Acta Cryst. (1974). A**30**, 631

Structure Factor Algebra in the Probabilistic Procedure for Phase Determination. II

BY C. GIACOVAZZO

Istituto di Mineralogia, Università di Bari, Italy

(*Received* 14 *December* 1973; *accepted* 11 *March* 1974)

Some distribution functions deduced in the previous paper [Giacovazzo, C. (1974). *Acta Cryst.* A30, 626–630] are further developed. A new form of the Cochran relation $\langle E_{\mathbf{h}}\rangle = E_{\mathbf{k}}E_{\mathbf{h-k}}/N^{1/2}$ is suggested, which is valid in all space groups. A new generalized tangent formula is pointed out which takes the statistical weights of the reflexions into account, as well as their contingent centrosymmetric nature. Experimental tests gave satisfactory results.

Theoretical considerations

If $E_{\mathbf{h}}$ is a non-centrosymmetric reflexion, (I.23), (I.24), (I.25), (I.26) suggest [the prefix I denotes equations of part I of this series (Giacovazzo, 1974)] that the distribution (I.9) is always valid, provided a suitable weight $W_{\mathbf{h},\mathbf{k}}$ is applied to the quantity $(2/\sqrt{N})|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|$. This weight has been specified by (I.28) for some numerical examples in the space group $P222$. A generalization of this formula is now necessary to deal with all space groups.

Because

$$E_{\mathbf{h}} = \frac{1}{\sqrt{p_{\mathbf{h}}}}\sum_1^t{}_j\, v_j\xi_j(\mathbf{h}) = \frac{1}{\sqrt{p_{\mathbf{h}}}}\sum_1^t{}_j\, v_j[\psi_j(\mathbf{h})+i\eta_j(\mathbf{h})]\,,$$

where

$$v_j = f_j/(\sum_1^n{}_j f_j^2)^{1/2},$$

by putting

$$\psi'_j(\mathbf{h}) = \psi_j(\mathbf{h})/\sqrt{p_{\mathbf{h}}},\quad \eta'_j(\mathbf{h}) = \eta_j(\mathbf{h})/\sqrt{p_{\mathbf{h}}},$$

(I.23) and (I.24) can be written

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\rangle = \frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}| \times\left\{\frac{\langle\psi'(\mathbf{h})\psi'(\mathbf{k})\psi'(\mathbf{h-k})\rangle}{\langle\psi'^2(\mathbf{k})\rangle\langle\psi'^2(\mathbf{h-k})\rangle}\cos\varphi_{\mathbf{k}}\cos\varphi_{\mathbf{h-k}} + \frac{\langle\psi'(\mathbf{h})\eta'(\mathbf{k})\eta'(\mathbf{h-k})\rangle}{\langle\eta'^2(\mathbf{k})\rangle\langle\eta'^2(\mathbf{h-k})\rangle}\sin\varphi_{\mathbf{k}}\sin\varphi_{\mathbf{h-k}}\right\}, \quad (1)$$

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\rangle = \frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}| \times\left\{\frac{\langle\eta'(\mathbf{h})\eta'(\mathbf{k})\psi'(\mathbf{h-k})\rangle}{\langle\eta'^2(\mathbf{k})\rangle\langle\psi'^2(\mathbf{h-k})\rangle}\sin\varphi_{\mathbf{k}}\cos\varphi_{\mathbf{h-k}} + \frac{\langle\eta'(\mathbf{h})\psi'(\mathbf{k})\eta'(\mathbf{h-k})\rangle}{\langle\psi'^2(\mathbf{k})\rangle\langle\eta'^2(\mathbf{h-k})\rangle}\cos\varphi_{\mathbf{k}}\sin\varphi_{\mathbf{h-k}}\right\}. \quad (2)$$

The considerations given in the Appendix allow us to state that, if $E_{\mathbf{h}}$ is a non-centrosymmetric reflexion,

$$\langle E_{\mathbf{h}}|E_{\mathbf{k}},E_{\mathbf{h-k}}\rangle = \frac{\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h-k})\rangle}{m\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h-k}}}}\,\frac{1}{\sqrt{N}}E_{\mathbf{k}}E_{\mathbf{h-k}}\,. \quad (3)$$

