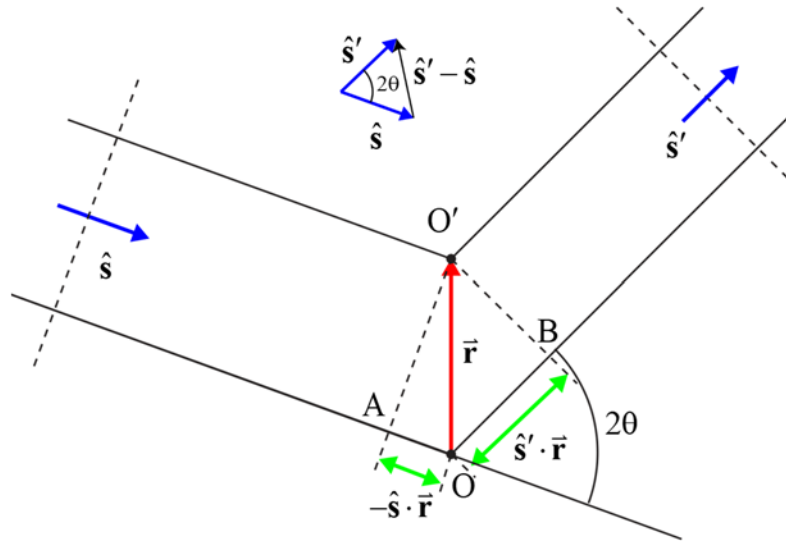


5. Structure Factors

Coherent scattering

We can understand diffraction from materials by considering a parallel incident wave that is scattered coherently through an angle designated as 2θ from some point O' in the specimen, which is offset by a vector \mathbf{r} from the origin O . In the diagram below, the length of the path through O is longer than that of the path through O' by $\Delta\ell = |A - O| + |O - B| = (\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{r}$. The phase difference for the two paths is then $\delta = 2\pi \cdot (\Delta\ell/\lambda)$, where λ is the wavelength. So

$$\delta = 2\pi \cdot \left(\frac{\hat{\mathbf{s}}' - \hat{\mathbf{s}}}{\lambda} \right) \cdot \mathbf{r}$$



The vector $\mathbf{r}^* = (\hat{\mathbf{s}}' - \hat{\mathbf{s}})/\lambda$, with dimensions of inverse length, is a reciprocal-space vector called the scattering vector. It is related to the momentum change of the X-ray photon (or electron) by $\Delta\mathbf{p} = h\mathbf{r}^*$, where h is Planck's constant. The length of $\hat{\mathbf{s}}' - \hat{\mathbf{s}}$ is

$$|\hat{\mathbf{s}}' - \hat{\mathbf{s}}| = \sqrt{1 + 1 - 2\cos(2\theta)} = \sqrt{4\left[\frac{1}{2}(1 - 2\cos(2\theta))\right]} = 2\sin\theta$$

So $|\mathbf{r}^*| = 2\sin\theta/\lambda$.

Scattering amplitude

Each scattering center in a specimen has a different scattering amplitude that depends on the type of scatterer at that point. The contribution of the scatterer at point j to the total scattering amplitude includes the scattering strength at an angle 2θ , which depends on the internal structure of the scattering center, and the phase difference for the path of the ray through that point, i.e.,

$$A_j(\theta) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}_j)$$

The scattering amplitude $A_j(\theta)$ is written as a function of θ , rather than 2θ , for reasons that will become clear later. If we have N discrete point scatters, the total scattering amplitude is

$$F(\mathbf{r}^*) = \sum_{j=1}^N A_j(\theta) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}_j)$$

More realistically, the scattering centers are distributed continuously within the specimen, so we integrate over the volume

$$F(\mathbf{r}^*) = \int_V \rho(\mathbf{r}) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) \cdot d^3 r = \mathfrak{F}[\rho(\mathbf{r})]$$

where $\rho(\mathbf{r})$ represents the concentration of scattering strength at point \mathbf{r} and the volume integral corresponds to a 3-D Fourier transform. In diffraction experiments, it is the intensity that is measured

$$I(\mathbf{r}^*) \propto |F(\mathbf{r}^*)|^2$$

Atomic scattering amplitude

We saw that the scattered X-ray intensity from a charged particle varies as the inverse mass squared of the particle. Thus, X-ray scattering from materials results almost entirely from the constituent electrons, rather than protons. The probability density for an electron in orbital j in an atom of type k is

$$\rho_j^{(k)}(\mathbf{r}) = |\psi_j^{(k)}(\mathbf{r})|^2$$

where $\psi_j^{(k)}(\mathbf{r})$ is the wave function. For a neutral atom, we can add together Z (the atomic number) such electron concentrations to find the total concentration

$$\rho^{(k)}(\mathbf{r}) = \sum_{j=1}^Z \rho_j^{(k)}(\mathbf{r})$$

Filled electron shells are spherically symmetric, and it is generally assumed that the entire electron density for the atom also has spherical symmetry, in which case we can center the atom at the origin and write $\rho^{(k)}(\mathbf{r}) \rightarrow \rho^{(k)}(r)$. The atomic scattering amplitude, also called the *atomic form factor*, is

$$f^{(k)}(r^*) = \mathfrak{F}[\rho^{(k)}(r)] = \int_V \rho^{(k)}(r) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) \cdot d^3 r$$

Using the spherical symmetry

$$f^{(k)}(r^*) = \int_V 4\pi r^2 \cdot \frac{\sin(2\pi r^* r)}{2\pi r^* r} \rho^{(k)}(r) \cdot dr$$

As an aside, it may be noticed that this is equivalent to

$$f^{(k)}(r^*) = \int_V \frac{\sin(2\pi r^* r)}{2\pi r^* r} U^{(k)}(r) \cdot dr$$

where $U^{(k)}(r) = 4\pi r^2 \cdot \rho^{(k)}(r)$ is the radial distribution function. Notice that we expect $f^{(k)}(0) = Z$, that is, the atomic scattering amplitude for X rays in the forward direction is equal to the atomic number.

