viously, emphasis might be laid on the Al–O and Al–O–OH linkages rather than on the Si–O linkage. The framework of the structure consists of the AlO_4 and AlO_3OH chains which are similar in shape to those found in cyanite and other alumino-silicate minerals (see Bragg, 1937). The chains are formed by O and O–OH octahedra around Al holding the O–O edges in common. They are stretched parallel to each other and to the b axis and are bound together sidewise by Al(Fe), Ca and Si atoms, each of which is oxygen-coordinated as mentioned above.

The chemical analysis of epidote (see for example, Dana, 1900) has invariably demonstrated that the atomic ratio Fe:Al is no more than 1:2. This may be explained if we recognize the fact that Fe atoms do not replace Al atoms of the chains.

The balance of valency is illustrated in Fig. 6 and the interatomic distances are given in Table 3. It is to be noted that they have been considerably improved by the present refinement.

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On the Shape of Cylindrical Patterson Function Peaks*

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In the course of an investigation of cylindrical Patterson functions as applied to the structures of fibrous polypeptides, the shape function for Gaussian distributions surrounding interatomic vectors in three-dimensional Patterson space projected cylindrically about a unique axis has been determined. This shape function is the Patterson space analogue of an electron distribution function in real space. The projected shape function is such that for the large temperature and disorientation factors associated with fibrous polypeptides there are significant deviations in both peak location and size from an ordinary Patterson projection.

An approach to the deduction of the structures of fibrous proteins and synthetic polypeptides from their X-ray diffraction diagrams lies in the calculation and interpretation of cylindrical Patterson projections for these substances. Such functions were first described by MacGillavry & Bruins (1948), and have recently been calculated for poly-γ-methyl-L-glutamate and collagen (Yakel & Schatz, to be published). In the interpretation of these projections, it proved desirable to compare the experimental results with Patterson functions calculated from the distribution of interatomic vectors for one or more suggested models of the folded polypeptide chain. Simple comparison of the observed functions with maps containing the interatomic vectors represented by suitably weighted points yielded little information, presumably owing to the poor resolution of the observed functions caused by

limited data and large temperature and disorientation factors. An attempt was therefore made to obtain a mathematical expression for the shape of the peaks in cylindrical Patterson projections which would contain variable parameters depending on temperature factor, etc. It was hoped that a more representative picture of what might be expected in the experimental projections could then be derived from the theoretical shape functions.

It can be shown that a three-dimensional Patterson peak shape function, $P_{ij}(r)$, may be defined by the equation

$$P_{ij}(r) = 4\pi \int_0^\infty f_i f_j \cdot \frac{\sin 2\pi r H}{2\pi r H} \cdot H^2 . dH , \qquad (1)$$

where f_i and f_j are the atomic scattering factors of the two atoms involved in the interaction, H equals $2 \sin \theta / \lambda$, and r is a radial coordinate measured from the end of the interatomic vector between atoms i and j in Patterson space, as indicated in Fig. 1. The function $P_{ij}(r)$ may be identified with a distribution func-

tion in Patterson space analogous to an electron distribution function in real crystal space. Equation (1) may be derived by a method roughly similar to that
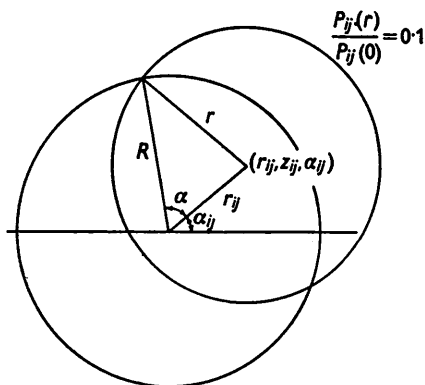

Fig. 1. A diagrammatic representation of the cylindrical projection of an interatomic vector whose cylindrical coordinates in Patterson space are r_{ij}, z_{ij}, and α_{ij}, and whose shape is given by the Gaussian function $P_{ij}(r)$. The z axis of Patterson space is perpendicular to the plane of the paper. The integral of the function $P_{ij}(r)$ around a circle of radius R, drawn at arbitrary height z, gives the contribution of the interatomic vector to the cylindrical Patterson projection at R and z. A circle of radius r, such that $P_{ij}(r) = 0.1P_{ij}(0)$, is also shown in the diagram.

