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# Symmetry of Fourier Space*

By Arthur Bienenstock

*Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass., U.S.A.*

and P. P. Ewald

19 *Fordyce Road, New Milford, Conn., U.S.A.*

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The symmetry group represented in crystal space by the array of symmetry elements, or by the coordinates of equivalent points, is equally contained in the expressions of the geometrical structure factor; it should therefore be possible to derive the 'symmetry' of the latter directly in Fourier space without any reference to crystal space. This program involves the distribution of complex weights on the lattice points of the reciprocal lattice. The relative phases of the weights at symmetry-related points can be determined by considerations of uniqueness. This leads to the Fourier-space equivalent of complex symmetry groups in crystal space (including the black-white and colored groups). In order thence to arrive at the 230 Fourier transforms of the Schoenflies–Fedorov groups a restriction has to be placed on the phase relations which corresponds to the exclusion of complex and antisymmetry elements in crystal space.

## 1. The problem and plan of this paper

The Fourier transform of a function in physical space, e.g. the charge density, $\varrho(x, y, z)$, in a crystal, is a complete image of this function in reciprocal or Fourier space. Hence any transformation property of the function in physical space, such as produced by symmetry elements, must have its equivalent in Fourier space. In fact, the 'geometrical structure factors' as listed for each space group in the *International Tables for X-ray Crystallography* (1952) contain implicitly the symmetry properties in Fourier space. These symmetry properties are not easily recognizable. Only those point symmetry elements which pass through the origin in physical space give rise to equivalent symmetry elements about the origin of Fourier space, whereas other symmetry elements in physical space lead to phase relations between equivalent points in Fourier space. These can, of course, be found from the explicit geometrical structure factors (Buerger, 1949, 1960; Waser, 1955; Nowacki, 1950), but it should be possible to derive them in a direct and, in that sense, more satisfactory manner by applying the essential group-theoretical properties of space groups directly to Fourier space, instead of following the present circuitous way of first operating in physical space so as to find the possible combinations of symmetry elements (i.e. the 230 space groups), then listing the coordinates of equivalent points, next making the Fourier transformation by writing down the geometrical structure factors and finally discussing these in view of relations expressing the symmetry in Fourier space.

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In the following, a direct approach to this problem is offered. It differs from the problem of establishing the 230 Schoenflies–Fedorov space groups in physical space in two characteristic respects:

(i) Periodicity in physical space does *not* correspond to periodicity in Fourier space, but instead to the reduction of Fourier space to the set of reciprocal lattice points—i.e., Fourier space is reduced to the '*index space*' of the Fourier coefficients $F(h, k, l)$, and is not a continuous space. It is reduced to one of the 14 Bravais lattices, and may have any compatible symmetry.

(ii) Even though the function in physical space may be real (or even positive like $\varrho(x, y, z)$), the function in Fourier space is, in general, complex. For this reason the symmetry we expect to recognize is compounded of symmetry elements of three-dimensional space character (as in physical space) *and* of symmetry elements appropriate to the Gaussian plane of complex numbers.

In order not to unnecessarily restrict the generality of our method, and so as to preserve, as long as convenient, the duality between physical and Fourier space, we start by defining what we understand by complex symmetry elements, point groups, and space groups. Applying these definitions to physical space, the black-white groups (Belov, Neronova & Smirnova, 1957) follow when the phase changes are restricted to 0 or $\pi$, and the colored (Belov & Tarkhova, 1956) space groups include more general phase changes. If no phase change is allowed, the complex symmetry elements are restricted to those from which the 230 Schoenflies–Fedorov groups follow.

To make the problem tractable, we only consider inhomogeneous linear symmetry operators. In addition, we consider as symmetry related only such

points at which the complex function has equal magnitude.

## 2. Definition of complex symmetry elements and complex point and space groups

*1. definition*

A *complex symmetry element* is the combination of an ordinary three-dimensional point or glide symmetry element, $S$, with a compatible symmetry element, $\sigma$, of the Gaussian plane; the complex symmetry element is denoted $\Sigma=(S, \sigma)$. Let $n$ be the order of $S$, so that $S^n=I$, the identity. Then, for uniqueness of the complex function, the order of $\sigma$ must be $n$ or a factor of $n$, so that $\sigma^n=I$. This is the condition of compatibility. This condition is indefinite for symmetry elements, $S$, which contain glide elements. For such symmetries, $n$ is infinite. We distinguish between what we shall term *closed* and *open* complex symmetry elements. Let $S'$ be the rotation-reflection portion of $S$ (i.e. excluding glides), and $n'$ the order of $S'$. If the order of $\sigma$ is $n'$ or a factor of $n'$, we call the operator a closed operator. All other operators are open operators. It should be observed that there is no possibility of open operators in the space groups of positive real functions. The simplest example of an open operator is the three-fold screw axis in which, with each rotation-translation, the function changes sign (i.e. $\sigma$ is a rotation of $\pi$ in the Gaussian plane). The order of $S'$ is three, while the order of $\sigma$ is two. The total operator, $\Sigma$, produces a unit cell which is twice as long as that which would be measured by an observer who is insensitive to the sign of the function.

With each of the crystallographically significant glide symmetry operators an infinite number of *open* complex symmetry operators can be constructed, whereas the number of *closed* compatible operators is finite.

