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Partial Fourier syntheses.

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Buerger (1956, 1959) has shown how partial Fourier syntheses can be used in the solution of crystal structures which have superstructure characteristics. Summarizing, we can divide such structures into two parts: (i) the substructure, comprising that part of the electron density which conforms to the periodicity of the sub-cell (or pseudocell), and (ii) the complement structure, comprising the rest of the electron density, which has only the periodicity of the true cell. At least one of the identity periods of the true cell or superstructure is a multiple of the corresponding period of the substructure. Therefore the reciprocal lattice of the superstructure contains an extra set of points (the 'excess points') compared with the reciprocal lattice points derived from the substructure cell. The complement structure alone is responsible for these excess points. Buerger (1959) gives a diagram for a simple example involving the doubling of one axis of the sub-cell.

The question is then posed, what is the Fourier transform of these excess superstructure points alone? The answer given is that it is simply a pattern of the scaled down electron density of the complement structure. The justification is quoted in the next paragraph.

'To see this, consider the Fourier transform of a single unit cell of the complement structure. This transform is a continuously varying function. The Fourier transform of the repetition of these cells on a lattice is a periodic sampling of the Fourier transform of the unit cell, the sampling occurring at the points of the reciprocal lattice of the complement structure. *If the sampling interval is arbitrarily changed, the result is the same, except for scale of weighting*'. (My italics, J.W.J.)

Actually the result is not the same, in two ways:

(1) If the sampling interval is changed the repeat period in real space is changed. In particular, if the sampling period is increased the real period will be decreased and the transforms (the unit-cell contents) at each of the new lattice points will overlap.

(ii) The sampling interval must be regular, *starting from the origin*. This is not the case with the excess points.

However, the transform of the excess points is undoubtedly something like the complement structure, in some cases at least, and a rather more elaborate justification of its use is given below, in terms of the subtraction of transforms, for the simple case of one doubled axis.

The Fourier transform of the excess points

(i) Form the transform of the whole reciprocal lattice. This is the true cell contents.

(ii) Separate out that part of the structure factor at the sub-cell reciprocal points which is due to the substructure alone. Subtract the transform of these parts (*i.e.* the substructure) from (i). We are then left with the complement structure.

(iii) The remaining parts of the structure factors at the sub-cell points then constitute a sampling of the complement structure transform at twice the normal repeat distance. This will transform to the complement structure with one half the actual electron density, repeated on a lattice one half the size of the true lattice (*i.e.* a set of overlapping complement structures centred on the sub-cell lattice points). If we then proceed to subtract this from the complement structure left at (ii) above, we first of all reduce it to half the previous electron density and then we have to subtract the overlapping parts of the electron density centred on neighbouring sub-cell lattice points. Since there can be no coincident peaks produced by this overlap the only effect will be to produce dips in the background and the complement structure peaks will stand out clearly.

So far only the simplest case of a sub-cell formed by a halving in one direction has been considered. The situation may be improved if the volume of the sub-cell is a smaller fraction of that of the true cell. If halving occurs in three directions the electron density to be subtracted in (iii) will be only one eighth of that left in (ii) and there will be seven overlapping cells contributing to a negative background which will obviously tend to be much more uniform than for the case considered above.

In the above analysis it has been tacitly assumed, following Buerger, that we are dealing with real electron density. If this restriction is relaxed so that we can deal with negative electron densities, the substructure can be defined as the average electron density of the sub-cells comprising the complete superstructure. The complement structure is obtained by subtracting this substructure from each of the sub-cells of the superstructure. The complement structure will then contain as much negative electron density distribution as positive, so that

$$\sum_{n=1}^{N} \varrho(\mathbf{r}_n + \mathbf{R}) = 0$$

for all **R**, where $\mathbf{r}_n$ define the origins of the N sub-cells. The structure factors for such a complement structure at the sub-cell reciprocal points are zero. It follows that the transform of the excess points (together with the zero weight sub-cell points) *is* the complement structure when defined in this way.

The Patterson transform of the excess points

The Patterson transform of the excess points is likewise the Patterson transform of this complement structure with equal totals of positive and negative electron density, and Frueh (1953) has shown that this can be interpreted in a simple case of segregation of atoms of two kinds in the equivalent sub-cell positions. However, in some cases it may be easier to interpret such a Patterson transform in terms of positive electron density, as was done previously for Fourier transforms. This is certainly at least as easy in the case considered by Frueh as is his interpretation in terms of a 'difference structure' containing equal positive and negative peaks. It may be, in fact, that the negative electron density approach is the best way of deriving a complement Patterson transform from a given structure, but that the reverse, the derivation of the complement structure from a given excess points Patterson transform, is best done in terms of real electron density. In terms of real electron density, if $\mathbf{F}_s$ is the structure factor for the sub-cells and $\mathbf{F}_c$ for the complement structure, then at the sub-cell reciprocal lattice points

$$I_{s+c}=(\mathbf{F}_s+\mathbf{F}_c)^2 = F_s^2+2\mathbf{F}_s.\mathbf{F}_c+F_c^2.$$

