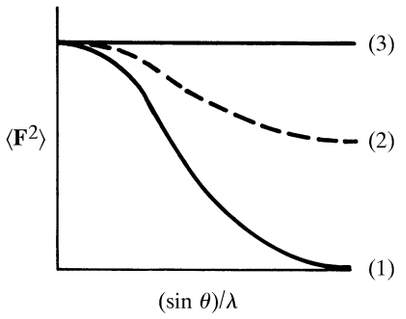

Fig. 2.3.1.1. Effect of 'sharpening' Patterson coefficients. (1) shows a mean distribution of $|\mathbf{F}|^2$ values with resolution, $(\sin\theta)/\lambda$. The normal decline of this curve is due to increasing destructive interference between different portions within diffuse atoms at larger Bragg angles. (2) shows the distribution of 'sharpened' coefficients. (3) shows the theoretical distribution of $|\mathbf{F}|^2$ 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.

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

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,

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

which they rationalize as the sum of a scaled exponentially sharpened Patterson and a gradient Patterson function (the value 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 24*d* 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 means for describing homometric structures [Buerger (1959, pp. 41–50), Menzer (1949), Bullough (1961, 1964), Hoppe (1962)].

Since a Patterson function is centrosymmetric, the Pattersons of a crystal structure and of its mirror image are identical. Thus the enantiomeric ambiguity present in noncentrosymmetric crystal structures cannot be overcome by using the Patterson alone and represents a special case of homometric structures. Assignment of the correct enantiomorph in a crystal structure analysis is generally not possible unless a recognizable fragment of known chirality emerges (*e.g.* L-amino acids in proteins, D-riboses in nucleic acids, the known framework of steroids and other natural products, the right-handed twist of α-helices, the left-handed twist of successive strands in a β-sheet, the fold of a known protein subunit *etc.*) or anomalous-scattering information is available and can be used to resolve the ambiguity (Bijvoet *et al.*, 1951).

It is frequently necessary to select arbitrarily one enantiomorph over another in the early stages of a structure solution. Structure-factor phases calculated from a single heavy atom in space group $P1$, $P2$ or $P2_1$ (for instance) will be centrosymmetric and both enantiomorphs will be present in Fourier calculations based on these phases. In other space groups (*e.g.* $P2_12_12_1$), the selected heavy atom is likely to be near one of the planes containing the 2_1 axes and thus produce a weaker 'ghost' image of the opposite enantiomorph. The mixture of the two overlapped enantiomorphic solutions can cause interpretive difficulties. As the structure solution progresses, the 'ghosts' are exorcized owing to the dominance of the chosen enantiomorph in the phases.

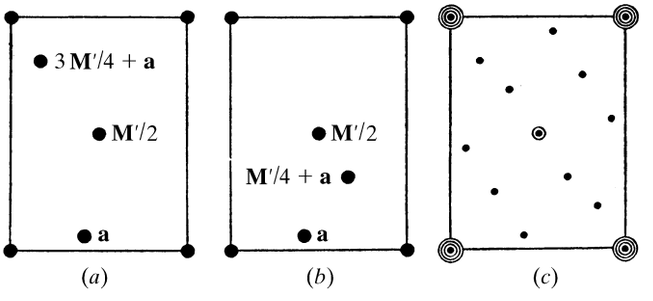

Fig. 2.3.1.2. (*c*) The point Patterson of the two homometric structures in (*a*) and (*b*). The latter are constructed by taking points at $\mathbf{a}$ and $\frac{1}{2}\mathbf{M}'$, where $\mathbf{M}'$ is a cell diagonal, and adding a third point which is (*a*) at $\frac{3}{4}\mathbf{M}' + \mathbf{a}$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

references