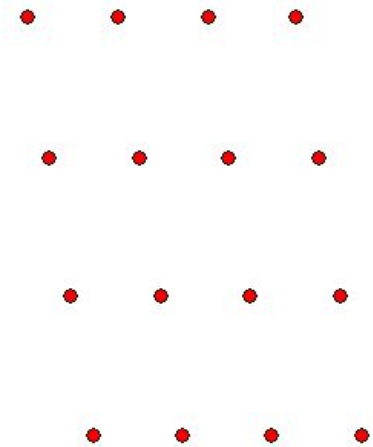
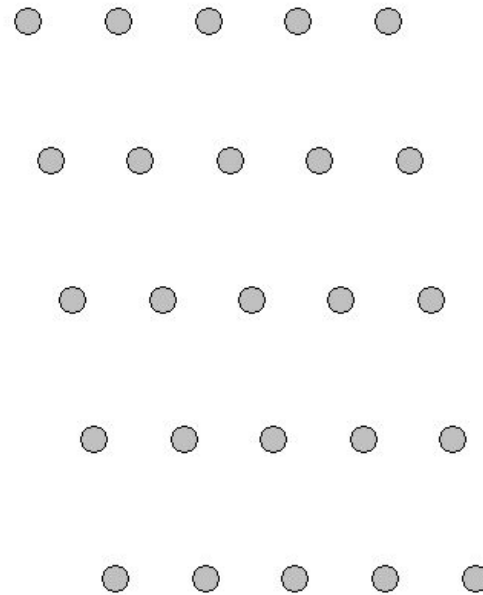
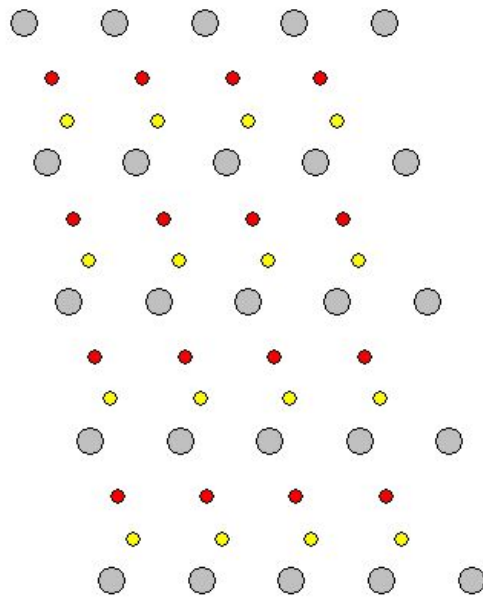
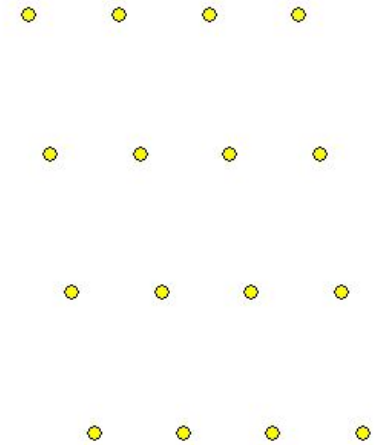


# Structure Factors

Until now, we have only typically considered reflections arising from planes in a hypothetical lattice containing one atom in the asymmetric unit. In practice we will generally deal with structures of molecules containing several atoms. In a crystal, each of the (independent) sets of atoms will make lattices so we need a way to determine the relationship between these lattices and the X-rays that we can observe – this information is provided by the Structure Factors.



# Structure Factors

Structure factors,  $F(hkl)$ , are the useful result of the diffraction data we collect. The  $F(hkl)$  values are complex numbers that express both the **amplitude** and **phase** of the reflection off of the (hkl) family of planes – structure factors are the quantities that we need to obtain for each of the reciprocal lattice points. The set of structure factors that we obtain for a crystal are the data that we use to model the unit cell contents.

The actual data that we use looks something like this:

2	0	2	7.66	0.70
2	0	2	7.25	0.70
-2	0	-2	6.35	0.69
-2	0	-2	6.93	0.70
1	1	2	1000.00	89.30
1	1	2	985.38	88.65
1	1	2	928.03	88.64
-1	-1	-2	871.24	88.63
0	2	2	7.88	0.72
0	2	2	6.63	0.72
0	-2	-2	7.91	0.73

In a real data set, there are usually thousands of structure factors. Note that these are in the format:

h k l  $|F_o^2|$   $\sigma(F_o^2)$

Where the magnitude of the structure factor and the error in its measurement are recorded for each of the reciprocal lattice points (hkl).