The F_c^2, together with those for the excess points, are the transform of the Patterson function of the (real) complement structure. $F_s^2+2\mathbf{F}_s.\mathbf{F}_c$ transforms to the Patterson function of the sub-structure plus the cross vectors between the sub-structure and the complement structure. The transform of the excess points, weighted with the intensities, is thus the scaled down version of the Patterson function of the complement structure, with a background of overlapping negative Patterson functions of the complement structure, exactly analogous to the Fourier case. However, even in the most favourable case of a Patterson function, it will be necessary to allow for the large negative origin peaks at the sub-cell lattice points, and where the superstructure is due to small displacements from ideal positions the cluster of positive and negative peaks round the ideal position will tend to cancel out. This is a particular case of the general possibility, which occurs in the case of Patterson functions, of coincident or near coincident positive and negative peaks. Projections will tend to suffer more from such cancellations than three-dimensional syntheses.

The referee's help, especially in pointing out many of the implications of the negative electron density approach, is gratefully acknowledged.

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Single-crystal studies of β-F_2 and of γ-O_2.

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Techniques for the growth, orientation and X-ray diffraction study of single crystals of β-N_2 (Streib & Lipscomb, 1962; Streib, Jordan & Lipscomb, 1962) have been extended to single crystal studies of β-F_2 at 50 °K and γ-O_2 at 50 °K. These phases have, surprisingly, the same structure-type (Fig. 1). Unit-cell dimensions are $a = 6{\cdot}67 \pm 0{\cdot}07$ Å for β-F_2 and $6{\cdot}83 \pm 0{\cdot}05$ Å for γ-O_2, and there are eight diatomic molecules in the unit cell. Systematic absences of hhl when l is odd suggest space groups $P\bar{4}3n$ or $Pm3n$, but our results indicate an orientationally disordered structure in $Pm3n$.

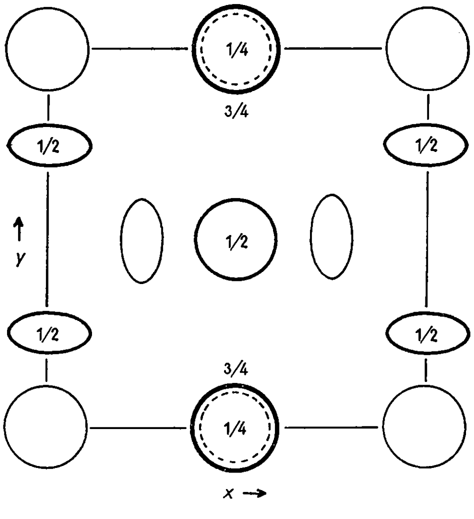

Fig. 1. Crystal structure of β-F_2 and of γ-O_2. Out-of-plane coordinates are indicated for each molecular center, except for those at $z=0$, which are unlabeled. The two molecules at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ are approximately spherically disordered. The other six molecules, at $\frac{1}{4}\frac{1}{2}0$, $0\frac{1}{4}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{3}{4}\frac{1}{2}0$, $0\frac{3}{4}\frac{1}{2}$ and $\frac{1}{2}0\frac{3}{4}$, show an oblate spheroidal distribution of electron density such that the ratio of major to minor axis is about two. Minor axes are aligned along the shortest intermolecular contacts (3·3 Å in F_2, 3·4 Å in O_2) along $x(y=\frac{1}{2}, z=0)$, along $y(x=0, z=\frac{1}{2})$ and along $z(x=\frac{1}{2}, y=0)$. Bond distances of 1·21 Å for O_2 and 1·42 Å for F_2 were assumed.

In β-F_2 each F_2 at 000 or at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ has 12 F_2 neighbors at 3·7 Å between molecular centers. Each of the other F_2's has $2F_2$'s at 3·3 Å, 4 F_2's at 3·7 Å and 8 F_2's at 4·1 Å. Van der Waals contacts are 2·7 Å if two F_2's have their molecular axes perpendicular to, or 4·1 Å if their axes are along, the line of contact. Thus, the disorder is strongly hindered along the infinite linear chains of F_2 molecules separated by 3·3 Å. We have verified the presence of a major transition, suspected by Murphy & Rubin (1952) because of an entropy discrepancy, and found by Hu, White & Johnston (1953), but we have obtained only powder photographs of α-F_2 by cooling single crystals of β-F_2 through the transition point at 45·55 °K.

The essential identity of the γ-O_2 and β-F_2 structures makes untenable any description of γ-O_2 based upon dimers of O_2 (Ruhemann, 1932; Vegard, 1935), and further suggests that the unusual magnetic properties of γ-O_2 (Kanda, Haseda & Otsubo, 1955) do not determine the structure. The presence of infinite linear chains of O_2 molecules is consistent with the very short range interactions suspected by Kanda *et al.* (1955) (Knobler, 1961; Lien & Phillips, 1961), but this structure raises serious questions about the existence of dimers in the other solid phases and in solution (Lewis, 1924; Pauling, 1960). Even the nearly spherically disordered molecules at 000