

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

The factor $\sum_{j=1}^n A_j \varphi_{\mathbf{h}_j}$ is the phase of the product (2.2.3.5). A structure invariant (s.i.) is a product (2.2.3.5) such that

$$\sum_{j=1}^n A_j \mathbf{h}_j = 0. \quad (2.2.3.6)$$

Since $|F_{\mathbf{h}_j}|$ are usually known from experiment, it is often said that s.i.'s are combinations of phases

$$\sum_{j=1}^n A_j \varphi_{\mathbf{h}_j}, \quad (2.2.3.7)$$

for which (2.2.3.6) holds.

$F_0, F_{\mathbf{h}} F_{-\mathbf{h}}, F_{\mathbf{h}} F_{\mathbf{k}} F_{\overline{\mathbf{h}+\mathbf{k}}}, F_{\mathbf{h}} F_{\mathbf{k}} F_{\mathbf{l}} F_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}}}, F_{\mathbf{h}} F_{\mathbf{k}} F_{\mathbf{l}} F_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{p}}}$ are examples of s.i.'s for $n = 1, 2, 3, 4, 5$.

The value of any s.i. does not change with an arbitrary shift of the space-group origin and thus it will depend on the crystal structure only.

(e) A structure seminvariant (s.s.) is a product of structure factors [or a combination of phases (2.2.3.7)] whose value is unchanged when the origin is moved by an allowed translation.

Let \mathbf{X}_p 's be the permissible origin translations of the space group. Then the product (2.2.3.5) [or the sum (2.2.3.7)] is an s.s., if, in accordance with (2.2.3.1),

$$\sum_{j=1}^n A_j (\mathbf{h}_j \cdot \mathbf{X}_p) = r, \quad p = 1, 2, \dots \quad (2.2.3.8)$$

where r is a positive integer, null or a negative integer.

Conditions (2.2.3.8) can be written in the following more useful form (Hauptman & Karle, 1953):

$$\sum_{j=1}^n A_j \mathbf{h}_{s_j} \equiv 0 \pmod{\omega_s}, \quad (2.2.3.9)$$

where \mathbf{h}_{s_j} is the vector seminvariantly associated with the vector \mathbf{h}_j and ω_s is the seminvariant modulus. In Tables 2.2.3.1–2.2.3.4, the reflection \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$, the seminvariant modulus ω_s and seminvariant phases are given for every H–K group.

The symbol of any group (cf. Giacovazzo, 1974) has the structure $\mathbf{h}_s L \omega_s$, where L stands for the lattice symbol. This symbol is underlined if the space group is cs.

By definition, if the class of permissible origin has been chosen, that is to say, if the algebraic form of the symmetry operators has been fixed, then the value of an s.s. does not depend on the origin but on the crystal structure only.

(f) Suppose that we have chosen the symmetry operators \mathbf{C}_s and thus fixed the functional form of the s.f.'s and the set of allowed origins. In order to describe the structure in direct space a unique reference origin must be fixed. Thus the phase-determining process must also require a unique permissible origin congruent to the values assigned to the phases. More specifically, at the beginning of the structure-determining process by direct methods we shall assign as many phases as necessary to define a unique origin among those allowed (and, as we shall see, possibly to fix the enantiomorph). From the theory developed so far it is obvious that arbitrary phases can be assigned to one or more s.f.'s if there is at least one allowed origin which, fixed as the origin of the unit cell, will give those phase values to the chosen reflections. The concept of linear dependence will help us to fix the origin.

(g) n phases $\varphi_{\mathbf{h}_j}$ are linearly semidependent (Hauptman & Karle, 1956) when the n vectors \mathbf{h}_{s_j} seminvariantly associated with the \mathbf{h}_j are linearly dependent modulo ω_s , ω_s being the seminvariant modulus of the space group. In other words, when

$$\sum_{j=1}^n A_j \mathbf{h}_{s_j} \equiv 0 \pmod{\omega_s}, \quad A_q \not\equiv 0 \pmod{\omega_s} \quad (2.2.3.10)$$

is satisfied. The second condition means that at least one A_q exists that is not congruent to zero modulo each of the components of ω_s . If (2.2.3.10) is not satisfied for any n -set of integers A_j , the phases $\varphi_{\mathbf{h}_j}$ are linearly semidependent. If (2.2.3.10) is valid for $n = 1$ and $A = 1$, then \mathbf{h}_1 is said to be linearly semidependent and $\varphi_{\mathbf{h}_1}$ is an s.s. It may be concluded that a seminvariant phase is linearly semidependent, and, vice versa, that a phase linearly semidependent is an s.s. In Tables 2.2.3.1–2.2.3.4 the allowed variations (which are those due to the allowed origin translations) for the semidependent phases are given for every H–K group. If $\varphi_{\mathbf{h}_1}$ is linearly semidependent its value can be fixed arbitrarily because at least one origin compatible with the given value exists. Once $\varphi_{\mathbf{h}_1}$ is assigned, the necessary condition to be able to fix a second phase $\varphi_{\mathbf{h}_2}$ is that it should be linearly semidependent of $\varphi_{\mathbf{h}_1}$.