If $E_{\mathbf{h}}$ is centrosymmetric, we obtain

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}|E_{\mathbf{k}},E_{\mathbf{h-k}}\rangle = \frac{\mu}{m}\,\frac{\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h-k})\rangle}{\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h-k}}}} \times\frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}}) \quad (4)$$

or

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}|E_{\mathbf{k}},E_{\mathbf{h-k}}\rangle = \frac{\mu}{m}\,\frac{\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h-k})\rangle}{\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h-k}}}} \times\frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\,. \quad (5)$$

$\mu=1$ if both $E_{\mathbf{k}}$ and $E_{\mathbf{h-k}}$ are centrosymmetric, $\mu=2$ if $E_{\mathbf{k}}$ and (or) $E_{\mathbf{h-k}}$ are non-centrosymmetric.

Equation (3) can be usefully compared with the formula (I.14) valid for centrosymmetric crystals. In the case in which all the reflexions are general, (3) is equivalent to the well-known relation (Cochran, 1955)

$$\langle E_{\mathbf{h}}\rangle = \frac{1}{\sqrt{N}}E_{\mathbf{k}}E_{\mathbf{h-k}}\,. \quad (6)$$

The same general role is played by (4) and (5) with respect to the well-known

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\rangle = \frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\,, \quad (7)$$

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\rangle = \frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\,. \quad (8)$$

Equations (3), (4) and (5), however, are more general than (6), (7) and (8). In this connexion we emphasize two aspects of the question:

(*a*) The algebraic form of the relation (6) is not invariant when non-primitive cells are chosen. Let **h**, **k**, **h**−**k** be three indices in a primitive cell of order m (N is the total number of atoms) and **H**, **K**, **H**−**K** the corresponding indices in a τ-centred cell ($N_c=\tau N$ is the total number of atoms). Even though $E_{\mathbf{H}}$, $E_{\mathbf{K}}$, $E_{\mathbf{H-K}}$ are general reflexions, formula (6) is inadequate to symbolize the statistical relation between $E_{\mathbf{H}}$ and $E_{\mathbf{K}}E_{\mathbf{H-K}}$: in fact we should write

$$\langle E_{\mathbf{H}}\rangle = (N_c/\tau)^{-1/2}E_{\mathbf{K}}E_{\mathbf{H-K}}\,.$$

On the contrary, the algebraic form of (6) does not change when a centred cell is chosen: in fact, because

$$p_{\mathbf{H}}=\tau p_{\mathbf{h}},\ \xi(\mathbf{H})=\tau\xi(\mathbf{h})\ \text{and}\ m_c=\tau m,$$

we have the result

$$\frac{\langle\xi(\mathbf{H})\xi(\mathbf{K})\xi(\mathbf{H}-\mathbf{K})\rangle}{m_c\sqrt{N_c}\sqrt{p_{\mathbf{H}}p_{\mathbf{K}}p_{\mathbf{H}-\mathbf{K}}}}=\frac{\langle\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle}{m\sqrt{N}\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}-\mathbf{k}}}}\,.$$

(*b*) The occurrence of a strong triplet $|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|$ is not always a sufficient condition for deriving $\varphi_{\mathbf{h}}$ from knowledge of $\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}$. For example, in the space group $P2_12_12_1$ the knowledge of the phases $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{h}-\mathbf{k}}$, where $\mathbf{k}=(0,g,u)$ and $\mathbf{h}-\mathbf{k}=(g,g,0)$, gives no contribution to the knowledge of $\varphi_{\mathbf{h}}=\varphi_{g0u}$ (see Table 1). In particular, $\varphi_{\mathbf{h}}\simeq(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})$ cannot be the case as in (6): the crystallographic symmetry restrains the values of the phases to

$$\varphi_{\mathbf{k}},\varphi_{\mathbf{h}-\mathbf{k}}=0;\quad \varphi_{\mathbf{h}}=\pm\pi/2\,.$$

