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Vector Maps of Structures Containing Helical Chains

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A cylindrically symmetrical Patterson is calculated for a simple structure containing straight, parallel helical chains. This is used to calculate composite vector maps representing structures in which the chains run in different directions. These maps show considerable spreading of the vector density. It is concluded that the features exhibited by the Patterson function for horse methaemoglobin, in the regions approximately 5 and 10 Å from the origin, do not conflict with the idea that the structure contains helical chains.

1. Introduction

The helix shown in Fig. 1 arose in connection with another problem (Bunn & Howells, 1954). It has a back-bone consisting of 13 carbon atoms per repeat length, in which there are 6 turns. Two fluorine atoms are attached to each carbon. Although the helix is of such a simple nature the conclusions we shall reach will be capable of extension to structures containing more complex chains. The presence of side groups containing several atoms would merely result in greater complexity in the vector map and would increase the smoothing effects discussed below. Again, the composite vector maps we shall construct correspond to rather special arrangements of chains which are chosen so as to simplify the Patterson calculations. The configurations studied do not correspond in detail to a physically plausible structure for haemoglobin, but they are likely to result in less smoothing of vectors than would occur in the actual molecule. On both counts, therefore, we tend to underestimate the spreading of vectors associated with the haemoglobin crystal.

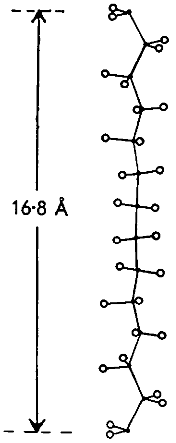

Fig. 1. Helical chain used in the Patterson calculations. One repeat length, containing thirteen CF_2 groups, is shown.

2. The cylindrical Patterson

The X-ray intensities were calculated, for the above helix, at reciprocal lattice points corresponding to a regular hexagonal lattice with $a = 5{\cdot}5$, $c = 16{\cdot}8$ Å. These intensity values, $I(l, \xi)$, were used to calculate a cylindrical Patterson function given by the MacGillavry & Bruins (1948) equations

$$\varphi_l(x) = \Sigma I(l, \xi) . J_0(2\pi\xi x)$$

and

$$\varphi(z, x) = \sum_l \varphi_l(x) \cos(2\pi l z) ,$$

where $\xi\lambda$ is the Bernal coordinate and J_0 is the zero-order Bessel function.

A Debye–Waller temperature factor, with $B = 8{\cdot}0 \times 10^{-16}$ cm.^{2}, was applied to the calculated intensities. All reflexions from planes of spacing greater than 1·3 Å were included in the summation; those from planes of spacing equal to 1·29 Å, or less, were omitted. The reason for not including the 1·29 Å reflexion, which corresponds to planes perpendicular to the helix axis through each carbon atom, will be obvious in the discussion below.

Fig. 2 shows the Patterson map. Contours are drawn at intervals of 5 units on an arbitrary scale and those below average are broken. The origin peak is 90. $I(000)$, which has been included, has the value 16. The distribution of vectors forms what may be called a face-centred array of regions of above-average vector density. The series of peaks along $x = 0$, spaced at intervals of 2·5 Å, corresponds to multiples of the C–C–C distance in one chain. A similar system of peaks along $x = 5{\cdot}5$ Å corresponds to the vectors between nearest neighbour chains. Peaks occur at the same z coordinate on these two lines because each chain in the structure is at the same height in the c direction.

It is noticeable that certain of the peaks are elongated (or even split) in the x direction. This is because the helix operation acting on a vector which is not parallel to the chain axis reproduces it in several positions in the surface of a cone. The above-average areas of density along $x = 2{\cdot}7$ Å are due to vectors between side groups separated by an odd number of