Similarly, the necessary condition to be able arbitrarily to assign a third phase $\varphi_{\mathbf{h}_3}$ is that it should be linearly semidependent from $\varphi_{\mathbf{h}_1}$ and $\varphi_{\mathbf{h}_2}$.

In general, the number of linearly semidependent phases is equal to the dimension of the seminvariant vector ω_s (see Tables 2.2.3.1–2.2.3.4). The reader will easily verify in $(h, k, l) P(2, 2, 2)$ that the three phases $\varphi_{\text{oee}}, \varphi_{\text{eoe}}, \varphi_{\text{eoo}}$ define the origin (o indicates odd, e even).

(h) From the theory summarized so far it is clear that a number of semidependent phases $\varphi_{\mathbf{h}_j}$, equal to the dimension of the seminvariant vector ω_s , may be arbitrarily assigned in order to fix the origin. However, it is not always true that only one allowed origin compatible with the given phases exists. An additional condition is required such that only one permissible origin should lie at the intersection of the lattice planes corresponding to the origin-fixing reflections (or on the lattice plane \mathbf{h} if one reflection is sufficient to define the origin). It may be shown that the condition is verified if the determinant formed with the vectors seminvariantly associated with the origin reflections, reduced modulo ω_s , has the value ± 1 . In other words, such a determinant should be primitive modulo ω_s .

For example, in $P\bar{1}$ the three reflections

$$\mathbf{h}_1 = (345), \mathbf{h}_2 = (139), \mathbf{h}_3 = (784)$$

define the origin uniquely because

$$\begin{vmatrix} 3 & 4 & 5 \\ 1 & 3 & 9 \\ 7 & 8 & 4 \end{vmatrix} \xrightarrow{\text{reduced mod } (2,2,2)} \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 0 \end{vmatrix} = -1.$$

Furthermore, in $P4mm$ [$\mathbf{h}_s = (h + k, l)$, $\omega_s = (2, 0)$]

$$\mathbf{h}_1 = (5, 2, 0), \quad \mathbf{h}_2 = (6, 2, 1)$$

define the origin uniquely since

$$\begin{vmatrix} 7 & 0 \\ 8 & 1 \end{vmatrix} \xrightarrow{\text{reduced mod } (2,0)} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1.$$

(i) If an s.s. or an s.i. has a general value φ for a given structure, it will have a value $-\varphi$ for the enantiomorph structure. If $\varphi = 0, \pi$ the s.s. has the same value for both enantiomorphs. Once the origin has been assigned, in ncs. space groups the sign of a given s.s. $\varphi \neq 0, \pi$ can be assigned to fix the enantiomorph. In practice it is often advisable to use an s.s. or an s.i. whose value is as near as possible to $\pm\pi/2$.

2.2.4. Normalized structure factors

2.2.4.1. Definition of normalized structure factor

The normalized structure factors E (see also Chapter 2.1) are calculated according to (Hauptman & Karle, 1953)

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}|^2 / \langle |F_{\mathbf{h}}|^2 \rangle, \quad (2.2.4.1)$$

2.2. DIRECT METHODS

Table 2.2.3.1. Allowed origin translations, seminvariant moduli and phases for centrosymmetric primitive space groups

