

## 2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

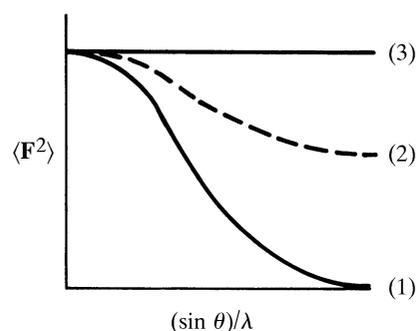


Fig. 2.3.1.1. Effect of 'sharpening' Patterson coefficients. (1) shows a mean distribution of  $|F|^2$  values with resolution,  $(\sin \theta)/\lambda$ . The normal decline of this curve is due to increasing destructive interference between different portions within diffuse atoms at larger Bragg angles. (2) shows the distribution of 'sharpened' coefficients. (3) shows the theoretical distribution of  $|F|^2$  produced by a point-atom structure. To represent such a structure with a Fourier series would require an infinite series in order to avoid large errors caused by truncation.

A common formulation for this type of sharpening expresses the atomic scattering factors at a given angle in terms of an overall isotropic thermal parameter  $B$  as

$$f(s) = f_0 \exp(-Bs^2).$$

The Patterson coefficients then become

$$\mathbf{F}_{\mathbf{h}, \text{sharp}} = \frac{Z_{\text{total}}}{\sum_{i=1}^N f(s)} \mathbf{F}_{\mathbf{h}}.$$

The normalized structure factors,  $E$  (see Chapter 2.2), which are used in crystallographic direct methods, are also a common source of sharpened Patterson coefficients ( $E^2 - 1$ ). Although the centre positions and total contents of Patterson peaks are unaltered by sharpening, the resolution of individual peaks may be enhanced. The degree of sharpening can be controlled by adjusting the size of the assumed  $B$  factor; Lipson & Cochran (1966, pp. 165–170) analysed the effect of such a choice on Patterson peak shape.

All methods of sharpening Patterson coefficients aim at producing a point atomic representation of the unit cell. In this quest, the high-resolution terms are enhanced (Fig. 2.3.1.1). Unfortunately, this procedure must also produce a serious Fourier truncation error which will be seen as large ripples about each Patterson peak (Gibbs, 1898). Consequently, various techniques have been used (mostly unsuccessfully) in an attempt to balance the advantages of sharpening with the disadvantages of truncation errors.

Schomaker and Shoemaker [unpublished; see Lipson & Cochran (1966, p. 168)] used a function

$$|\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = \frac{|\mathbf{F}_{\mathbf{h}}|^2}{\tilde{f}^2} s^2 \exp\left[-\frac{\pi^2}{p} s^2\right],$$

in which  $s$  is the length of the scattering vector, to produce a Patterson synthesis which is less sensitive to errors in the low-order terms. Jacobson *et al.* (1961) used a similar function,

$$|\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = \frac{|\mathbf{F}_{\mathbf{h}}|^2}{\tilde{f}^2} (k + s^2) \exp\left[-\frac{\pi}{p} s^2\right],$$

which they rationalize as the sum of a scaled exponentially sharpened Patterson and a gradient Patterson function (the value

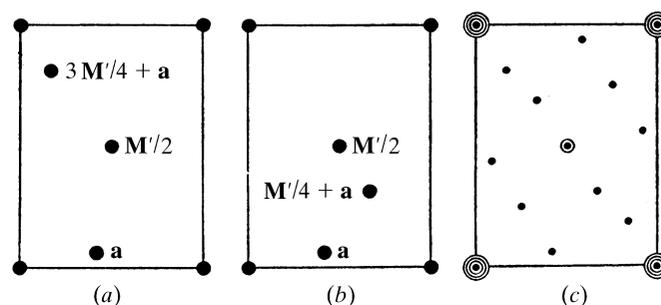


Fig. 2.3.1.2. (c) The point Patterson of the two homometric structures in (a) and (b). The latter are constructed by taking points at  $\mathbf{a}$  and  $\frac{1}{2}\mathbf{M}'$ , where  $\mathbf{M}'$  is a cell diagonal, and adding a third point which is (a) at  $\frac{3}{4}\mathbf{M}' + \mathbf{a}$  or (b) at  $\frac{1}{4}\mathbf{M}' + \mathbf{a}$ . [Reprinted with permission from Patterson (1944).]

of  $k$  was empirically chosen as  $\frac{2}{3}$ ). This approach was subsequently further developed and generalized by Wunderlich (1965).

#### 2.3.1.4. Homometric structures and the uniqueness of structure solutions; enantiomorphic solutions

Interpretation of any Patterson requires some assumption, such as the existence of discrete atoms. A complete interpretation might also require an assumption of the number of atoms and may require other external information (*e.g.* bond lengths, bond angles, van der Waals separations, hydrogen bonding, positive density *etc.*). To what extent is the solution of a Patterson function unique? Clearly the greater is the supply of external information, the fewer will be the number of possible solutions. Other constraints on the significance of a Patterson include the error involved in measuring the observed coefficients and the resolution limit to which they have been observed. The larger the error, the larger the number of solutions. When the error on the amplitudes is infinite, it is only the other physical constraints, such as packing, which limit the structural solutions. Alternative solutions of the same Patterson are known as homometric structures.

During their investigation of the mineral bixbyite, Pauling & Shappell (1930) made the disturbing observation that there were two solutions to the structure, with different arrangements of atoms, which yielded the same set of calculated intensities. Specifically, atoms occupying equipoint set  $24d$  in space group  $I(2_1/a)\bar{3}$  can be placed at either  $x, 0, \frac{1}{4}$  or  $-x, 0, \frac{1}{4}$  without changing the calculated intensities. Yet the two structures were not chemically equivalent. These authors resolved the ambiguity by placing the oxygen atoms in question at positions which gave the most acceptable bonding distances with the rest of the structure.

Patterson interpreted the above ambiguity in terms of the  $F^2$  series: the distance vector sets or Patterson functions of the two structures were the same since each yielded the same calculated intensities (Patterson, 1939). He defined such a pair of structures a homometric pair and called the degenerate vector set which they produced a homometric set. Patterson went on to investigate the likelihood of occurrence of homometric structures and, indeed, devoted a great deal of his time to this matter. He also developed algebraic formalisms for examining the occurrence of homometric pairs and multiplets in selected one-dimensional sets of points, such as cyclotomic sets, and also sets of points along a line (Patterson, 1944). Some simple homometric pairs are illustrated in Fig. 2.3.1.2.

Drawing heavily from Patterson's inquiries into the structural uniqueness allowed by the diffraction data, Hosemann, Bagchi and others have given formal definitions of the different types of homometric structures (Hosemann & Bagchi, 1954). They suggested a classification divided into pseudohomometric structures and homomorphs, and used an integral equation representing a convolution operation to express their examples of finite homometric structures. Other workers have chosen various