In real materials, there is likely to be some reorganization of the outer, valence electrons involved in bonding, in which case we could write

$$f^{(k)}(r^*) = f_{\text{core}}^{(k)}(r^*) + f_{\text{valence}}^{(k)}(r^*)$$

again assuming spherical symmetry. The valence term will mainly contribute to low-angle scattering, and is likely to be significantly smaller than the core term for atoms with relatively large Z . Thus, in practice, it is typical to assume the atoms are neutral and spherically symmetric.

Unit-cell scattering amplitude

The electron concentration within a unit cell of a crystal is typically computed by assuming a collection of atoms, with electron concentrations $\rho^{(k)}(\mathbf{r})$, located at positions $\mathbf{d}^{(k)}$

$$\rho_m(\mathbf{r}) = \sum_k \rho^{(k)}(\mathbf{r} - \mathbf{d}^{(k)})$$

The scattering amplitude from the unit cell is

$$\begin{aligned} F_m(\mathbf{r}^*) &= \mathfrak{F}[\rho_m(\mathbf{r})] = \sum_k \mathfrak{F}[\rho^{(k)}(\mathbf{r} - \mathbf{d}^{(k)})] \\ &= \sum_k \int_V \rho^{(k)}(\mathbf{r} - \mathbf{d}^{(k)}) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) \cdot d^3 r \end{aligned}$$

Defining $\mathbf{r}^{(k)} = \mathbf{r} - \mathbf{d}^{(k)}$, we can center each integral on the origin

$$\begin{aligned} F_m(\mathbf{r}^*) &= \mathfrak{F}[\rho_m(\mathbf{r})] = \sum_k \mathfrak{F}[\rho^{(k)}(\mathbf{r} - \mathbf{d}^{(k)})] \\ &= \sum_k \int_{\mathbf{r}^{(k)}} \rho^{(k)}(\mathbf{r}^{(k)}) \cdot \exp[2\pi i \mathbf{r}^* \cdot (\mathbf{r}^{(k)} + \mathbf{d}^{(k)})] \cdot d^3 r^{(k)} \\ &= \sum_k \mathfrak{F}[\rho^{(k)}(\mathbf{r}^{(k)})] \exp(2\pi i \mathbf{r}^* \cdot \mathbf{d}^{(k)}) \\ F_m(\mathbf{r}^*) &= \sum_k f^{(k)}(\mathbf{r}^*) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{d}^{(k)}) \end{aligned}$$

where we have used the spherical symmetry of the atoms in the last step.

Structure factors

The X-ray scattering amplitude for a crystal is proportional to the Fourier transform of the total electron density.

$$F(\mathbf{r}^*) = \mathfrak{F}[\rho(\mathbf{r})]$$

The total electron density can be evaluated by sum over unit cells.

$$\rho(\mathbf{r}) = \lim_{N \rightarrow \infty} \sum_{n=1}^N \rho_m(\mathbf{r} - \mathbf{r}_n)$$

where n indicates a lattice point and $\mathbf{r}_n = u_n \mathbf{a} + v_n \mathbf{b} + w_n \mathbf{c}$, with $(u_n, v_n, w_n) \in \mathbb{Z}^3$. Another way to evaluate this uses the convolution

$$\rho(\mathbf{r}) = \rho_m(\mathbf{r}) * L(\mathbf{r})$$

where

$$L(\mathbf{r}) = \lim_{N \rightarrow \infty} \sum_{n=1}^N \delta(\mathbf{r} - \mathbf{r}_n)$$

is called the lattice sum. From the convolution theorem

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$$F(\mathbf{r}^*) = \mathfrak{F}[\rho_m(\mathbf{r})] \cdot \mathfrak{F}[X(\mathbf{r})]$$

Recall that we have already determined

$$F_m(\mathbf{r}^*) = \sum_k f^{(k)}(\mathbf{r}^*) \cdot e^{2\pi i \mathbf{r}^* \cdot \mathbf{d}^{(k)}}$$

Now

$$\begin{aligned} \mathfrak{F}[X(\mathbf{r})] &= \lim_{V \rightarrow \infty} \lim_{N \rightarrow \infty} \sum_{n=1}^N \int_{\mathbf{r} \in V} \delta(\mathbf{r} - \mathbf{r}_n) \cdot e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}} \\ &= \lim_{N \rightarrow \infty} \sum_{n=1}^N e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}_n} = X(\mathbf{r}^*) \end{aligned}$$

Writing $\mathbf{r}^* = \bar{\mathbf{A}}^* \cdot \mathbf{X}^*$, where $\bar{\mathbf{X}}^* = (x^* \ y^* \ z^*)$, we have $\mathbf{r}^* \cdot \mathbf{r}_n = x^* u_n + y^* v_n + z^* w_n$.