The most general complex symmetry element contains both glide elements in $S$ and phase transformations, $\sigma$, which are a function of the point $\mathbf{r}=(x, y, z)$ on which $\Sigma$ is acting. Basic characteristics of the two spaces (physical and Fourier) limit the type of operators acting within them. Consider a symmetry operation $\Sigma$ defined by

$$F(S\mathbf{r})=F(\mathbf{r})\exp j\xi(\mathbf{r}) \tag{1}$$

where $j=2\pi i=2\pi(-1)^{\frac{1}{2}}$, and $\xi(\mathbf{r})$ is any function of $(x, y, z)$. The compatibility condition places restrictions on the form of $\xi(\mathbf{r})$. The restrictions are considerably less severe in an index space than in a continuous periodic space, as in the latter space they must be satisfied at every point in the space. Consider, for example, a relationship of the form $F(-x, y, z) = F(x, y, z)\exp j\xi(x, y, z)$. Applying this twice we obtain the equation

$$F(x, y, z)=F(x, y, z)\exp j[\xi(x, y, z)+\xi(-x, y, z)]. \tag{2}$$

In both spaces this implies that either

$$\xi(x, y, z)+\xi(-x, y, z)=\text{integer} \tag{3a}$$

or

$$F(x, y, z)=0\,. \tag{3b}$$

In the continuous space, equation (3$a$) implies that the integer be a piece-wise constant function in the regions where equation (3$b$) is not satisfied. In index space no such restriction exists. If, however, continuous space is also periodic, then it is also required that either $F(\frac{1}{2}, y, z)=0$ or that $\xi(\frac{1}{2}, y, z)$ be a half-integer. (In all that follows we shall measure physical space coordinates in fractions of repeat distances, so that the index space coordinates are integers.) In our linear formalism this means that $\xi(x, y, z)=nx$, where $n$ is an integer. The important thing to note is that symmetries of the form of equation (1) are compatible with complex periodic functions and must form an important part of any complex groups formalism.

In addition to operators which depend on coordinates there are simple rotations of $\mu$th order in the complex plane which change the complex quantity $|F|\exp j\xi$ to $|F|\exp j(\xi+1/\mu)$ and reflections across a line under complex angle $2\pi\Omega$ which transform $|F|\exp j\xi$ to $|F|\exp j(2\Omega-\xi)$. For $\Omega=0$, this operation of order 2 describes the transition to the complex conjugate and is denoted as $*$. Two planar examples of such complex operators are given in Fig. 1.

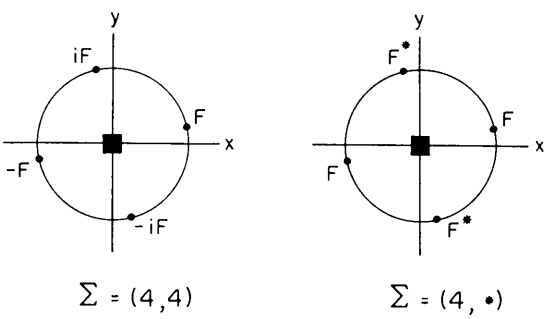


Fig. 1. Two planar examples of complex operators. $x$ and $y$ are space coordinates.

It should be noted that at some points along the symmetry operators the function must vanish if phase symmetry relations (other than the identity) are to hold. This is the complex analogue of the requirement that an anti-symmetric function vanish at the origin.

*2. definition*

A *complex point group* is a combination of complex symmetry elements, all of which pass through a single point (the origin), have no glide components, and produce a single-valued function.

The enumeration of these groups can be divided into three overlapping parts: (i) the groups in which

$\sigma$ is independent of $(x, y, z)$, (ii) the groups in which $\sigma$ is compatible with the periodic, continuous space, (iii) the groups in which $\sigma$ is compatible with an index space. The groups of the first set have been enumerated by us. We find 267 such complex crystal classes. Their tabulation will be published separately, as their knowledge is not essential for the further development of our main problem. The third set of groups are the major concern of this paper and will be discussed in detail below.

*3. definition*

By a *complex space group* we understand any combination of complex symmetry elements which produces a single-valued, three-dimensionally periodic function.

From these definitions onwards we can proceed in two different ways. *Either* all possible combinations of complex symmetry elements could be enumerated in physical space and thence the equivalent of the coordinate lists of the Schoenflies–Fedorov space groups could be found *or* we can operate directly in Fourier space. Since the special cases for physical space

$\sigma = I$: Schoenflies–Ferodov groups
$\sigma = \pm$: Heesch–Shubnikov black-white groups
$\sigma = \mu$: Belov's color groups with $\mu$ colors
$\sigma = *$: another form of the black-white groups

have been widely discussed (*International Tables for X-ray Crystallography*, 1952; Belov *et al.*, 1956, 1957), the former procedure would lead to much repetition. Hence, it is the direct derivation in Fourier space to which we proceed.

## 3. Symmetry transformations in Fourier space

To facilitate manipulation of Fourier space symmetry operators, we express them in matrix form. As stated above, we restrict ourselves to linear transformations which leave the magnitude of the structure factor invariant. This leaves the four independent variables $h, k, l$, and $\varphi$, where $h, k$, and $l$ are the index space coordinates and $\varphi$ is the complex phase of the structure factor, measured in multiples of $2\pi$. The most general such linear transformation is given by the matrix equation (writing $(h, k, l)$ instead of $(h_1, h_2, h_3)$)

$$\begin{pmatrix} h' \\ k' \\ l' \\ \varphi' \end{pmatrix} = (\alpha_{ij}) \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} + (\beta_j) \qquad (4)$$

where $\alpha_{ij}$ and $\beta_j$ must be real.

These transformation matrices can be reduced immediately. Since, for fixed arbitrary symmetry, $\varphi$ can vary continuously, while the index space coordinates are discontinuous and restricted to integer values, the entries in the fourth column of the first three rows of $\alpha_{ij}$ must be zero. In addition, since the index space forms a Bravais lattice which must be kept invariant, the submatrix of $\alpha_{ij}$ for which $i$ and $j$ take on the values 1 to 3 must be the matrix representation of a three-dimensional point group operator. We denote such a representation $R_p$.

