

tion, such as particle size, strain, dislocation density *etc.* (Mitra & Chattopadhyay, 1972), but as these samples are well annealed, it is evident that they are free of all these defects. Thus this change of Debye characteristic temperature must be due to a change in local ordering. Fig. 3 shows the variation of Debye characteristic temperature with the ordering as calculated from equation (5). This graph was drawn after the constant $\Theta_{AB}^2 M_{AB}$ had been calculated from the known value of $\Theta_{AB(pq)}^2 M_{AB(pq)}$ at a heat-treatment temperature of 400°C when s can safely be taken to be zero, *i.e.* the alloy can be considered to be fully disordered. Thus, by determining the Debye characteristic temperatures of the samples quenched from different temperatures, the corresponding ordering parameter s can be found from the graph. The plot of ordering parameter s against temperature is shown in Fig. 4 from which it can be observed that the ordering decreases, as expected, with increase of temperature.

Shri A. K. Chaudhuri is indebted to the Council of Scientific and Industrial Research, New Delhi, for financial help.

References

CHIPMAN, D. R. & PASKIN, A. (1959). *J. Appl. Phys.* **30**, 1998–2001.

Acta Cryst. (1974). **A30**, 390

A New Scheme for Seminvariant Tables in All Space Groups

BY C. GIACOVAZZO

Istituto di Mineralogia, Università di Bari, Italy

(Received 12 January 1973; accepted 16 July 1973)

A new scheme is proposed to make the Hauptman–Karle Tables on structure seminvariants conform with international notation. An alternative derivation of the Tables for conventionally centred cells is presented.

The fundamental papers of Hauptman & Karle (1953, 1956, 1959; Karle & Hauptman, 1961) have excellently solved the problem of choosing an origin by specifying the values of an appropriate set of phases. Four tables, containing among other things the permissible origins and seminvariant moduli, have been presented in these papers; subsequently they were slightly modified (Karle, 1970).

Because of the considerable increase in the use of direct methods, these tables could be usefully issued in the new *International Tables for X-ray Crystallography*; nevertheless some modifications could be made for two reasons:

(a) to simplify their use, by a suitable notation similar to other crystallographic notations,

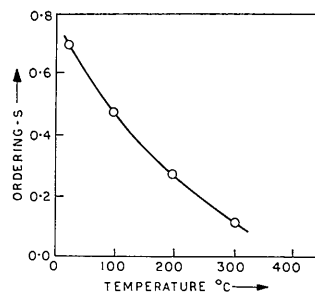


Fig. 4. Variation of ordering with temperature.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DAMASK, A. C. (1956). *J. Appl. Phys.* **27**, 610–616.

MITRA, G. B. & CHATTOPADHYAY, T. (1972). *Phys. Stat. Sol. (a)*, **9**, 89–96.

MITRA, G. B. & CHAUDHURI, A. K. (1974). *Acta Cryst.* **A30**, 385–387.

MITRA, G. B. & MISRA, N. K. (1966). *Brit. J. Appl. Phys.* **17**, 1319–1328.

JAMES, R. W. (1962). *The Optical Principles of the Diffraction of X-rays*. London: Bell and Sons.

JONES, F. W. & SYKES, C. (1937). *Proc. Roy. Soc. Lond.* **A161**, 440–446.

(b) to allow, in space groups with conventional centred cells also, the automatic search for permissible origins and seminvariant reflexions by the use of symmetry transformations (Hall, 1970; Gramaccioli & Zechmeister, 1972).

To pursue these two aims, some new definitions are necessary.

(1) *Permissible origins*: Hauptman & Karle (here H–K) define the permissible origins for primitive centrosymmetric space groups to be the eight points

$$\varepsilon_1, \varepsilon_2, \varepsilon_3; \varepsilon_i = 0 \text{ or } \frac{1}{2}, \quad i = 1, 2, 3. \quad (1)$$

For the primitive non-centrosymmetric space groups the permissible origins are defined to be those points which are equivalent to at least one of the eight points

(1). The unsuitability of this definition (particularly in non-centrosymmetric groups) for practical structure determination suggests a new definition; thus:

“permissible origins are the points which, taken as origins, retain the same functional form of the structure factor. They are related each other by the ‘permissible translations’”.

(2) *Permissible translations*: In the primitive space groups point symmetry defines possible translations.