For reciprocal-lattice vectors $\mathbf{r}_H^* = \bar{\mathbf{A}}^* \cdot \mathbf{H}$, where $\bar{\mathbf{H}} = (h \ k \ \ell)$, we have $\mathbf{r}_H^* \cdot \mathbf{r}_n = h u_n + k v_n + \ell w_n$. The sum becomes

$$\sum_{n=1}^N e^{2\pi i \mathbf{r}_H^* \cdot \mathbf{r}_n} = \sum_{n=1}^N (1) = N$$

So

$$\lim_{N \rightarrow \infty} \sum_{n=1}^N e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}_n} = \lim_{N \rightarrow \infty} \sum_{\mathbf{H}} \begin{cases} N, & \mathbf{r}^* = \mathbf{r}_H^* \\ 0, & \text{otherwise} \end{cases}$$

We can write

$$\begin{aligned} \Delta(\mathbf{r}^* - \mathbf{r}_H^*) &= \lim_{V \rightarrow \infty} \int_{\mathbf{r} \in V} d^3 r \cdot (1) \cdot e^{2\pi i (\mathbf{r}^* - \mathbf{r}_H^*) \cdot \mathbf{r}} \\ &= \lim_{V \rightarrow \infty} \begin{cases} V, & \mathbf{r}^* = \mathbf{r}_H^* \\ 0, & \text{otherwise} \end{cases} \\ \Delta(\mathbf{r}^* - \mathbf{r}_H^*) &= v \cdot \lim_{V \rightarrow \infty} \begin{cases} N, & \mathbf{r}^* = \mathbf{r}_H^* \\ 0, & \text{otherwise} \end{cases} \end{aligned}$$

using $V = Nv$, where v is the unit-cell volume. Now we have

$$X(\mathbf{r}^*) = \frac{1}{v} \cdot \sum_{\mathbf{H}} \Delta(\mathbf{r}^* - \mathbf{r}_H^*)$$

We can abbreviate $F_H = F_m(\mathbf{r}_H^*)$ — the *structure factors* — to write

$$F(\mathbf{r}^*) = \frac{1}{v} \cdot \sum_{\mathbf{H}} F_H \cdot \Delta(\mathbf{r}^* - \mathbf{r}_H^*)$$

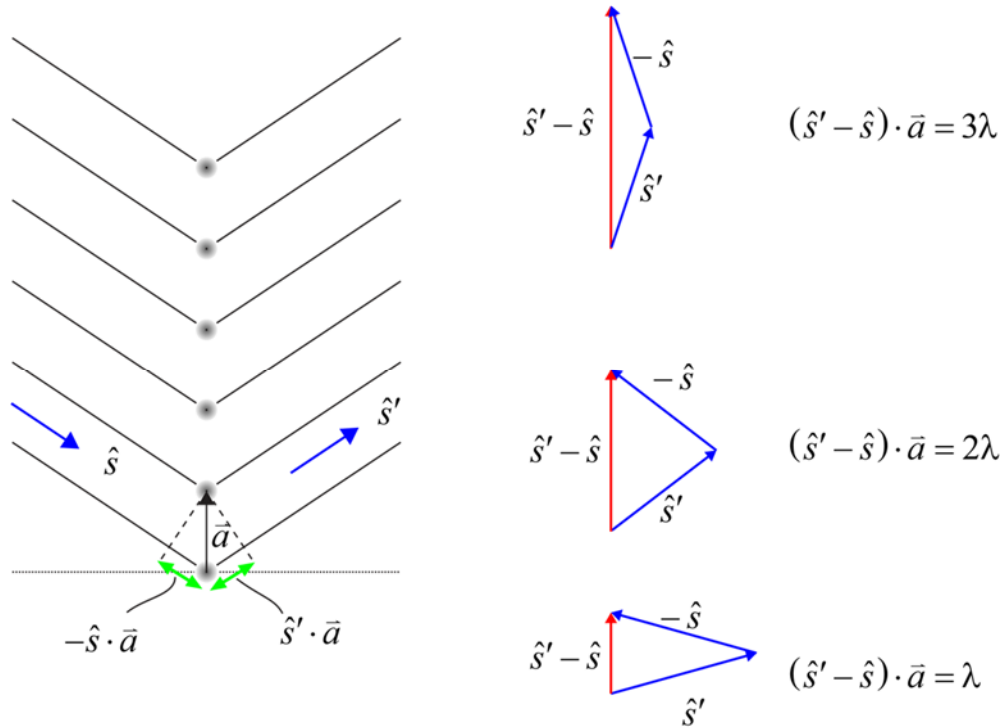
Electron density from structure factors

Now that we know $F(\mathbf{r}^*)$, we can find the Fourier series for $\rho(\mathbf{r})$:

$$\begin{aligned}\rho(\mathbf{r}) &= \mathfrak{F}^{-1}[F(\mathbf{r}^*)] \\ &= \frac{1}{v} \cdot \sum_{\mathbf{H}} F_{\mathbf{H}} \cdot \left[\lim_{V^* \rightarrow \infty} \int_{\mathbf{r}^* \in V^*} d^3 r^* \cdot \Delta(\mathbf{r}^* - \mathbf{r}_{\mathbf{H}}^*) \cdot e^{-2\pi i \mathbf{r}^* \cdot \mathbf{r}} \right] \\ \rho(\mathbf{r}) &= \frac{1}{v} \cdot \sum_{\mathbf{H}} F_{\mathbf{H}} \cdot e^{-2\pi i \mathbf{H} \cdot \mathbf{r}}\end{aligned}$$

Laue equations

Laue considered scattering from rows of atoms. The contribution to the scattering amplitude from each atom contains the phase factor $\exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}_j)$, where \mathbf{r}_j specifies the atom's location. If the atoms are aligned along the lattice direction \mathbf{a} , then $\mathbf{r}_j = u_j \cdot \mathbf{a}$, where $u_j \in \mathbb{Z}$. By definition, $\mathbf{r}^* = (\hat{\mathbf{s}}' - \hat{\mathbf{s}})/\lambda$, so $\mathbf{r}^* \cdot \mathbf{r}_j = u_j \cdot (\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{a}/\lambda$. Constructive interference will occur when $\mathbf{r}^* \cdot \mathbf{r}_j$ is an integer for each u_j , so we need $(\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{a}/\lambda$ to equal an integer. We will call this integer h and write $(\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{a} = h\lambda$. For a given incident beam direction \mathbf{s} , each value of h specifies a cone of scattered intensity in directions \mathbf{s}' satisfying $\hat{\mathbf{s}}' \cdot \mathbf{a} = \hat{\mathbf{s}} \cdot \mathbf{a} + h\lambda$.



