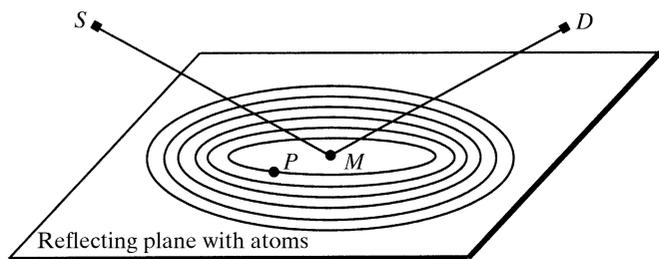


2.1. INTRODUCTION TO BASIC CRYSTALLOGRAPHY


Figure 2.1.4.6

S is the X-ray source and D is the detector. The scattering is by the atoms in a plane. The shortest distance between S and D via a point in the plane is through M . Path lengths via points in the plane further out from M are longer, and when these beams reach the detector they lag behind in phase with respect to the MD beam. The plane is divided into zones, such that from one zone to the next the path difference is $\lambda/2$.

the radius is slightly smaller, because the intensity radiated by more distant zones decreases (Kauzmann, 1957). Therefore, the sum of vectors pointing upwards is shorter than that of those pointing downwards, and the resulting scattered wave lags $\pi/2$ in phase behind the scattering by the atom at M .

2.1.4.4. Anomalous dispersion

In classical dispersion theory, the scattering power of an atom is derived by supposing that the atom contains dipole oscillators. In units of the scattering of a free electron, the scattering of an oscillator with eigen frequency ν_n and moderate damping factor κ_n was found to be a complex quantity:

$$f_n = \nu^2 / (\nu^2 - \nu_n^2 - i\kappa_n\nu), \quad (2.1.4.4)$$

where ν is the frequency of the incident radiation [James, 1965; see also *IT C* (2004), equation (4.2.6.8)]. When $\nu \gg \nu_n$ in equation (2.1.4.4), f_n approaches unity, as is the case for scattering by a free electron; when $\nu \ll \nu_n$, f_n approaches zero, demonstrating the lack of scattering from a fixed electron. Only for $\nu \cong \nu_n$ does the imaginary part have an appreciable value.

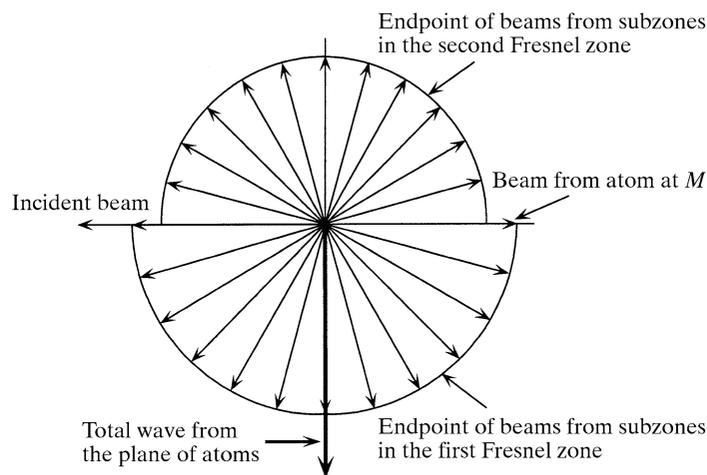
Fortunately, quantum mechanics arrives at the same result by adding a rational meaning to the damping factors and interpreting ν_n as absorption frequencies of the atom (Hönl, 1933). For heavy atoms, the most important transitions are to a continuum of energy states, with $\nu_n \geq \nu_K$ or $\nu_n \geq \nu_L$ etc., where ν_K and ν_L are the frequencies of the K and L absorption edges.

