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Seminvariants for Centrosymmetric Space Groups with Conventional Centered Cells

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The nature of the dependence of phase on the choice of origin is clarified for those centrosymmetric space groups, for which the conventional unit cell is not primitive, by means of special linear combinations of the phases, the structure seminvariants. The theory leads to simple procedures for selecting the origin by first fixing the functional form for the structure factor and then specifying arbitrarily the values of a suitable set of phases.

1. Introduction

The development of formulas for the determination of the values of phases directly from observed intensities makes necessary a study of the relationship of phase to the specification of origin. This problem has already been treated for those centrosymmetric and

Table 1. *Coordinates for centered centrosymmetric space groups referred to a primitive unit cell*

Space group	Coordinates (+ and −)			
$C2/m$	x, y, z	y, x, z		
$C2/c$	x, y, z	$y, x, z+\frac{1}{2}$		
$Cmcm$	x, y, z	$y, x, z+\frac{1}{2}$	$y, x, \bar{z}$	$x, y, \bar{z}+\frac{1}{2}$
$Cmca$	x, y, z	$y, x, z+\frac{1}{2}$	$y+\frac{1}{2}, x+\frac{1}{2}, \bar{z}$	$x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$
$Cmmm$	x, y, z	y, x, z	$y, x, \bar{z}$	$x, y, \bar{z}$
$Cccm$	x, y, z	$y, x, z+\frac{1}{2}$	$y, x, \bar{z}+\frac{1}{2}$	$x, y, \bar{z}$
$Cmma$	x, y, z	y, x, z	$y+\frac{1}{2}, x+\frac{1}{2}, \bar{z}$	$x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$
$Ccca$	x, y, z	$y, x, z+\frac{1}{2}$	$y+\frac{1}{2}, x+\frac{1}{2}, \bar{z}+\frac{1}{2}$	$x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$
$Fmmm$	x, y, z	$x+y+z, \bar{z}, \bar{y}$	$\bar{z}, x+y+z, \bar{x}$	$\bar{y}, \bar{x}, x+y+z$
$Fddd$	x, y, z	$x+y+z+\frac{1}{2}, \bar{z}, \bar{y}$	$\bar{z}, x+y+z+\frac{1}{2}, \bar{x}$	$\bar{y}, \bar{x}, x+y+z+\frac{1}{2}$
$Fm3$	x, y, z z, x, y y, z, x	$x+y+z, \bar{z}, \bar{y}$ $x+y+z, \bar{y}, \bar{x}$ $x+y+z, \bar{x}, \bar{z}$	$\bar{z}, x+y+z, \bar{x}$ $\bar{y}, x+y+z, \bar{z}$ $\bar{x}, x+y+z, \bar{y}$	$\bar{y}, \bar{x}, x+y+z$ $\bar{x}, \bar{z}, x+y+z$ $\bar{z}, \bar{y}, x+y+z$