In a 3-D crystal, we expect atoms to also be aligned along lattice directions \mathbf{b} and \mathbf{c} . Altogether, we have three Laue equations.

$$(\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{a} = h\lambda, \quad (\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{b} = h\lambda, \quad (\hat{\mathbf{s}}' - \hat{\mathbf{s}}) \cdot \mathbf{c} = h\lambda$$

The simultaneous solutions to any two of these specify a line, whereas all three specify a point.

Bragg's law from the Laue equations

Let's write an arbitrary vector in terms of the reciprocal-lattice basis vectors as

$$\mathbf{r} = u\mathbf{a}^* + v\mathbf{b}^* + w\mathbf{c}^*$$

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Using the fact that $A^* = (A^T)^{-1}$, where $A^T = (\mathbf{a} \ \mathbf{b} \ \mathbf{c})$ and $(A^*)^T = (\mathbf{a}^* \ \mathbf{b}^* \ \mathbf{c}^*)$, we can write $u = \mathbf{r} \cdot \mathbf{a}$, $v = \mathbf{r} \cdot \mathbf{b}$, and $w = \mathbf{r} \cdot \mathbf{c}$, so

$$\mathbf{r} = (\mathbf{r} \cdot \mathbf{a})\mathbf{a}^* + (\mathbf{r} \cdot \mathbf{b})\mathbf{b}^* + (\mathbf{r} \cdot \mathbf{c})\mathbf{c}^*$$

Now let's examine the vector $\mathbf{r} = \hat{\mathbf{s}}' - \mathbf{s}$. We can write

$$\mathbf{r} = [(\hat{\mathbf{s}}' - \mathbf{s}) \cdot \mathbf{a}]\mathbf{a}^* + [(\hat{\mathbf{s}}' - \mathbf{s}) \cdot \mathbf{b}]\mathbf{b}^* + [(\hat{\mathbf{s}}' - \mathbf{s}) \cdot \mathbf{c}]\mathbf{c}^*$$

Using the Laue equations

$$\mathbf{r} = \lambda \cdot (h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^*)$$

We recognize the last factor as the reciprocal-lattice vector $\mathbf{r}_H^* = h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^*$, so $\hat{\mathbf{s}}' - \mathbf{s} = \lambda \cdot \mathbf{r}_H^*$. We now know that diffraction peaks from 3-D crystals occur when $\mathbf{r}^* = (\hat{\mathbf{s}}' - \mathbf{s})/\lambda = \mathbf{r}_H^*$, that is, when the scattering vector is a reciprocal-lattice vector. The length of a reciprocal-lattice vector is the inverse of the spacing of the corresponding planes, i.e., $|\mathbf{r}_H^*| = 1/d$, and we know that $|\mathbf{r}^*| = 2 \sin \theta / \lambda$, so $2d \sin \theta = \lambda$, which is Bragg's law.

Symmetry and structure factors

We can write the electron density as either

$$\rho(\mathbf{r}) = \frac{1}{v} \cdot \sum_H F_H \cdot e^{-2\pi i \mathbf{h} \cdot \mathbf{r}}$$

or

$$\rho(\mathbf{X}) = \frac{1}{v} \cdot \sum_H F_H \cdot e^{-2\pi i \bar{\mathbf{H}} \cdot \mathbf{X}}$$

After performing a transformation (R,T), we have

$$\begin{aligned} \rho(\mathbf{RX} + \mathbf{T}) &= \frac{1}{v} \cdot \sum_H F_H \cdot e^{-2\pi i \bar{\mathbf{H}} \cdot (\mathbf{RX} + \mathbf{T})} \\ &= \frac{1}{v} \cdot \sum_H (F_H \cdot e^{-2\pi i \bar{\mathbf{H}} \cdot \mathbf{T}}) \cdot e^{-2\pi i (\bar{\mathbf{H}}\mathbf{R})\mathbf{X}} \\ \rho(\mathbf{RX} + \mathbf{T}) &= \frac{1}{v} \cdot \sum_H (F_H \cdot e^{-2\pi i \bar{\mathbf{H}} \cdot \mathbf{T}}) \cdot e^{-2\pi i (\overline{\mathbf{RH}})\mathbf{X}} \end{aligned}$$

Now we define $H' = \overline{\mathbf{RH}}$. So $H = \overline{\mathbf{R}}^{-1}H' = \mathbf{RH}'$, since R is unitary. Now $\bar{\mathbf{H}} = \overline{\overline{\mathbf{RH}'}}$. Substituting $H' \rightarrow H$:

$$\rho(\mathbf{RX} + \mathbf{T}) = \frac{1}{v} \cdot \sum_H (F_{\mathbf{RH}} \cdot e^{-2\pi i (\overline{\mathbf{RH}})\mathbf{T}}) \cdot e^{-2\pi i \bar{\mathbf{H}}\mathbf{X}}$$

