Chapter 2

Reciprocal Lattice

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DIFFRACTION OF WAVES BY CRYSTALS

Bragg Law

We study crystal structure through the diffraction of photons, neutrons, and electrons (Fig. 1). The diffraction depends on the crystal structure and on the wavelength.

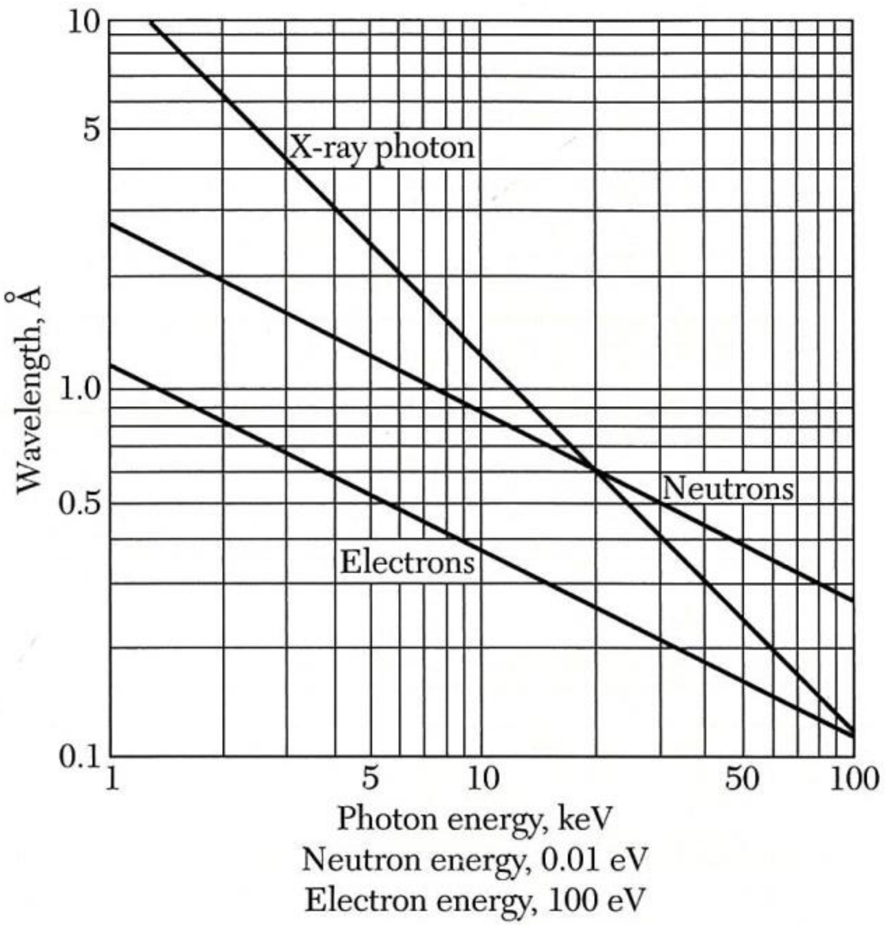
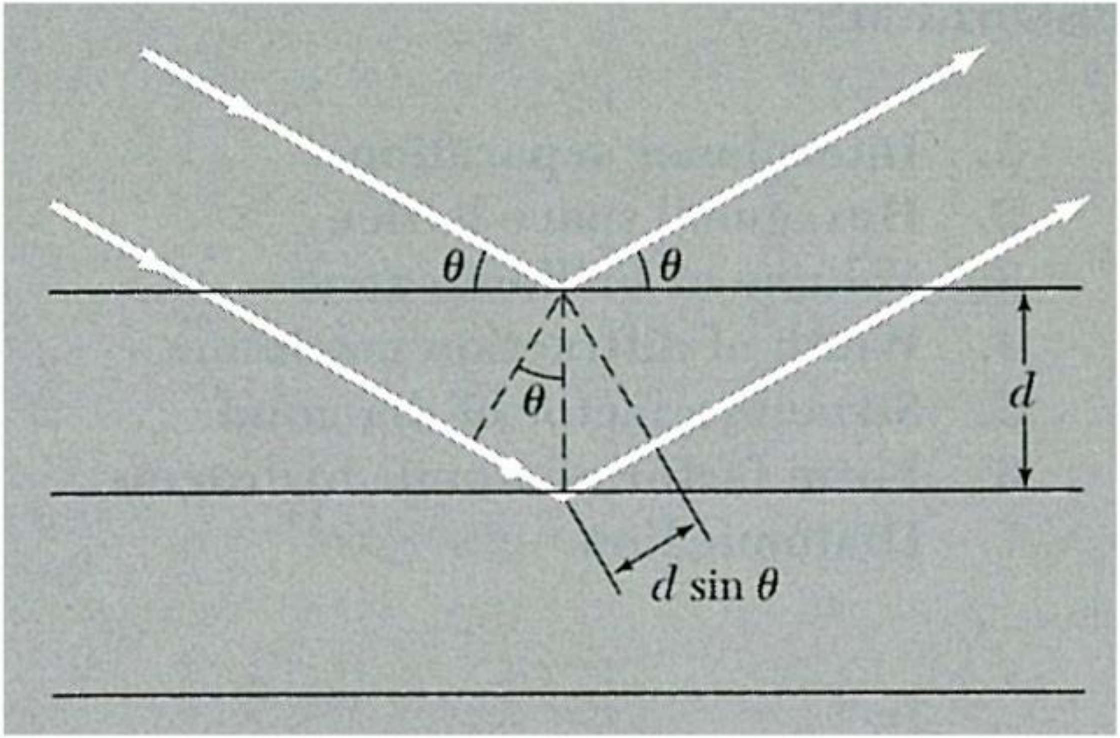