$Fd3$	x, y, z z, x, y y, z, x	$x+y+z+\frac{1}{2}, \bar{z}, \bar{y}$ $x+y+z+\frac{1}{2}, \bar{y}, \bar{x}$ $x+y+z+\frac{1}{2}, \bar{x}, \bar{z}$	$\bar{z}, x+y+z+\frac{1}{2}, \bar{x}$ $\bar{y}, x+y+z+\frac{1}{2}, \bar{z}$ $\bar{x}, x+y+z+\frac{1}{2}, \bar{y}$	$\bar{y}, \bar{x}, x+y+z+\frac{1}{2}$ $\bar{x}, \bar{z}, x+y+z+\frac{1}{2}$ $\bar{z}, \bar{y}, x+y+z+\frac{1}{2}$
$Fm3m$	coordinates of $Fm3$ +			
	x, z, y y, x, z z, y, x	$x+y+z, \bar{y}, \bar{z}$ $x+y+z, \bar{z}, \bar{x}$ $x+y+z, \bar{x}, \bar{y}$	$\bar{y}, x+y+z, \bar{x}$ $\bar{z}, x+y+z, \bar{y}$ $\bar{x}, x+y+z, \bar{z}$	$\bar{z}, \bar{x}, x+y+z$ $\bar{x}, \bar{y}, x+y+z$ $\bar{y}, \bar{z}, x+y+z$
$Fm3c$	coordinates of $Fm3$ +			
	$x+\frac{1}{2}, z+\frac{1}{2}, y+\frac{1}{2}$ $y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}$ $z+\frac{1}{2}, y+\frac{1}{2}, x+\frac{1}{2}$	$x+y+z+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}+\frac{1}{2}$ $x+y+z+\frac{1}{2}, \bar{z}+\frac{1}{2}, \bar{x}+\frac{1}{2}$ $x+y+z+\frac{1}{2}, \bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}$	$\bar{y}+\frac{1}{2}, x+y+z+\frac{1}{2}, \bar{x}+\frac{1}{2}$ $\bar{z}+\frac{1}{2}, x+y+z+\frac{1}{2}, \bar{y}+\frac{1}{2}$ $\bar{x}+\frac{1}{2}, x+y+z+\frac{1}{2}, \bar{z}+\frac{1}{2}$	$\bar{z}+\frac{1}{2}, \bar{x}+\frac{1}{2}, x+y+z+\frac{1}{2}$ $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, x+y+z+\frac{1}{2}$ $\bar{y}+\frac{1}{2}, \bar{z}+\frac{1}{2}, x+y+z+\frac{1}{2}$
$Fd3m$	coordinates of $Fd3$ +			
	x, z, y y, x, z z, y, x	$x+y+z+\frac{1}{2}, \bar{y}, \bar{z}$ $x+y+z+\frac{1}{2}, \bar{z}, \bar{x}$ $x+y+z+\frac{1}{2}, \bar{x}, \bar{y}$	$\bar{y}, x+y+z+\frac{1}{2}, \bar{x}$ $\bar{z}, x+y+z+\frac{1}{2}, \bar{y}$ $\bar{x}, x+y+z+\frac{1}{2}, \bar{z}$	$\bar{z}, \bar{x}, x+y+z+\frac{1}{2}$ $\bar{x}, \bar{y}, x+y+z+\frac{1}{2}$ $\bar{y}, \bar{z}, x+y+z+\frac{1}{2}$
$Fd3c$	coordinates of $Fd3$ +			
	$x+\frac{1}{2}, z+\frac{1}{2}, y+\frac{1}{2}$ $y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}$ $z+\frac{1}{2}, y+\frac{1}{2}, x+\frac{1}{2}$	$x+y+z, \bar{y}+\frac{1}{2}, \bar{z}+\frac{1}{2}$ $x+y+z, \bar{z}+\frac{1}{2}, \bar{x}+\frac{1}{2}$ $x+y+z\ \bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}$	$\bar{y}+\frac{1}{2}, x+y+z, \bar{x}+\frac{1}{2}$ $\bar{z}+\frac{1}{2}, x+y+z, \bar{y}+\frac{1}{2}$ $\bar{x}+\frac{1}{2}, x+y+z, \bar{z}+\frac{1}{2}$	$\bar{z}+\frac{1}{2}, \bar{x}+\frac{1}{2}, x+y+z$ $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, x+y+z$ $\bar{y}+\frac{1}{2}, \bar{z}+\frac{1}{2}, x+y+z$