It is well known that in a primitive space group of order m , a general space-group symmetry operation

$$\mathbf{r}_{js} = \mathbf{R}_s \mathbf{r}_j + \mathbf{T}_s$$

is modified, by a origin translation \mathbf{X}_p , to

$$\mathbf{r}'_{js} = \mathbf{R}'_s \mathbf{r}'_j + \mathbf{T}'_s,$$

where

$$\mathbf{R}'_s = \mathbf{R}_s \quad \mathbf{T}'_s = \mathbf{T}_s + (\mathbf{R}_s - \mathbf{I})\mathbf{X}_p. \quad (2)$$

Hence \mathbf{X}_p is a permissible origin translation when

$$(\mathbf{R}_s - \mathbf{I})\mathbf{X}_p = \mathbf{V} \quad \text{for } s = 1, 2, \dots, m \quad (3)$$

where \mathbf{V} is a vector with arbitrary integer components.

In centred space groups the permissible translations are not determined exclusively by the point symmetry. In the H-K (1959, 1961) papers the centred rotation matrices \mathbf{R}_c are transformed into primitive rotation

matrices \mathbf{R}_p before equation (3) can be used. In these papers the primitive rotation matrices \mathbf{R}_p are tabulated for space groups with conventionally centred cells.

In contrast with the H-K derivation, the permissible translations can be specified for centred space groups without transforming them to appropriate primitive cells (this is very convenient in crystallographic computing).

Indeed, if $\mathbf{B}_v = (B_{1v}, B_{2v}, B_{3v})$ is a translation vector of the centred cell $[(\frac{1}{2}, \frac{1}{2}, 0)]$ for C cells, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for I cells, etc., from equations (2) and (3) we can deduce that a permissible translation \mathbf{X}_p must satisfy the equations

$$(\mathbf{R}_s - \mathbf{I})\mathbf{X}_p = \mathbf{V} + a\mathbf{B}_v \quad s = 1, 2, \dots, m; \quad a = 0, 1. \quad (4)$$

For example, one can verify that condition (4) is satisfied, in the space group $F222$, by the points

$$\begin{aligned} &(0, 0, 0); (\frac{1}{2}, \frac{1}{2}, 0); (0, \frac{1}{2}, \frac{1}{2}); (\frac{1}{2}, 0, \frac{1}{2}); \\ &(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}); (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}); (\frac{3}{4}, \frac{1}{4}, \frac{3}{4}); \\ &(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}); (\frac{1}{4}, \frac{1}{4}, \frac{3}{4}); (\frac{3}{4}, \frac{1}{4}, \frac{1}{4}); (\frac{1}{4}, \frac{3}{4}, \frac{1}{4}); \\ &(\frac{1}{2}, 0, 0); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); (0, \frac{1}{2}, 0); (0, 0, \frac{1}{2}). \end{aligned}$$

The third row of Tables 3 and 4 can be deduced directly from equation (4). We write in this row only the permissible translations not related by a combination of translation vectors: in the example of the $F222$ group,

$$(0, 0, 0); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}); (\frac{3}{4}, \frac{3}{4}, \frac{3}{4}).$$

Table 1. *Permissible translations, moduli and seminvariant phases for the primitive centrosymmetric space groups*