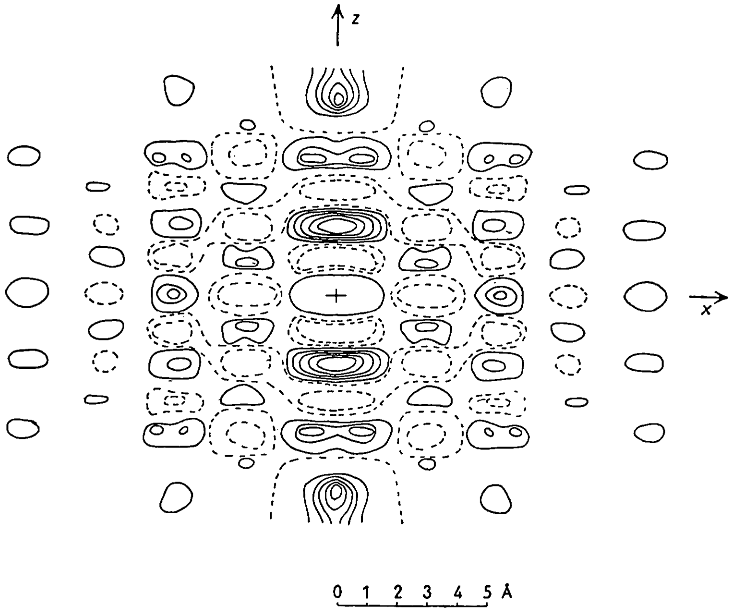

Fig. 2. Cylindrical Patterson function of a structure composed of infinite parallel helices (as in Fig. 1) arranged on a hexagonal lattice for which $a = 5{\cdot}5$ Å and $c = 16{\cdot}8$ Å. Contours in the origin peak are omitted.

C–C distances in the same chain, and between side groups in neighbouring chains. It is to be expected that these two kinds of vector should have an average x component of about one-half the distance between chains. Finally, we note the general feature of the Patterson diagram, namely, that its appearance clearly indicates the chain direction. For, although the position of peaks could be interpreted in terms of chains running in a number of directions, the general peak shape and the outstanding height of those along the c axis leaves no doubt that the chains are parallel to c.

3. Composite vector maps

We now try to obtain a qualitative picture of the vector distributions corresponding to more complex arrangements of chains. Consider a bundle of helical chains packed together straight and parallel, as in the ideal structure above. Suppose we construct a molecule consisting of a number of such bundles with their chain directions distributed uniformly in the surface of a cone of semi-vertical angle 10°. The axis of the cone may be called the mean chain direction of the molecule. Let the molecules form a crystal structure with the mean chain direction of each lying parallel to the Z axis.

It is clear that the cylindrical Patterson of such a structure will be similar to that for the case of parallel chains but there will be a spreading of vector density caused by the misorientation introduced.

Neglecting the vectors between different bundles of chains, the vector map may be formed by drawing the Z axis at 10° to z in Fig. 2, and rotating about Z. This approximation is justifiable on the grounds that when the bundles of chains are large the Patterson function of the whole array is, near the origin, just the superposition of all the self-Pattersons of the bundles. 'Near the origin' here means within a sphere of radius equal approximately to the distance between chains. The cylindrical Patterson constructed in this way (Fig. 3) illustrates how a structure containing helices which are all approximately parallel to one direction can give a considerable smearing of

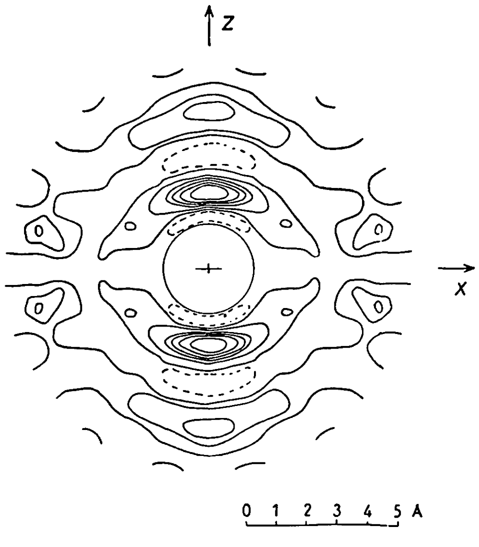

Fig. 3. Composite cylindrical vector map representing a structure in which the helices are allowed to deviate by 10° from the mean chain direction (Z). Contours in the origin peak are omitted.

the inter-side-group vectors (~ 3 Å) and of the vectors about 5·5 Å long. The vector density in spherical shells of radii about 3 Å and 5·5 Å is everywhere above average. There is, however, a marked concentration of density (for the 3 Å vectors) into spherical caps centred on the Z axis. Thus the diagram is uniaxial and there could hardly be an ambiguity in selecting the mean chain direction.