Equations (3), (4) and (5) resolve the question because

$$\langle\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle=0\,.$$

Following Cochran's (1955) arguments, we can conclude that, if $\varphi_{\mathbf{h}}$ is a non-centrosymmetric reflexion, the conditional distribution of $\varphi_{\mathbf{h}}$ can be still written in the form

$$P(\varphi_{\mathbf{h}})=\exp\{G_{\mathbf{h},\mathbf{k}}\cos(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})\}/2\pi I_0(G_{\mathbf{h},\mathbf{k}}),\quad (9)$$

where

$$G_{\mathbf{h},\mathbf{k}}=\frac{\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle}{\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}-\mathbf{k}}}}\,\frac{2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|}{\sqrt{N}}\,.\quad (10)$$

The weight $W_{\mathbf{h},\mathbf{k}}$ introduced in equation (I.28) is so defined in all space groups.

If r 'addition pairs' $\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}$ are fixed, following Karle & Karle (1966), we may multiply the individual probability (9) and obtain

$$\textstyle\sum_r G_{\mathbf{h},\mathbf{k}}\sin(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})=0\,.$$

From this relation we can derive the generalized tangent formula

$$\tan\varphi_{\mathbf{h}}=\frac{\sum_r G_{\mathbf{h},\mathbf{k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}{\sum_r|G_{\mathbf{h},\mathbf{k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}\,.\quad (11)$$

In the same way we generalize the equations (3.35) and (3.36) of Karle & Karle (1966) as

$$\langle\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle=\frac{I_1(G_{\mathbf{h},\mathbf{k}})}{I_0(G_{\mathbf{h},\mathbf{k}})}\cos\varphi_{\mathbf{h}}\,,\quad (12)$$

$$\langle\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle=\frac{I_1(G_{\mathbf{h},\mathbf{k}})}{I_0(G_{\mathbf{h},\mathbf{k}})}\sin\varphi_{\mathbf{h}}\,,\quad (13)$$

where I_0 and I_1 are modified Bessel functions.

If $E_{\mathbf{h}}$ is a centrosymmetric reflexion ($\eta_{\mathbf{h}}=0$) in a non-centrosymmetric space group, relation (14) can be used. The probability $P_+(E_{\mathbf{h}})$ is then

$$P_+(E_{\mathbf{h}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{\mu\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle}{m\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}-\mathbf{k}}}}\,\frac{1}{N}\times|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\right].\quad (14)$$

If both $E_{\mathbf{k}}$ and $E_{\mathbf{h}-\mathbf{k}}$ are centrosymmetric, $\mu=1$: formula (14) coincides then with equation (I.17). It can be useful to emphasize that (14) evaluates correctly the probability $P_+(E_{\mathbf{h}})$ in the cases, recalled above, in which $\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle=0$. Equation (14), besides, is suitable to deal, in non-centrosymmetric structures, with reflexions having restricted values of the phases. A good criterion to assign phase values to the zonal reflexions whose phases are fixed by space-group symmetry is to evaluate the argument of tanh in (14) and to specify that this quantity is larger than a threshold value.

Experimental

The tangent formula (I.10) and its modified form (11) have been applied to the 102 largest normalized structure factors of the tincalconite (Giacovazzo, Menchetti & Scordari (1973)). 20 iterative cycles have been performed with both (I.10) and (11): 80 jointly assigned phase values resulted. Table 2 compares the true values φ of these phases with the values φ_t obtained by (I.10) and the phases φ_W obtained by (11).

As one can see, formula (11) seems more accurate than (I.10): the average values $\langle|\varphi-\varphi_W|\rangle$ and $\langle|\varphi-\varphi_t|\rangle$ are respectively 20 and 35°.