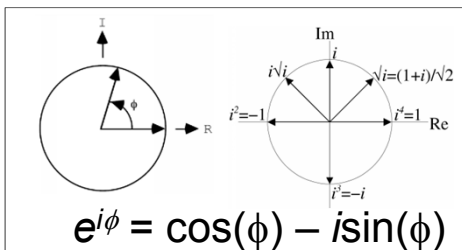
# Atomic Scattering Factors

To understand how structure factors are constructed, one must first examine the atomic scattering factors. Atomic scattering factors,  $f$ , provide a measure of the scattering power of all of the electrons in an atom of a given type.

Let the electron density at a distance  $\mathbf{r}$  from the center of an atom be  $\rho(\mathbf{r})$ . Consider the wave scattered at the position  $\mathbf{r}$  in a direction  $\mathbf{s}$  relative to the incident beam of radiation in the direction  $\mathbf{s}_0$ . The scattered intensity depends on the phase difference,  $\delta$ , which is  $2\pi / \lambda$  times the path length difference, is given by:

$$\delta = (2\pi / \lambda)[\mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0)] = 2\pi / \lambda \mathbf{r} \cdot \mathbf{S}$$

where  $\mathbf{S} = (\mathbf{s} - \mathbf{s}_0)$ . The vector  $\mathbf{S}$  is a vector in reciprocal space. The wave scattered by the volume element  $dv$  at  $\mathbf{r}$  will have an amplitude with a maximum of  $\rho(\mathbf{r}) dv$ . Combining this with the phase (  $\exp(i\phi)$  ) then the amplitude of the wave at  $\mathbf{r}$  must be  $\rho(\mathbf{r}) \exp(2\pi i \mathbf{r} \cdot \mathbf{S}) dv$ . The total scattering power of the atom is given by summing over all volume elements  $dv$  of the atom giving:



$$f(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{r} \cdot \mathbf{S}) dv$$

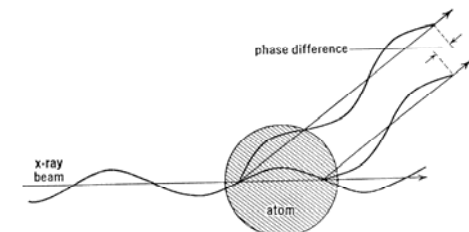


FIG. 32.

## Displacement Factor

The expression for the scattering factor function represents the scattering by an atom at 0 K. Changes in temperature affect the thermal motion of atoms, and this in turn affects the scattered intensities. In 1913 Peter Debye originally proposed and later Ivar Waller modified a relation describing the effect of the thermal motion of atoms on intensity. The Debye-Waller equation assumes the form:

$$f = f^{\circ} \exp[-B(\sin^2\theta/\lambda^2)]$$

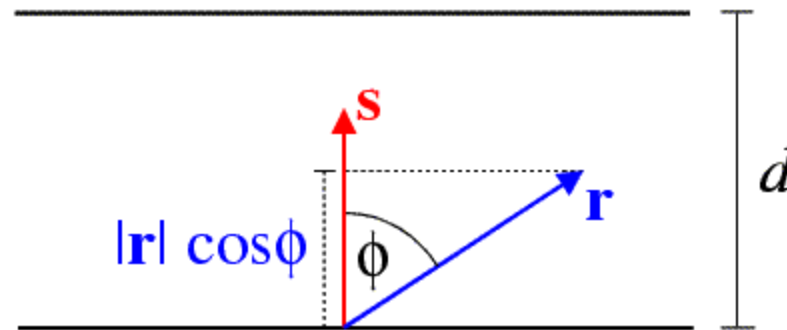
where  $f$  is the corrected scattering factor for a given atom type;  $f^{\circ}$  is the scattering factor for a given atom calculated at zero Kelvin;  $B = 8\pi^2 u^2$  and  $u^2$  is the mean square displacement of the atoms. This factor only reduces the intensity of the peaks and does not change the sharpness or shape of the peaks. This *displacement factor* was used originally to correct calculated intensities for thermal motion of the atoms. However, this factor also takes into account a variety of other factors such as static disorder, absorption, how tightly an atom is bound in the structure, wrong scaling of measurements, and incorrect atomic scattering functions. When the displacement parameter for a given atom is expressed as a single term  $B$ , it is said to represent an *isotropic* model of motion. Atoms that do not vibrate the same amount in all directions may be represented with an ellipsoidal *anisotropic* model rather than the spherical isotropic model. Ellipsoid models require six displacement variables for each atom – we will look at this when we discuss refinement.