	H-K group					
	$(h, k, l)\underline{P}(2, 2, 2)$		$(h + k, l)\underline{P}(2, 2)$		$(l)\underline{P}(2)$	$(h + k + l)\underline{P}(2)$
Space group	$P\bar{1}$	$Pmna$	$P\frac{4}{m}$	$P\frac{4}{n}mm$	$P\bar{3}$	$R\bar{3}$
	$P\frac{2}{m}$	$Pcca$	$P\frac{4_2}{m}$	$P\frac{4}{n}cc$	$P\bar{3}1m$	$R\bar{3}m$
	$P\frac{2_1}{m}$	$Pbam$	$P\frac{4}{n}$	$P\frac{4_2}{m}mc$	$P\bar{3}1c$	$R\bar{3}c$
	$P\frac{2}{c}$	$Pccn$	$P\frac{4_2}{n}$	$P\frac{4_2}{m}cm$	$P\bar{3}m1$	$Pm\bar{3}$
	$P\frac{2_1}{c}$	$Pbcm$	$P\frac{4}{m}mm$	$P\frac{4_2}{n}bc$	$P\bar{3}c1$	$Pn\bar{3}$
	$Pmmm$	$Pnmm$	$P\frac{4}{m}cc$	$P\frac{4_2}{n}nm$	$P\frac{6}{m}$	$Pa\bar{3}$
	$Pnnn$	$Pmnn$	$P\frac{4}{n}bm$	$P\frac{4_2}{m}bc$	$P\frac{6_3}{m}$	$Pm\bar{3}m$
	$Pccm$	$Pbcn$	$P\frac{4}{n}nc$	$P\frac{4_2}{m}nm$	$P\frac{6}{m}mm$	$Pn\bar{3}n$
	$Pban$	$Pbca$	$P\frac{4}{m}bm$	$P\frac{4_2}{n}mc$	$P\frac{6}{m}cc$	$Pm\bar{3}n$
	$Pnma$	$Pnma$	$P\frac{4}{m}nc$	$P\frac{4_2}{n}cm$	$P\frac{6_3}{m}cm$	$Pn\bar{3}m$
	$Pnna$				$P\frac{6_3}{m}mc$	
Allowed origin translations	$(0, 0, 0);$ $(\frac{1}{2}, 0, 0);$ $(0, \frac{1}{2}, 0);$ $(0, 0, \frac{1}{2});$	$(0, \frac{1}{2}, \frac{1}{2});$ $(\frac{1}{2}, 0, \frac{1}{2});$ $(\frac{1}{2}, \frac{1}{2}, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2});$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$		$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
Vector \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, k, l)		$(h + k, l)$		(l)	$(h + k + l)$
Seminvariant modulus ω_s	$(2, 2, 2)$		$(2, 2)$		(2)	(2)
Seminvariant phases	φ_{eee}		$\varphi_{eee}; \varphi_{ooo}$		$\varphi_{eee}; \varphi_{eoe}$ $\varphi_{ooo}; \varphi_{ooe}$	$\varphi_{eee}; \varphi_{ooc}$ $\varphi_{ooo}; \varphi_{ooo}$
Number of semindependent phases to be specified	3		2		1	1

where $|F_{\mathbf{h}}|^2$ is the squared observed structure-factor magnitude on the absolute scale and $\langle |F_{\mathbf{h}}|^2 \rangle$ is the expected value of $|F_{\mathbf{h}}|^2$.

$\langle |F_{\mathbf{h}}|^2 \rangle$ depends on the available *a priori* information. Often, but not always, this may be considered as a combination of several typical situations. We mention:

(a) No structural information. The atomic positions are considered random variables. Then

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \sum_{j=1}^N f_j^2 = \varepsilon_{\mathbf{h}} \sum_N$$

so that

$$E_{\mathbf{h}} = \frac{F_{\mathbf{h}}}{(\varepsilon_{\mathbf{h}} \sum_N)^{1/2}}. \quad (2.2.4.2)$$

$\varepsilon_{\mathbf{h}}$ takes account of the effect of space-group symmetry (see Chapter 2.1).

(b) P atomic groups having a known configuration but with unknown orientation and position (Main, 1976). Then a certain number of interatomic distances $r_{j_1 j_2}$ are known and

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \left(\sum_N + \sum_{i=1}^P \sum_{j_1 \neq j_2=1}^{M_i} f_{j_1} f_{j_2} \frac{\sin 2\pi q r_{j_1 j_2}}{2\pi q r_{j_1 j_2}} \right),$$

where M_i is the number of atoms in the i th molecular fragment and $q = |\mathbf{h}|$.