used in a derivation of an electron distribution function given by James (1948, p. 404). If the atomic scattering factor is approximated by the equation

$$f_i = Z_i \cdot \exp(-0.8H^2) \cdot \exp(-\tfrac{1}{4}BH^2), \qquad (2)$$

where Z_i is the atomic number of the ith atom and B is a Debye temperature coefficient, equation (1) may be integrated in closed form to give

$$P_{ij}(r) = Z_i Z_j \left(\frac{2\pi}{B+3.2}\right)^{3/2} \cdot \exp\left[\frac{-2\pi^2 r^2}{B+3.2}\right]. \qquad (3)$$

This simple Gaussian distribution for a vector whose cylindrical coordinates are r_{ij}, z_{ij}, and α_{ij} must now be subjected to a cylindrical projection around the z axis of Patterson space. The value of the projected function at a distance R from the z axis is given by

$$Q_{ij}(R, z, r_{ij}, z_{ij}) = \int_0^{2\pi} R \cdot P_{ij}'(R, z, r_{ij}, z_{ij}) \cdot d\alpha, \qquad (4)$$

where $P_{ij}'(R, z, r_{ij}, z_{ij})$ is the value of the three-dimensional Patterson peak shape function (3) along a circle of radius R centered on the z axis. As can be seen from Fig. 1, we have

$$P_{ij}'(R, z, r_{ij}, z_{ij})$$
$$= Z_i Z_j (M/\pi)^{3/2} \cdot \exp\left[-M(z-z_{ij})^2\right]$$
$$\times \exp\left[-M(R^2+r_{ij}^2-2Rr_{ij}\cos\alpha)\right]. \qquad (5)$$

Here, M equals $2\pi^2/(B+3.2)$, a function of the temperature coefficient. It seems clear that the α_{ij} coordinate of the interatomic vector does not need to be taken into account for the evaluation of $Q_{ij}(R,z,r_{ij},z_{ij})$

so that all the vectors may be arbitrarily placed in a plane containing the z axis whose azimuth angle is chosen as zero degrees. With the introduction of (5), equation (4) becomes

$$Q_{ij}(R, z, r_{ij}, z_{ij})$$
$$= 2R \cdot Z_i Z_j \cdot (M/\pi)^{3/2} \cdot \exp\left[-M(z-z_{ij})^2\right]$$
$$\times \exp\left[-M(R^2+r_{ij}^2)\right] \cdot \int_0^{\pi} \exp\left[2MRr_{ij} \cdot \cos\alpha\right] \cdot d\alpha$$
$$= 2R \cdot Z_i Z_j \cdot (M/\pi)^{3/2} \cdot \exp\left[-M(z-z_{ij})^2\right]$$
$$\times \exp\left[-M(R^2+r_{ij}^2)\right] \cdot I_0(2MRr_{ij}), \qquad (6)$$

where $I_0(2MRr_{ij})$ is the zero-order Bessel function of the first kind for imaginary arguments.

In order to investigate the nature of the projected peak shape function (6), curves of $2R \cdot \exp[-M(R^2+r_{ij}^2)] \cdot I_0(2MRr_{ij})$ versus R for various r_{ij} and M values were calculated. These curves showed several interesting properties. First, all the peak maxima were displaced to values of R greater
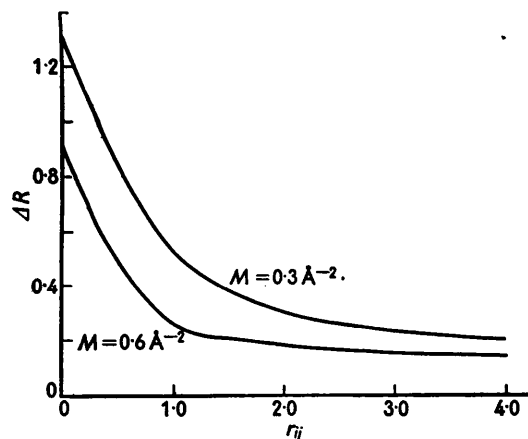