Thus, purely from considerations of periodicity in crystal space and retention of the most general functional form for the Fourier transform, the linear transformation can be reduced to

$$\begin{pmatrix} h' \\ k' \\ l' \\ \varphi' \end{pmatrix} = \begin{pmatrix} R_p & \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} \\ \alpha_{41}\ \alpha_{42}\ \alpha_{43} & \alpha_{44} \end{pmatrix} \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} + \begin{pmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \end{pmatrix}. \qquad (5)$$

Since all phase equations are understood to hold (mod. 1), the $\alpha_{4j}$ $(j = 1, 2, 3)$ can be chosen in the range $0 \leq \alpha < 1$. The same holds for $\beta$.

## 4. Index space point operators

The operators exhibited in equation (5) contain translations in the index space. To obtain point operators we set these translations, $\beta_1, \beta_2$, and $\beta_3$ equal to zero.

The final reduction of the form of the operator occurs when we demand that the function be single-valued. This implies that the entire transformation be of the same order, $n$, as $R_p$. Applying the transformation $n$ times we obtain an equation in which a function of the $\alpha_{4j}$'s, $\beta_4, h, k$, and $l$ plus a term $(\alpha_{44})^n\varphi$ must be equal to $\varphi$ (mod. 1). Treating $\varphi$ as an independent variable, this equation can be satisfied for a number of choices of the $\alpha_{4j}$'s with $(\alpha_{44})^n$ equal to unity. For operators of odd order this implies that $\alpha_{44}$ equals unity while for the even order operators $\alpha_{44}$ can take on the values plus or minus one. The form of the linear transformations which are of interest is then:

$$\begin{pmatrix} h' \\ k' \\ l' \\ \varphi' \end{pmatrix} = \begin{pmatrix} R_p & \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} \\ \alpha_{41}\ \alpha_{42}\ \alpha_{43} & \pm 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \\ \beta_4 \end{pmatrix}. \qquad (6)$$

We can now impose further conditions on the index space concerning its symmetry and thereby obtain restrictions on the coefficients $\alpha_{41}, \alpha_{42}, \alpha_{43}, \beta_4$ and the sign of $\alpha_{44}$. Such conditions will be compatibility of the weights in index space with the group properties of $R_p$, or intrinsic symmetry properties of the weights (which are not determined by $R_p$) like *hermitian character*. The latter demands that $F(h, k, l) = F^*(-h, -k, -l)$ and is the condition for interpreting the weights as the Fourier transforms of a *real* periodic function in physical space. (In the case of Patterson space the intrinsic conditions on the weights would be a center of symmetry with respect to the origin and positiveness). A discussion of $R_p$ induced symmetry will be given for the tetragonal case in section 8.

### 5. Hermitian index space operators

If we demand the hermitian character of a pair of centrosymmetrically related points $= \pm(h, k, l)$ as well as of a second, symmetrically equivalent, pair $= \pm(h', k', l')$, we obtain the equation

$$\varphi(h', k', l') = -\varphi(-h', -k', -l') \tag{7}$$

or

$$\alpha_{41}h + \alpha_{42}k + \alpha_{43}l + \alpha_{44}\varphi(h, k, l) + \beta_4 = -[-\alpha_{41}h - \alpha_{42}k - \alpha_{43}l + \alpha_{44}\varphi(-h, -k, -l) + \beta_4].$$

Since $\varphi(h, k, l) = -\varphi(-h, -k, -l)$ we obtain

$$2\beta_4 = 0 \text{ (mod. 1)}$$

or

$$\beta_4 = 0, \tfrac{1}{2}. \tag{8}$$

In addition to this restriction on $\beta$, it is only necessary to consider those transformations for which $\alpha_{44} = +1$. Because the negative identity matrix is an element of each hermitian space, we have the equality

$$\begin{pmatrix} R_p & \vdots & 0 \\ & \vdots & 0 \\ & \vdots & 0 \\ \cdots & \cdots & \cdots \\ \alpha_{41}\ \alpha_{42}\ \alpha_{43} & & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} \bar{R}_p & \vdots & 0 \\ & \vdots & 0 \\ & \vdots & 0 \\ \cdots & \cdots & \cdots \\ -\alpha_{41}\ -\alpha_{42}\ -\alpha_{43} & & +1 \end{pmatrix} = \begin{pmatrix} \bar{R}_p & \vdots & 0 \\ & \vdots & 0 \\ & \vdots & 0 \\ \cdots & \cdots & \cdots \\ 1-\alpha_{41}\ 1-\alpha_{42}\ 1-\alpha_{43} & & 1 \end{pmatrix}. \tag{9}$$

Hence, inclusion of $\alpha_{44} = -1$ leads to redundancy in the derivation of those groups in Fourier space which correspond to space groups of real functions in physical space.

### 6. Hermitian index-space operators for space with positive origin weight

Finally, the restriction that $\varphi(0)$ equal 0 for the Fourier transform of a *positive function* implies that $\beta_4$ equals zero. This is a necessary but, by no means, sufficient condition for making the weights the Fourier transform of a positive function. Thus, the form of the index space transformation for the Fourier transforms of positive real functions is:

$$\begin{pmatrix} h' \\ k' \\ l' \\ \varphi' \end{pmatrix} = \begin{pmatrix} R_p & \vdots & 0 \\ & \vdots & 0 \\ & \vdots & 0 \\ \cdots & \cdots & \cdots \\ \alpha_{41}\ \alpha_{42}\ \alpha_{43} & & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} \tag{10}$$

with $\varphi(0, 0, 0) = 0$.

### 7. Index-space point groups

With the operators in the form of equation (6) we can construct point groups. The condition that the index space weight function be single-valued implies that these transformations obey, in combination, the point group generating relations obeyed by the $R_p$ submatrices. Substitution of the matrices into the relations leads to restrictions on the relative and absolute values of the $\alpha_{4j}$'s and $\beta_4$. For the operators of the form of equation (6) there are an infinite number of such combinations. This corresponds to the existence of an infinite number of open symmetry operators for complex functions in physical space. However, for the operators of equations (8) and (10) the number of such combinations is finite. In section 10 the derivation of the tetragonal point groups constructed from operators of equation (10) is exhibited.