H-K groups	$(h, k, l)P(2, 2, 2)$	$(h+k, l)P(2, 2)$	$(l)P(2)$	$(h+k+l)P(2)$
Space groups	$P\bar{1}$ $Pmna$ $P2_1/m$ $Pcca$ $P2_1/m$ $Pbam$ $P2_1/c$ $Pccn$ $P2_1/c$ $Pbcm$ $Pmmm$ Pnm Pnn $Pmnn$ $Pccm$ $Pbcn$ $Pban$ $Pbca$ $Pmma$ $Pnma$ $Pnna$	$P4/m$ $P4/nmm$ $P4_2/m$ $P4/ncc$ $P4/n$ $P4_2/mmc$ $P4_2/n$ $P4_2/mcm$ $P4/mmm$ $P4_2/nbc$ $P4/mcc$ $P4_2/nnm$ $P4/nbm$ $P4_2/mbc$ $P4/nnc$ $P4_2/mnm$ $P4/nbm$ $P4_2/nmc$ $P4/mnc$ $P4_2/ncm$	$P\bar{3}$ $P\bar{3}1m$ $P\bar{3}1c$ $P\bar{3}m1$ $P\bar{3}c1$ $P6/m$ $P6_3/m$ $P6/mmm$ $P6/mcc$ $P6_3/mcm$ $P6_3/mmc$	$R\bar{3}$ $R\bar{3}m$ $R\bar{3}c$ $Pm\bar{3}$ $Pn\bar{3}$ $Pa\bar{3}$ $Pm\bar{3}m$ $Pn\bar{3}n$ $Pm\bar{3}n$ $Pn\bar{3}m$
Permissible translations of the origin	$(0, 0, 0); (0, \frac{1}{2}, \frac{1}{2});$ $(\frac{1}{2}, 0, 0); (\frac{1}{2}, 0, \frac{1}{2});$ $(0, \frac{1}{2}, 0); (\frac{1}{2}, \frac{1}{2}, 0);$ $(0, 0, \frac{1}{2}); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$	$(0, 0, 0);$ $(0, 0, \frac{1}{2});$ $(\frac{1}{2}, \frac{1}{2}, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$	$(0, 0, 0);$ $(0, 0, \frac{1}{2}).$	$(0, 0, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$
Vector \mathbf{h}_s seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, k, l)	$(h+k, l)$	(l)	$(h+k+l)$
Seminvariant modulus	$(2, 2, 2)$	$(2, 2)$	(2)	(2)
Seminvariant phases	φ_{ggg}	$\varphi_{ggg}; \varphi_{uug};$	$\varphi_{ggg}; \varphi_{guu};$ $\varphi_{ugg}; \varphi_{uug};$	$\varphi_{ggg}; \varphi_{uug};$ $\varphi_{ugu}; \varphi_{guu};$
Number of phases linearly semi-independent to be specified	3	2	1	1

Table 2. Permissible translations, moduli and seminvariant phases for primitive non-centrosymmetric space groups

H-K groups	(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) - $P(2, 2, 0)$	$(h+k, l)$ - $P(2, 0)$	$(h+k, l)$ - $P(2, 2)$	$(h-k, l)$ - $P(3, 0)$	$(h-k, l)$ - $P(3, 2)$	(l) - $P(0)$	(l) - $P(2)$	$(h+k+l)$ - $P(0)$	$(h+k+l)$ - $P(2)$
Space groups	P1	P2 P ₂₁	Pm Pc	P222 P22 ₁ P2 ₁ 2 ₁ P2 ₁ 2 ₁ 2 ₁	Pmm2 Pmc2 ₁ Pcc2 Pma2 Pca2 ₁ Pnc2 Pmm2 ₁ Pba2 Pna2 ₁ Pmn2	P4 P4 ₁ P4 ₂ P4 ₃ P4mm P4bm P4 ₃ cm P4 ₂ nm P4cc P4nc P4 ₂ nc P4 ₂ bc	P4 P422 P42 ₁ P4 ₂ 2 ₁ P4 ₃ 2 ₁ P4 ₂ m P4 ₂ c P4 ₂ 1 ₁ P4 ₂ 1 ₂ P4 ₂ m2 P4c2 P4b2 P4m2	P3 P3 ₁ P3 ₂ P3m1 P3c1	P312 P3 ₁ 12 P3 ₂ 12 P6 P6 ₁ P6 ₂ P6 ₃ P6 ₄ P6 ₅ P6 ₆ P6 ₇ P6 ₈ P6 ₉ P6 ₁₀ P6 ₁₁ P6 ₁₂	P321 P3 ₁ 21 P3 ₂ 21 P622 P6 ₁ 22 P6 ₂ 22 P6 ₃ 22 P6 ₄ 22 P6 ₅ 22 P6 ₆ 22 P6 ₇ 22 P6 ₈ 22 P6 ₉ 22 P6 ₁₀ 22 P6 ₁₁ 22 P6 ₁₂ 22	R32 P23 P2 ₁ 3 P432 P4 ₃ 32 P4 ₃ 32 P4 ₃ 32 P4 ₃ m P4 ₃ n		
Permissible translations of the origin	(x, y, z)	$(0, y, 0)$ $(0, y, \frac{1}{2})$ $(\frac{1}{2}, y, 0)$ $(\frac{1}{2}, y, \frac{1}{2})$	$(x, 0, z)$ $(x, \frac{1}{2}, z)$	$(0, 0, 0)$ $(\frac{1}{2}, 0, 0)$ $(0, \frac{1}{2}, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	(x, x, x)	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
Vector h , seminvariantly associated with $h = (h, k, l)$	(h, k, l)												
Seminvariant modulus	$(0, 0, 0)$	$(2, 0, 2)$	$(0, 2, 0)$	$(2, 2, 2)$	$(2, 2, 0)$	$(2, 0)$	$(2, 2)$	$(3, 0)$	$(3, 2)$	(l)	(2)	(0)	(2)
Seminvariant phases	φ_{000}	φ_{202}	φ_{020}	φ_{222}	φ_{220}	φ_{200} φ_{200}	φ_{222} φ_{222}	φ_{300} , if $h-k \equiv 0 \pmod{3}$	φ_{320} , if $h+k \equiv 0 \pmod{3}$	φ_{hk0}	φ_{hkg}	φ_{h+k+l}	φ_{222} , φ_{222} , φ_{222}
Permissible variations for semi-independent phases	$\ \infty\ $	$\ \infty\ $, $\ 2\ $ if $k=0$	$\ \infty\ $, $\ 2\ $ if $h=l=0$	$\ 2\ $	$\ \infty\ $, $\ 2\ $ if $l=0$	$\ \infty\ $, $\ 2\ $ if $l=0$	$\ 2\ $	$\ \infty\ $, $\ 3\ $ if $l=0$	$\ 2\ $ if $h \equiv k \pmod{3}$, $\ 3\ $ if $l \equiv 0 \pmod{3}$	$\ 2\ $	$\ 2\ $	$\ \infty\ $	$\ 2\ $
Number of phases linearly semi-independent to be specified	3			2			1			1			