We are interested in symmetry transformations, so $\rho(\mathbf{RX} + \mathbf{T}) = \rho(\mathbf{X})$. Thus

$$F_H = F_{\mathbf{RH}} \cdot e^{-2\pi i (\overline{\mathbf{RH}})\mathbf{T}}$$

Now define $H' = \mathbf{RH}$. So $H = \overline{\mathbf{RH}'}$. Again substituting $H' \rightarrow H$:

$$F_{\bar{R}H} = F_H \cdot e^{-2\pi i \bar{H} \cdot T}$$

This equation is very useful for relating the structure factors of symmetry-equivalent reflections. We know two things just by inspection: 1) the magnitudes of F_H and $F_{\bar{R}H}$ must be equal

$$|F_{\bar{R}H}| = |F_H|$$

and 2) the phases of F_H and $F_{\bar{R}H}$ are related by

$$\phi_{\bar{R}H} = \phi_H - 2\pi \bar{H} \cdot T$$

Systematic absences

Consider some symmetry transformation (R,T) under which $\bar{R}H = H$ for a particular reflection H. Then

$$F_H = F_H \cdot e^{-2\pi i \bar{H} \cdot T}$$

So either

- i) $2\pi \bar{H} \cdot T = 2\pi n$, where $n \in \mathbb{Z}$, or
- ii) $|F_H| = 0$

In other words, if $\bar{H} \cdot T \neq n$, then the reflection is absent. For a particular crystal with the symmetry (R,T), we can say that all reflections satisfying $\bar{R}H = H$ with $\bar{H} \cdot T \neq n$ are *systematically absent*.

Periodic absences

Centered lattices have at least one built-in symmetry transformation (R,T), where R=I and T indicates the centered position. For example, a C-centered lattice has $T = \frac{1}{2}(A + B)$, i.e.,

$$\rho(\mathbf{r}) = \rho[\mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$$

Because R=I, all reflections satisfy $\bar{R}H = H$. Now,

$$\bar{H} \cdot T = (h \quad k \quad \ell) \cdot \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \end{pmatrix} = \frac{h+k}{2}$$

So

$$F_{hk\ell} = F_{hk\ell} \cdot e^{\pi i (h+k)}$$

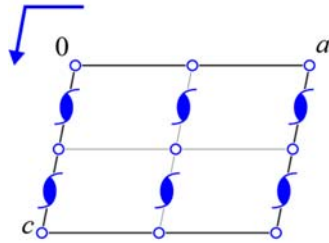
If $h+k = \text{odd}$, then $F_{hk\ell} = 0$. We conclude that reflections with $h+k$ odd are absent.

Unambiguous space-group determination

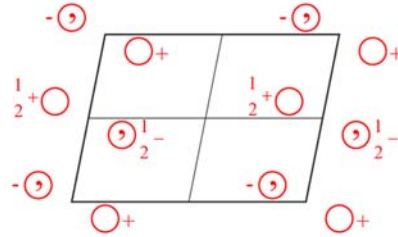
Certain space groups can be identified unambiguously from their diffraction pattern symmetries.

Consider group $P2_1/c$:

$P2_1/c$
No. 14



Monoclinic



We have the following symmetry elements.

- 1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity
- 2: $\rho(\mathbf{r}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{c}/4) + \mathbf{c}/4 + \mathbf{b}/2]$ // 2_b @ $\mathbf{c}/4$
- 3: $\rho(\mathbf{r}) = \rho[m_b \cdot (\mathbf{r} - \mathbf{b}/4) + \mathbf{b}/4 + \mathbf{c}/2]$ // c_b @ $\mathbf{b}/4$
- 4: $\rho(\mathbf{r}) = \rho(-\mathbf{r})$ // $\bar{1}$ @ $\mathbf{0}$

In order to write these in matrix forms, let's first convert 2 and 3 to their general forms

$$\rho(\mathbf{r}) = \rho[2_b \cdot \mathbf{r} + (\mathbf{b} + \mathbf{c})/2] \text{ and}$$

$$\rho(\mathbf{r}) = \rho[m_b \cdot \mathbf{r} + (\mathbf{b} + \mathbf{c})/2]$$

The matrices are

- 1: $R = I, T = 0$
- 2: $R = 2_b, T = (\mathbf{X}_b + \mathbf{X}_c)/2$
- 3: $R = m_b, T = (\mathbf{X}_b + \mathbf{X}_c)/2$
- 4: $R = -I, T = 0$

Systematic absences may occur for reflections satisfying $\bar{R}\mathbf{H} = \mathbf{H}$. Consider 2:

$$2_b \cdot \begin{pmatrix} h \\ k \\ \ell \end{pmatrix} = \begin{pmatrix} -h \\ k \\ -\ell \end{pmatrix} = \begin{pmatrix} h \\ k \\ \ell \end{pmatrix} \rightarrow h = \ell = 0$$

Reflections of the type $(0k0)$ will be absent if $\bar{\mathbf{H}} \cdot \mathbf{T} \neq n$.

$$\bar{\mathbf{H}} \cdot \mathbf{T} = (0 \quad k \quad 0) \cdot \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix} = \frac{k}{2}$$

We have

$$F_{0k0} = F_{0k0} \cdot e^{-\pi i k} = \begin{cases} F_{0k0}, & k \text{ even} \\ -F_{0k0}, & k \text{ odd} \end{cases}$$

Therefore, reflections $(0k0)$ with k odd are absent. Viewed along the \mathbf{c} axis, the diffraction pattern from a material with Now consider 3:

$$m_b \cdot \begin{pmatrix} h \\ k \\ \ell \end{pmatrix} = \begin{pmatrix} h \\ -k \\ \ell \end{pmatrix} = \begin{pmatrix} h \\ k \\ \ell \end{pmatrix} \rightarrow k = 0$$

Reflections of the type $(h0\ell)$ will be absent if $\bar{\mathbf{H}} \cdot \mathbf{T} \neq n$.