(c) P atomic groups with a known configuration, correctly oriented, but with unknown position (Main, 1976). Then a certain group of interatomic vectors $\mathbf{r}_{j_1 j_2}$ is fixed and

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \left(\sum_N + \sum_{i=1}^P \sum_{j_1 \neq j_2=1}^{M_i} f_{j_1} f_{j_2} \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_{j_1 j_2} \right).$$

The above formula has been derived on the assumption that primitive positional random variables are uniformly distributed over the unit cell. Such an assumption may be considered unfavourable (Giacovazzo, 1988) in space groups for which the allowed shifts of origin, consistent with the chosen algebraic form for the symmetry operators \mathbf{C}_s , are arbitrary displacements along any polar axes. Thanks to the indeterminacy in the choice of origin, the first of the shifts τ_i (to be applied to the i th fragment in order to translate atoms in the correct positions) may be restricted to a region which is smaller than the unit cell (*e.g.* in $P2$ we are free to specify the origin along the diad axis by restricting τ_1 to the family of vectors $\{\tau_1\}$ of type $[x0z]$). The practical consequence is that $\langle |F_{\mathbf{h}}|^2 \rangle$ is significantly modified in polar space groups if \mathbf{h} satisfies

$$\mathbf{h} \cdot \tau_1 = 0,$$

where τ_1 belongs to the family of restricted vectors $\{\tau_1\}$.

(d) Atomic groups correctly positioned. Then (Main, 1976; Giacovazzo, 1983a)

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$$\langle |F_{\mathbf{h}}|^2 \rangle = |F_{p,\mathbf{h}}|^2 + \varepsilon_{\mathbf{h}} \sum_q,$$

where $F_{p,\mathbf{h}}$ is the structure factor of the partial known structure and q are the atoms with unknown positions.

(e) A pseudotranslational symmetry is present. Let $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, \dots$ be the pseudotranslation vectors of order n_1, n_2, n_3, \dots , respectively. Furthermore, let p be the number of atoms (symmetry equivalents included) whose positions are related by pseudotranslational symmetry and q the number of atoms (symmetry equivalents included) whose positions are not related by any pseudotranslation. Then (Casarano *et al.*, 1985a,b)

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} (\zeta_{\mathbf{h}} \sum_p + \sum_q),$$

where

$$\zeta_{\mathbf{h}} = \frac{(n_1 n_2 n_3 \dots) \gamma_{\mathbf{h}}}{m}$$

and $\gamma_{\mathbf{h}}$ is the number of times for which algebraic congruences

$$\mathbf{h} \cdot \mathbf{R}_s \mathbf{u}_i \equiv 0 \pmod{1} \quad \text{for } i = 1, 2, 3, \dots$$

are simultaneously satisfied when s varies from 1 to m . If $\gamma_{\mathbf{h}} = 0$ then $F_{\mathbf{h}}$ is said to be a *superstructure reflection*, otherwise it is a *substructure reflection*.

Often substructures are not ideal: *e.g.* atoms related by pseudotranslational symmetry are ideally located but of different type (replacive deviations from ideality); or they are equal but not ideally located (displacive deviations); or a combination of the two situations occurs. In these cases a correlation exists between the substructure and the superstructure. It has been shown (Mackay, 1953; Cascarano *et al.*, 1988a) that the scattering power of the substructural part may be estimated *via* a statistical analysis of diffraction data for ideal pseudotranslational symmetry or for displacive deviations from it, while it is not estimable in the case of replacive deviations.

2.2.4.2. Definition of quasi-normalized structure factor

When probability theory is not used, the *quasi-normalized structure factors* $\varepsilon_{\mathbf{h}}$ and the *unitary structure factors* $U_{\mathbf{h}}$ are often used. $\varepsilon_{\mathbf{h}}$ and $U_{\mathbf{h}}$ are defined according to

$$|\varepsilon_{\mathbf{h}}|^2 = \varepsilon_{\mathbf{h}} |E_{\mathbf{h}}|^2$$

$$U_{\mathbf{h}} = F_{\mathbf{h}} / \left(\sum_{j=1}^N f_j \right).$$

Since $\sum_{j=1}^N f_j$ is the largest possible value for $F_{\mathbf{h}}$, $U_{\mathbf{h}}$ represents the fraction of $F_{\mathbf{h}}$ with respect to its largest possible value. Therefore

Table 2.2.3.2. Allowed origin translations, seminvariant moduli and phases for noncentrosymmetric primitive space groups