(3) *Equivalence classes.* H-K assemble all the permissible origins defined by (1) into equivalence classes.

In our notation, all the permissible origins corresponding to a fixed functional form of the structure factor constitute an equivalence class. Hence it is not necessary, as in the H-K papers, to divide the space groups into categories according to the number of equivalence classes associated with each group.

(4) *Seminvariant phases, vectors and moduli:* As in the H-K papers, the structure seminvariants are phases or linear combination of phases whose value, for a fixed functional form of the structure factor, is independent of the choice of cell origin. Therefore $\sum_j A_j \varphi_{h_j}$ with integer A_j is a structure seminvariant if the condition

$$\sum_j A_j (\mathbf{h}_j \mathbf{X}_p) \equiv 0 \pmod{1} \quad p=1,2,\dots \quad (5)$$

is verified; \mathbf{X}_p is a permissible translation. Equation (5) indeed implies that any shift between permissible origins changes the value of $\sum_j A_j \varphi_{h_j}$ by an integer multiple of 2π . It is easily verified that this definition of the structure seminvariant is the same as in the H-K papers.

This notation requires no modification, for primitive space groups, in the meanings of the seminvariant vector \mathbf{h}_s and the seminvariant modulus ω_s (see Tables 1, 2), as defined by H-K.

In conventionally centred cells the systematic absences can be suitably associated with equation (5) to define \mathbf{h}_s , and ω_s . For example, in space group *I222*

equation (5) by itself defines a seminvariant vector $\mathbf{h}'_s=(h,k,l)$ and a seminvariant modulus $\omega'_s=(2,2,2)$. But if we note that non-zero reflexions are characterized by the condition $h+k+l \equiv 0 \pmod{2}$, we can choose a seminvariant vector $\mathbf{h}_s=(h,k)$ and a seminvariant modulus $\omega_s=(2,2)$.

This procedure gives the result that the dimensions of seminvariant moduli are equal to the number of phases which have to be specified in fixing the origin.

(5) *Structure invariants:* In the H-K papers (and in their tables for primitive space groups), the structure invariants are phases or linear combinations of phases whose value is independent of the choice of origin among the permissible origins defined by (1).

This definition is in contrast with the concept of structure invariant widely used in the literature, according to which structure invariants are phases or linear combination of phases, for example $\sum_j A_j \varphi_{h_j}$, whose value is independent of cell origins: for example $\sum_j A_j \mathbf{h}_j=0$.

In this notation the concept of structure invariant, as defined by H-K, is not necessary: this simplification results because we do not confide a special role, as do Gramaccioli & Zechmeister (1972), to the operation 'centre of symmetry'.

(6) *Symbols used in the Tables:* We say that all the space groups which present the same permissible translations of the origin form a H-K group.