In the remainder of this section some general features of Index Space symmetries will be discussed.

Of major importance is the distinction between primitive and centered index spaces which arises when the $(h, k, l)$ coordinates are chosen so as to automatically express a particular symmetry of the Bravais lattice. In a primitive index space, $h$, $k$, and $l$ assume, independently, any integer values. In non-primitive index spaces certain values, or combinations of values are excluded so that conditions arise such as

$h + k = 2n$ ($c$-centered lattice),
$h + k + l = 2n$ (face-centered lattice),
$h$, $k$, $l$ of same parity only (body-centered lattice).

These conditions affect the conclusions that can be drawn from the substitution of the matrices in the generating relations because they reduce the number of points at which the generating relations have to hold.

Some general properties of the Index space of hermitian symmetry should be noted:

(i) If the transformations lead to $\varphi(h, k, l) = \varphi(-h, -k, -l)$, then $\varphi$ must be 0 or $\frac{1}{2}$ and all such $F(h, k, l)$ are real.

(ii) Similarly, if $\varphi(h, k, l) = \varphi(-h, -k, +l)$, then it follows that the plane $l = 0$ of index space is a conjugate reflection plane; therefore $\varphi(h, k, 0)$ is 0 or $\frac{1}{2}$.

(iii) If $\varphi(h, k, l) = -\varphi(-h, -k, +l)$ then the plane $l = 0$ is a reflection plane and has itself a center of conjugate inversion at the origin $\varphi(h, k, 0) = -\varphi(-h, -k, 0)$.

(iv) In case the transformation adds a non-integral number to the phase of a point $(h', k', l')$ of index space which is transformed into itself, the preservation of uniqueness demands that $|F(h', k', l')| = 0$.

Most of the operators of equation (6) require, in addition to (iv), that the index space weight functions vanish along planes of non-invariant points. If such operators are excluded from consideration, there exist a finite number of index space point groups which correspond to the Fourier transforms of complex functions with only closed symmetry operators.

## 8. Index space symmetry. The tetragonal system

In this section the method is illustrated by considering the possible weight distributions under operators of the type of equation (10) in the case of tetragonal symmetry of the index space. There are, according to Bravais, two different space lattices in this system. The first is primitive. The second may be either face or body centered, depending on the choice of axes. In order to obtain the normal body-centered setting in physical space, we choose a face-centered setting for the index space, so that $h+k+l=2n$.

The Bravais lattices have holohedral symmetry $4/mmm$, but the distribution of weights can reduce the symmetry of the index space function to that of any of the complex point sub-groups of $4/mmm$ formed by the equation (10) type operators, namely those based on $4mm$, $4/m$, 4, $\bar{4}2m$ and $\bar{4}$.

We begin with the *simplest symmetry*, 4. There is a four-fold axis parallel to the $l$ axis which we denote by the matrix operator $(\alpha)$. Then

$$(\alpha) = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \alpha_{41} & \alpha_{42} & \alpha_{43} & 1 \end{pmatrix}. \tag{11}$$

The generating relation for the class is

$$\begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} = (\alpha)^4 \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} \tag{12}$$

or $(\alpha)^4 = I$ on the index space.

Raising $(\alpha)$ to the fourth power, we obtain the matrix equation

$$\begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} = \begin{pmatrix} I & \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 & 4\alpha_{43} \end{matrix} & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix} \tag{13}$$

or $\varphi = 4\alpha_{43} l + \varphi$, (mod. 1), which implies that

$$4\alpha_{43} l = 0 \pmod 1 . \tag{14}$$

Hence,

$$\alpha_{43} = 0, \tfrac{1}{4}, \tfrac{1}{2}, \tfrac{3}{4} . \tag{15}$$

This is a typical example of the compatibility requirements. They fix the absolute value of certain of the $\alpha$'s. In particular, the order relations always fix the $\alpha$'s corresponding to the directions parallel to rotation axes or mirror planes, and leave the other $\alpha$'s as arbitrary parameters. We shall consider as equivalent all those groups which differ only by the values of such arbitrary parameters. Finally, we note that equation (15) holds in both the primitive and face-centered index space, as $l$ can take on all values in each.

Thus, in the primitive index space there are four complex point groups, corresponding to the four values of $\alpha_{43}$. It should be noted that because the direction of phase changes differs in sign with the sign of $l$, the groups for which $\alpha_{43} = \frac{3}{4}$ cannot be made equivalent to that for which $\alpha_{43} = \frac{1}{4}$. This is not the case in the groups formed of operators of the type of equation (6) in the special case $\alpha_{41} = \alpha_{42} = \alpha_{43} = 0$, $\alpha_{44} = 1$ and $\beta_4 = \frac{1}{4}$ or $\frac{3}{4}$ (i.e., phase changes which are independent of coordinates). Here the two groups are identical and correspond to opposite ways of looking down the $l$-axis. We shall now show that for entirely different reasons, the groups are identical in the face-centered index space. We can write the transformation corresponding to the operator $(\alpha)$ as

$$F(-k, h, l) = F(h, k, l) \exp jl/4$$

for $\alpha_{43} = \frac{1}{4}$. Since $\alpha_{41}$ and $\alpha_{42}$ are arbitrary, we can also write this as

$$F(-k, h, l) = F(h, k, l) \exp j[(h+k)/2 + l/4] .$$

For the centered group, $h+k+l=2n$. When $l=4p+1$, where $p$ is an integer, $h+k$ is odd and we have a phase change equivalent to $\alpha_{43} = \frac{3}{4}$, as $(h+k)/2 = \frac{1}{2}$, (mod. 1). When $l=4p+2$, $(h+k)/2 = 0$, (mod. 1), but $3l/4 = l/4$, (mod. 1). When $l=4p+3$ or $4p$ the situations are exactly the same. Thus the restriction $h+k+l=2n$ makes the group of $\alpha_{43} = \frac{1}{4}$ equivalent to the group of $\alpha_{43} = \frac{3}{4}$. In the same way, $\alpha_{43} = \frac{1}{2}$ is equivalent to $\alpha_{43} = 0$. We have, then, six non-equivalent groups of class 4 in the index space.