	H-K group					
	(h, k, l)P(0, 0, 0)	(h, k, l)P(2, 0, 2)	(h, k, l)P(0, 2, 0)	(h, k, l)P(2, 2, 2)	(h, k, l)P(2, 2, 0)	(h + k, l)P(2, 0)
Space group	P1	P2 P2 ₁	Pm Pc	P222 P222 ₁ P2 ₁ 2 ₁ 2 P2 ₁ 2 ₁ 2 ₁	Pmm2 Pmc2 ₁ Pcc2 Pma2 Pca2 ₁ Pnc2 Pmn2 ₁ Pba2 Pna2 ₁ Pnn2	P4 P4 ₁ P4 ₂ P4 ₃ P4mm P4bm P4 ₂ cm P4 ₂ nm P4cc P4nc P4 ₂ mc P4 ₂ bc
Allowed origin translations	(x, y, z)	(0, y, 0) (0, y, ½) (½, y, 0) (½, y, ½)	(x, 0, z) (x, ½, z)	(0, 0, 0) (½, 0, 0) (0, ½, 0) (0, 0, ½) (0, ½, ½) (½, 0, ½) (½, ½, 0) (½, ½, ½)	(0, 0, z) (0, ½, z) (½, 0, z) (½, ½, z)	(0, 0, z) (½, ½, z)
Vector \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, k, l)	(h, k, l)	(h, k, l)	(h, k, l)	(h, k, l)	(h + k, l)
Seminvariant modulus ω_s	(0, 0, 0)	(2, 0, 2)	(0, 2, 0)	(2, 2, 2)	(2, 2, 0)	(2, 0)
Seminvariant phases	φ_{000}	φ_{c0c}	φ_{0c0}	φ_{ccc}	φ_{cc0}	φ_{cc0} φ_{o00}
Allowed variations for the semindependent phases	$\ \infty\ $	$\ \infty\ , \ 2\ $ if $k = 0$	$\ \infty\ , \ 2\ $ if $h = l = 0$	$\ 2\ $	$\ \infty\ , \ 2\ $ if $l = 0$	$\ \infty\ , \ 2\ $ if $l = 0$
Number of semindependent phases to be specified	3	3	3	3	3	2

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$$0 \leq |U_{\mathbf{h}}| \leq 1.$$

If atoms are equal, then $U_{\mathbf{h}} = \epsilon_{\mathbf{h}}/N^{1/2}$.

assumed that all the atoms are at rest. $\langle |F^0|^2 \rangle$ depends upon the structural information that is available (see Section 2.2.4.1 for some examples).

Equation (2.2.4.3) may be rewritten as

$$\ln \left\{ \frac{\langle I \rangle}{\langle |F^0|^2 \rangle} \right\} = -\ln K - 2Bs^2,$$

2.2.4.3. The calculation of normalized structure factors

N.s.f.'s cannot be calculated by applying (2.2.4.1) to observed s.f.'s because: (a) the observed magnitudes $I_{\mathbf{h}}$ (already corrected for Lp factor, absorption, ...) are on a relative scale; (b) $\langle |F_{\mathbf{h}}|^2 \rangle$ cannot be calculated without having estimated the vibrational motion of the atoms.

This is usually obtained by the well known Wilson plot (Wilson, 1942), according to which observed data are divided into ranges of $s^2 = \sin^2 \theta / \lambda^2$ and averages of intensity $\langle I_{\mathbf{h}} \rangle$ are taken in each shell. Reflection multiplicities and other effects of space-group symmetry on intensities must be taken into account when such averages are calculated. The shells are symmetrically overlapped in order to reduce statistical fluctuations and are restricted so that the number of reflections in each shell is reasonably large. For each shell

$$K \langle I \rangle = \langle |F|^2 \rangle = \langle |F^0|^2 \rangle \exp(-2Bs^2) \quad (2.2.4.3)$$

should be obtained, where K is the scale factor needed to place X-ray intensities on the absolute scale, B is the overall thermal parameter and $\langle |F^0|^2 \rangle$ is the expected value of $|F|^2$ in which it is

which plotted at various s^2 should be a straight line of which the slope ($2B$) and intercept ($\ln K$) on the logarithmic axis can be obtained by applying a linear least-squares procedure.

Very often molecular geometries produce perceptible departures from linearity in the logarithmic Wilson plot. However, the more extensive the available *a priori* information on the structure is, the closer, on the average, are the Wilson-plot curves to their least-squares straight lines.

Accurate estimates of B and K require good strategies (Rogers & Wilson, 1953) for:

(1) treatment of weak measured data. If weak data are set to zero, there will be bias in the statistics. Methods are, however, available (French & Wilson, 1978) that provide an *a posteriori* estimate of weak (even negative) intensities by means of Bayesian statistics.

Table 2.2.3.2 (cont.)