Table 1 (*cont.*)

Space group	Coordinates (+ and −)			
Immm	x, y, z	$\bar{x}, \bar{x}+z, \bar{x}+y$	$\bar{y}+z, \bar{y}, x+\bar{y}$	$y+\bar{z}, x+\bar{z}, \bar{z}$
Ibam	x, y, z	$\bar{x}+\frac{1}{2}, \bar{x}+z+\frac{1}{2}, \bar{x}+y$	$\bar{y}+z+\frac{1}{2}, \bar{y}+\frac{1}{2}, x+\bar{y}$	$y+\bar{z}, x+\bar{z}, \bar{z}$
Ibca	x, y, z	$\bar{x}+\frac{1}{2}, \bar{x}+z+\frac{1}{2}, \bar{x}+y$	$\bar{y}+z, \bar{y}+\frac{1}{2}, x+\bar{y}+\frac{1}{2}$	$y+\bar{z}+\frac{1}{2}, x+\bar{z}, \bar{z}+\frac{1}{2}$
Imma	x, y, z	$\bar{x}, \bar{x}+z, \bar{x}+y$	$\bar{y}+z+\frac{1}{2}, \bar{y}, x+\bar{y}+\frac{1}{2}$	$y+\bar{z}+\frac{1}{2}, x+\bar{z}, \bar{z}+\frac{1}{2}$
*I*4/*m*	x, y, z	$x+\bar{z}, x, x+\bar{y}$	$y, y+\bar{z}, \bar{x}+y$	$\bar{y}+z, \bar{x}+z, z$
$I4_1/a$	x, y, z	$x+\bar{z}, x, x+\bar{y}+\frac{1}{2}$	$y, y+\bar{z}+\frac{1}{2}, \bar{x}+y$	$\bar{y}+z+\frac{1}{2}, \bar{x}+z, z+\frac{1}{2}$
*I*4/*mmm*	x, y, z y, x, z	$x+\bar{z}, x, x+\bar{y}$ $x, x+\bar{z}, x+\bar{y}$	$y, y+\bar{z}, \bar{x}+y$ $y+\bar{z}, y, \bar{x}+y$	$\bar{y}+z, \bar{x}+z, z$ $\bar{x}+z, \bar{y}+z, z$
*I*4/*mcm*	x, y, z $y+\frac{1}{2}, x+\frac{1}{2}, z$	$x+\bar{z}, x, x+\bar{y}$ $x+\frac{1}{2}, x+\bar{z}+\frac{1}{2}, x+\bar{y}$	$y, y+\bar{z}, \bar{x}+y$ $y+\bar{z}+\frac{1}{2}, y+\frac{1}{2}, \bar{x}+y$	$\bar{y}+z, \bar{x}+z, z$ $\bar{x}+z+\frac{1}{2}, \bar{y}+z+\frac{1}{2}, z$
$I4_1/amd$	x, y, z $y, x, z+\frac{1}{2}$	$x+\bar{z}, x, x+\bar{y}+\frac{1}{2}$ $x, x+\bar{z}, x+\bar{y}$	$y, y+\bar{z}+\frac{1}{2}, \bar{x}+y$ $y+\bar{z}+\frac{1}{2}, y, \bar{x}+y+\frac{1}{2}$	$\bar{y}+z+\frac{1}{2}, \bar{x}+z, z+\frac{1}{2}$ $\bar{x}+z, \bar{y}+z+\frac{1}{2}, z$
$I4_1/acd$	x, y, z $y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}$	$x+\bar{z}, x, x+\bar{y}+\frac{1}{2}$ $x+\frac{1}{2}, x+\bar{z}+\frac{1}{2}, x+\bar{y}$	$y, y+\bar{z}+\frac{1}{2}, \bar{x}+y$ $y+\bar{z}, y+\frac{1}{2}, \bar{x}+y+\frac{1}{2}$	$\bar{y}+z+\frac{1}{2}, \bar{x}+z, z+\frac{1}{2}$ $\bar{x}+z+\frac{1}{2}, \bar{y}+z, z$
*Im*3	x, y, z z, x, y y, z, x	$x, x+\bar{z}, x+\bar{y}$ $z, \bar{y}+z, \bar{x}+z$ $y, \bar{x}+y, y+\bar{z}$	$y+\bar{z}, y, \bar{x}+y$ $x+\bar{y}, x, x+\bar{z}$ $\bar{x}+z, z, \bar{y}+z$	$\bar{y}+z, \bar{x}+z, z$ $\bar{x}+y, y+\bar{z}, y$ $x+\bar{z}, x+\bar{y}, x$
*Ia*3	x, y, z z, x, y y, z, x	$x+\frac{1}{2}, x+\bar{z}+\frac{1}{2}, x+\bar{y}$ $y+\frac{1}{2}, \bar{y}+z+\frac{1}{2}, \bar{x}+z$ $z+\frac{1}{2}, \bar{x}+y+\frac{1}{2}, y+\bar{z}$	$y+\bar{z}, y+\frac{1}{2}, \bar{x}+y+\frac{1}{2}$ $x+\bar{y}, x+\frac{1}{2}, x+\bar{z}+\frac{1}{2}$ $\bar{x}+z, z+\frac{1}{2}, \bar{y}+z+\frac{1}{2}$	$\bar{y}+z+\frac{1}{2}, \bar{x}+z, z+\frac{1}{2}$ $\bar{x}+y+\frac{1}{2}, y+\bar{z}, y+\frac{1}{2}$ $x+\bar{z}+\frac{1}{2}, x+\bar{y}, x+\frac{1}{2}$
*Im*3*m*	coordinates of *Im*3 +			
	x, z, y z, y, x y, x, z	$x, x+\bar{y}, x+\bar{z}$ $z, \bar{x}+z, \bar{y}+z$ $y, y+\bar{z}, \bar{x}+y$	$\bar{y}+z, z, \bar{x}+z$ $\bar{x}+y, y, y+\bar{z}$ $x+\bar{z}, x, x+\bar{y}$	$y+\bar{z}, \bar{x}+y, y$ $x+\bar{y}, x+\bar{z}, x$ $\bar{x}+z, \bar{y}+z, z$
*Ia*3*d*	coordinates of *Ia*3 +			
	$x+\frac{1}{2}, z+\frac{1}{2}, y+\frac{1}{2}$ $z+\frac{1}{2}, y+\frac{1}{2}, x+\frac{1}{2}$ $y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2}$	$x, x+\bar{y}+\frac{1}{2}, x+\bar{z}$ $z, \bar{x}+z+\frac{1}{2}, \bar{y}+z$ $y, y+\bar{z}+\frac{1}{2}, \bar{x}+y$	$\bar{y}+z, z, \bar{x}+z+\frac{1}{2}$ $\bar{x}+y, y, y+\bar{z}+\frac{1}{2}$ $x+\bar{z}, x, x+\bar{y}+\frac{1}{2}$	$y+\bar{z}+\frac{1}{2}, \bar{x}+y, y$ $x+\bar{y}+\frac{1}{2}, x+\bar{z}, x$ $\bar{x}+z+\frac{1}{2}, \bar{y}+z, z$