Some centrosymmetric reflexions have been inspected in order to test equation (12). Table 3 shows, when $\mathbf{h}=(0,0,12)$, the pairs $E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$ arranged in decreasing order of $A=(2/\sqrt{N})\,|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|$. We have considered three intervals of A and, for each interval, we have written the value $\langle\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle$ in the last

Table 1. *Values for space group* $P2_12_12_1$

$\mathbf{h}$	ggu	ggu	ggu	$g0u$	$0gu$	$g0u$	$g0u$	ggu	ggu	ggu	$0gu$	$0gu$
$\mathbf{k}$	ggu	ggu	$g0u$	ggu	ggu	$0gu$	$0gu$	ggu	$0gu$	$0gu$	$0gu$	$0gu$
$\mathbf{h}-\mathbf{k}$	ggg	$gg0$	ggg	ggg	ggg	ggg	$gg0$	$g00$	$g00$	$g0g$	$0gg$	$00g$
$\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h}-\mathbf{k})\rangle$	1	2	0	0	2	0	0	4	8	4	4	8
$\langle\eta(\mathbf{h})\eta(\mathbf{k})\psi(\mathbf{h}-\mathbf{k})\rangle$	1	2	2	2	0	0	0	4	0	0	0	0
$\langle\eta(\mathbf{h})\psi(\mathbf{k})\eta(\mathbf{h}-\mathbf{k})\rangle$	1	0	0	2	0	4	0	0	0	0	0	0
$\langle\psi(\mathbf{h})\eta(\mathbf{k})\eta(\mathbf{h}-\mathbf{k})\rangle$	−1	0	−2	0	−2	0	0	0	0	0	0	0
$\langle\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle$	0	0	0	−4	4	−4	0	0	8	4	4	8
$\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle$	4	4	4	4	4	4	0	8	8	4	4	8
$\frac{\mu}{m}\frac{\langle\xi(-\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle}{\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}-\mathbf{k}}}}$	1	1	1	2	2	2	0	$\sqrt{2}$	$\sqrt{2}$	1	1	$\sqrt{2}$

Table 2. *Values of phases derived by different methods*

h	*k*	*l*	*E*	φ	φ_t	φ_W	$\|\varphi-\varphi_t\|$	$\|\varphi-\varphi_W\|$
4	6	1	2·99	68	90	90	22	22
6	3	9	2·64	179	164	176	15	3
0	9	3	2·62	180	180	180	0	0
6	4	11	2·50	30	112	83	82	53
5	0	11	2·45	0	0	0	0	0
7	0	1	2·44	0	0	0	0	0
9	0	6	2·33	0	0	0	0	0
9	1	5	2·10	207	−139	−150	14	3
3	3	0	1·97	−22	−91	−42	69	20
3	3	3	1·94	199	−132	−159	29	2
1	4	9	1·92	88	107	58	19	30
5	3	11	1·91	−83	−121	−79	38	4
6	6	3	1·89	181	131	172	50	9
4	2	2	1·87	−45	−4	−26	41	19
7	3	1	1·83	240	−122	−103	2	17
4	7	9	1·83	78	−3	29	81	49
2	6	11	1·82	23	78	38	55	15
3	1	5	1·82	229	−132	−131	1	0
0	6	6	1·80	0	0	0	0	0
9	4	2	1·78	−37	−5	1	32	38
0	4	8	1·77	0	0	0	0	0
2	10	1	1·75	123	141	100	18	23
0	3	9	1·72	180	180	180	0	0
0	2	10	1·68	0	0	0	0	0
9	3	3	1·68	197	−141	−139	22	24
3	7	5	1·68	204	−134	−158	22	2
2	8	9	1·68	269	170	−71	99	20
10	0	1	1·67	0	180	180	180	180
4	0	4	1·65	0	0	0	0	0
3	5	1	1·61	−49	−115	−70	66	21
8	2	3	1·61	249	−177	−115	66	4
8	2	9	1·59	22	100	48	78	26
1	3	7	1·59	241	−119	−115	0	4
3	7	2	1·58	250	−109	−72	1	38
8	0	5	1·56	180	180	180	0	0
2	8	0	1·54	52	84	86	32	34
1	9	1	1·51	−55	−117	−78	62	23
1	8	5	1·49	93	105	114	12	21
4	1	3	1·48	68	114	87	46	19
5	1	4	1·46	141	−125	−171	94	48
4	7	0	1·44	−49	−12	−67	37	28
5	1	13	1·44	224	−126	−154	10	18
7	5	5	1·44	157	−134	178	69	21
0	12	3	1·43	180	180	180	0	0
6	8	1	1·43	214	166	−167	48	21
0	7	11	1·38	0	0	0	0	0
7	1	3	1·38	119	−171	159	70	40
5	5	3	1·37	265	−123	−85	28	10