*The next crystal class is* $\bar{4}$. This group has a four-fold rotary-inversion axis parallel to $l$, denoted $(\nu)$.

$$(\nu) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ \nu_{41} & \nu_{42} & \nu_{43} & 1 \end{pmatrix}. \tag{15}$$

We require that $(\nu)^4 = I$ on the index space. We find, however, by matrix multiplication, that

$$(\nu)^4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{16}$$

Thus, $\nu_{41}$, $\nu_{42}$, and $\nu_{43}$ are arbitrary parameters and there are two groups in the class, corresponding to the two index spaces.

*In class* $4/m$ we introduce a mirror plane normal to $(\alpha)$, which we denote $(\gamma)$. Then

$$(\gamma) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ \gamma_{41} & \gamma_{42} & \gamma_{43} & 1 \end{pmatrix}. \tag{17}$$

The group has the three generating relations,

$$(\gamma)^2 = \mathrm{I}, \quad (\alpha)(\gamma) = (\gamma)(\alpha), \quad \text{and} \quad (\alpha)^4 = I . \tag{18}$$

The phase relation obtained from $(\gamma)^2 = I$ is

$$2\gamma_{41}h+2\gamma_{42}k=0,\ (\text{mod. } 1)\ . \tag{19}$$

In both spaces this implies

$$\begin{matrix}\gamma_{41}=0 \text{ or } \tfrac{1}{2}\\ \gamma_{42}=0 \text{ or } \tfrac{1}{2}\end{matrix} \tag{20}$$

and $\gamma_{43}$ is arbitrary.

The second generating relation yields the equation

$$\begin{aligned}(\alpha_{41}+\gamma_{41})h+(\alpha_{42}+\gamma_{42})k+(\gamma_{43}-\alpha_{43})l\\ =(\gamma_{42}+\alpha_{41})h+(\alpha_{42}-\gamma_{41})k+(\gamma_{43}+\alpha_{43})l\end{aligned}$$

or

$$(\gamma_{41}-\gamma_{42})h+(\gamma_{41}+\gamma_{42})k-2\alpha_{43}l=0\ . \tag{21}$$

For the primitive lattice this implies

$$\begin{matrix}\alpha_{43}=0 \text{ or } \tfrac{1}{2}\\ \gamma_{41}=\gamma_{42}\ .\end{matrix} \tag{22}$$

It should be noted that the alternative solution, $\gamma_{41}=1-\gamma_{42}$, yields no new information as $\gamma_{42}=0$ or $\frac{1}{2}$. For the centered lattice we can have either equation (22) holding or

$$\alpha_{43}=\tfrac{1}{4} \text{ or } \tfrac{3}{4} \tag{23a}$$

$$\begin{matrix}\gamma_{41}=0,\ \gamma_{42}=\tfrac{1}{2}\\ \gamma_{41}=\tfrac{1}{2},\ \gamma_{42}=0\ .\end{matrix} \tag{23b}$$

Since the $h$ and $k$ axes are identical, the two situations described in equation (23$b$) are equivalent.

This example also shows how the existence of a smaller number of index space points on which the compatibility relations must hold allows operator combinations which are inconsistent with a primitive index space. Then, for the primitive lattice, the possible combinations of determined parameters are listed in Table 1.

Table 1. *Allowed groups, class* $4/m$*, primitive index space*

| $\alpha_{43}$ | $\gamma_{41}=\gamma_{42}$ | Space group |
|---|---|---|
| 0 | 0 | $P4/m$ |
| 0 | $\frac{1}{2}$ | $P4/n$ |
| $\frac{1}{2}$ | 0 | $P4_2/m$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | $P4_2/n$ |

For the centered index space, the possible combinations are listed in Table 2.

Table 2. *Allowed groups, class* $4/m$*, face-centered index space*

| $\alpha_{43}$ | $\gamma_{41}$ | $\gamma_{42}$ | Space group |
|---|---|---|---|
| 0 | 0 | 0 | $I4/m$ |
| $\frac{1}{2}$ | 0 | 0 | |
| 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | |
| $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | |
| $\frac{1}{4}$ | $\frac{1}{2}$ | 0 | $I4_1/a$ |
| $\frac{3}{4}$ | $\frac{1}{2}$ | 0 | |

However, examining Table 2 we find that the first and second, third and fourth, and fifth and sixth sets of values are equivalent, respectively, for the same reasons that the axes were equivalent in the face-centered groups of class 4. In addition, using the first set of values we have

$$F(h,\ k,\ -l)=F(h,\ k,\ l) \tag{24}$$

while the third set gives the relation

$$F(h,\ k,\ -l)=F(h,\ k,\ l)\exp\left[j(h+k)/2\right]\ . \tag{25}$$

We note that $\gamma_{43}$ is arbitrary. Setting $\gamma_{43}=\frac{1}{2}$ in the third set, equation (25) becomes

$$F(h,\ k,\ -l)=F(h,\ k,\ l)\exp\left[j(h+k+l)/2\right]=F(h,\ k,\ l) \tag{26}$$

as $(h+k+l)=2n$. Thus, the independent groups are the first and fifth, all others being equivalent to these.