In practice, the complex atomic scattering factor, $f_{\text{anomalous}}$, is separated into three parts: $f_{\text{anomalous}} = f + f' + if''$. f is the contribution to the scattering if the electrons are free electrons and it is a real number (Section 2.1.4.3). f' is the real part of the correction to be applied and f'' is the imaginary correction; f'' is always $\pi/2$ in phase ahead of f (Fig. 2.1.4.8). $f + f'$ is the total real part of the atomic scattering factor.

The imaginary correction if'' is connected with absorption by oscillators having $\nu_n \cong \nu$. It can be calculated from the atomic absorption coefficient of the anomalously scattering element. For each of the K , L etc. absorption edges, f'' is virtually zero for frequencies below the edge, but it rises steeply at the edge and decreases gradually at higher frequencies.

The real correction f' can be derived from f'' by means of the Kramers–Kronig transform [*IT C* (2004), Section 4.2.6.2.2]. For frequencies close to an absorption edge, f' becomes strongly negative.

Values for f , f' and f'' are always given in units equal to the scattering by one free electron. f values are tabulated in *IT C* (2004) as a function of $\sin \theta/\lambda$, and the anomalous-scattering


Figure 2.1.4.7

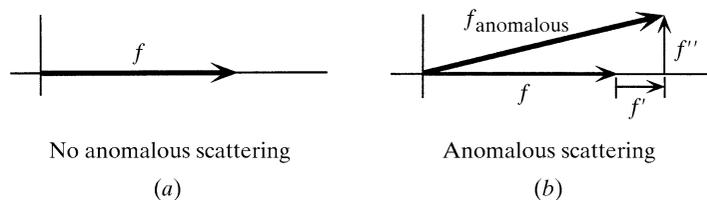
Schematic picture of the Argand diagram for the scattering by atoms in a plane. All electrons are considered free. The vector of the incident beam points to the left. The atom at M (see Fig. 2.1.4.6) has a phase difference of π with respect to the incident beam. Subzones in the first Fresnel zone have the endpoints of their vectors on the lower half circle. For the next Fresnel zone, they are on the upper half circle, which has a smaller radius because the amplitude decreases gradually for subsequent Fresnel zones (Kauzmann, 1957). The sum of all vectors points down, indicating a phase lag of $\pi/2$ with respect to the beam scattered by the atom at M .

corrections for forward scattering as a function of the wavelength. Because the anomalous contribution to the atomic scattering factor is mainly due to the electrons close to the nucleus, the value of the corrections diminishes much more slowly than f as a function of the scattering angle.

2.1.4.5. Scattering by a crystal

A unit cell contains a large number of electrons, especially in the case of biological macromolecules. The waves scattered by these electrons interfere with each other, thereby reducing the effective number of electrons in the scattered wave. The exception is scattering in the forward direction, where the beams from all electrons are in phase and add to each other. The effective number of scattering electrons is called the *structure factor* F because it depends on the structure, i.e. the distribution of the atoms in the unit cell. It also depends on the scattering direction. If small electron-density changes due to chemical bonding are neglected, the structure factor can be regarded as the sum of the scattering by the atoms in the unit cell, taking into consideration their positions and the corresponding phase differences between the scattered waves. For n atoms in the unit cell

$$F(\mathbf{S}) = \sum_{j=1}^n f_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{S}), \quad (2.1.4.5)$$


Figure 2.1.4.8

The atomic scattering factor as a vector in the Argand diagram. (a) When the electrons in the atom can be regarded as free. (b) When they are not completely free and the scattering becomes anomalous with a real anomalous contribution f' and an imaginary contribution if'' . Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.

2. BASIC CRYSTALLOGRAPHY

where \mathbf{S} is a vector perpendicular to the plane reflecting the incident beam at an angle θ ; the length of \mathbf{S} is given by $|\mathbf{S}| = 2 \sin \theta / \lambda$ [equation (2.1.4.3) in Section 2.1.4.2].