non-centrosymmetric space groups for which the conventional unit cell is primitive (Hauptman & Karle, 1953, 1956). It was seen there that certain linear combinations of the phases, called the structure seminvariants, played a central role. The seminvariants show which phases are uniquely determined by the intensities alone and which are to be specified in order to fix the origin.

In this paper we are concerned with those centrosymmetric space groups for which the conventional unit cell is non-primitive. The treatment here involves the use of well-known transformations to replace the conventional centered cell by an appropriate primitive unit cell. The methods referred to above are then immediately applicable. If desired, the final results may be readily expressed in terms of the conventional cell by means of appropriate transformations.

2. Primitive unit cells

The coordinates representing the space group relative to a primitive unit cell are obtained from those corresponding to a non-primitive unit cell (*International Tables*, 1952) by means of the following matrices:

$$C \rightarrow P, \quad \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{2·1}$$

$$I \rightarrow P, \quad \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \tag{2·2}$$

and

$$F \rightarrow P, \quad \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}. \tag{2·3}$$

The results are shown in Table 1. For some of the space groups the origin has been shifted to exhibit the relationship between group and subgroup.

3. Equivalence

For the centrosymmetric space groups, the permissible origins are the eight centers of symmetry in the primitive unit cell. However, not all of these need be equivalent, since different centers of symmetry may be situated differently with respect to the symmetry elements. The non-equivalent origins are associated with different functional forms for the structure

Table 2. *Equivalence classes, seminvariant vectors and seminvariant moduli for the centered centrosymmetric space groups, referred to a primitive unit cell*

