International Tables for Crystallography (2006). Vol. B, Figure 2.4.2.3, p. 266.

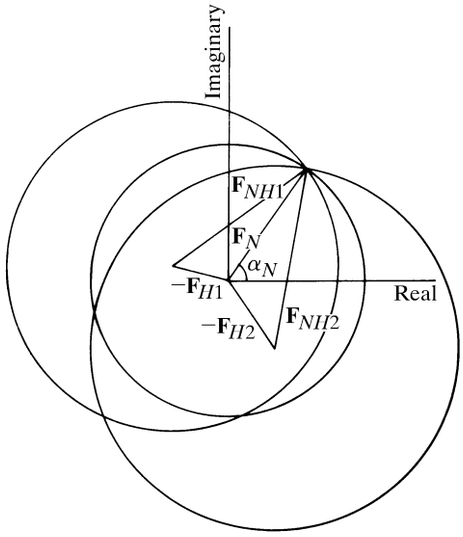

Fig. 2.4.2.3. Harker construction when two heavy-atom derivatives are available.

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

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

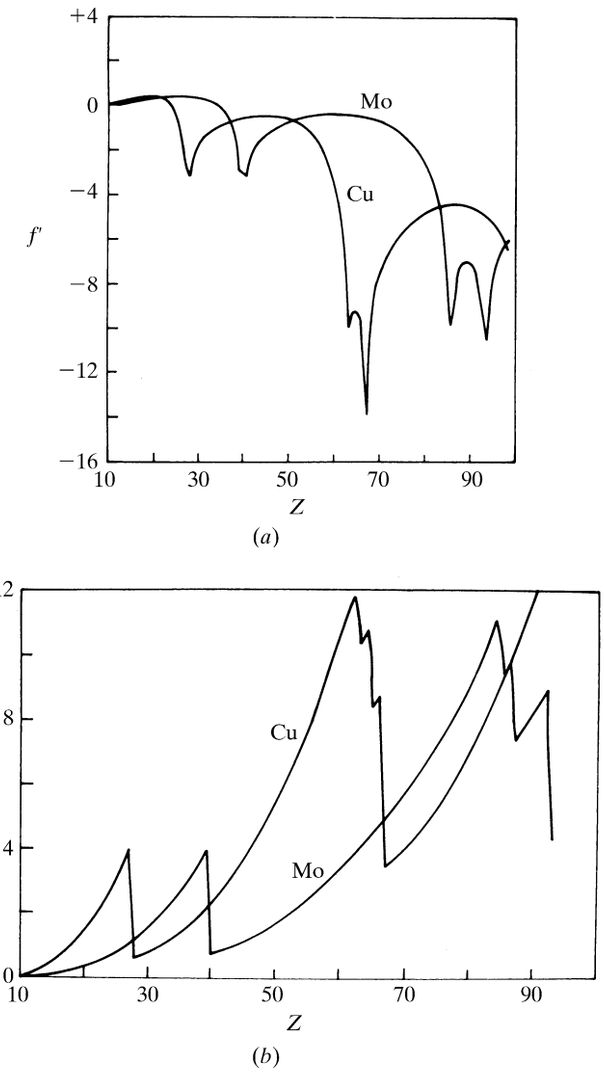

Fig. 2.4.3.1. Variation of (*a*) f' and (*b*) f'' as a function of atomic number for Cu $K\alpha$ and Mo $K\alpha$ radiations. Adapted from Fig. 3 of Srinivasan (1972).

$\mathbf{F}''_Q$ 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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