The next step is to enquire into the effect of having more than one chain direction in the molecule. Suppose that the molecule contains one set of chains in the direction of the Z axis (with the same departure from exact parallelism as above), and another similar set with its mean chain direction perpendicular to Z. The Patterson map of such a structure may be calculated approximately by superposing two maps at right angles, one for each half of the molecule. This takes no account of the vectors between the two halves, but these may be considered negligible if the molecule is large. The features of the resultant three-dimensional vector distribution may be summarized by drawing two central sections. Fig. 4 shows a section parallel to the plane of the two chain directions. It is seen to be almost completely circularly symmetrical in that the 3 Å and 5·5 Å shells of above-average vector density show only faint indication of the chain directions. A central section perpendicular to one chain direction will be practically identical to Fig. 3.

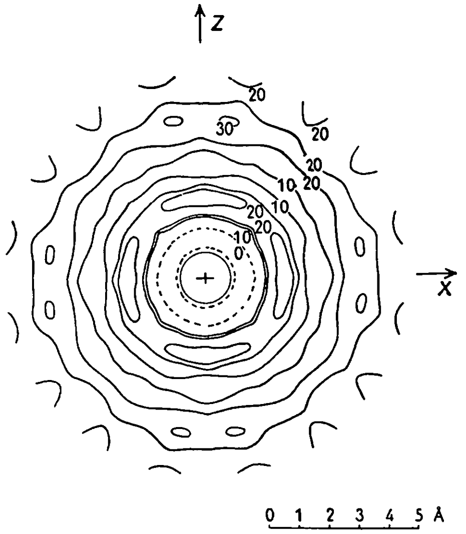

Fig. 4. Central section of the three-dimensional Patterson function of a structure containing two sets of chains. The mean chain direction of one set is along Z, and of the other is along X. Where ambiguity exists, contours are numbered, on an arbitrary scale. Origin peak contours are omitted.

Summing up, the three-dimensional Patterson of the kind of structure we have envisaged is noticeably biaxial. However, the spread of vectors is larger than might be expected in view of the small departure from parallelism permitted in the chains of each half of the molecule.

4. Horse methaemoglobin

The diameters (3 Å and 5 Å) of the shells of vector density, discussed above, result directly from the average inter-side-group distances and from the distance between chains. If we had taken the Pauling α-helix as the basis of calculations, the main features of the Patterson diagrams would have been similar but the shells of high vector density would have had diameters of 5 and 10 Å approximately. These vector shells are observed in the three-dimensional Patterson of horse methaemoglobin (Perutz, 1949) and there arises the question, 'Is the vector distribution in them compatible with a structure comprising α-helices (or similar helical chains)?'. Wrinch (1953*a*, *b*) describes the 5 Å vectors as an 'essentially three-dimensional distribution' and concludes that 'there is no confirmation of the hypothesis of rod-like polypeptide chains in the crystal'. The present investigation indicates that Wrinch's conclusion is unjustified. In the first place the 5 Å vectors in haemoglobin do not approximate closely to spherical symmetry. As Perutz describes it, 'the vector density varies within wide limits in different parts of the shell'. Thus the distribution can be called essentially three-dimensional only in the limited sense that the vector density is above average everywhere at a distance of 5 Å from the origin. This is equally true of the approximate vector map we calculated above for a chain-like structure with two widely different chain directions. In fact the general appearance of the vector distribution in the hypothetical case we have considered is similar to that observed in haemoglobin. This is especially noticeable in looking at Fig. 3 here and Perutz's (1949) Fig. 1(*b*). It is likely on general packing grounds that Pauling α-helices should pack together with *neighbouring* chains making an angle of about 20° with each other at any point (Crick, 1953). Consequently, the departure from parallelism in the actual haemoglobin molecule would be of a different kind from that in our model, where neighbouring chains are parallel and the misorientation occurs between widely separated groups. Thus a more physically real model would involve additional dispersion of the vectors between neighbouring helices. Therefore, the vector diagrams obtained here probably underestimate the smearing to be expected in Pattersons of structures in which helical chains are packed with the side-groups of one fitting into the spaces between the side-groups of its neighbours.