Fig. 2. A plot of the difference between the position of the maximum of the function $2R \cdot \exp[-M(R^2+r_{ij}^2)] \cdot I_0(2MRr_{ij})$ and r_{ij} for various values of r_{ij} and for $M = 0.3$ and 0.6 Å^{-2}.
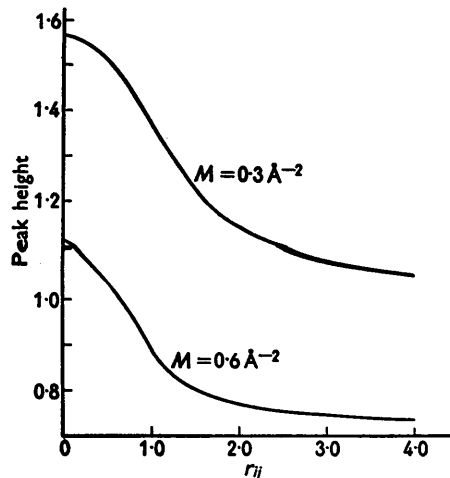

Fig. 3. A plot of the variation in the maximum height of the function $2R \cdot \exp[-M(R^2+r_{ij}^2)] \cdot I_0(2MRr_{ij})$ with r_{ij} for values of M equal to 0.3 and 0.6 Å^{-2}.

than r_{ij}. This effect was largest for small values of r_{ij} and amounted to about 1 Å for $r_{ij} = 0$ Å and $M = 0.6$ Å^{-2}. Fig. 2 shows the magnitude of these shifts as a function of r_{ij} for two representative values of M. Secondly, the relative maximum peak heights decrease with increasing r_{ij}, as shown in Fig. 3. Although calculations have been made for only two M values, 0.3 and 0.6 Å^{-2}, the results show that both of the above-mentioned effects decrease in importance with increasing M, that is, with smaller temperature factors. With single-crystal data, for example, a Gaussian distribution would probably give a good approximation to the peak shapes of a cylindrical Patterson projection for all values of r_{ij}.

It should be noted that at large values of r_{ij} (over 4.0 Å for $M = 0.6$ Å^{-2}), the shape given by (6) is closely approximated by a Gaussian function whose maximum is displaced to a larger value of R by an amount given by extrapolation of a curve like that shown in Fig. 2. The larger the value of M, the smaller is the shift and also the smaller the value of r_{ij} at which the approximation can be made. The maximum of the shifted Gaussian is similarly given by extrapolation of a curve such as that shown in Fig. 3.

Some idea of the appropriate value of M to use in the construction of a synthetic cylindrical Patterson projection can be obtained by examination of the origin peak of the observed Patterson to which the theoretical function is compared. Equation (6) has a simple form for $r_{ij} = 0$ and the variation of the position of the maximum with M may be easily derived. For example, a value of 0.6 Å^{-2} for M was suggested by the origin peak shape in the observed cylindrical Patterson projection for poly-γ-methyl-L-glutamate. This corresponds to a value of about 30 Å^2 for the temperature coefficient B, a not altogether unanticipated figure for fibrous substances with a relatively large degree of disorientation.

The complete calculation of $Q_{ij}(R, z, r_{ij}, z_{ij})$ for a set of interatomic vectors from a given model is obviously a tedious task, but some applications of IBM digital computing methods to the problem shorten the time required for such a calculation considerably.

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The Statistical Theory of Sign Relationships

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A statistical investigation of the relation between the signs of structure factors shows that the probability of the result $s(h)s(h') = s(h+h')$ is $Q/(1+Q)$, where

$$Q = \exp(2\varepsilon^{-1}|U_h U_{h'} U_{h+h'}|) \quad \text{and} \quad \varepsilon = \sum_{j=1}^{N} n_j^2.$$

These theoretical predictions are found to agree well with observation.

1. Introduction

Sayre (1952), Cochran (1952) and Zachariasen (1952) have shown that, for a centrosymmetrical structure, the signs of structure-factors of indices (hkl), $(h'k'l')$ and $(h+h',k+k',l+l')$ tend to be related so that the product

$$U_{hkl} U_{h'k'l'} U_{h+h',k+k',l+l'}$$

is a positive quantity. This tendency increases with the magnitude of the product of the unitary structure factors.

If the signs of some structure factors can be found unequivocally by the use of inequality relations (Harker & Kasper, 1948; Gillis, 1948; Karle & Hauptmann, 1950) then the range of known signs may be extended by assuming that the sign relationship holds when the structure factors involved are all large. It is even possible to allow for some inconsistencies which arise from occasional breakdowns of the relationship (Zachariasen, 1952).

It would obviously be useful to be able to calculate in advance the probability that the sign relationship will be obeyed, and this may be done by using the results of the theory developed in this paper.

2. The statistical theory

For a structure containing N atoms and having a centre of symmetry, the unitary structure factor $U_{h+h',k+k',l+l'}$ may be expressed as