The origin of the system is chosen at the origin of the selected unit cell. Atom j is at position \mathbf{r}_j with respect to the origin. Another unit cell has its origin at $t \times \mathbf{a}$, $u \times \mathbf{b}$ and $v \times \mathbf{c}$, where t , u and v are whole numbers, and \mathbf{a} , \mathbf{b} and \mathbf{c} are the basis vectors of the unit cell. With respect to the first origin, its scattering is

$$F(\mathbf{S}) \exp(2\pi i t \mathbf{a} \cdot \mathbf{S}) \exp(2\pi i u \mathbf{b} \cdot \mathbf{S}) \exp(2\pi i v \mathbf{c} \cdot \mathbf{S}).$$

The wave scattered by a crystal is the sum of the waves scattered by all unit cells. Assuming that the crystal has a very large number of unit cells ($n_1 \times n_2 \times n_3$), the amplitude of the wave scattered by the crystal is

$$W_{\text{cr}}(\mathbf{S}) = F(\mathbf{S}) \sum_{t=0}^{n_1} \exp(2\pi i t \mathbf{a} \cdot \mathbf{S}) \sum_{u=0}^{n_2} \exp(2\pi i u \mathbf{b} \cdot \mathbf{S}) \times \sum_{v=0}^{n_3} \exp(2\pi i v \mathbf{c} \cdot \mathbf{S}). \quad (2.1.4.6)$$

For an infinitely large crystal, the three summations over the exponential functions are delta functions. They have the property that they are zero unless

$$\mathbf{a} \cdot \mathbf{S} = h, \quad \mathbf{b} \cdot \mathbf{S} = k \quad \text{and} \quad \mathbf{c} \cdot \mathbf{S} = l, \quad (2.1.4.7)$$

where h , k and l are whole numbers, either positive, negative or zero. These are the Laue conditions. If they are fulfilled, all unit cells scatter in phase and the amplitude of the wave scattered by the crystal is proportional to the amplitude of the structure factor F . Its intensity is proportional to $|F|^2$.

\mathbf{S} vectors satisfying equation (2.1.4.7) are denoted by $\mathbf{S}(hkl)$ or $\mathbf{S}(\mathbf{h})$, and the corresponding structure factors as $F(hkl)$ or $F(\mathbf{h})$.

Bragg's law for scattering by a crystal is better known than the Laue conditions:

$$2d \sin \theta = \lambda, \quad (2.1.4.8)$$

where d is the distance between reflecting lattice planes, θ is the reflecting or glancing angle and λ is the wavelength (Fig. 2.1.4.9). It can easily be shown that the Laue conditions and Bragg's law are equivalent by combining equation (2.1.4.7) with the following information:

- (1) Vector \mathbf{S} is perpendicular to a reflecting plane (Section 2.1.4.2).
- (2) The Laue conditions for scattering [equation (2.1.4.7)] can be written as

$$\frac{\mathbf{a}}{h} \cdot \mathbf{S} = 1; \quad \frac{\mathbf{b}}{k} \cdot \mathbf{S} = 1; \quad \frac{\mathbf{c}}{l} \cdot \mathbf{S} = 1. \quad (2.1.4.9)$$

- (3) Lattice planes always divide the unit-cell vectors \mathbf{a} , \mathbf{b} and \mathbf{c} into a number of equal parts (Section 2.1.1). If the lattice planes divide the \mathbf{a} vector of the unit cell into h equal parts, the first index for this set of planes is h . The second index, k , is related to the division of \mathbf{b} and the third index, l , to the division of \mathbf{c} .

