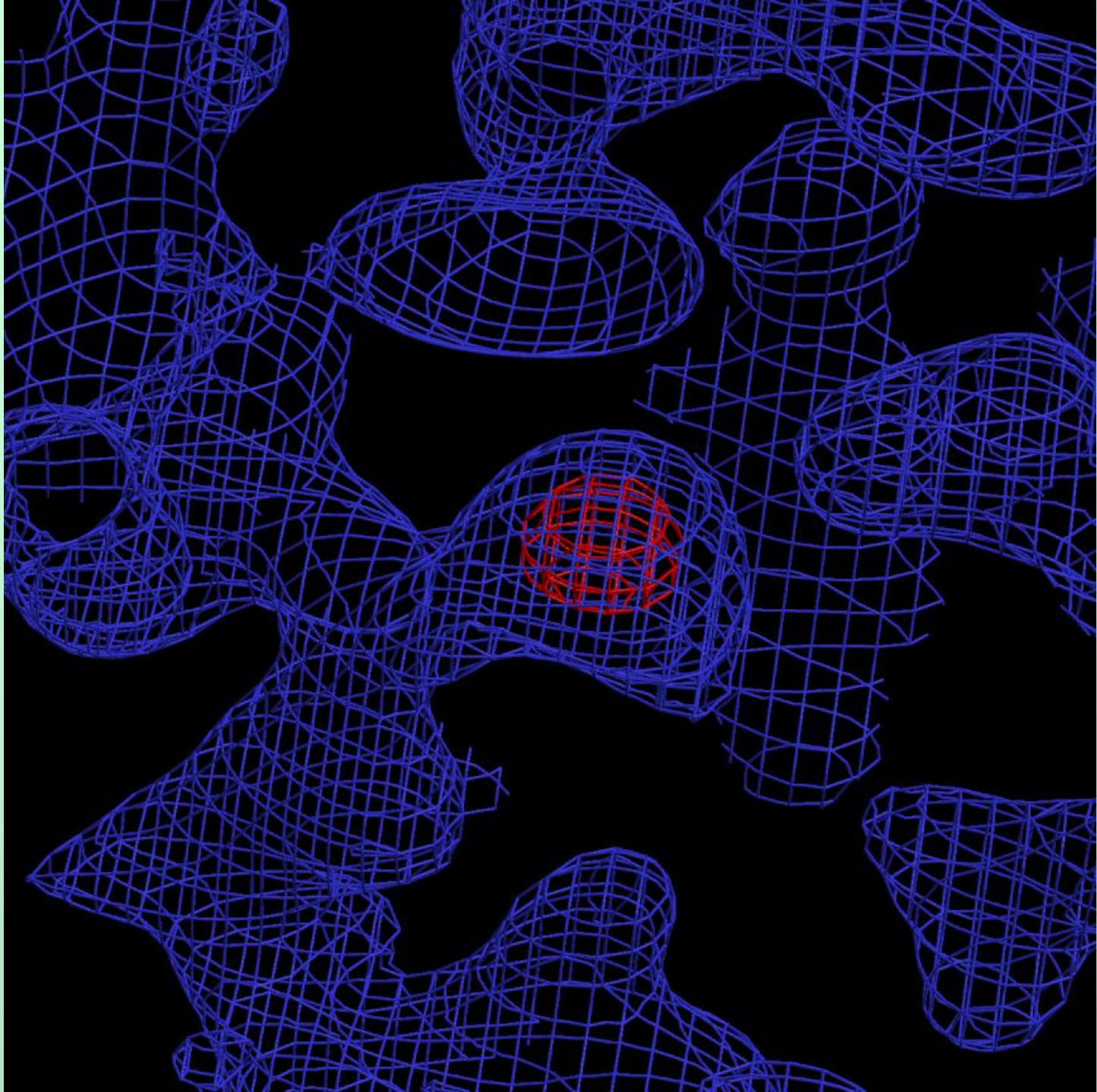
The electron density function is related to the scattered amplitudes by a Fourier-transform. Since in a crystal $\mathbf{F}(\mathbf{S})$ is sampled at the nodes of the reciprocal lattice, the electron density can be expressed as a Fourier series:

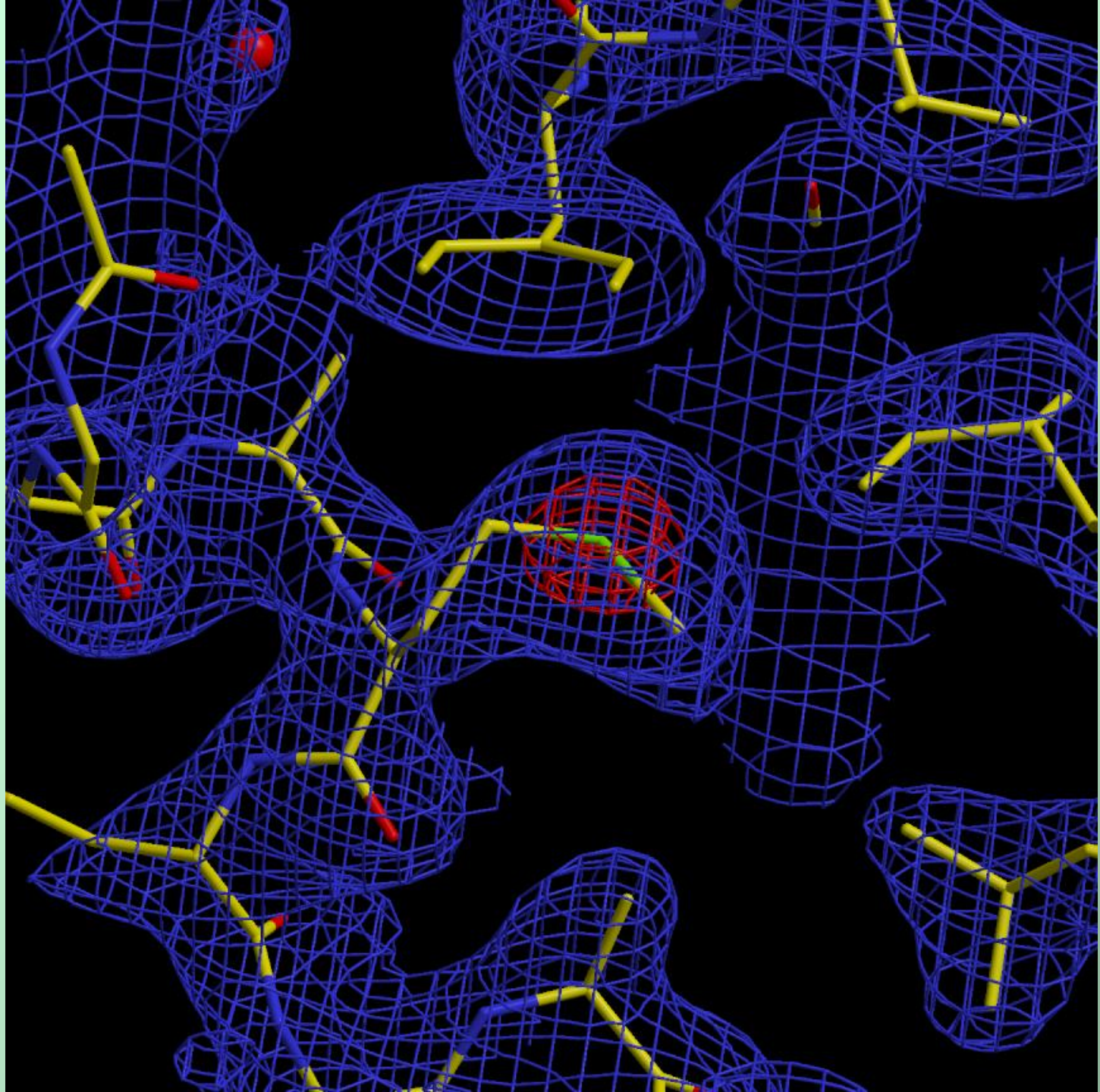
$$\rho(\mathbf{r}) \equiv \rho(xyz) = 1/V \sum_h \sum_k \sum_l \mathbf{F}(hkl) e^{-2\pi i(hx + ky + lz)}$$