We now examine the *class* $4mm$. In addition to $(\alpha)$ we have the mirror planes given by

$$(\delta)=\begin{pmatrix}\bar{1} & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ \delta_{41} & \delta_{42} & \delta_{43} & 1\end{pmatrix}\quad(\varepsilon)=\begin{pmatrix}0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 1 & 0\\ \varepsilon_{41} & \varepsilon_{42} & \varepsilon_{43} & 1\end{pmatrix} \tag{27}$$

and the generating relations

$$(\alpha)^4=(\delta)^2=(\varepsilon)^2=I\ , \tag{28}$$

$$(\alpha)(\delta)=(\delta)(\alpha)^3=(\varepsilon)\ . \tag{29}$$

$(\delta)^2=I$ implies that

$$2(\delta_{42}k+\delta_{43}l)=0,\ (\text{mod. } 1) \tag{30}$$

while $(\varepsilon)^2=I$ requires

$$(\varepsilon_{41}+\varepsilon_{42})(h+k)+2\varepsilon_{43}l=0,\ (\text{mod. } 1)\ . \tag{31}$$

Finally, the condition that $(\alpha)(\delta)=(\varepsilon)$ yields

$$\begin{aligned}(\delta_{41}-\alpha_{41}-\varepsilon_{41})h+(\delta_{42}+\alpha_{42}-\varepsilon_{42})k\\ +(\delta_{43}+\alpha_{43}-\varepsilon_{43})l=0,\ (\text{mod. } 1)\ .\end{aligned} \tag{32}$$

In the primitive index space, equations (30) and (31) imply that

$$\begin{matrix}\delta_{42}=0,\ \tfrac{1}{2}\\ \delta_{43}=0,\ \tfrac{1}{2}\\ \varepsilon_{42}=0,\ \tfrac{1}{2}\\ \varepsilon_{41}=\varepsilon_{42}\ .\end{matrix} \tag{33}$$

Finally, the coefficient of $l$ in equation (32) combined with equation (23) implies that $\alpha_{43}$ cannot be $\frac{1}{4}$ or $\frac{3}{4}$, but that

$$\alpha_{43}=0,\ \tfrac{1}{2}\ . \tag{34}$$

Table 3. *Allowed groups, class* $4mm$*, primitive index space*

| $\alpha_{43}$ | $\delta_{42}$ | $\delta_{43}$ | $\varepsilon_{43}$ | Space group |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | $P4mm$ |
| 0 | $\frac{1}{2}$ | 0 | 0 | $P4bm$ |
| $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | 0 | $P4_2cm$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | $P4_2nm$ |
| 0 | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | $P4cc$ |
| 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $P4nc$ |
| $\frac{1}{2}$ | 0 | 0 | $\frac{1}{2}$ | $P4_2mc$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | $P4_2bc$ |

We thus have four parameters which can take on the values 0 or $\frac{1}{2}$. The possible combinations of these parameters are those which fulfill equation (32). These are listed in Table 3. We also note that although the parameters $\delta_{41}$, $\alpha_{41}$, $\alpha_{42}$, $\varepsilon_{41}$, and $\varepsilon_{42}$ are not absolutely determined, their relative values are fixed.

In the face-centered index space, in addition to the possibilities listed above, equation (31) admits the solution

$$\varepsilon_{43}=\tfrac{1}{4},\ \tfrac{3}{4} \tag{35a}$$

and

$$\varepsilon_{41}=\varepsilon_{42}=\tfrac{1}{4}\ \text{or}\ \tfrac{3}{4}\,. \tag{35b}$$

With $\varepsilon_{43}=\frac{1}{4}$ or $\frac{3}{4}$, the third term of equation (32) combined with equation (30) implies that $\alpha_{43}=\frac{1}{4}$ or $\frac{3}{4}$. Under these restrictions, some 30 combinations of parameters are possible. Of these, only four are independent. These are listed in Table 4. It should be noted that the mirror planes for which $\alpha_{41}$, $\alpha_{42}$, and $\alpha_{43}$ are all $\frac{1}{4}$, rather than the usual 0 or $\frac{1}{2}$, are a new phenomenon which appears only for the diagonally placed mirror plane in the centered index space. This crystal class is the first in which the relative values of the otherwise arbitrary parameters are determined.

Table 4. *Allowed independent groups, class 4mm, face-centered index space*

| $\alpha_{43}$ | $\delta_{42}$ | $\delta_{43}$ | $\varepsilon_{43}$ | $\varepsilon_{41}=\varepsilon_{42}$ | Space group |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | $I4mm$ |
| $\frac{1}{4}$ | 0 | 0 | $\frac{1}{4}$ | $\frac{1}{4}$ | $I4_1md$ |
| $\frac{1}{4}$ | 0 | $\frac{1}{2}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | $I4_1cd$ |
| 0 | 0 | $\frac{1}{2}$ | 0 | 0 | $I4cm$ |

The groups which we have derived thus far illustrate all the phenomena which are encountered in a complete derivation of the groups formed by operators of the type of equation (10). To avoid repetition, we leave the remainder of the groups unlisted.

## 9. Physical interpretation of the index-space point groups

It has been shown, thus far, that there exists a set of operators which express the possible linear point symmetries of a complex function defined on an index space. These operators form complex point groups on the index space. By restricting the operators to be compatible with hermitian symmetry and to contain no index-independent phase transformations the symmetries of the point groups must be those of the structure factors, since these are the Fourier transforms of positive real, *periodic* functions. The more general operators express the symmetry properties of the structure factors belonging to black-white, colored, or complex space groups.