Each group can be denoted by a maximum of seven symbols which are:

Table 3. Permissible translations, moduli and seminvariant phases for centrosymmetric space groups with conventional centred cells

H-K groups	$(h,l)\underline{C}(2,2)$	$(k,l)\underline{I}(2,2)$	$(h+k+l)\underline{F}(2)$	$(l)\underline{I}(2)$	\underline{I}
Space groups	<i>C2/m</i> <i>C2/c</i> <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>Fm3</i> <i>Fd3</i> <i>Fm3m</i> <i>Fm3c</i> <i>Fd3m</i> <i>Fd3c</i>	<i>I4/m</i> <i>I4₁/a</i> <i>I4/mmm</i> <i>I4/mcm</i> <i>I4₁/amd</i> <i>I4₁/acd</i>	<i>Im3</i> <i>Ia3</i> <i>Im3m</i> <i>Ia3d</i>
Permissible translations of the origin	$(0,0,0)$ $(0,0,\frac{1}{2})$ $(\frac{1}{2},0,0)$ $(\frac{1}{2},0,\frac{1}{2})$	$(0,0,0)$ $(0,0,\frac{1}{2})$ $(0,\frac{1}{2},0)$ $(\frac{1}{2},0,0)$	$(0,0,0)$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$(0,0,0)$ $(0,0,\frac{1}{2})$	$(0,0,0)$
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	$(2,2)$	$(2,2)$	(2)	(2)	$(1,1,1)$
Seminvariant phases	$\varphi_{g\bar{g}\bar{g}}$	$\varphi_{g\bar{g}\bar{g}}$	$\varphi_{g\bar{g}\bar{g}}$	$\varphi_{g\bar{u}\bar{g}}$; $\varphi_{g\bar{g}\bar{g}}$ $\varphi_{u\bar{u}\bar{g}}$; $\varphi_{u\bar{g}\bar{g}}$	any φ_{hkl}
Number of phases linearly semi-independent to be specified	2		1		0

Table 4. Permissible translations, moduli and seminvariant phases for non-centrosymmetric space groups with conventional centred cells

H-K groups	(k, l) - $C(0, 2)$	(h, l) - $C(2, 0)$	(h, l) - $C(2, 2)$	(h, l) - $A(2, 0)$	(h, l) - $I(2, 0)$	(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
Space groups	$C2$	Cm Cc	$C222$ $C222_1$ $Ccc2$	$Amm2$ $Abm2$ $Ama2$ $Abc2$	$Imm2$ $Iba2$ $Ima2$	$I222$ $I2_12_12_1$	$F432$ $F4_32$	$F222$ $F23$ $F\bar{4}3m$ $F\bar{4}3c$	$I4$ $I4_1$ $I4mm$ $I4cm$ $I4_1md$ $I4_1cd$	$I422$ $I4_122$	$I\bar{4}$ $I\bar{4}m2$ $I\bar{4}c2$ $I\bar{4}2m$ $I\bar{4}2d$	$Fmm2$ $Fdd2$	$I23$ $I2_13$ $I432$ $I4_132$ $I\bar{4}3m$ $I\bar{4}3d$
Permissible translations of the origin	$(0, y, 0)$ $(0, y, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(0, \frac{1}{2}, 0)$ $(\frac{1}{2}, 0, 0)$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, z)$	$(0, 0, 0)$ $(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, z)$	$(0, 0, z)$	$(0, 0, 0)$
Vector \mathbf{h} , seminvariantly associated with $\mathbf{h}=(h, k, l)$	(k, l)	(h, l)											
Seminvariant modulus	$(0, 2)$	$(0, 0)$	$(2, 2)$	$(2, 0)$	$(2, 0)$	$(2, 2)$	(2)	(4)	(0)	(2)	(4)	(0)	$(1, 1, 1)$
Seminvariant phases	φ_{gg}	φ_{ggo}	φ_{ggg}	φ_{ggo}	φ_{ggo}	φ_{ggg}	φ_{ggg}	φ_{hkt} , if $h+k+l \equiv 0 \pmod{4}$	φ_{kno}	φ_{hkg}	φ_{hkt} , if $(2k-l) \equiv 0 \pmod{4}$	φ_{hko}	any φ_{hkt}
Permissible variations for semi-independent phases	$\ \infty\ $, $\ 2\ $ if $k=0$	$\ \infty\ $, $\ 2\ $ if $l=0$	$\ 2\ $	$\ \infty\ $, $\ 2\ $ if $l=0$	$\ \infty\ $, $\ 2\ $ if $l=0$	$\ 2\ $	$\ 2\ $	$\ 2\ $ if $h+k+l \equiv 0 \pmod{2}$, $\ 4\ $ if $h+k+l \equiv 1 \pmod{2}$	$\ \infty\ $	$\ 2\ $	$\ 2\ $ if $2k-l \equiv 0 \pmod{2}$, $\ 4\ $ if $2k-l \equiv 1 \pmod{2}$	$\ \infty\ $	any φ_{hkt}
Number of phases lin. semi-independent to be specified		2		2			1		1				0

(1) the components of the vectors \mathbf{h} , seminvariantly associated with $\mathbf{h}=(h,k,l)$; it can be useful to preserve this information in the symbol of the H-K group.