### Physical interpretation of $\mathbf{s} \cdot \mathbf{r}$

To get a more intuitive feel for the meaning of the structure factor equation, which will be developed below, it is useful to consider the physical interpretation of  $\mathbf{s} \cdot \mathbf{r}$ . Remember that a dot product can be interpreted as the projection of one vector on the other (the component of one vector that is parallel to the other vector), multiplied by the length of the other vector.

$$\mathbf{s} \cdot \mathbf{r} = |\mathbf{s}| |\mathbf{r}| \cos\phi$$



In this figure,  $|\mathbf{r}| \cos\phi$  is the component of the position vector  $\mathbf{r}$  in the direction of  $\mathbf{s}$ , which is perpendicular to the Bragg planes. Since the length of the diffraction vector,  $|\mathbf{s}|$ , is equal to  $1/d$ ,  $\mathbf{s} \cdot \mathbf{r}$  is equal to the **fraction of the distance from one Bragg plane to the next** that the position vector  $\mathbf{r}$  has travelled from the origin. (Of course,  $\mathbf{s} \cdot \mathbf{r}$  can be any real number, so it can be greater than one.) We define a wave diffracted from the Bragg plane passing through the origin to have a phase of zero. Waves diffracted from the next Bragg plane have a phase of  $2\pi$  (which is equivalent to a phase of zero) and, in general, diffraction from any point  $\mathbf{r}$  will have a phase of  $2\pi\mathbf{s} \cdot \mathbf{r}$ .

The derivation of the phase (with respect to the origin) found in the handout, is simply a proof of the  $\mathbf{s} \cdot \mathbf{r}$  relationship earlier in the notes. In this derivation,  $xyz$  are not in fractional coordinates.

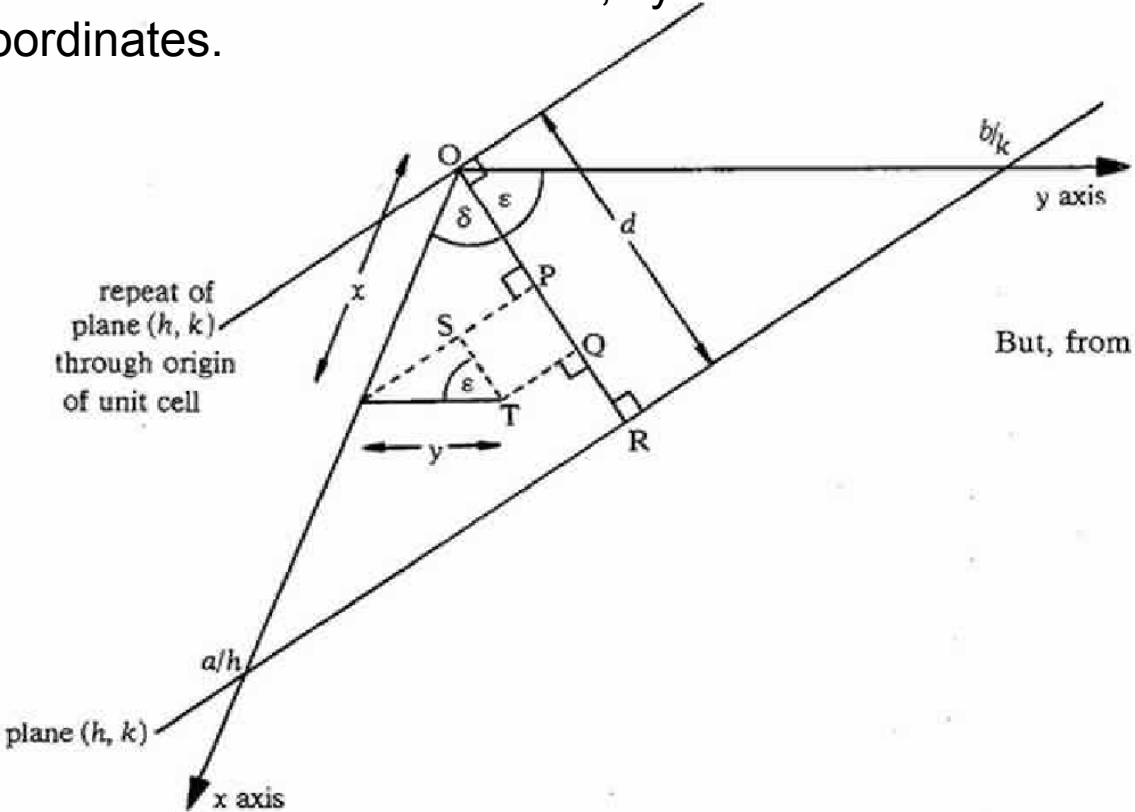
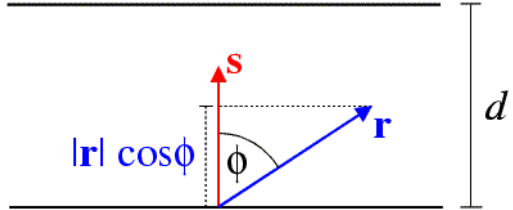


