2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION
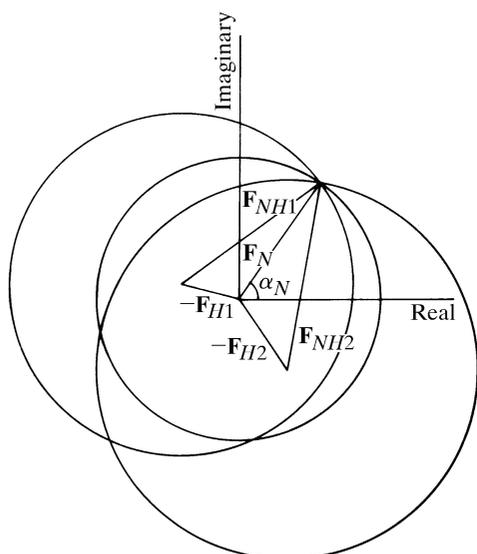

Fig. 2.4.2.3. Harker construction when two heavy-atom derivatives are available.

Fig. 2.4.3.1. Variation of (*a*) f' and (*b*) f'' as a function of atomic number for Cu $K\alpha$ and Mo $K\alpha$ radiations. Adapted from Fig. 3 of Srinivasan (1972).

$$f_0 + f' + if'', \qquad (2.4.3.1)$$

where f_0 is a real positive number and corresponds to the atomic scattering factor for a spherically symmetric collection of free electrons in the atom. The second and third terms are, respectively, referred to as the real and the imaginary components of the 'dispersion correction' (*IT* IV, 1974). f' is usually negative whereas f'' is positive. For any given atom, f'' is obviously 90° ahead of the real part of the scattering factor given by

$$f = f_0 + f'. \qquad (2.4.3.2)$$

The variation of f' and f'' as a function of atomic number for two typical radiations is given in Fig. 2.4.3.1 (Srinivasan, 1972; Cromer, 1965). The dispersion effects are pronounced when an absorption edge of the atom concerned is in the neighbourhood of the wavelength of the incident radiation. Atoms with high atomic numbers have several absorption edges and the dispersion-correction terms in their scattering factors always have appreciable values. The values of f' and f'' do not vary appreciably with the angle of scattering as they are caused by core electrons confined to a very small volume around the nucleus. An atom is usually referred to as an anomalous scatterer if the dispersion-correction terms in its scattering factor have appreciable values. The effects on the structure factors or intensities of Bragg reflections resulting from dispersion corrections are referred to as anomalous-dispersion effects or anomalous-scattering effects.

2.4.3.2. *Violation of Friedel's law*

Consider a structure containing N atoms of which P are normal atoms and the remaining Q anomalous scatterers. Let $\mathbf{F}_P$ denote the contribution of the P atoms to the structure, and $\mathbf{F}_Q$ and $\mathbf{F}''_Q$ the real and imaginary components of the contribution of the Q atoms. The relation between the different contributions to a reflection $\mathbf{h}$ and its Friedel equivalent $-\mathbf{h}$ is illustrated in Fig. 2.4.3.2. For simplicity we assume here that all Q atoms are of the same type. The phase angle of $\mathbf{F}''_Q$ is then exactly 90° ahead of that of $\mathbf{F}_Q$. The structure factors of $\mathbf{h}$ and $-\mathbf{h}$ are denoted in the figure by $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$, respectively. In the absence of anomalous scattering, or when the imaginary component of the dispersion correction is zero, the magnitudes of the two structure factors are equal and Friedel's law is obeyed; the phase angles have equal magnitudes, but opposite signs. As can be seen from Fig. 2.4.3.2, this is no longer true when
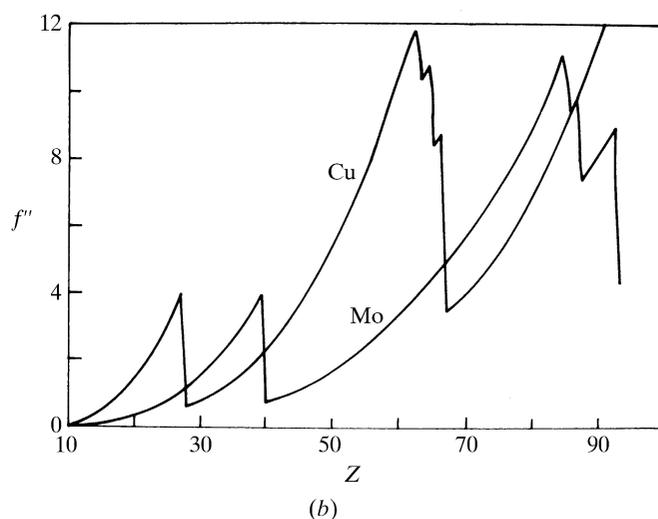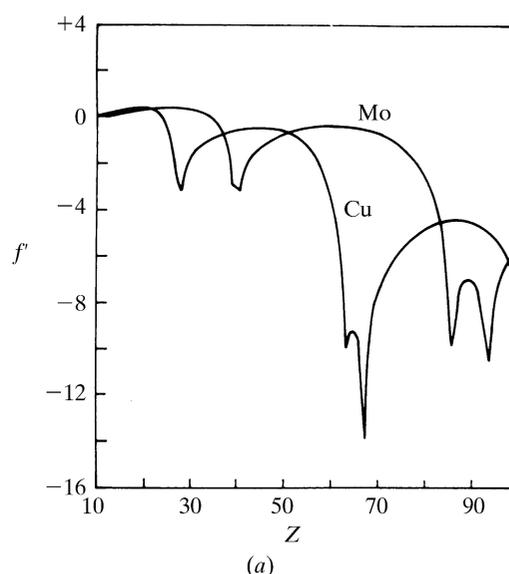
$\mathbf{F}''_Q$ has a nonzero value. Friedel's law is then violated. A composite view of the vector relationship for $\mathbf{h}$ and $-\mathbf{h}$ can be obtained, as in Fig. 2.4.3.3, by reflecting the vectors corresponding to $-\mathbf{h}$ about the real axis of the vector diagram. $\mathbf{F}_P$ and $\mathbf{F}_Q$ corresponding to the two reflections superpose exactly, but $\mathbf{F}''_Q$ do not. $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$ then have different magnitudes and phases.