Table 2 (*cont.*)

h	*k*	*l*	*E*	φ	φ_t	φ_W	$\|\varphi-\varphi_t\|$	$\|\varphi-\varphi_W\|$
3	6	0	1·36	20	62	11	42	9
2	6	5	1·34	172	142	173	30	1
10	1	6	1·31	181	159	−153	22	26
6	4	5	1·31	194	144	154	50	40
1	11	5	1·31	168	176	145	8	23
2	8	3	1·30	1	103	−19	102	20
4	6	7	1·29	221	172	−165	49	26
1	7	6	1·26	230	−110	−135	20	5
10	1	9	1·25	83	129	58	46	25
6	4	8	1·24	56	89	80	33	24
5	2	12	1·23	82	57	96	25	14
7	2	11	1·23	63	14	39	49	24
0	2	1	1·21	0	0	0	0	0
3	10	2	1·21	−17	−77	−52	60	35
4	8	2	1·19	55	100	75	45	20
6	7	2	1·17	35	−5	19	40	16
7	1	6	1·17	228	−113	−136	19	4
5	5	9	1·16	−89	−120	−67	31	22
4	5	2	1·15	−47	8	−35	55	12
3	9	3	1·14	181	−143	−164	36	15
2	5	9	1·12	−32	27	−12	59	20
6	8	4	1·11	57	105	122	48	65
1	9	4	1·11	252	−137	−144	30	36
6	5	1	1·11	4	22	−12	18	16
3	9	6	1·10	−31	−88	−64	57	33
11	0	5	1·10	0	0	0	0	0
7	6	1	1·09	3	−30	−32	33	35
0	10	11	1·09	180	180	180	0	0
1	6	4	1·06	76	15	109	51	33
2	11	3	1·06	−64	−24	−47	40	17
4	9	1	1·03	−76	−21	−31	55	45
5	1	10	1·00	−41	−86	−75	45	34

column of Table 3. In each of these intervals $\langle G\rangle$ is closer than $\langle A\rangle$ to the theoretical value which corresponds, in (12), to the observed value of $\langle\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle$.

Conclusions

In the part I of this paper we have take into account, for centrosymmetric structures, the statistical weights of the reflexions. Formulae (I.14) and (I.17) have been deduced, which improve on the previous Cochran–Woolfson results. In non-centrosymmetric structures, the centrosymmetric nature of the reflexions as well as

Table 3. *Pairs* $E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$ *for* $E_{0,0,12}=+1{\cdot}05$

k			**h−k**			*A*	*G*	$\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})$	$\langle\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle$
6	4	11	4	6	1	7·84	13·57	0·788	
4	0	4	0	4	8	3·07	3·07	1·0	
3	1	5	1	3	7	3·04	5·26	0·978	
4	1	3	1	4	9	2·98	5·16	0·940	0·914
2	8	0	2	8	12	2·92	5·06	0·839	
8	2	3	2	8	9	2·84	4·91	0·940	
7	6	10	6	7	2	2·58	4·47	0·985	
2	2	6	2	2	6	2·49	4·31	1·0	
3	6	0	3	6	12	2·48	4·29	0·985	
8	2	9	2	8	3	2·17	3·75	0·933	0·965
3	8	1	3	8	13	1·98	3·42	0·965	
3	9	0	3	9	12	1·97	3·41	0·920	
6	4	5	4	6	7	1·77	3·07	0·891	
5	4	10	4	5	2	1·67	2·89	0·809	
5	5	9	5	5	3	1·67	2·89	0·994	0·867
8	5	6	5	8	6	1·58	2·73	0·642	
7	1	6	1	7	6	1·52	2·63	0·998	

the statistical weights have been taken into account. By the mathematical device of the joint probability distributions we have shown that the Cochran formula [equation (6)] is inadequate for centred space groups and for some reflexion classes in certain space groups. A new conditional distribution function [equation (9)] and a generalized tangent formula [equation (11)] have been suggested: some experimental tests proved satisfactory.