Fig. 6. Construction for calculating the phase of scattering from a point  $x, y$  in two dimensions for a reflection  $h, k$ .

Since  $OR/d = 2\pi$ ,  $d = OR/2\pi$ ,  $OQ/OR = 2\pi(hx/a + ky/b)$   
 Thus, in 3-D, the phase of the scattering of an atom at  $xyz$  is:  
 (note if  $xyz$  is in fractional coordinates, this is just the expression  $2\pi(hx + ky + lz)$  that is listed in the equations I have shown you.

But, from the triangle defined by  $O, R$  and the point  $a/h$ ,

$$OP = x \cos \delta$$

$$PQ = ST = y \cos \epsilon.$$

$$\cos \delta = \frac{OR}{a/h} = \frac{d}{a/h} = \frac{dh}{a}$$

$$\cos \epsilon = \frac{OR}{b/k} = \frac{d}{b/k} = \frac{dk}{b}$$

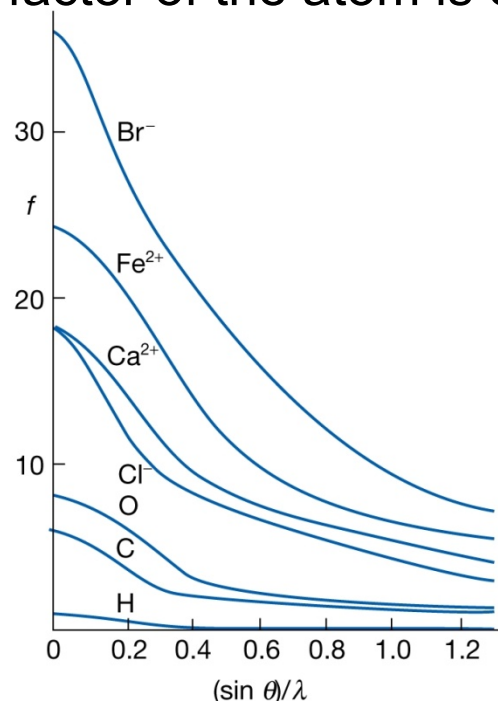
$$\therefore OP = x \cdot \frac{dh}{a} \quad \text{and} \quad PQ = y \cdot \frac{dk}{b}$$