It is easily seen that Friedel's law is obeyed in centric data even when anomalous scatterers are present. $\mathbf{F}_P$ and $\mathbf{F}_Q$ are then parallel to the real axis and $\mathbf{F}''_Q$ perpendicular to it. The vector sum of the three components is the same for $\mathbf{h}$ and $-\mathbf{h}$. It may, however, be noted that the phase angle of the structure factor is then no longer 0 or 180°. Even when the structure is noncentrosymmetric, the effect of anomalous scattering in terms of intensity differences between Friedel equivalents varies from reflection to reflection. The difference between $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$ is zero when $\alpha_P = \alpha_Q$ or $\alpha_Q + 180°$. The difference tends to the maximum possible value $(2F''_Q)$ when $\alpha_P = \alpha_Q \pm 90°$.

Intensity differences between Friedel equivalents depend also on the ratio (in terms of number and scattering power) between anomalous and normal scatterers. Differences obviously do not occur when all the atoms are normal scatterers. On the other hand, a structure containing only anomalous scatterers of the same type also
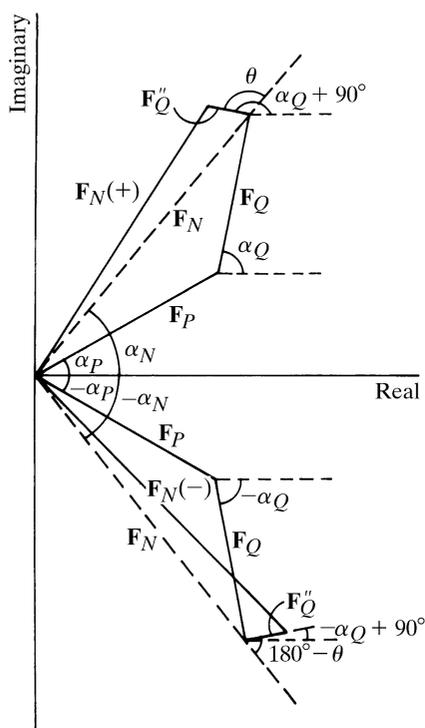
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Fig. 2.4.3.2. Vector diagram illustrating the violation of Friedel's law when $\mathbf{F}_Q'' \neq 0$.