$(h+k, l)P(2, 2)$	$(h-k, l)P(3, 0)$	$(2h+4k+3l)P(6)$	$(l)P(0)$	$(l)P(2)$	$(h+k+l)P(0)$	$(h+k+l)P(2)$
$P\bar{4}$	$P3$	$P312$	$P31m$	$P321$	$R3$	$R32$
$P422$	$P3_1$	$P3_112$	$P31c$	$P3_121$	$R3m$	$P23$
$P42_12$	$P3_2$	$P3_212$	$P6$	$P3_221$	$R3c$	$P2_13$
$P4_122$	$P3m1$	$P6$	$P6_1$	$P622$		$P432$
$P4_12_12$	$P3c1$	$P\bar{6}m2$	$P6_5$	$P6_122$		$P4_232$
$P4_222$		$P\bar{6}c2$	$P6_4$	$P6_522$		$P4_332$
$P4_22_12$			$P6_3$	$P6_222$		$P4_132$
$P4_322$			$P6_2$	$P6_422$		$P\bar{4}3m$
$P4_32_12$			$P6mm$	$P6_322$		$P\bar{4}3n$
$P\bar{4}2m$			$P6cc$	$P\bar{6}2m$		
$P\bar{4}2c$			$P6_3cm$	$P\bar{6}2c$		
$P\bar{4}2_1m$			$P6_3mc$			
$P\bar{4}2_1c$						
$P\bar{4}m2$						
$P\bar{4}c2$						
$P\bar{4}b2$						
$P\bar{4}n2$						
$(0, 0, 0)$	$(0, 0, z)$	$(0, 0, 0)$	$(0, 0, z)$	$(0, 0, 0)$	(x, x, x)	$(0, 0, 0)$
$(0, 0, \frac{1}{2})$	$(\frac{1}{3}, \frac{2}{3}, z)$	$(0, 0, \frac{1}{2})$		$(0, 0, \frac{1}{2})$		$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{2}{3}, \frac{1}{3}, z)$	$(\frac{1}{3}, \frac{2}{3}, 0)$				
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$		$(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$				
		$(\frac{2}{3}, \frac{1}{3}, 0)$				
		$(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$				
$(h+k, l)$	$(h-k, l)$	$(2h+4k+3l)$	(l)	(l)	$(h+k+l)$	$(h+k+l)$
$(2, 2)$	$(3, 0)$	(6)	(0)	(2)	(0)	(2)
φ_{eoc} φ_{ooe}	φ_{hk0} if $h-k=0$ (mod 3)	φ_{hkl} if $2h+4k+3l=0$ (mod 6)	φ_{hk0}	φ_{hkc}	$\varphi_{h, k, \bar{h}+\bar{k}}$	$\varphi_{\text{eoc}}; \varphi_{\text{ooe}}$ $\varphi_{\text{oco}}; \varphi_{\text{ooe}}$
$\ 2\ $	$\ \infty\ , \ 3\ $ if $l=0$	$\ 2\ $ if $h \equiv k \pmod{3}$ $\ 3\ $ if $l \equiv 0 \pmod{2}$	$\ \infty\ $	$\ 2\ $	$\ \infty\ $	$\ 2\ $
2	2	1	1	1	1	1

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Table 2.2.3.3. Allowed origin translations, seminvariant moduli and phases for centrosymmetric non-primitive space groups

	H-K group				
	$(h, l)C(2, 2)$	$(k, l)I(2, 2)$	$(h + k + l)F(2)$	$(l)I(2)$	I
Space groups	$C\frac{2}{m}$ $C\frac{2}{c}$ <i>Cmcm</i> <i>Cmca</i> <i>Cmmm</i> <i>Cccm</i> <i>Cmma</i> <i>Ccca</i>	<i>Immm</i> <i>Ibam</i> <i>Ibca</i> <i>Imma</i>	<i>Fmmm</i> <i>Fddd</i> <i>Fm\bar{3}</i> <i>Fd\bar{3}</i> <i>Fm\bar{3}m</i> <i>Fm\bar{3}c</i> <i>Fd\bar{3}m</i> <i>Fd\bar{3}c</i>	$I\frac{4}{m}$ $I\frac{4}{a}$ $I\frac{4}{m}mm$ $I\frac{4}{m}cm$ $I\frac{4}{a}md$ $I\frac{4}{a}cd$	$Im\bar{3}$ $Ia\bar{3}$ $Im\bar{3}m$ $Ia\bar{3}d$
Allowed origin translations	(0, 0, 0) (0, 0, $\frac{1}{2}$) ($\frac{1}{2}$, 0, 0) ($\frac{1}{2}$, 0, $\frac{1}{2}$)	(0, 0, 0) (0, 0, $\frac{1}{2}$) (0, $\frac{1}{2}$, 0) ($\frac{1}{2}$, 0, 0)	(0, 0, 0) ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)	(0, 0, 0) (0, 0, $\frac{1}{2}$)	(0, 0, 0)
Vector \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, l)	(k, l)	$(h + k + l)$	(l)	(h, k, l)
Seminvariant modulus ω_s	(2, 2)	(2, 2)	(2)	(2)	(1, 1, 1)
Seminvariant phases	φ_{eee}	φ_{eee}	φ_{eee}	$\varphi_{eoe}; \varphi_{eee}$ $\varphi_{oee}; \varphi_{oee}$	All
Number of semindependent phases to be specified	2	2	1	1	0