The use of equation (11) in the automatic procedures for the phase assignment is expensive in computing time: nevertheless equation (11) seems suitable in the refinement stages of the phases.

APPENDIX

By the definition of normalized structure factor (Hauptman & Karle, 1953; Bertaut, 1959)

$$\langle \xi'^2(\mathbf{h})\rangle = \langle \psi'^2(\mathbf{h})\rangle + \langle \eta'^2(\mathbf{h})\rangle \doteq m\,,$$

where m is the order of the space group.

If $E_\mathbf{h}$ is a general reflexion

$$\langle \psi'^2(\mathbf{h})\rangle = \langle \eta'^2(\mathbf{h})\rangle = \frac{m}{2}\,. \tag{A1}$$

If $E_\mathbf{h}$ is a centrosymmetric reflexion with $\eta'(\mathbf{h})=0$ or $\psi'(\mathbf{h})=0$,

$$\langle \psi'^2(\mathbf{h})\rangle = m \text{ or } \langle \eta'^2(\mathbf{h})\rangle = m\,. \tag{A2}$$

By linearization theory we can write, in analogy with equation (I.A2)

$$\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle = \sum_{s,r=1}^{m} a_s(\mathbf{h})a_r(\mathbf{k}) \times \xi[\mathbf{h}(\mathbf{R}_s+\mathbf{I})+\mathbf{k}(\mathbf{R}_r-\mathbf{I})]\,. \tag{A3}$$

Some interesting algebraical features of the expressions (I.A2) and (A3) can be shown:

(1) Unlike $\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(-\mathbf{h}-\mathbf{k})\rangle$, $\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle$ is in general equal to zero: in fact the condition $\mathbf{h}(\mathbf{R}_s+\mathbf{I})+\mathbf{k}(\mathbf{R}_r-\mathbf{I})=0$ requires either a centrosymmetric reflexion $\mathbf{h}$ or a suitable arrangement of the vectors $\mathbf{h}(\mathbf{R}_s+\mathbf{I})$ and $\mathbf{k}(\mathbf{R}_r-\mathbf{I})$.

We refer for an example to the space group $P2_12_12_1$ (some numerical values are shown in Table 1): the symmetry operations are

$$\mathbf{R}_1=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix};\quad \mathbf{R}_2=\begin{bmatrix}1&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{bmatrix};$$

$$\mathbf{R}_3=\begin{bmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{bmatrix};\quad \mathbf{R}_4=\begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix};$$

$$\mathbf{T}_1=\begin{bmatrix}0\\0\\0\end{bmatrix};\quad \mathbf{T}_2=\begin{bmatrix}\frac{1}{2}\\\frac{1}{2}\\0\end{bmatrix};$$

$$\mathbf{T}_3=\begin{bmatrix}0\\\frac{1}{2}\\\frac{1}{2}\end{bmatrix};\quad \mathbf{T}_4=\begin{bmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{bmatrix}.$$

If $\mathbf{h}=(g,0,u)$ is a centrosymmetric reflexion, $\mathbf{k}=(0,g,u)$, $\mathbf{h}-\mathbf{k}=(g,g,g)$, we obtain from equation (A3)

$$\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}-\mathbf{k})\rangle = -\xi(0) = -4\,. \tag{A4}$$

In fact, for $s=3$ and $r=1$ the condition $\mathbf{h}(\mathbf{R}_s+\mathbf{I})+\mathbf{k}(\mathbf{R}_r-\mathbf{I})=0$ is satisfied: the negative sign in (A4) derives from the a ($\mathbf{h}$) value.