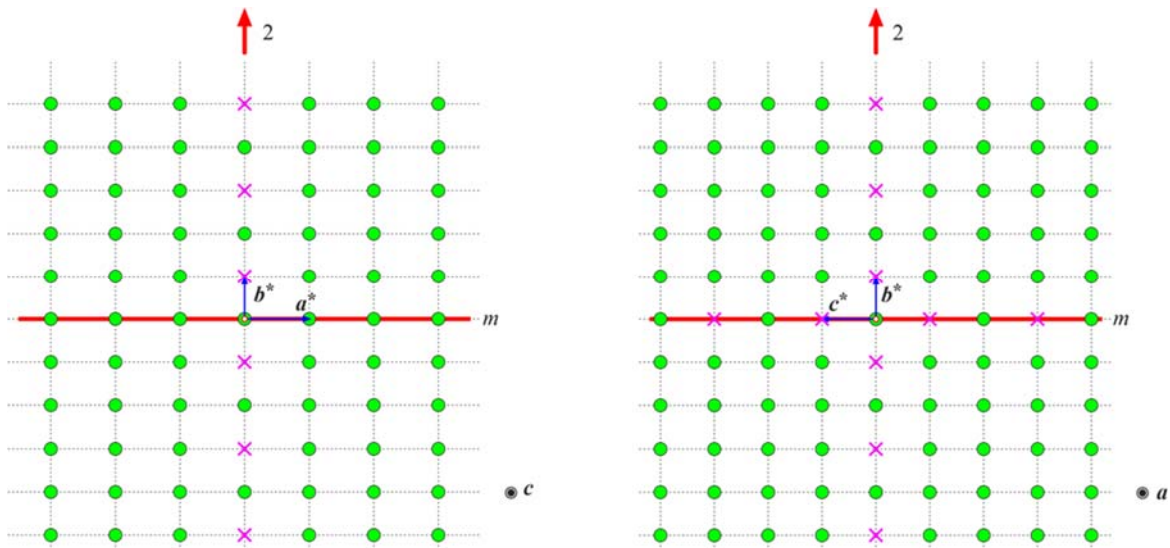
$$\bar{\mathbf{H}} \cdot \mathbf{T} = (h \ 0 \ \ell) \cdot \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix} = \frac{\ell}{2}$$

We have

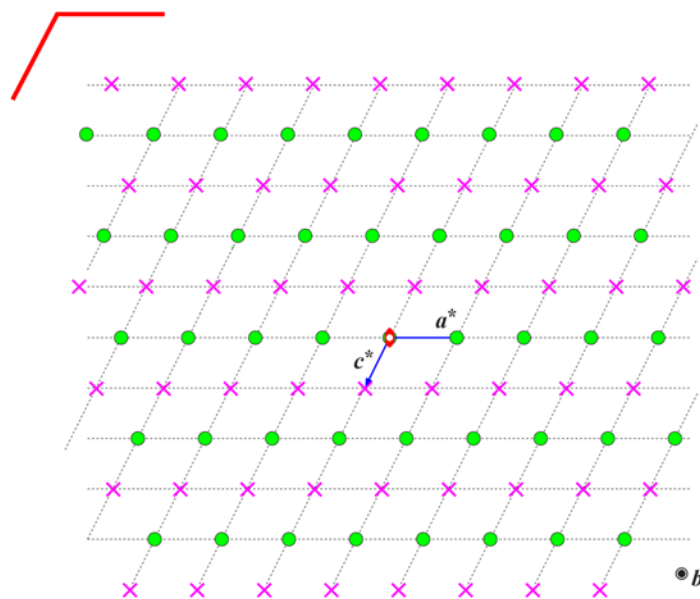
$$F_{h0\ell} = F_{h0\ell} \cdot e^{-\pi i \ell} = \begin{cases} F_{h0\ell}, & \ell \text{ even} \\ -F_{h0\ell}, & \ell \text{ odd} \end{cases}$$

Therefore, reflections $(h0\ell)$ with ℓ odd are also absent.

As for all monoclinic crystals, the entire collection of diffraction spots will have $2/m$ symmetry. Viewed along the \mathbf{c} axis, the ZOLZ contains a rectangular net of diffraction spots. In particular, along the row of spots $(0k0)$, those with k odd are absent. Viewed along the \mathbf{a} axis, the same $(0k0)$ spots are absent, as well as the (00ℓ) with ℓ odd.



Viewed along the **b** (unique) axis, the spots are arranged in an oblique net, with the absence of alternating rows ($h0\ell$) having ℓ odd. Of course, the absence of these rows is not evident without the additional observations of parallel rows ($hk\ell$), with $k \neq 0$.



We also observe that there are no periodic absences in these diffraction patterns, indicated that the lattice is primitive. Comparison with the arrangements of diffraction spots from all other monoclinic space groups shows that these observations are only consistent with $P2_1/c$. The space group has been determined unequivocally.