Category	2		3		4
No. of equivalence classes	2		4		8
Type	$2P$	$2P_1$	$3P_2$	$3P_3$	$4P$
Space groups	$C2/m$ $C2/c$ $Cmcm$ $Cmca$ $Cmmm$ $Cccm$ $Cmma$ $Ccca$	$Immm$ $Ibam$ $Ibca$ $Imma$	$Fmmm$ $Fddd$ $Fm3$ $Fd3$ $Fm3m$ $Fm3c$ $Fd3m$ $Fd3c$	$I4/m$ $I4_1/a$ $I4/mmm$ $I4/mcm$ $I4_1/amd$ $I4_1/acd$	$Im3$ $Ia3$ $Im3m$ $Ia3d$
Equivalence classes of origins	0, 0, 0 0, 0, ½ ½, ½, 0 ½, ½, ½ ½, 0, 0 ½, 0, ½ 0, ½, 0 0, ½, ½	0, 0, 0 ½, ½, 0 ½, 0, ½ 0, ½, ½ ½, 0, 0 0, ½, 0 0, 0, ½ ½, ½, ½	0, 0, 0 ½, ½, ½ ½, 0, 0 0, ½, ½ 0, ½, 0 ½, 0, ½ 0, 0, ½ ½, ½, 0	0, 0, 0 ½, ½, 0 ½, 0, 0 0, ½, 0 0, 0, ½ ½, ½, ½ ½, 0, ½ 0, ½, ½	0, 0, 0 ½, 0, 0 0, ½, 0 0, 0, ½ ½, ½, 0 ½, 0, ½ 0, ½, ½ ½, ½, ½
Seminvariant vector, $\mathbf{h}_s$, referred to primitive cell	$(h+k, l)$	$(h+k, k+l, l+h)$	$(h+k+l)$	$(h+k)$	(h, k, l)
Seminvariant modulus, ω_s	(2, 2)	(2, 2, 2)	(2)	(2)	(1, 1, 1)
No. of phases linearly semi-independent to be specified arbitrarily	2	2	1	1	0

factors. This leads logically to the concept of equivalence. Two origins are said to be equivalent if they are geometrically related in the same way to all the symmetry elements or, alternatively, if they lead to the same functional form for the structure factor. In this way the set of eight permissible origins is divided into one or more equivalence classes; two origins in the same class being equivalent, while no two origins taken from different classes are equivalent. According as the number of equivalence classes is one, two, four or eight, the corresponding space group is said to be in category one, two, three or four. The various categories may be further subdivided as to type depending upon the nature of the equivalence classes (Table 2).

4. Seminvariance

Once a functional form for the structure factor has been chosen, i.e. a particular equivalence class has been selected, then the values of certain linear combinations of the phases are determined by the crystal structure, or, for centrosymmetric structures, by the observed intensities (independently of the choice of origin within the particular equivalence class). These linear combinations of the phases are called the structure seminvariants (Hauptman & Karle, 1953, 1956). The aims of this paper are attained with the identification of the structure seminvariants for each space group. To this end it is convenient to define the seminvariant vector and seminvariant modulus associated with the vector $\mathbf{h} = (h, k, l)$, as indicated in rows 6 and 7 of Table 2; and to develop the concept of linear dependence and independence.

5. Linear dependence and independence

5·1. *Vectors*

In order to develop the concepts of linear dependence and independence we proceed as previously, (Hauptman & Karle, 1956), and consider vectors $\mathbf{h} = (h_1, h_2, \ldots, h_p)$ and $\boldsymbol{\omega} = (\omega_1, \omega_2, \ldots, \omega_p)$, where the h_i's and ω_i's are integers. In this paper the ω_i's are restricted to the values 1 and 2. The vector $\mathbf{h}$ is said

to be divisible by the vector ω if each h_i is devisible by ω_i. In this case we write

$$\mathbf{h} \equiv 0 \pmod{\omega} . \qquad (5\cdot1\cdot1)$$

Two vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ are congruent modulo ω if the difference $\mathbf{h}_1-\mathbf{h}_2$ is divisible by ω; and the notation

$$\mathbf{h}_1 \equiv \mathbf{h}_2 \pmod{\omega} \qquad (5\cdot1\cdot2)$$

is used.

A set of n vectors $\mathbf{h}_j, j = 1, 2, \ldots, n, (n \geq 1)$, is said to be linearly dependent modulo ω if there exists a set of n integers $a_j, j = 1, 2, \ldots, n$, at least one of which is odd such that

$$\sum_{j=1}^{n} a_j \mathbf{h}_j \equiv 0 \pmod{\omega} . \qquad (5\cdot1\cdot3)$$

If each ω_i is equal to 2, this definition is included in the one previously given (1956). If each ω_i is equal to 1, this definition supplements the previous one (1956) which is no longer applicable. We note that if each ω_i is equal to unity, then every set of vectors is linearly dependent modulo ω. If the set $\mathbf{h}_j$ is not linearly dependent modulo ω, it is said to be linearly independent modulo ω.