Figure 1 Wavelength versus particle energy, for photons, neutrons, and electrons.

Bragg Law of Diffraction

- W. L. Bragg presented a simple explanation of the law of diffraction beams from a crystal.
- The incident waves are reflected specularly (mirror-like) from parallel planes of atoms in the crystals. In the specular reflection, the angle of incidence is equal to the angle of reflection. 鏡面反射
- The diffracted beams are found when the reflections from parallel planes of atoms interfere constructively.
- Elastic scattering is considered here that the energy of x-rays is not changed upon reflection

Consider parallel lattice planes spaced d apart. The radiation is incident in the plane of the paper. The path difference for rays reflected from adjacent planes is $2d \sin\theta$, where θ is measured from the plane. Constructive interference of the radiation from successive planes occurs when the path difference is an integral number n of wavelengths λ, so that



Bragg Equation

$$\boxed{2d \sin\theta = n\lambda \quad .}$$

Figure 2 Derivation of the Bragg equation $2d \sin\theta = n\lambda$; here d is the spacing of parallel atomic planes and $2\pi n$ is the difference in phase between reflections from successive planes. The reflecting planes have nothing to do with the surface planes bounding the particular specimen.

Although the reflection from each plane is specular, for only certain values of θ will the reflections from all periodic parallel planes add up in phase to give a strong reflected beam.

The Bragg law is a consequence of the periodicity of the lattice. Notice that the law does not refer to the composition of the basis of atoms associated with every lattice point. We shall see, however, that the composition of the basis determines the relative intensity of the various orders of diffraction (denoted by n above) from a given set of parallel planes.