(2) treatment of missing weak data (Rogers *et al.*, 1955; Vicković & Viterbo, 1979). All unobserved reflections may assume

$$\mu = |F_{o\min}|^2/3 \text{ for cs. space groups}$$

$$\mu = |F_{o\min}|^2/2 \text{ for ncs. space groups,}$$

where the subscript 'o min' refers to the minimum observed intensity.

Once K and B have been estimated, $E_{\mathbf{h}}$ values can be obtained from experimental data by

$$|E_{\mathbf{h}}|^2 = \frac{KI_{\mathbf{h}}}{\langle |F_{\mathbf{h}}^o|^2 \rangle \exp(-2Bs^2)},$$

Table 2.2.3.4. Allowed origin translations, seminvariant moduli and phases for noncentrosymmetric non-primitive space groups

	H-K group					
	$(k, l)C(0, 2)$	$(h, l)C(0, 0)$	$(h, l)C(2, 0)$	$(h, l)C(2, 2)$	$(h, l)A(2, 0)$	$(h, l)I(2, 0)$
Space group	<i>C2</i>	<i>Cm</i> <i>Cc</i>	<i>Cmm2</i> <i>Cmc2₁</i> <i>Ccc2</i>	<i>C222</i> <i>C222₁</i>	<i>Amm2</i> <i>Abm2</i> <i>Ama2</i> <i>Aba2</i>	<i>Imm2</i> <i>Iba2</i> <i>Ima2</i>
Allowed origin translations	(0, y, 0) (0, y, $\frac{1}{2}$)	(x, 0, z)	(0, 0, z) ($\frac{1}{2}$, 0, z)	(0, 0, 0) (0, 0, $\frac{1}{2}$) ($\frac{1}{2}$, 0, 0) ($\frac{1}{2}$, 0, $\frac{1}{2}$)	(0, 0, z) ($\frac{1}{2}$, 0, z)	(0, 0, z) ($\frac{1}{2}$, 0, z)
Vector \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$	(k, l)	(h, l)	(h, l)	(h, l)	(h, l)	(h, l)
Seminvariant modulus ω_s	(0, 2)	(0, 0)	(2, 0)	(2, 2)	(2, 0)	(2, 0)
Seminvariant phases	φ_{e0e}	φ_{0e0}	φ_{ee0}	φ_{eee}	φ_{ee0}	φ_{ee0}
Allowed variations for the semindependent phases	$\ \infty\ , \ 2\ $ if $k = 0$	$\ \infty\ $	$\ \infty\ , \ 2\ $ if $l = 0$	$\ 2\ $	$\ \infty\ , \ 2\ $ if $l = 0$	$\ \infty\ , \ 2\ $ if $l = 0$
Number of semindependent phases to be specified	2	2	2	2	2	2

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where $\langle |F_{\mathbf{h}}^0|^2 \rangle$ is the expected value of $|F_{\mathbf{h}}^0|^2$ for the reflection \mathbf{h} on the basis of the available *a priori* information.

2.2.4.4. Probability distributions of normalized structure factors

Under some fairly general assumptions (see Chapter 2.1) probability distribution functions for the variable $|E|$ for cs. and ncs. structures are (see Fig. 2.2.4.1)

$${}_1P(|E|) d|E| = \sqrt{\frac{2}{\pi}} \exp\left(-\frac{E^2}{2}\right) d|E| \quad (2.2.4.4)$$

and

$${}_1P(|E|) d|E| = 2|E| \exp(-|E|^2) d|E|, \quad (2.2.4.5)$$

respectively. Corresponding cumulative functions are (see Fig. 2.2.4.2)

$${}_1N(|E|) = \sqrt{\frac{2}{\pi}} \int_0^{|E|} \exp\left(-\frac{t^2}{2}\right) dt = \operatorname{erf}\left(\frac{|E|}{\sqrt{2}}\right),$$

$${}_1N(|E|) = \int_0^{|E|} 2t \exp(-t^2) dt = 1 - \exp(-|E|^2).$$

Some moments of the distributions (2.2.4.4) and (2.2.4.5) are listed in Table 2.2.4.1. In the absence of other indications for a given crystal structure, a cs. or an ncs. space group will be preferred according to whether the statistical tests yield values closer to column 2 or to column 3 of Table 2.2.4.1.