The Fourier transform of a helix has a marked feature which we have so far left out of account. For the α-helix this corresponds to the strong diffraction by planes perpendicular to the chain axis and 1·5 Å apart. This high-angle diffracted intensity is concentrated into one reflexion when all the chains are straight and parallel. In the type of structure discussed above the misorientation would cause a slight spread, but there would not be spherical smoothing to the same extent as in the 5 and 10 Å reflexions, which are more numerous and at lower angles. The 1·5 Å reflexion is, therefore, of considerable significance in deciding between a chain structure and a three-dimensional net, and it is more profitable to study the diffraction pattern at high angles rather than the near-origin regions of the Patterson function. If, for example, there are found to be several areas of high intensity on the surface of the 1·5 Å sphere in reciprocal space, there is a strong presumption that the structure contains chains parallel to the directions joining these areas to the origin.

References

Bunn, C. W. & Howells, E. R. (1954). *Nature, Lond.* **174**, 549.
Crick, F. H. C. (1953). *Acta Cryst.* **6**, 689.
MacGillavry, C. H. & Bruins, E. M. (1948). *Acta Cryst.* **1**, 156.
Perutz, M. F. (1949). *Proc. Roy. Soc.* A, **195**, 474.
Wrinch, D. (1953*a*). *Acta Cryst.* **6**, 562.
Wrinch, D. (1953*b*). *Acta Cryst.* **6**, 638.

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The Determination of the Crystal Structure of the σ Phase in the Iron–Chromium and Iron–Molybdenum Systems*

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The crystal structure of the σ phase in the iron–chromium system at 46·5 atomic % chromium was determined by the application of powder and single-crystal X-ray diffraction methods. The crystal structure of this phase in the iron–molybdenum system was also determined by the use of powder and single-crystal methods, and found to be essentially the same as that for the iron–chromium phase. Reliable information regarding the distribution of iron and chromium among the various positions could not be obtained directly for σ-FeCr. However, reasonably reliable information regarding the distribution of iron and molybdenum in σ-FeMo was obtained, and probably the chromium atoms in σ-FeCr occupy substantially the same positions as the molybdenum atoms in σ-FeMo.

The iron–chromium σ-phase structure has space group D_{4h}^{14}–$P4_2/mnm$, with $a_0 = 8{\cdot}800$ Å and $c_0 = 4{\cdot}544$ Å. The iron–molybdenum presumably has the same space group, and has $a_0 = 9{\cdot}188$ Å and $c_0 = 4{\cdot}812$ Å. There are 30 atoms in the unit cell. The positions of the atoms are at the points of two pseudo-hexagonal nets normal to **c** at $z = 0$ and $z = \frac{1}{2}$. Eight of the 30 atoms are displaced parallel to **c** by approximately the distance $\frac{1}{4}c_0$, so that there are four atoms at $z \approx \frac{1}{4}$ and four at $z \approx \frac{3}{4}$. The structure is nearly identical with that found independently by Tucker for β-uranium.

1. Introduction

The σ phase is a brittle phase of complex structure which occurs in a number of binary and ternary systems involving transition-group elements, in particular vanadium through nickel in the first long period and molybdenum in the second. Systems in which the σ phase has been found to occur, with compositions as determined after annealing at elevated temperatures, are listed in Table 1 (Duwez & Baen, 1950; Greenfield & Beck, 1954).

The σ phase has a characteristic powder diffraction pattern. It contains a group of about eight strong lines with spacings close to 2 Å, only a few very weak lines at larger spacings, and only a few weak lines with spacings in the range 1·8–1·3 Å. These general features are not unique to the σ phase; other phases, such as the μ phase (Fe_7W_6 and Fe_7Mo_6, Arnfelt & Westgren, 1935; Co_7W_6, Magneli & Westgren, 1938; Co_7Mo_6, Henglein & Kohsok, 1949), and the phases designated δ, *P*, and *R* (in the respective systems Ni–Mo, Cr–Ni–Mo, and Cr–Co–Mo; Rideout *et al.*, 1951) give similar powder diffraction patterns. The σ phase has often been described as non-magnetic, but it has been found to be ferromagnetic with a low Curie temperature (about −113° C.; Beck, 1952). The σ phase in the iron–chromium system is of some technological importance in connection with stainless steels.

Previous attempts to determine the crystal structure of the σ phase have been unsuccessful for the

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