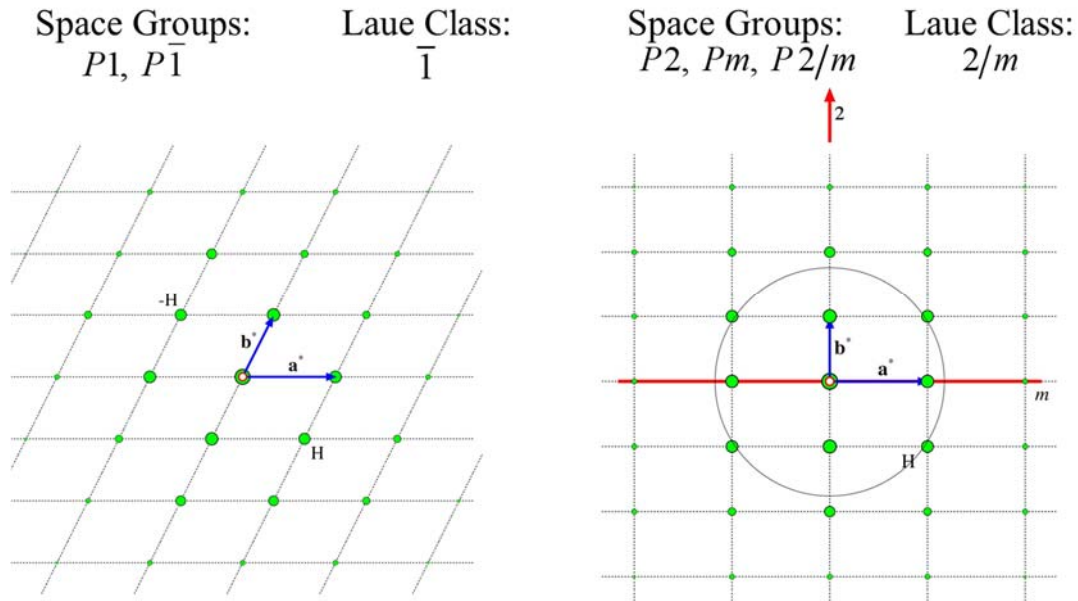
Friedel's law

We expect $\rho(X)$ from any actual crystal to be a real number. Mathematically, this is $\rho^*(\mathbf{r}) = \rho(\mathbf{r})$. So

$$\rho^*(\mathbf{r}) = \frac{1}{v} \cdot \sum_{\mathbf{H}} F_{\mathbf{H}}^* \cdot e^{+2\pi i \mathbf{r} \cdot \mathbf{H}} = \frac{1}{v} \cdot \sum_{\mathbf{H}} F_{-\mathbf{H}} \cdot e^{-2\pi i \mathbf{r} \cdot \mathbf{H}}$$

where the sum variable is altered to retain the negative sign in the exponent. From the Fourier series for $\rho(\mathbf{r})$, we can conclude $F_{-\mathbf{H}}^* = F_{\mathbf{H}}$, or $F_{-\mathbf{H}} = F_{\mathbf{H}}^*$.

Let us write $F_{\mathbf{H}} = |F_{\mathbf{H}}| \cdot e^{i\phi_{\mathbf{H}}}$ and $F_{-\mathbf{H}} = |F_{-\mathbf{H}}| \cdot e^{i\phi_{-\mathbf{H}}}$. Now we can see that $F_{\mathbf{H}}^* = |F_{\mathbf{H}}| \cdot e^{-i\phi_{\mathbf{H}}} = |F_{-\mathbf{H}}| \cdot e^{i\phi_{-\mathbf{H}}}$, so $|F_{-\mathbf{H}}| = |F_{\mathbf{H}}|$ and $\phi_{-\mathbf{H}} = -\phi_{\mathbf{H}}$. The scattered intensity $I_{\mathbf{H}} \propto |F_{\mathbf{H}}|^2$ and $I_{-\mathbf{H}} \propto |F_{-\mathbf{H}}|^2$, so $I_{\mathbf{H}} = I_{-\mathbf{H}}$. We can describe this result, called Friedel's law, by the statement that the collection of diffracted intensities has a center of symmetry. Thus, the arrangement of diffracted intensities has a center of symmetry. The overall symmetry of the diffracted intensity for a particular space group corresponds to that of the point group from which the space group was derived with the addition of an inversion center at the origin. This results in ten distinct Laue classes.



Restricted phase reflections

Consider some symmetry transformation (R,T) under which $\bar{R}H = -H$ for a particular reflection H. Then

$$\phi_{\bar{R}H} = \phi_{-H} = -\phi_H = \phi_H - 2\pi\bar{H} \cdot T$$

So

$$\phi_{\bar{R}H} = \phi_{-H} = 2\phi_H = 2\pi\bar{H} \cdot T + 2\pi n, \text{ where } n \in \mathbb{Z}$$

observing that we can always add integer multiples of 2π to a phase. So the phase for this reflection must satisfy

$$\phi_H = \pi\bar{H} \cdot T + \pi n$$

If there is no T associated with this symmetry operation (it is an inversion, rotation, or reflection for which the symmetry element intersects the origin), then $\bar{H} \cdot T = 0$ and $\phi_H = \pi n$. In other words, F_H is real, i.e., $F_H = \pm |F_H|$. Regardless, the reflections satisfying $\bar{R}H = -H$ have *restricted phase*.

Structure invariants (I)

It is useful to identify quantities that remain unchanged under a shift (translation) in coordinates. Such quantities are called structure invariants. For example, the placement of a symmetry element at a particular location, especially the origin, often leads to a simplification in the forms of a particular subset of structure factors. Structure-invariant quantities that were determined in the original coordinates can be retained in the shifted coordinates to facilitate analysis.