We now examine in greater detail some further aspects of the duality between physical and Fourier Index space. We begin with equation (6). This equation states, choosing $\alpha_{44}=+1$, that

$$F(R_p\mathbf{K})=F(\mathbf{K})\exp\left[j(\alpha_{41}h+\alpha_{42}k+\alpha_{43}l)+j\beta_4\right] \tag{36}$$

where $\mathbf{K}=(h,k,l)$. $F(\mathbf{K})$ is the coefficient in the Fourier series which describes the complex function $\varrho(x,y,z)$ or $\varrho(\mathbf{r})$. Hence

$$\varrho(\mathbf{r})=\Sigma_{\mathbf{K}}F(\mathbf{K})\exp j(\mathbf{K}.\mathbf{r})\,. \tag{37}$$

This can also be written, by a change of the order of summation, as

$$\begin{aligned}\varrho(\mathbf{r})&=\Sigma_{\mathbf{K}}F(R_p\mathbf{K})\exp j(R_p\mathbf{K}.\mathbf{r})\\&=\Sigma_{\mathbf{K}}F(R_p\mathbf{K})\exp j(R_p^{-1}R_p\mathbf{K}.R_p^{-1}\mathbf{r})\end{aligned}$$

as the scalar product is invariant under such a transformation. Furthermore, using equation (36),

$$\varrho(\mathbf{r})=\Sigma_{\mathbf{K}}F(\mathbf{K})\exp\left\{j[(\mathbf{K}.R_p^{-1}\mathbf{r})+\mathbf{K}.\alpha+\beta_4]\right\}$$

where $\alpha=(\alpha_{41},\alpha_{42},\alpha_{43})$. Hence,

$$\varrho(\mathbf{r})=\exp(j\beta_4)\Sigma_{\mathbf{K}}F(\mathbf{K})\exp\left[j\mathbf{K}.(R_p^{-1}\mathbf{r}+\alpha)\right].$$

But, examining equation (37), we find that this implies

$$\varrho(\mathbf{r})=\exp(j\beta_4)\varrho(R_p^{-1}\mathbf{r}+\alpha)\,. \tag{38}$$

Thus, for each symmetry operator in Fourier space there is a complex symmetry operator in physical space. The physical space operator is a space group operator, in general, as $\alpha$ represents it translational part. Thus the groups derived and listed in the tables bear a one-to-one correspondence to the Schoenflies–Federov space groups. For this reason, the tables contain the space group symbol. We have found that when $\beta_4=0$, the condition that the Index space operators be of the same order as $R_p$ leads to restrictions on the components of $\alpha$ parallel to the operator. These are just the conditions for the glide elements to be some multiple of $1/n$, e.g., that a four-fold screw axis have a pitch of 1, 2, or 3 quarters of an identity period. This rule was broken by the diagonal mirror plane of $4mm$ in the centered index space. Here there could be $\alpha_{41}=\alpha_{42}=\alpha_{43}=\frac{1}{4}$. This is because the $d$ glide is an allowed operation in the body-centered physical space. What we have termed the arbitrary components of $\alpha$ correspond to translation portions of the physical space operator which arise from the displacement of the operator from the origin. In space groups where the relative positions of the operators remain arbitrary, such as $4/m$, these components of $\alpha$ remain arbitrary. In a group where the relative positions of the operators are fixed, as, for example, in class $4mm$ where the positions of the four-fold axis relative to the intersection of the mirror planes is determined by space group consistency relations, we have conditions in Fourier space which fix the relative values of the corresponding components of $\alpha$.

Similarly, the properties (i) and (ii) listed in the section Index-Space Point Groups correspond to a center of symmetry in physical space forcing the structure factor to be real. Property (iv) is a representation of the fact that screw axes and glide planes lead to systematic absences in the index space.

We have noted that if $\beta_4=0$ or $\frac{1}{2}$, the symmetry operator (6) represents the symmetry of a real function. The groups of such operators are the structure factor symmetry groups corresponding to the black-white groups.

With $\beta_4$ free to take on all values permitted by the compatibility relations, we have, as demonstrated by equation (37), the index-space analogues of the possible groups in which the phase change in independent of the coordinates. These groups have, in general, restrictions which do not appear with the other groups. That is, they require the vanishing of the function on planes of non-invariant points. Consider an $n$-fold axis parallel to $l$ in index space and denoted by $(\alpha_n)$. Then

$$(\alpha_n)=\begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \alpha_{41} & \alpha_{42} & \alpha_{43} & 1 \end{pmatrix}+\begin{pmatrix} 0 \\ 0 \\ 0 \\ \beta_4 \end{pmatrix}. \quad (39)$$

Raising this operator to the $n$th power we get

$$(\alpha_n)^n=\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & n\alpha_{43} & 1 \end{pmatrix}+\begin{pmatrix} 0 \\ 0 \\ 0 \\ n\beta_4 \end{pmatrix}. \quad (40)$$

Then

$$(n\alpha_{43})l+n\beta_4=0, \text{ (mod. 1)}. \quad (41)$$

In discussing this equation, we have to distinguish two cases:

(*a*) The equation is to be fulfilled for all values of $l$. It then shows (for $l=0$) that $\beta_4=s/n$, where $s$ is any integer, and, by forming the difference of the conditions for $l$ and $l+1$, that $\alpha_{43}=q/n$, with $q$ an integer. These solutions give the normal screw axes with phase change. Similarly, complex glide mirror planes are obtained.

(*b*) The equation is to be fulfilled only on an equidistant set of planes. This is the case if $F(h, k, l)=0$ for all values $l\neq L_t$, where $L_t=tl+L_0$ ($t$, $L_0$ integers). The same procedure as before now determines $\alpha_{43}$ and $\beta_4$ as

$$\alpha_{43}=q'/tn, \quad \beta_4=s'/n-L_0\alpha_{43}, \quad (42)$$

where $q'$ and $s'$ are arbitrary integers, and $t$ and $L_0$ assumed integers. These values of the coefficients describe 'open' complex screw axes. If $c$ is the identity period which would be obtained with the 'closed' operation of an $n$-fold screw axis, the 'open' operator characterized by (42) yields, after $n$-fold application, the glide $c/t$ and phase shift $-L_0q'/t$. The true identity period is therefore $tc$ and the order of the operator $tn$.