The vector $\mathbf{h}$ is linearly dependent modulo ω on, or linearly independent modulo ω of, the set $\mathbf{h}_j, j = 1, 2, \ldots, n(n \geq 1)$, according as there exist or do not exist n integers $a_j, j = 1, 2, \ldots, n$, some or all of which may be zero, such that

$$\mathbf{h} \equiv \sum_{j=1}^{n} a_j \mathbf{h}_j \pmod{\omega} . \qquad (5\cdot1\cdot4)$$

If every ω_i is equal to unity, then any vector is evidently linearly dependent modulo ω on any set of vectors. If every ω_i is equal to two, then any vector $\mathbf{h}$, each of whose components is even, is linearly dependent modulo ω on any set of vectors since each a_j in (5·1·4) may be chosen to be zero.

5·2. *Phases*

The seminvariant vector $\mathbf{h}_s$ and the seminvariant modulus ω_s associated with the vector $\mathbf{h} \equiv (h, k, l)$, or, alternatively, with the phase $\varphi_{\mathbf{h}}$, have already been defined (Table 2). We use these to define the concept of linear semi-dependence and semi-independence of phases.

For each of the types described in Table 2, a set of phases $\varphi_{\mathbf{h}_j}$ is said to be linearly semi-dependent or semi-independent according as the set of seminvariantly associated vectors is linearly dependent or independent modulo ω_s, where ω_s is the seminvariant modulus of the type.

The phase $\varphi_{\mathbf{h}}$ is linearly semi-dependent on, or linearly semi-independent of, the set of phases $\varphi_{\mathbf{h}_j}$ according as the vector seminvariantly associated with $\varphi_{\mathbf{h}}$ is linearly dependent modulo ω_s on, or linearly independent modulo ω_s of, the set of vectors seminvariantly associated with the set $\varphi_{\mathbf{h}_j}$.

As already noted, for each fixed functional form of a structure factor, the observed intensities determine the values of all structure seminvariants. The identity of the seminvariants is given by the following:

Theorem 1. For each type, the structure seminvariants are the linear combinations

$$\dot{\sum_{\mathbf{h}}} A_{\mathbf{h}} \varphi_{\mathbf{h}} , \qquad (5\cdot2\cdot1)$$

where the $A_{\mathbf{h}}$ are integers satisfying

$$\sum_{\mathbf{h}} A_{\mathbf{h}} \mathbf{h}_s \equiv 0 \pmod{\omega_s} , \qquad (5\cdot2\cdot2)$$

$\mathbf{h}_s$ is the vector seminvariantly associated with the phase $\varphi_{\mathbf{h}}$, ω_s is the seminvariant modulus of the type, and the symbol $\dot{\sum}$ in (5·2·1) means that the sum in (5·2·1) is to be reduced modulo 2π and $-\pi < \dot{\sum_{\mathbf{h}}} \leq \pi$.

The proof of this theorem, based upon an analysis of the equivalence classes shown in Table 2, follows the same lines as that given in Monograph I (1953).

6. Specification of origin

In the determination of phase by some direct procedure, it is presumed, of course, that a sufficiently large number of intensities have been observed to determine the structure uniquely. It is also necessary to choose one of the possible functional forms of the structure factor, e.g. by means of the coordinates listed in Table 1. This corresponds to selecting one of the possible equivalence classes listed in Table 2. Only when this is done will the values of the seminvariants be uniquely determined by the observed intensities. It is therefore to be expected that fixing the functional form of the structure factor is an integral part of any direct procedure for determining the values of phases from measured intensities.