Take $\rho'(\mathbf{r}) = \rho(\mathbf{r} - \mathbf{r}_0)$. The X-ray scattering amplitude is the Fourier transform:

$$F'(\mathbf{r}^*) = \mathfrak{F}[\rho'(\mathbf{r})] = \int_V \rho(\mathbf{r} - \mathbf{r}_0) \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) \cdot d^3r$$

Defining $\mathbf{r}' = \mathbf{r} - \mathbf{r}_0$.

$$\begin{aligned}
F'(\mathbf{r}^*) &= \int_V \rho(\mathbf{r}') \cdot \exp[2\pi i \mathbf{r}^* \cdot (\mathbf{r}' + \mathbf{r}_0)] \cdot d^3 r' \\
&= \left[\int_V \rho(\mathbf{r}') \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}') \cdot d^3 r' \right] \cdot \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}_0) \\
F'(\mathbf{r}^*) &= F(\mathbf{r}^*) \cdot e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}_0}
\end{aligned}$$

So the only effect of the translation is a shift in phase of the scattering amplitude. For illustration, consider a material composed of atoms with form factors $f^{(k)}$ at locations $\mathbf{d}^{(k)}$ within the unit cell. The structure factors are

$$F_H = \sum_k f^{(k)} \cdot \exp(2\pi i \mathbf{r}_H^* \cdot \mathbf{d}^{(k)}) = |F_H| \cdot e^{i\phi_H}$$

If we shift the origin from $\mathbf{0}$ to \mathbf{r}_0 , the structure factors become

$$F'_H = \sum_k f^{(k)} \cdot \exp[2\pi i \mathbf{r}_H^* \cdot (\mathbf{d}^{(k)} - \mathbf{r}_0)] = |F_H| \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}_0}$$

Whereas the phase has changed, we can conclude that the magnitudes of the structure factors are independent of the placement of the origin, that is $|F'_H| = |F_H|$, so $|F_H|$ is a *structure invariant*.

Structure invariants (II)

The product of a collection of structure factors can be written

$$F_{H_1} \cdot F_{H_2} \cdots F_{H_m} = |F_{H_1}| \cdot |F_{H_2}| \cdots |F_{H_m}| \cdot \exp[i(\phi_{H_1} + \phi_{H_2} + \cdots + \phi_{H_m})]$$

If we shift the origin to \mathbf{r}_0 , the product of structure factors in the new coordinates is

$$F'_{H_1} \cdot F'_{H_2} \cdots F'_{H_m} = F_{H_1} \cdot F_{H_2} \cdots F_{H_m} \cdot \exp[-2\pi i(\mathbf{r}_{H_1}^* + \mathbf{r}_{H_2}^* + \cdots + \mathbf{r}_{H_m}^*) \cdot \mathbf{r}_0]$$

If $\mathbf{r}_{H_1}^* + \mathbf{r}_{H_2}^* + \cdots + \mathbf{r}_{H_m}^* = \mathbf{0}$ (which occurs when $H_1 + H_2 + \cdots + H_m = 0$), then

$$F'_{H_1} \cdot F'_{H_2} \cdots F'_{H_m} = F_{H_1} \cdot F_{H_2} \cdots F_{H_m}$$

The product $F_{H_1} \cdot F_{H_2} \cdots F_{H_m}$ is a structure invariant. We can write it as $F_{H_1} \cdot F_{H_2} \cdots F_{-H_1-H_2-\dots}$.

Structure semi-invariants

The symmetry of a crystal can allow identifying quantities that are invariant under particular coordinate shifts. Given a crystal with a symmetry relationship (R,T), such that $\rho(\mathbf{X}) = \rho(\mathbf{RX} + \mathbf{T})$, we know that the structure factor of a reflection $\bar{\mathbf{R}}\mathbf{H}$ is related to that of the reflection \mathbf{H} by $F_{\bar{\mathbf{R}}\mathbf{H}} = F_{\mathbf{H}} \cdot \exp(-2\pi i \bar{\mathbf{H}} \cdot \mathbf{T})$. This indicates that phases are related by $\phi_{\bar{\mathbf{R}}\mathbf{H}} = \phi_{\mathbf{H}} - 2\pi \bar{\mathbf{H}} \cdot \mathbf{T}$. The negative of this, $-\phi_{\bar{\mathbf{R}}\mathbf{H}} = -\phi_{\mathbf{H}} + 2\pi \bar{\mathbf{H}} \cdot \mathbf{T}$, is the phase of the reflection $-\bar{\mathbf{R}}\mathbf{H}$, so $\phi_{\mathbf{H}} + \phi_{-\bar{\mathbf{R}}\mathbf{H}} = 2\pi \bar{\mathbf{H}} \cdot \mathbf{T}$. Consider a third reflection $\bar{\mathbf{R}}\mathbf{H} - \mathbf{H} = (\bar{\mathbf{R}} - \mathbf{I})\mathbf{H}$. The triple product $F_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}} F_{\mathbf{H}} F_{-\bar{\mathbf{R}}\mathbf{H}}$ is structure invariant, with phase $\psi = \phi_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}} + \phi_{\mathbf{H}} + \phi_{-\bar{\mathbf{R}}\mathbf{H}}$. Substituting $\psi = \phi_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}} + 2\pi \bar{\mathbf{H}} \cdot \mathbf{T}$. Therefore, the phase

$$\phi_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}} = \psi - 2\pi \bar{\mathbf{H}} \cdot \mathbf{T}$$

Under a coordinate shift by Δ_X , the translation \mathbf{T} becomes $\mathbf{T}' = \mathbf{T} - \Delta_X$. If $\bar{\mathbf{H}} \cdot \mathbf{T}' = \bar{\mathbf{H}} \cdot \mathbf{T} - n$ ($n \in \mathbb{Z}$), then $\bar{\mathbf{H}} \cdot \Delta_X = n$, leaving $\phi_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}}$ unchanged. The quantity $\phi_{(\bar{\mathbf{R}}-\mathbf{I})\mathbf{H}}$ is a *structure semi-invariant*.