From equation (2.1.4.9) it follows that vector $\mathbf{S}(hkl)$ is perpendicular to a plane determined by the points \mathbf{a}/h , \mathbf{b}/k and \mathbf{c}/l , and according to conditions (3) this is a lattice plane. Therefore, scattering by a crystal can indeed be regarded as reflection by lattice planes. The projection of \mathbf{a}/h , \mathbf{b}/k and \mathbf{c}/l on vector $\mathbf{S}(hkl)$ is $1/|\mathbf{S}(hkl)|$ (Laue condition), but it is also equal to the spacing $d(hkl)$ between the lattice planes (see Fig. 2.1.1.3), and, therefore,

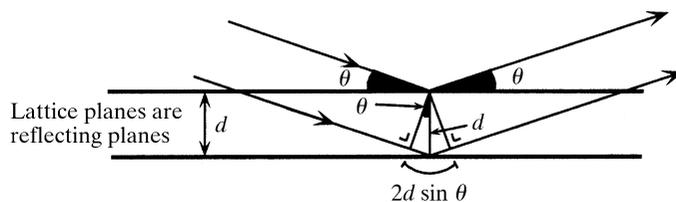


Figure 2.1.4.9

X-ray diffraction by a crystal is, in Bragg's conception, reflection by lattice planes. The beams reflected by successive planes have a path difference of $2d \sin \theta$, where d is the lattice-plane distance and θ is the reflecting angle. Positive interference occurs if $2d \sin \theta = \lambda$, 2λ , 3λ etc., where λ is the X-ray wavelength. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.

$|\mathbf{S}(hkl)| = 1/d(hkl)$. Combining this with equation (2.1.4.3) yields Bragg's law, $2d \sin \theta = \lambda$ [equation (2.1.4.8)].

2.1.4.6. The structure factor

For noncentrosymmetric structures, the structure factor,

$$F(\mathbf{S}) = \sum_{j=1}^n f_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{S}),$$

is an imaginary quantity and can also be written as²

$$F(\mathbf{S}) = \sum_{j=1}^n f_j \cos(2\pi \mathbf{r}_j \cdot \mathbf{S}) + i \sum_{j=1}^n f_j \sin(2\pi \mathbf{r}_j \cdot \mathbf{S}) = A(\mathbf{S}) + iB(\mathbf{S}).$$

It is sometimes convenient to split the structure factor into its real part, $A(\mathbf{S})$, and its imaginary part, $B(\mathbf{S})$. For centrosymmetric structures, $B(\mathbf{S}) = 0$ if the origin of the structure is chosen at the centre of symmetry.

The average value of the structure-factor amplitude $|F(\mathbf{S})|$ decreases with increasing $|\mathbf{S}|$ or, because $|\mathbf{S}| = 2 \sin \theta / \lambda$, with increasing reflecting angle θ .

This is caused by two factors:

- (1) A stronger negative interference between the electrons in the atoms at a larger scattering angle; this is expressed in the decrease of the atomic scattering factor as a function of \mathbf{S} .
- (2) The temperature-dependent vibrations of the atoms. Because of these vibrations, the apparent size of an atom is larger during an X-ray exposure, and the decrease in its scattering as a function of \mathbf{S} is stronger. If the vibration is equally strong in all directions, it is called isotropic, and the atomic scattering factor must be multiplied by a correction factor, the temperature factor, $\exp[-B(\sin^2 \theta) / \lambda^2]$. It can be shown that the parameter B is related to the mean-square displacement of the atomic vibrations, $\overline{u^2}$:

$$B = 8\pi^2 \overline{u^2}.$$

In protein crystal structures determined at high resolution, each atom is given its own individual thermal parameter B .³ Anisotropic thermal vibration is described by six parameters instead of one, and the evaluation of this anisotropic thermal vibration requires more data (X-ray intensities) than are usually available. Only at very high resolution (better than 1.5 Å) can one consider the incorporation of anisotropic temperature factors.

² For convenience, we write $F(\mathbf{S})$ when we mean $F(hkl)$ or $F(\mathbf{h})$, and \mathbf{S} instead of $\mathbf{S}(hkl)$ or $\mathbf{S}(\mathbf{h})$.

³ Do not confuse the thermal parameter B with the imaginary part $B(\mathbf{S})$ of the structure factor.