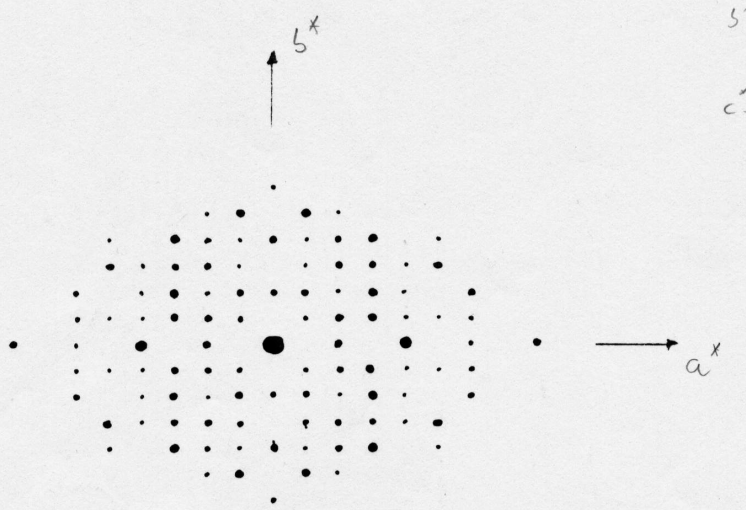
where:

$$\mathbf{F}(hkl) = |\mathbf{F}(hkl)| e^{i\phi}$$

$$\rho(xyz) = (2/V) \sum_h \sum_k \sum_l [A(hkl) \cos[-2\pi(hx + ky + lz)] + B(hkl) \sin[-2\pi(hx + ky + lz)]]$$



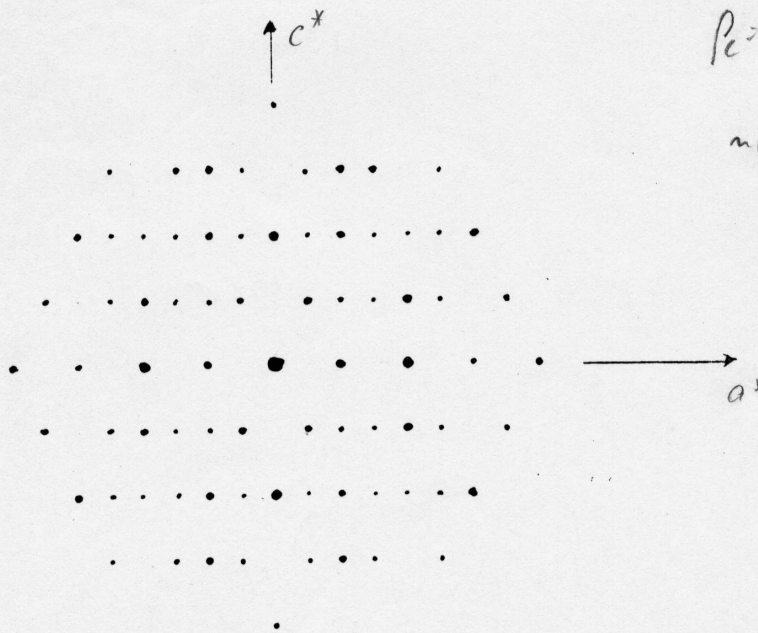




$$\mathbf{a}^* = 5 \text{ mm}/100\text{mm} = 0.05/1.5418\text{\AA} = 0.032 \text{ \AA}^{-1}$$