For further details about the distribution of intensities see Chapter 2.1.

2.2.5. Phase-determining formulae

From the earliest periods of X-ray structure analysis several authors (Ott, 1927; Banerjee, 1933; Avrami, 1938) have tried to determine atomic positions directly from diffraction intensities.

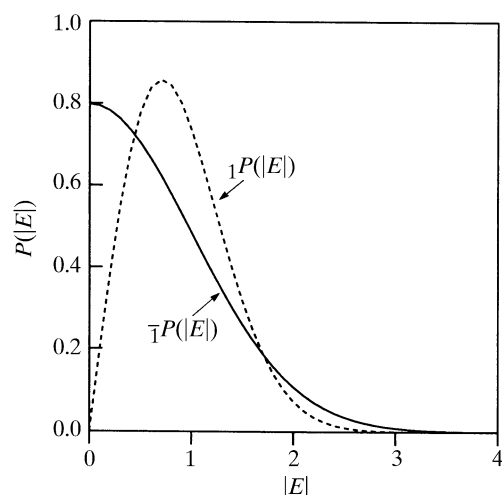


Fig. 2.2.4.1. Probability density functions for cs. and ncs. crystals.

Significant developments are the derivation of inequalities and the introduction of probabilistic techniques *via* the use of joint probability distribution methods (Hauptman & Karle, 1953).

2.2.5.1. Inequalities among structure factors

An extensive system of inequalities exists for the coefficients of a Fourier series which represents a positive function. This can restrict the allowed values for the phases of the s.f.'s in terms of measured structure-factor magnitudes. Harker & Kasper (1948) derived two types of inequalities:

Type 1. A modulus is bound by a combination of structure factors:

$$|U_{\mathbf{h}}|^2 \leq \frac{1}{m} \sum_{s=1}^m a_s(-\mathbf{h}) U_{\mathbf{h}(\mathbf{I}-\mathbf{R}_s)}, \quad (2.2.5.1)$$

where m is the order of the point group and $a_s(-\mathbf{h}) = \exp(-2\pi i \mathbf{h} \cdot \mathbf{T}_s)$.

Table 2.2.3.4 (cont.)

$(h, l)I(2, 2)$	$(h + k + l)F(2)$	$(h + k + l)F(4)$	$(l)I(0)$	$(l)I(2)$	$(2k - l)I(4)$	$(l)F(0)$	I
$I222$ $I2_12_12_1$	$F432$ $F4_132$	$F222$ $F23$ $F\bar{4}3m$ $F\bar{4}3c$	$I4$ $I4_1$ $I4mm$ $I4cm$ $I4_1md$ $I4_1cd$	$I422$ $I4_122$ $I\bar{4}2m$ $I\bar{4}2d$	$\bar{I}4$ $\bar{I}4m2$ $\bar{I}4c2$	$Fmm2$ $Fdd2$	$I23$ $I2_13$ $I432$ $I4_132$ $\bar{I}43m$ $\bar{I}43d$
$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(0, \frac{1}{2}, 0)$ $(\frac{1}{2}, 0, 0)$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$	$(0, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{3}{4})$ $(\frac{1}{2}, 0, \frac{1}{4})$	$(0, 0, z)$	$(0, 0, 0)$
(h, l)	$(h + k + l)$	$(h + k + l)$	(l)	(l)	$(2k - l)$	(l)	(h, k, l)
$(2, 2)$	(2)	(4)	(0)	(2)	(4)	(0)	$(1, 1, 1)$
φ_{eee}	φ_{eee}	φ_{hkl} with $h + k + l \equiv 0$ $(\text{mod } 4)$	φ_{hk0}	φ_{hkc}	φ_{hkl} with $(2k - l) \equiv 0$ $(\text{mod } 4)$	φ_{hk0}	All
$\ 2\ $	$\ 2\ $	$\ 2\ $ if $h + k + l \equiv 0$ $(\text{mod } 2)$ $\ 4\ $ if $h + k + l \equiv 1$ $(\text{mod } 2)$	$\ \infty\ $	$\ 2\ $	$\ 2\ $ if $h + k + l \equiv 0$ $(\text{mod } 2)$ $\ 4\ $ if $2k - l \equiv 1$ $(\text{mod } 2)$	$\ \infty\ $	All
2	1	1	1	1	1	1	0