There are apparently two types of operators on complex physical-space functions which have not appeared in the index-space formalism. The first is complex conjugation. Equation (6), with $\alpha_{44}=-1$ states

$$F(R_p\mathbf{K})=F^*(\mathbf{K})\exp[j(\alpha.\mathbf{K}+\beta_4)]. \quad (44)$$

Writing

$$\varrho(\mathbf{r})=\Sigma_{\mathbf{K}}F(R_p\mathbf{K})\exp[j(R_p\mathbf{K}.\mathbf{r})]$$

we have

$$\varrho(\mathbf{r})=\Sigma_{\mathbf{K}}F^*(\mathbf{K})\exp\{j[\mathbf{K}.(R_p^{-1}\mathbf{r}+\alpha)+\beta_4]\}$$

or

$$\varrho(\mathbf{r})=\exp(j\beta_4)\varrho^*(\overline{R_p}\mathbf{r}-\alpha), \quad (45)$$

where $\overline{R_p}$ is the product of the inversion and $R_p^{-1}$. It follows that a set of complex point groups can be constructed in index space for which $\alpha_{44}=-1$, and where the corresponding physical space groups have crystal classes which are determined by $\overline{R_p}$ rather than by $R_p$.

The second type of complex space groups which do not appear to have Fourier space analogues are those in which the operators have phase transformations which vary with the coordinates. We have shown that such an operation in the index space implies a translational component in physical space. It follows that the Fourier space analogues of such physical space groups are the above-derived index space point groups consistently displaced from the origin. By consistently, we mean that they leave the Bravais lattice invariant and can still obey the compatibility relations. The simplest example of this is the mirror operator normal to $h$ displaced $n/2$ from the origin in the $h$ direction. The matrix representation of this is

$$\begin{pmatrix} h' \\ k' \\ l' \\ \varphi' \end{pmatrix}=\begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} h \\ k \\ l \\ \varphi \end{pmatrix}-\begin{pmatrix} n \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (46)$$

or

$$F(\overline{h+n}, k, l)=F(h, k, l) \quad (47)$$

which implies

$$\varrho(x, y, z)=\varrho(\bar{x}, y, z)\exp(jnx). \quad (48)$$

For $n$ odd we have the operators discussed immediately after equation (3) for which $F(\frac{1}{2}, y, z)=0$, while for $n$ even this requirement need not hold.

Other types of combinations of operators appear to be possible forms for the index space symmetry corresponding to the last-named groups. An example is a group in which the four-fold axis is separated from the intersection of the mirror planes in an index-space group of the form $4mm$. It is easily shown, however, that such a configuration generates periodicity in the index space and thus robs physical space of its continuity in one or more directions.

## 10. Duality of index space and physical space

The results of the work may be summarized as follows. There is an exact correspondence between

point groups in physical and Fourier space under the following condition. The physical space point group has no phase changes which are a function of coordinates. A space group isomorphous with a point group also yields this point group as the index space symmetry. Translations introduced in one space imply, in the other, phase factors which are linear functions of the coordinates.

There is a special type of physical space structure in which the groups possible in the two spaces become identical. Consider the case in which the physical space structure consists of complex point masses located at points which are rational fractions of the repeat distances. The complex density can be written

$$\varrho(\mathbf{r}) = \Sigma_p g(\mathbf{p}) \delta(\mathbf{r}-\mathbf{p}) \tag{47}$$

where $\delta(\mathbf{r}-\mathbf{p})$ is the Dirac delta function and

$$\mathbf{p} = (p_1/n_1, p_2/n_2, p_3/n_3), \text{ with } p_i = 0, 1, 2, \ldots, n_i. \tag{48}$$

Then

$$\begin{aligned} F(\mathbf{K}) &= \int \Sigma_p g(\mathbf{p}) \delta(\mathbf{r}-\mathbf{p}) \exp(-j\mathbf{K}.\mathbf{r}) dV \\ &= \Sigma_p (g(\mathbf{p}) \exp(-j\mathbf{K}.\mathbf{p}) . \end{aligned} \tag{49}$$

In this case Fourier space is periodic with repeat distances $(n_1, n_2, n_3)$. Similarly, with the simple rescaling of coordinates, $x_i' = n_i x_i$, physical space becomes an index space in the sense in which we have defined it. The two spaces are both periodic index spaces of complex functions and must have the same symmetry groups. The Fourier space symmetry group corresponding to a given physical space group is not, of course, identical to that physical space groups, but the sets of possible groups are identical.

Still another interesting limit exists. This is the transition from an index space to a continuous Fourier space. It can be shown, as a generalization of the discussion of equation (1) in section 2, that only the parameters called arbitrary, i.e. those which do not enter into the order equation can be non-zero. This is because the order equation cannot hold otherwise in a continuous space. We know that the non-arbitrary parameters correspond to glide elements which generate infinite periodicity in one or more directions. Thus, the existence of a continuous Fourier space rules out those Fourier space operators which correspond to operators in physical space which generate infinite periodicity.

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# The Crystal Structure of the Low-Melting Form of Oleic Acid


BY SIXTEN ABRAHAMSSON AND INGER RYDERSTEDT-NAHRINGBAUER

*Crystallography Group, Institute of Medical Biochemistry, University of Göteborg and Institute of Chemistry, University of Uppsala, Sweden*


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The low-melting form of oleic acid is pseudoorthorhombic with $a = 9{\cdot}51$, $b = 4{\cdot}74$ and $c = 40{\cdot}6$ Å. The space group is $P2_1/a$ and there are four molecules per cell. The molecules are bent at the *cis*-double bond. The two chain parts have the usual planar zig-zag conformation and adopt a side packing $0'$ || not previously found in long-chain compounds. The chain axes of the two parts have equal angles of tilt (56·5°) to the (001) planes but are tilted in opposite directions. The acid dimers are held together by hydrogen bonds (2·64 Å) around centres of symmetry and form a layer structure normal for long-chain compounds.


## Introduction

It has long been known (Kirschner, 1912) that oleic acid is dimorphous. Several observations of two melting points have been reported; Lutton (1946) gives the values 13·3° and 16·2°. He investigated the X-ray powder patterns of the two forms and reported the long spacing, $d(001)$, values of 40·5 Å and 42·2 (84·4) Å respectively.

The only single-crystal data given for unsaturated