does not give rise to intensity differences. Expressions for intensity differences between Friedel equivalents have been derived by Zachariasen (1965) for the most general case of a structure containing normal as well as different types of anomalous scatterers. Statistical distributions of such differences under various conditions have also been derived (Parthasarathy & Srinivasan, 1964; Parthasarathy, 1967). It turns out that, with a single type of anomalous scatterer in the structure, the ratio

$$\frac{|F_N^2(+) - F_N^2(-)|}{F_N^2(+) + F_N^2(-)}$$

has a maximum mean value when the scattering powers of the anomalous scatterers and the normal scatterers are nearly the same (Srinivasan, 1972). Also, for a given ratio between the scattering powers, the smaller the number of anomalous scatterers, the higher is the mean ratio.
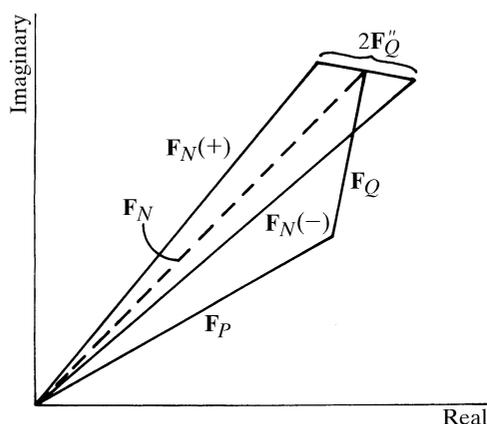

Fig. 2.4.3.3. A composite view of the vector relationship between $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$.

2.4.3.3. Friedel and Bijvoet pairs

The discussion so far has been concerned essentially with crystals belonging to space groups $P1$ and $P\bar{1}$. In the centrosymmetric space group, the crystal and the diffraction pattern have the same symmetry, namely, an inversion centre. In $P1$, however, the crystals are noncentrosymmetric while the diffraction pattern has an inversion centre, in the absence of anomalous scattering. When anomalous scatterers are present in the structure ($\mathbf{F}_Q'' \neq 0$), Friedel's law breaks down and the diffraction pattern no longer has an inversion centre. Thus the diffraction pattern displays the same symmetry as that of the crystal in the presence of anomalous scattering. The same is true with higher-symmetry space groups also. For example, consider a crystal with space group $P222$, containing anomalous scatterers. The magnitudes of $\mathbf{F}_P$ are the same for all equivalent reflections; so are those of $\mathbf{F}_Q$ and $\mathbf{F}_Q''$. Their phase angles, however, differ from one equivalent to another, as can be seen from Table 2.4.3.1. When $\mathbf{F}_Q'' = 0$, the magnitudes of the vector sum of $\mathbf{F}_P$ and $\mathbf{F}_Q$ are the same for all the equivalent reflections. The intensity pattern thus has point-group symmetry $2/m\ 2/m\ 2/m$. When $\mathbf{F}_Q'' \neq 0$, the equivalent reflections can be grouped into two sets in terms of their intensities: hkl, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}l$; and $\bar{h}\bar{k}\bar{l}$, $\bar{h}kl$, $h\bar{k}l$ and $hk\bar{l}$. The equivalents belonging to the first group have the same intensity; so have the equivalents in the second group. But the two intensities are different. Thus the symmetry of the pattern is 222, the same as that of the crystal.

In general, under conditions of anomalous scattering, equivalent reflections generated by the symmetry elements in the crystal have intensities different from those of equivalent reflections generated by the introduction of an additional inversion centre in normal scattering. There have been suggestions that a reflection from the first group and another from the second group should be referred to as a 'Bijvoet pair' instead of a 'Friedel pair', when the two reflections are not inversely related. Most often, however, the terms are used synonymously. The same practice will be followed in this article.

2.4.3.4. Determination of absolute configuration

The determination of the absolute configuration of chiral molecules has been among the most important applications of anomalous scattering. Indeed, anomalous scattering is the only effective method for this purpose and the method, first used in the early 1950s (Peerdeman et al., 1951), has been extensively employed in structural crystallography (Ramaseshan, 1963; Vos, 1975).

Many molecules, particularly biologically important ones, are chiral in that the molecular structure is not superimposable on its mirror image. Chirality (handedness) arises primarily on account of the presence of asymmetric carbon atoms in the molecule. A tetravalent carbon is asymmetric when the four atoms (or groups) bonded to it are all different from one another. The substituents can then have two distinct arrangements which are mirror images of (or related by inversion to) each other. These optical isomers or enantiomers have the same chemical and physical properties except

Table 2.4.3.1. *Phase angles of different components of the structure factor in space group P222*

	Phase angle (°) of		
Reflection	$\mathbf{F}_P$	$\mathbf{F}_Q$	$\mathbf{F}_Q''$
$hkl,\ h\bar{k}\bar{l},\ \bar{h}k\bar{l},\ \bar{h}\bar{k}l$	α_P	α_Q	$90 + \alpha_Q$
$\bar{h}\bar{k}\bar{l},\ \bar{h}kl,\ h\bar{k}l,\ hk\bar{l}$	$-\alpha_P$	$-\alpha_Q$	$90 - \alpha_Q$

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