(2) The mean value $\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(-\mathbf{h}-\mathbf{k})\rangle$, as we have shown in the paper I, is in general equal to m: the statistical features of $E_\mathbf{h}$, $E_\mathbf{k}$, $E_{\mathbf{h}-\mathbf{k}}$ can modify this situation, but never make $\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(-\mathbf{h}-\mathbf{k})\rangle$ negative.

In fact the condition $\mathbf{h}_1(\mathbf{R}_s-\mathbf{I})+(\mathbf{h}_2(\mathbf{R}_r-\mathbf{I})=0$ is verified only when

(*a*) $\mathbf{h}_1\mathbf{R}_s=\mathbf{h}_1$, $\mathbf{h}_2\mathbf{R}_r=\mathbf{h}_2$

(*b*) $(\mathbf{h}_1+\mathbf{h}_2)\mathbf{R}_s=\mathbf{h}_1+\mathbf{h}_2$.

In accordance with Bertaut (1959)

$$\xi(\mathbf{h}\mathbf{C}_s)=\xi(\mathbf{h})\,, \tag{A5}$$

or, more explicitly,

$$\xi(\mathbf{h}\mathbf{C}_s)=\xi(\mathbf{h}\mathbf{R}_s)\exp 2\pi i\mathbf{h}\mathbf{T}_s=\xi(\mathbf{h}\mathbf{R}_s)a_s(\mathbf{h})\,.$$

When $\mathbf{h}\mathbf{R}_s=\mathbf{h}$, as in (*a*) or (*b*), then $\xi(\mathbf{h}\mathbf{C}_s)=\xi(\mathbf{h})a_s(\mathbf{h})$, and, from (A5), $a_s(\mathbf{h})=1$.

The values of $a_s(\mathbf{h})$ and $a_r(\mathbf{k})$ in (A3) can then be made equal to unity, and some computational time can thus be saved in the evaluation of

$$\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(-\mathbf{h}-\mathbf{k})\rangle\,.$$

It should be noticed that $\langle \xi(\mathbf{h})\xi(\mathbf{k})\xi(-\mathbf{h}-\mathbf{k})\rangle$ can be also equal to zero in certain space groups. An example is shown in Table 2, column 8: in fact we obtain a contribution equal to m for $r=s=1$, a contribution equal to $-m$ for $s=2$, $r=3$.

(3) In spite of the differences between

$$\langle \xi'(\mathbf{h})\xi'(\mathbf{k})\xi'(\mathbf{h}-\mathbf{k})\rangle$$

and

$$\langle \xi'(\mathbf{h})\xi'(\mathbf{k})\xi'(-\mathbf{h}-\mathbf{k})\rangle\,,$$

following equalities are valid:

$$|\langle \psi'(\mathbf{h})\psi'(\mathbf{k})\psi'(\mathbf{h}-\mathbf{k})\rangle| = |\langle \psi'(-\mathbf{h})\psi'(\mathbf{k})\psi'(\mathbf{h}-\mathbf{k})\rangle|$$
$$|\langle \eta'(\mathbf{h})\eta'(\mathbf{k})\eta'(\mathbf{h}-\mathbf{k})\rangle| = |\langle \eta'(-\mathbf{h})\eta'(\mathbf{k})\eta'(\mathbf{h}-\mathbf{k})\rangle|\,,\ldots \tag{A6}$$

The reason is trivial, and resides in the relations

$$\psi(\mathbf{h})=\psi(-\mathbf{h}),\quad \eta(\mathbf{h})=-\eta(-\mathbf{h})\,.$$

References

Bertaut, E. F. (1959). *Acta Cryst.* **12**, 541–549.

Cochran, W. (1955). *Acta Cryst.* **8**, 473–478.

Giacovazzo, C. (1974). *Acta Cryst.* A**30**, 626–630.

Giacovazzo, C., Menchetti, S. & Scordari, F. (1973). *Amer. Min.* **58**, 523–530.

Hauptman, H. & Karle, J. (1953). *Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.

Karle, J. & Karle, I. (1966). *Acta Cryst.* **21**, 849–859.