A monochromator Set up

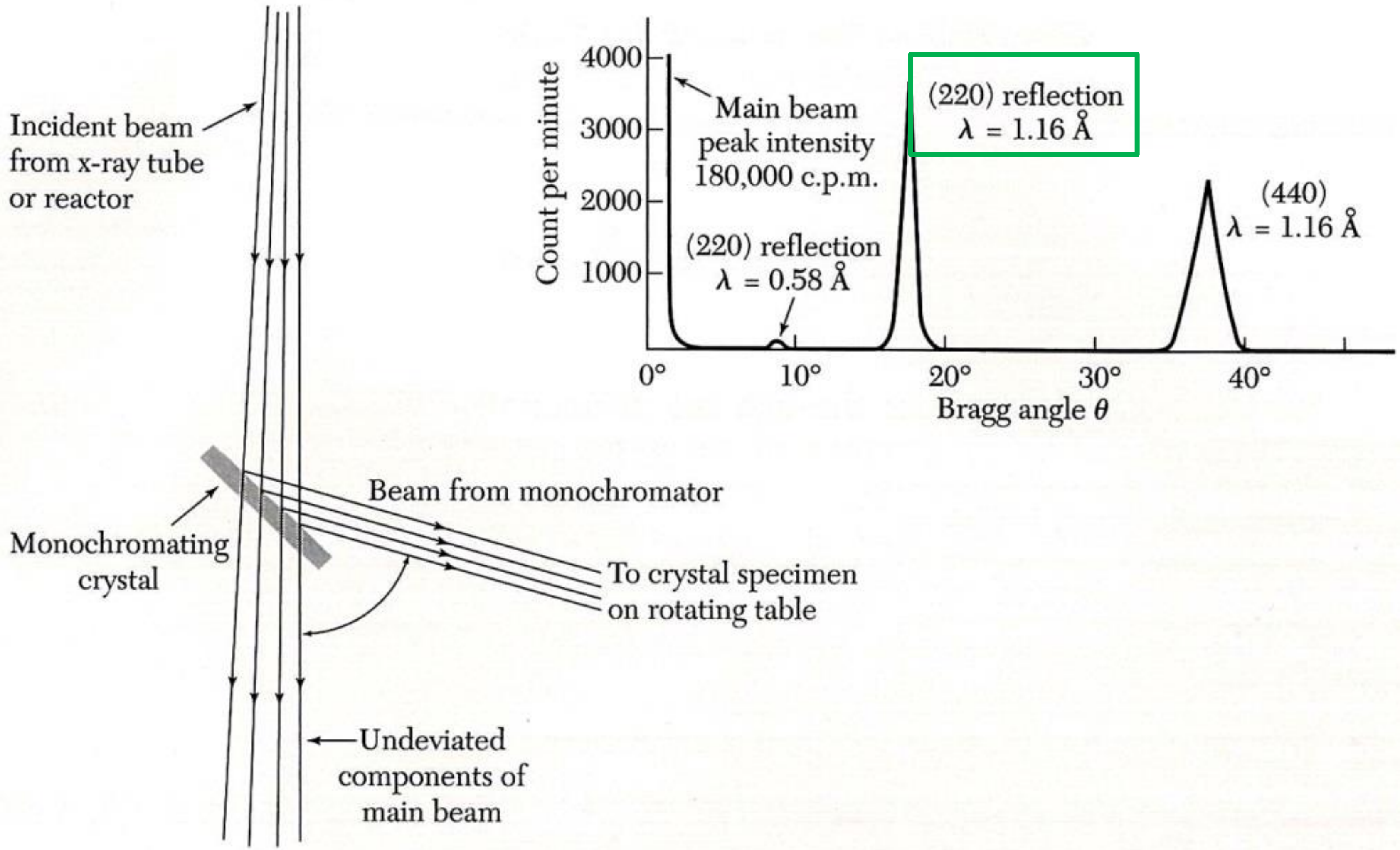


Figure 3 Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. (After G. Bacon.)

X-ray Powder diffraction pattern of Si

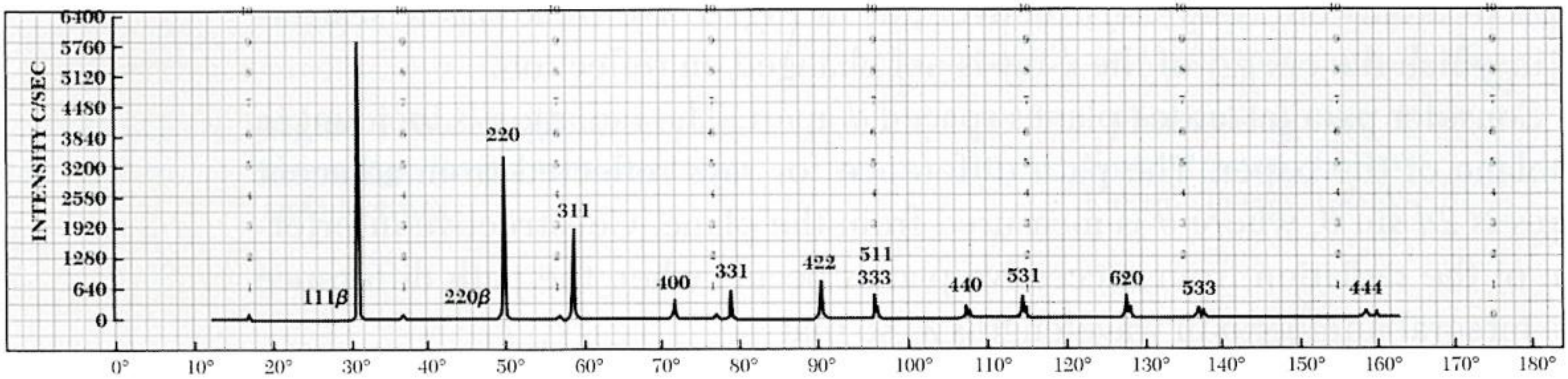


Figure 4 X-ray diffractometer recording of powdered silicon, showing a counter recording of the diffracted beams. (Courtesy of W. Parrish.)