(2) The type of the cell (P primitive, *etc.* . . .): following Rogers (1950, 1965), the lattice symbol is underlined if the point group is centrosymmetric.

(3) The seminvariant modulus ω_s .

The meaning of the symbols ($\|2\|$, $\|\infty\|$, . . .) used in the Tables 1-4 is the same as in Karle (1970).

References

- GRAMACCIOLI, C. M. & ZECHMEISTER, K. (1972). *Acta Cryst.* **A28**, 154-158.
- HALL, S. R. (1970). *Symmetry Considerations in the Application of the Structure Invariants*. Nato Advanced Study Institute on Direct and Patterson Methods. Parma, Italy.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.
- HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45-55.
- HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 93-97.
- KARLE, J. (1970). In *Crystallographic Computing*. Edited by F. R. AHMED. Copenhagen: Munksgaard.
- KARLE, J. & HAUPTMAN, H. (1961). *Acta Cryst.* **14**, 217-223.
- ROGERS, D. (1950). *Acta Cryst.* **3**, 455-464.
- ROGERS, D. (1965). In *Computing Methods in Crystallography*. Edited by J. S. ROLLETT. London: Pergamon Press.

Acta Cryst. (1974). **A30**, 395

Geometric Sources of Redundancy in Intensity Data and Their Use for Phase Determination

BY G. BRICOGNE

MRC Laboratory of Molecular Biology, Cambridge, England

(Received 14 November 1973; accepted 14 January 1974)

Linear equations are derived in direct space, which express the relation between the electron densities of crystals built from the same molecule, but with different lattices or several identical subunits in their asymmetric units. They are shown to be equivalent to the most general 'molecular-replacement' phase equations in reciprocal space. The solution of these phase equations by the method of successive projections is discussed. This algorithm, best implemented in direct space by averaging operations, is shown to be convergent for over-determined problems, and to be equivalent to a least-squares solution of the phase equations.

Introduction

The 'molecular-replacement' method has now a well documented literature, which has recently been collected in a book (Rossmann, 1972). It aims at exploiting the redundancies of geometrical origin which may be present in X-ray intensity data, in order to determine or refine phases. Such redundancies arise if a protein can crystallize with several identical molecules in the asymmetric unit, or in several crystal forms.

The basic equations expressing the phase constraints thus generated were derived by Rossmann & Blow (1963), Main & Rossmann (1966), and Crowther (1967). Their implementation was investigated by Rossmann & Blow (1963, 1964), Main (1967), Crowther (1969) and Jack (1973). All this work was done in reciprocal space *only*, although Main (1967) and Rossmann (1972) suggested that direct-space methods should be formally equivalent but of greater practical utility.

In this work, a rigorous proof of this formal equivalence is presented. The equations are first written in direct space, using an adequate linear operator formalism. A Fourier transformation then yields equations in reciprocal space, which are found to be the most general molecular-replacement equations in Crow-

ther's linear formulation. This proves the equivalence in question.

In both direct and reciprocal spaces, the equations express the fact that a certain vector, representing a set of structures built from a common subunit, is constrained to lie in the eigenspace of a certain orthogonal projector. In reciprocal space, this projector is represented by a matrix. In direct space, the projection operation consists in averaging the electron densities of all the crystallographically independent molecules present in all crystals, then rebuilding each crystal from this averaged molecule, the density outside the molecular boundaries being set to a uniform background value. The direct-space method has considerable computational advantages. Indeed, averaging is a simple operation, and the molecular boundaries can easily be given any desired shape.

If N subunits are thus averaged, the signal-to-noise ratio of the electron-density maps will increase, by a factor of at least \sqrt{N} since we also remove noise from the solvent regions. Therefore, combining the experimental amplitudes with the phases recomputed from these averaged maps - or, equivalently, with the phases of the projected structure factors - may be expected to give improved maps.