$$OQ = OP + PQ = x \cdot \frac{dh}{a} + y \cdot \frac{dk}{b}$$

$$\therefore \frac{OO}{d} = \left( \frac{hx}{a} + \frac{ky}{b} \right)$$

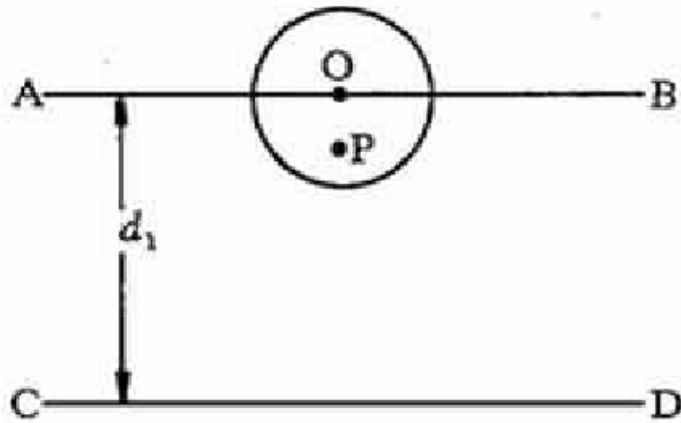
$$2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \text{ radians.}$$

The scattering factors are scaled with respect to the scattering that would be expected from a single electron and the intensity of the scattering is dependent on the scattering angle. At a scattering angle ( $\theta$ ) of 0 (i.e. straight through the atom in the same direction as the incident beam), the scattering factor of the atom is equal to the number of electrons on the atom.

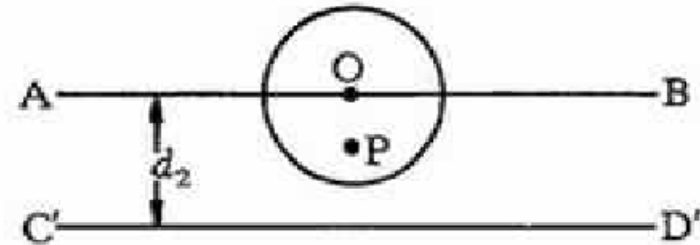


The atomic scattering factors are calculated values and the scattering factors for each of the elements are contained in most of the structure solution software packages. For most diffraction experiments, the electron density around an atom is assumed to be spherical – this can be a poor assumption for easily polarized atoms.

Note that the scattering factor is independent of the wavelength of the X-radiation used and depends only on the scattering angle and the electron density of the atom (note that  $\text{Ca}^{+2}$  and  $\text{Cl}^-$  have different behaviour at higher values of  $\theta$  because the electron density is different!)



(a)



(b)

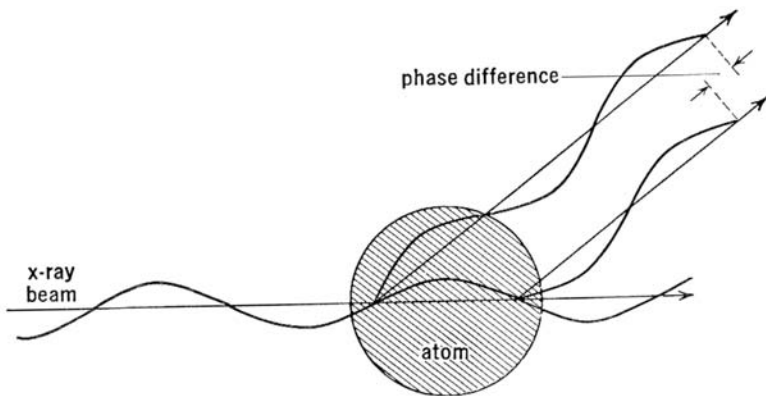


FIG. 32.

The decrease in the intensity of the scattering with increasing  $\theta$  can be understood in a manner similar to that which we examined earlier in the context of systematic absences. If distance between the electron density close to the nucleus (O) and the density at P is small compared the repeat distance ( $d$ ) then the scattered waves will have roughly the same phase. As the repeat distance becomes smaller, the waves will be more out-of-phase so destructive interference will reduce the overall intensity of the beam.



Consider that an atom  $j$  is located at  $\mathbf{r}_j$  from the origin in a unit cell of a crystal. This shift in origin from the center of the individual atom means that the distance  $\mathbf{r}$  in the equation for the scattering by an atom becomes  $\mathbf{r} + \mathbf{r}_j$ . Thus the scattering by atom  $j$  becomes:

$$\begin{aligned} \mathbf{f}_j &= \int \rho(\mathbf{r}) \exp[2\pi i (\mathbf{r} + \mathbf{r}_j) \cdot \mathbf{S}] dv \\ &= f_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{S}) \end{aligned}$$

where  $f_j = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{r} \cdot \mathbf{S}) dv$

This is just another way of saying that an atom will have the same scattering power no matter where it is located in the unit cell – the “ $\exp(2\pi i \mathbf{r}_j \cdot \mathbf{S})$ ” factor merely accounts for the **phase change** that occurs upon translation of the atom away from the origin of the cell.