SCATTERED WAVE AMPLITUDE

We need a deeper analysis to determine the scattering intensity from the basis of atoms, which means from the spatial distribution of electrons within each cell.

From (1, 3), a crystal is invariant under any translation of the form **$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$,** where u_1, u_2, u_3 are integers and a_1, a_2, a_3 are the crystal axes. **Any local physical property of the crystal is invariant under T**, such as the charge concentration, electron number density, or magnetic moment density.

Fourier Analysis

Electron number density $n(\mathbf{r})$ is a periodic function of $\mathbf{r}$,

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}) \qquad \mathbf{(2)}$$

Such periodicity creates an ideal situation for Fourier analysis.

The most interesting properties of crystals are directly related to the Fourier components of the electron density.

We consider first a function $n(x)$ in one dimension with period a in the direction x. We expand $n(x)$ in a Fourier series of sines and cosines:

1-D

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)\right] \ , \tag{3}$$

where the p are positive integers and C_p, S_p are real constants, called the Fourier coefficients of the expansion. The factor $2\pi/a$ in the arguments ensures that $n(x)$ has the period a:

$$\begin{aligned} n(x+a) &= n_0 + \sum [C_p \cos(2\pi px/a + 2\pi p) + S_p \sin(2\pi px/a + 2\pi p)] \\ &= n_0 + \sum [C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)] = n(x) \ . \end{aligned} \tag{4}$$

We say that $2\pi p/a$ is a point in the reciprocal lattice or Fourier space of the crystal. In one dimension these points lie on a line. The **reciprocal lattice points** tell us the allowed terms in the Fourier series (4) or (5). A term is allowed if it is consistent with the periodicity of the crystal, as in Fig. 5.