$$\mathbf{b}^* = 4 \text{ mm}/100\text{mm} = 0.04/1.5418\text{\AA} = 0.026 \text{ \AA}^{-1}$$

$$\mathbf{c}^* = 10 \text{ mm}/100\text{mm} = 0.001/1.5418\text{\AA} = 0.065 \text{ \AA}^{-1}$$



$$\mathbf{a} = 31.25\text{\AA}$$

$$\mathbf{b} = 38.46\text{\AA}$$

$$\mathbf{c} = 15.38 \text{ \AA}$$

$$\mathbf{a}^* = 5 \text{ mm}/100\text{mm} = 0.05/1.5418\text{\AA}=0.032 \text{ \AA}^{-1}$$

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$$\mathbf{a} = 31.25\text{\AA}$$

$$\mathbf{b} = 38.46\text{\AA}$$

$$\mathbf{c} = 15.38 \text{ \AA}$$

Systematic extinctions

2_1 axis: $x, y, z; -x, 1/2+y, -z$ if $h=0, l=0$

$$\begin{aligned} F(0k0) &= \sum f_j(s) \{ \exp(2\pi i k y_j) + \exp(2\pi i k/2 + 2\pi i k y_j) \} = \\ &= \sum f_j(s) \{ \exp(2\pi i k y_j) [1 + \exp(2\pi i k/2)] \} \end{aligned}$$

$$k=1 \quad \exp(2\pi i 1/2) = \exp(\pi i) = \cos\pi + i\sin\pi = -1$$

$$k=2 \quad \exp(2\pi i 2/2) = \exp(2\pi i) = \cos 2\pi + i\sin 2\pi = 1$$

$$\mathbf{a} = 58.4 \text{ \AA}$$

$$\mathbf{b} = 59.0 \text{ \AA}$$

$$\mathbf{c} = 74.6 \text{ \AA}$$

$$\alpha = \beta = \gamma = 90$$



$$V = 257042 \text{ \AA}^3$$

$$\mathbf{n}=1 \quad \mathbf{M}_{\text{tot}}=\mathbf{60000}$$

$$\mathbf{n}=2 \quad \mathbf{M}_{\text{tot}}=\mathbf{120000}$$

$$V_{\text{M}}=257042/60000 = 4.3 \quad \text{Solv}=0.71$$

$$V_{\text{M}}=257042/120000 = 2.14 \quad \text{Solv}=0.44$$

The thermal parameters

Atoms, also in the solid state, undergo thermal vibrations around their equilibrium position. If we assume that this oscillation is equal in all directions (isotropic displacement), the structure factor $F(hkl)$ is modified by an additional term:

$$F(hkl) = (1/V) \sum_j f_j(\mathbf{S}) e^{2\pi i(hx_j + ky_j + lz_j)} e^{-B_j \sin^2 \theta / \lambda^2}$$

Where $B = 8\pi^2 U$, U being the mean square displacement of the atom. A more accurate description considers anisotropic thermal displacement, which is described by an ellipsoid. The latter can be expressed as a 3x3 symmetric matrix B_{ij} .

The phase problem

We can measure:

$$I(hkl) = F(hkl)F^*(hkl) = |F(hkl)|^2$$

- Solution of the phase problem
- Refinement

- **Direct methods**
- Multiple isomorphous replacement
- **Molecular replacement**
- Anomalous Dispersion

The anomalous effect

The Friedel law:

$$|F(h,k,l)| = |F(-h,-k,-l)|$$

Bijvoët pair:

$$|F(h,k,l)| \neq |F(-h,-k,-l)|$$

Summary

The electron density

$$\rho(\mathbf{r}) \equiv \rho(xyz) = 1/V \sum_h \sum_k \sum_l \mathbf{F}(hkl) e^{-2\pi i(hx + ky + lz)}$$

