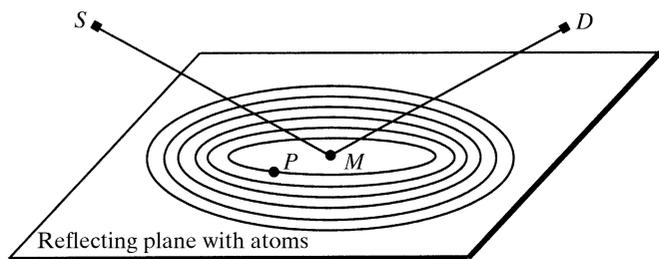2.1. INTRODUCTION TO BASIC CRYSTALLOGRAPHY

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:

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

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
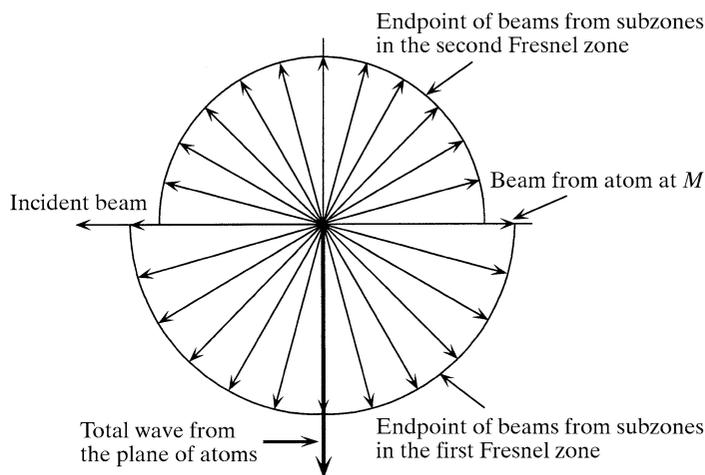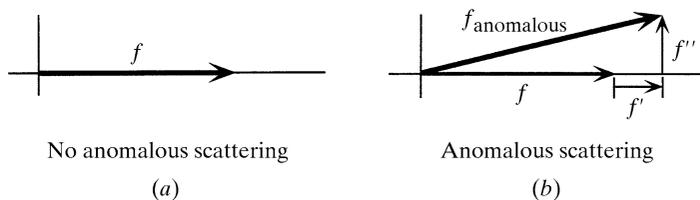

Figure 2.1.4.7
Schematic picture of the Argand diagram for the scattering by atoms in a plane. All electrons are considered free. The vector of the incident beam points to the left. The atom at *M* (see Fig. 2.1.4.6) has a phase difference of π with respect to the incident beam. Subzones in the first 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

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

No anomalous scattering
(*a*)

Anomalous scattering
(*b*)

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.

references