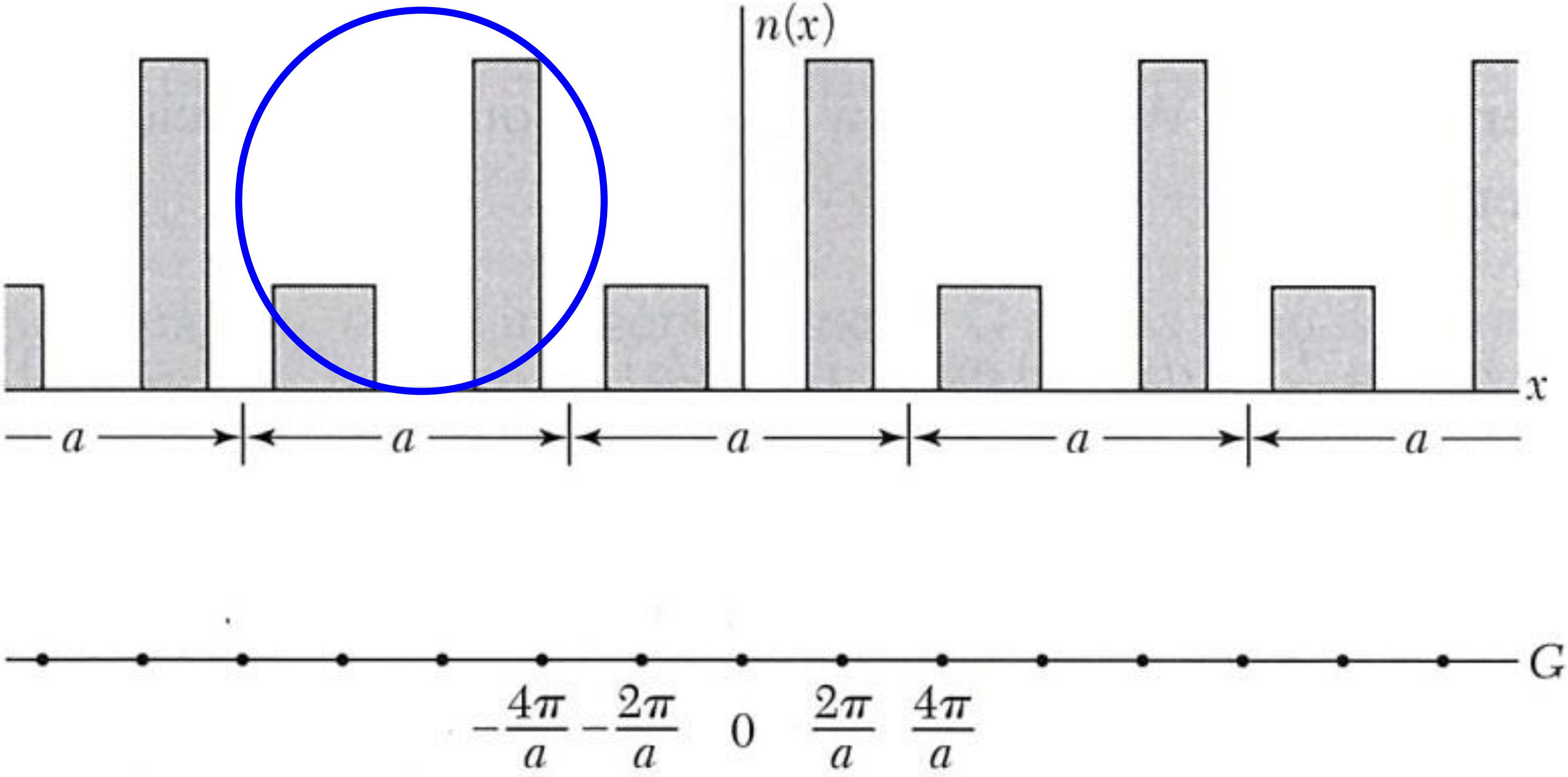


Figure 5 A periodic function $n(x)$ of period a, and the terms $2\pi p/a$ that may appear in the Fourier transform $n(x) = \Sigma\, n_p \exp(i2\pi px/a)$. The magnitudes of the individual terms n_p are not plotted.

It is convenient to write the series (4) in the compact form

1-D

$$\boxed{n(x) = \sum_p n_p \exp(i2\pi px/a) \ ,} \qquad (5)$$

where the sum is over all integers p: positive, negative, and zero. The coefficients n_p now are complex numbers. To ensure that $n(x)$ is a real function, we require

$$\boxed{n^*_{-p} = n_p \ , \qquad n_{-p} = n_p^*} \qquad (6)$$

for then the sum of the terms in p and $-p$ is real. The asterisk on n^*_{-p} denotes the complex conjugate of n_{-p}.

With $\varphi = 2\pi px/a$, the sum of the terms in p and $-p$ in (5) is real if (6) is satisfied. The sum is

$$\begin{aligned} &n_p(\cos\varphi + i\sin\varphi) + n_{-p}(\cos\varphi - i\sin\varphi) \\ &\qquad = (n_p + n_{-p})\cos\varphi + i(n_p - n_{-p})\sin\varphi \ , \end{aligned} \qquad (7)$$

which in turn is equal to the real function

$$2\mathrm{Re}\{n_p\}\cos\varphi - 2\mathrm{Im}\{n_p\}\sin\varphi \qquad (8)$$

if (6) is satisfied. Here $\mathrm{Re}\{n_p\}$ and $\mathrm{Im}\{n_p\}$ are real and denote the real and imaginary parts of n_p. Thus the number density $n(x)$ is a real function, as desired.

The extension of the Fourier analysis to periodic functions $n(\mathbf{r})$ in three dimensions is straightforward. We must find a set of vectors $\mathbf{G}$ such that

3-D

$$\boxed{n(\mathbf{r})=\sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})} \tag{9}$$

is invariant under all crystal translations $\mathbf{T}$ that leave the crystal invariant. It will be shown below that the set of Fourier coefficients $n_{\mathbf{G}}$ determines the x-ray scattering amplitude.

Inversion of Fourier Series. We now show that the Fourier coefficient n_p in the series (5) is given by

1-D

$$n_p = a^{-1}\int_0^a dx\, \underline{n(x)}\, \exp(-i2\pi px/a) \ . \tag{10}$$

is substituted by Eq. (5)

Substitute (5) in (10) to obtain

$$n_p = a^{-1}\sum_{p'} n_{p'}\int_0^a dx\, \exp[i2\pi(p'-p)x/a] \ . \tag{11}$$

If $p' \neq p$ the value of the integral is

$$\frac{a}{i2\pi(p'-p)}\left(e^{i2\pi(p'-p)}-1\right)=0 \ ,$$

because $p'-p$ is an integer and $\exp[i2\pi(\text{integer})]=1$. For the term $p'=p$ the integrand is $\exp(i0)=1$, and the value of the integral is a, so that $n_p = a^{-1}n_p a = n_p$, which is an identity, so that (10) is an identity.

Similarly, the inversion of (9) gives

3-D

$$\boxed{n_{\mathbf{G}} = V_c^{-1}\int_{\text{cell}} dV\, n(\mathbf{r})\exp(-i\mathbf{G}\cdot\mathbf{r}) \ .} \tag{12}$$

Here V_c is the volume of a cell of the crystal.