6·1. *Type 2P*

The phases which are the structure seminvariants, hence uniquely determined by the magnitudes of the structure factors alone, independent of the choice of origin, are of the form φ_{ggg} and φ_{uug} (g means even and u means odd). The value of any phase, φ_1, not of this form, may be specified arbitrarily, i.e. either 0 or π. Once this is done, the values of all phases, linearly semi-dependent on φ_1, are uniquely determined. The value of any phase, φ_2, linearly semi-independent of φ_1 may be specified arbitrarily. In this way the origin is fixed and the value of any remaining phase φ is determined. This is a consequence of Theorem 1, since φ is linearly semi-dependent on the pair φ_1 and φ_2, whence there exist integers A_1 and A_2 such that

$$\varphi + A_1\varphi_1 + A_2\varphi_2 \qquad (6\cdot1\cdot1)$$

is a structure seminvariant and therefore determined by the intensities.

As an illustration of the specification of origin,

φ_1 may be chosen to be a φ_{ugg}. Then the values of all phases φ_{ugg} and φ_{gug}, being linearly semi-dependent on φ_1, are determined. Next, φ_2 may be chosen to be a φ_{uuu}. Then the values of all phases φ_{uuu} and φ_{ggu}, linearly semi-dependent on φ_2, are determined. Finally the values of all phases φ_{ugu} and φ_{guu}, linearly semi-dependent on the pair φ_1, φ_2, are determined.

6·2. *Type* $2P_1$

The first paragraph of 6·1 carries over verbatim for Type $2P_1$ with the single exception that the seminvariant phases are now of the form φ_{ggg} and φ_{uuu}.

As an illustration of the specification of origin, φ_1 may be chosen to be a φ_{uug}. The values of all phases φ_{uug} and φ_{ggu}, linearly semi-dependent on φ_1, are determined. Next, φ_2 may be chosen to be a φ_{guu}. Then the values of all phases φ_{guu} and φ_{ugg}, linearly semi-dependent on φ_2, are determined. Finally the values of all phases φ_{ugu} and φ_{gug}, linearly semi-dependent on the pair φ_1, φ_2, are determined.

6·3. *Type* $3P_2$

The phases which are the structure seminvariants are of the form φ_{ggg}, φ_{uug}, φ_{ugu} and φ_{guu}. The value of any phase φ_1, not of this form, may be specified arbitrarily. Once this is done, the values of all phases, of necessity linearly semi-dependent on φ_1, are determined. For example, φ_1 may be chosen to be φ_{ggu}.

6·4. *Type* $3P_3$

The phases which are the structure seminvariants are of the form φ_{ggg}, φ_{ggu}, φ_{uug}, and φ_{uuu}. The value of any phase φ_1, not of this form, may be specified arbitrarily. Once this is done, the values of all phases, of necessity linearly semi-dependent on φ_1, are determined. For example, φ_1 may be chosen to be φ_{ugg}.

6·5. *Type* $4P$

Every phase is a structure seminvariant and its value is determined by the observed intensities. The value of no phase may be specified arbitrarily. In this type, the choice of the functional form of the structure factor is equivalent to the unique selection of the origin.

7. Concluding remarks

Monograph I (1953) and this paper present a detailed procedure for specifying the origin in any centrosymmetric space group. This has been done by demonstrating the existence of relationships between the observed intensities and values of the phases via the structure seminvariants. With the specific statement of the nature of these relationships, it is possible to go directly from observed intensities to the values of phases. It will be the aim of future publications to employ the formulas of our two recent papers (1958) to obtain specific procedures for phase determination for all the space groups.

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Structure Factor Calculations for some Helical Polypeptide Models

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Structure factors have been calculated for some helical polypeptide models, assuming random angular orientations of the molecules about the helical axis. The computations were carried out on IBM punched-card machines and a brief description is given of the method of computation.

Introduction

The theory of X-ray diffraction by helical molecules has been developed by Cochran, Crick & Vand (1952), who applied it to verify the presence of the α-helix (Pauling, Corey & Branson, 1951) in the synthetic polypeptide, poly-γ-methyl-L- glutamate. Since then, helical structures have been proposed for a number of molecules, e.g. desoxyribose nucleic acid (Watson & Crick, 1953); collagen (Rich & Crick, 1955). Although many helical structures have been proposed with no more than a qualitative prediction of the calculated intensities, it is important to point out that a structure with satisfactory screw dimensions will not necessarily result in a correct distribution of layer-line