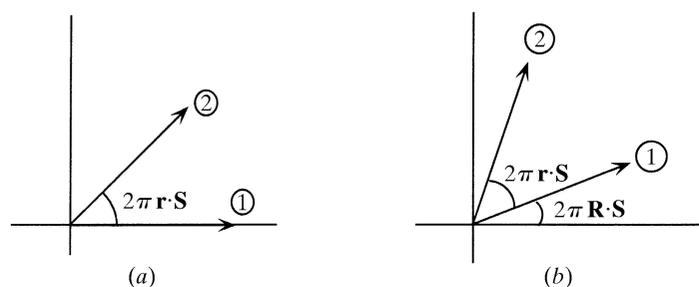


2. BASIC CRYSTALLOGRAPHY

**Figure 2.1.4.4**

An Argand diagram for the scattering by two electrons. In (a), the origin is at electron 1; electron 2 is at position \mathbf{r} with respect to electron 1. In (b), electron 1 is at position \mathbf{R} with respect to the new origin, and electron 2 is at position $\mathbf{R} + \mathbf{r}$.

The total scattering from the two-electron system is $1 + 1 \times \exp(2\pi i \mathbf{r} \cdot \mathbf{S})$ if the resultant amplitude of the waves from electrons 1 and 2 is set to 1. In an Argand diagram, the waves are represented by vectors in a two-dimensional plane, as in Fig. 2.1.4.4(a).¹ Thus far, the origin of the system was chosen at electron 1. Moving the origin to another position simply means an equal change of phase angle for all waves. Neither the amplitudes nor the intensities of the reflected beams change (Fig. 2.1.4.4b).

2.1.4.3. Scattering by atoms

2.1.4.3.1. Scattering by one atom

Electrons in an atom are bound by the nucleus and are – in principle – not free electrons.

However, to a good approximation, they can be regarded as such if the frequency of the incident radiation ν is greater than the natural absorption frequencies, ν_n , at the absorption edges of the scattering atom, or the wavelength of the incident radiation is shorter than the absorption-edge wavelength (Section 2.1.4.4). This is normally true for light atoms but not for heavy ones (Table 2.1.4.1).

If the electrons in an atom can be regarded as free electrons, the scattering amplitude of the atom is a real quantity, because the electron cloud has a centrosymmetric distribution, *i.e.* $\rho(\mathbf{r}) = \rho(-\mathbf{r})$.

A small volume, dv_r , at \mathbf{r} contains $\rho(\mathbf{r}) \times dv_r$ electrons, and at $-\mathbf{r}$ there are $\rho(-\mathbf{r}) \times dv_r$ electrons. The combined scattering of the two volume elements, in units of the scattering of a free electron, is

$$\rho(\mathbf{r})dv_r\{\exp(2\pi i \mathbf{r} \cdot \mathbf{S}) + \exp[2\pi i (-\mathbf{r}) \cdot \mathbf{S}]\} = 2\rho(\mathbf{r}) \cos(2\pi \mathbf{r} \cdot \mathbf{S})dv_r;$$

this is a real quantity.

The scattering amplitude of an atom is called the atomic scattering factor f . It expresses the scattering of an atom in terms of the scattering of a single electron. f values are calculated for spherically averaged electron-density distributions and, therefore, do not depend on the scattering direction. They are tabulated in *ITC* (2004) as a function of $\sin \theta/\lambda$. The f values decrease appreciably as a function of $\sin \theta/\lambda$ (Fig. 2.1.4.5). This is due to interference effects between the scattering from the electrons in the cloud. In the direction $\theta = 0$, all electrons scatter in phase and

¹ The plane is also called the ‘imaginary plane’. The real part of the vector in an Argand diagram is along the horizontal or real axis; the imaginary part is along the vertical or imaginary axis. Note also that $\exp(2\pi i \mathbf{r} \cdot \mathbf{S}) = \cos(2\pi \mathbf{r} \cdot \mathbf{S}) + i \sin(2\pi \mathbf{r} \cdot \mathbf{S})$. The cosine term is the real component and the sine term is the imaginary component.

Table 2.1.4.1

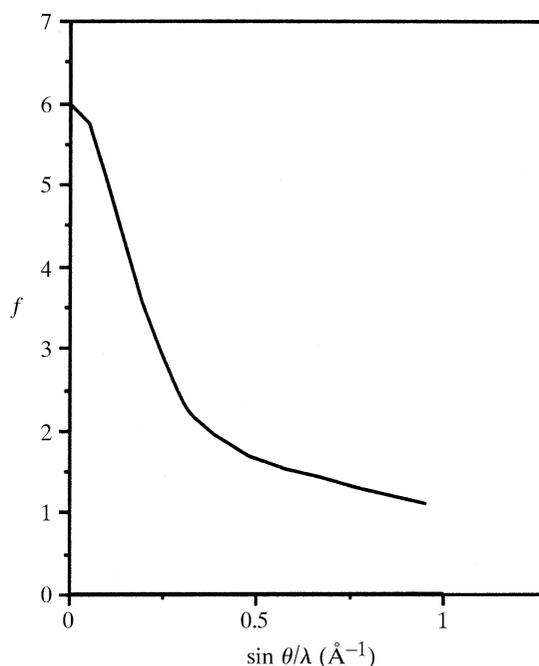
The position of the $K\alpha$ edge of different elements

| Atomic number | Element | $K\alpha$ edge (\AA) |
|---------------|---------|---------------------------------|
| 6 | C | 43.68 |
| 16 | S | 5.018 |
| 26 | Fe | 1.743 |
| 34 | Se | 0.980 |
| 78 | Pt | 0.158 |

the atomic scattering factor is equal to the number of electrons in the atom.

2.1.4.3.2. Scattering by a plane of atoms

A plane of atoms reflects an X-ray beam with a phase retardation of $\pi/2$ with respect to the scattering by a single atom. The difference is caused by the difference in path length from source (S) to atom (M) to detector (D) for the different atoms in the plane (Fig. 2.1.4.6). Suppose the plane is infinitely large. The shortest connection between S and D *via* the plane is $S-M-D$. The plane containing S , M and D is perpendicular to the reflecting plane, and the lines SM and MD form equal angles with the reflecting plane. Moving outwards from atom M in the reflecting plane, to P for instance, the path length $S-P-D$ is longer. At the edge of the first Fresnel zone, the path is $\lambda/2$ longer (Fig. 2.1.4.6). This edge is an ellipse with its centre at M and its major axis on the line of intersection between the plane SMD and the reflecting plane. Continuing outwards, many more elliptic Fresnel zones are formed. Clearly, the beams radiated by the many atoms in the plane interfere with each other. The situation is represented in the Argand diagram in Fig. 2.1.4.7. Successive Fresnel zones can be subdivided into an equal number of subzones. If the distribution of electrons is sufficiently homogeneous, it can be assumed that the subzones in one Fresnel zone give the same amplitude at D . Their phases are spaced at regular intervals and their vectors in the Argand diagram lie in a half circle. In the lower part of Fig. 2.1.4.7, this is illustrated for the first Fresnel zone. For the second Fresnel zone (upper part),

**Figure 2.1.4.5**

The atomic scattering factor f for carbon as a function of $\sin \theta/\lambda$, expressed in units of the scattering by one electron. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.