Again,  $\mathbf{S}$  is the scattering vector and is the bisector of  $\mathbf{s}_0$ , a unit vector in the incident beam direction, and  $\mathbf{s}$ , a unit vector in the diffracted beam direction. The angle between  $\mathbf{s}_0$  and  $\mathbf{s} = 2\theta$ , is called the scattering angle.

$$|\mathbf{S}| = 2 \sin \theta / \lambda = 1/d_{hkl}$$

Similar expressions may be derived for all of the other atoms in the unit cell. The total scattering power of all of the atoms is given by the sum of the individual scattering amplitudes.

$$\begin{aligned} F(\mathbf{S}) &= \sum \mathbf{f}_j \\ &= \sum f_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{S}) \end{aligned}$$

Bragg's Law requires that the phase difference between the waves scattered by successive unit cells must be equal to an integral multiple of  $2\pi/\lambda$ . Since the scattered wave may be considered as coming from  $1/n$  multiples of the cell edge vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , then

$$(2\pi / \lambda) (\mathbf{a} \cdot \mathbf{S}) = 2\pi h / \lambda$$

$$(2\pi / \lambda) (\mathbf{b} \cdot \mathbf{S}) = 2\pi k / \lambda$$

$$(2\pi / \lambda) (\mathbf{c} \cdot \mathbf{S}) = 2\pi l / \lambda$$

This is another way of expressing the *Laue equations*.

The coordinates of atoms, in fractional coordinates, for the  $j$ th atom are labelled  $x_j$ ,  $y_j$ , and  $z_j$ . The vector from the origin,  $\mathbf{r}_j$ , may be written as:

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

Thus the product  $\mathbf{r}_j \cdot \mathbf{S}$  may be written as:

$$\begin{aligned}\mathbf{r}_j \cdot \mathbf{S} &= x_j\mathbf{a} \cdot \mathbf{S} + y_j\mathbf{b} \cdot \mathbf{S} + z_j\mathbf{c} \cdot \mathbf{S} \\ &= h x_j + k y_j + l z_j\end{aligned}$$

Finally, the total scattering power for all of the atoms in the unit cell may be written as:

$$\mathbf{F}(hkl) = \sum f_j \exp[2\pi i (h x_j + k y_j + l z_j)]$$

The relation above is known as the *structure factor expression*. This relation may be recast in terms of its amplitude,  $|F(hkl)|$ , and its phase angle,  $\alpha(hkl)$  or in terms of its real,  $A$ , and imaginary,  $B$ , components in the following expressions.

$$\mathbf{F}(hkl) = |F(hkl)| \exp [i \alpha(hkl)]$$

$$\mathbf{F}(hkl) = A + iB$$



## Electron Density

If the structure factor expression is rewritten as a continuous summation over the volume of the unit cell then the expression becomes:

$$F(\mathbf{S}) = \int \rho(\mathbf{r}) \exp (2\pi i \mathbf{r}_j \cdot \mathbf{S}) dv$$

By multiplying both sides by  $\exp (-2\pi i \mathbf{r}_j \cdot \mathbf{S})$  and integrating over the volume of diffraction space,  $dvr$ , we get an expression for the electron density of the unit cell.

$$\rho(\mathbf{r}) = \int F(\mathbf{S}) \exp (-2\pi i \mathbf{r}_j \cdot \mathbf{S}) dvr$$

Since  $F(\mathbf{S})$  is nonzero only at the lattice points, The integral may be written as discrete sums over the three indices  $h$ ,  $k$ , and  $l$ :

$$\rho(xyz) = 1/V \sum \sum \sum F(hkl) \exp [-2\pi i (h x + k y + l z)]$$

or

$$\rho(xyz) = 1/V \sum \sum \sum |F(hkl)| \exp -2\pi i [(h x + k y + l z - \phi(hkl))]$$

where the three summations run over all values of  $h$ ,  $k$ , and  $l$ .