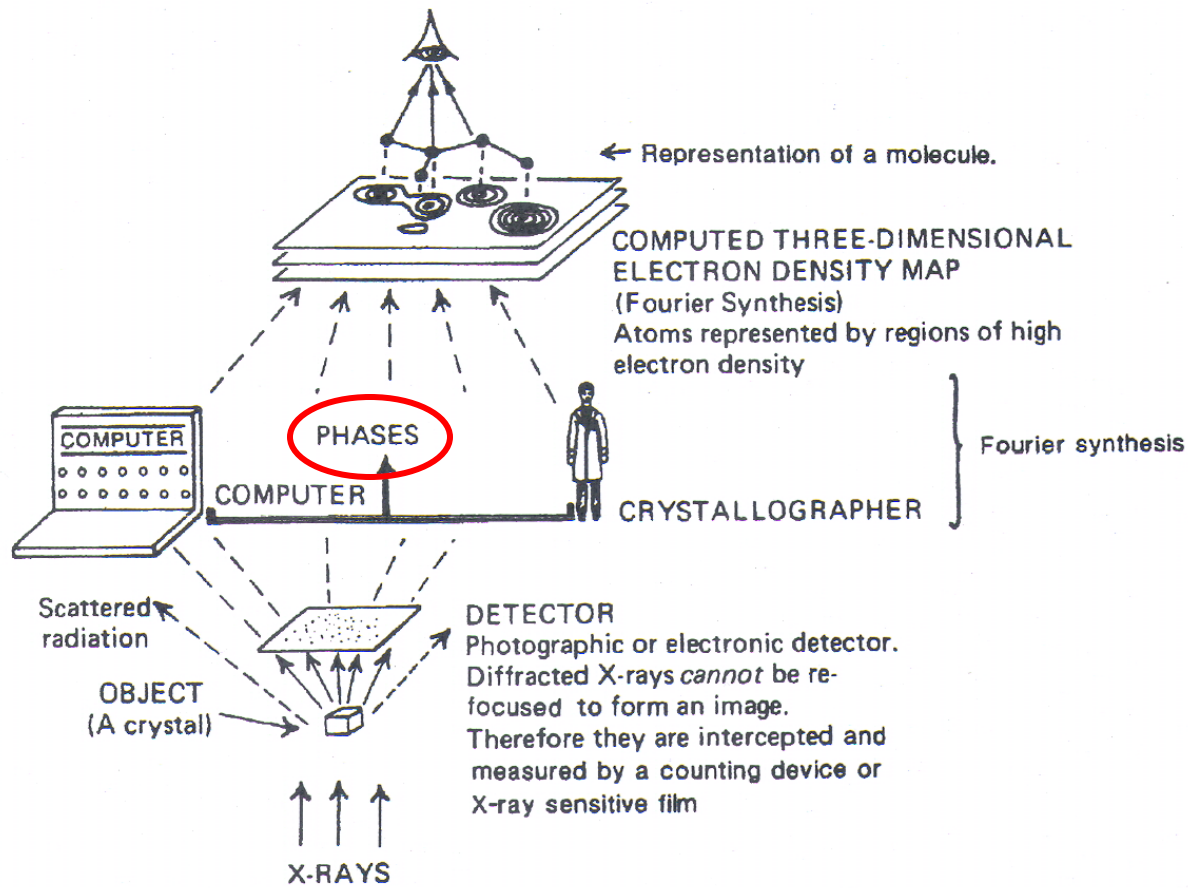
The structure factor

$$\mathbf{F}(hkl) = (1/V) \sum_j f_j(\mathbf{S}) e^{2\pi i(hx_j + ky_j + lz_j)}$$

where:

$$\mathbf{F}(hkl) = |\mathbf{F}(hkl)| e^{i\phi}$$

End of part I



(b) X-RAY DIFFRACTION