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Structure Factor Algebra in the Probabilistic Procedure for Phase Determination. IV. Quartets

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An investigation has been carried out on the influence of the space-group symmetry in the quartet relationships. New generalized formulae are derived which take the statistical weights of the reflexions into account. Cross-reflexions of special type may strongly modify formulae valid in $P1$ and $P\bar{1}$.

1. Introduction

In recent papers (Giacovazzo, 1974*a*, *b*, *c*) a combination of the joint probability distribution approach and of the space group algebra has been proposed. $\sum_1$, Sayre and tangent formulae were generalized so as to take the statistical weights of the reflexions into account as well as their contingent centrosymmetric nature. For example, the well known Cochran (1955) relation was rewritten in the form:

$$P(\varphi_{\mathbf{H}_1}) = \exp\left[G_{\mathbf{H}_1,\mathbf{H}_2} \cos\left(\varphi_{\mathbf{H}_1} - \varphi_{\mathbf{H}_2} - \varphi_{\mathbf{H}_1-\mathbf{H}_2}\right)\right] / 2\pi I_0(G_{\mathbf{H}_1,\mathbf{H}_2}) ,$$

where

$$G_{\mathbf{H}_1,\mathbf{H}_2} = \frac{\langle \xi(-\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1-\mathbf{H}_2)\rangle}{m\sqrt{(p_{\mathbf{H}_1}p_{\mathbf{H}_2}p_{\mathbf{H}_1-\mathbf{H}_2})}} \times \frac{2|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1-\mathbf{H}_2}|}{\sqrt{N}} ;$$

ξ is the trigonometric function for the structure factor, m is the order of the space group, $p_{\mathbf{H}}$ the statistical weight of $E_{\mathbf{H}}$. The weight $G_{\mathbf{H}_1,\mathbf{H}_2}$ is invariant under cell transformations and takes the full space-group symmetry into account. For example, in $P2_12_12_1$ the knowledge of $\varphi_{\mathbf{H}_2}$ and $\varphi_{\mathbf{H}_1-\mathbf{H}_2}$, when $\mathbf{H}_2=(0,g,u)$ and $H_1-H_2=(g,g,0)$, gives no contribution to the knowledge of $\varphi_{\mathbf{H}_1}=\varphi_{g0u}$. In accordance with this fact,

$$\langle \xi(-\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1-\mathbf{H}_2)\rangle = 0 .$$

In recent years (Hauptman, 1974*a*, *b*; 1975*a*, *b*; Green & Hauptman, 1976; Hauptman & Green, 1976; Giacovazzo, 1975; 1976*a*, *b*, *c*) some probabilistic theories of the cosine invariant $\cos(\varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}+\varphi_{\mathbf{H}_3}-\varphi_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})$ have been described in $P1$ and $P\bar{1}$. These theories lead to an estimate for the value of the cosine which may lie anywhere between -1 and $+1$ and depends on the values of the seven magnitudes $|E_{\mathbf{H}_1}|$, $|E_{\mathbf{H}_2}|$, $|E_{\mathbf{H}_3}|$, $|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|$, $|E_{\mathbf{H}_1+\mathbf{H}_2}|$, $|E_{\mathbf{H}_1+\mathbf{H}_3}|$, $|E_{\mathbf{H}_2+\mathbf{H}_3}|$.

A general theory of quartets valid in all the space groups has not been given. One would expect that the phase relationships as stated in $P1$ or $P\bar{1}$ are valid respectively in any non-centrosymmetric or centrosymmetric space group if all seven $|E|$ magnitudes correspond to general reflexions. When special reflexions are involved, however, the phase relationships valid in $P1$ and $P\bar{1}$ may be affected in a remarkable way. The aim of this paper is to generalize to all space groups the probabilistic approaches proposed by Giacovazzo (1975, 1976*a*) and Hauptman (1975*a*). Giacovazzo's approach involves a Gram–Charlier expansion of the characteristic function in terms of the statistical cumulants. Hauptman's formulation directly uses the same cumulants in an exponential expression of the characteristic function. In order to give phase relationships valid in all the space groups, it will be enough to obtain the general expressions of the cumulants by space group algebra. Five Appendices are devoted to this algebraic analysis.

2. The mathematical approach

The Gram–Charlier expansion used (Giacovazzo, 1975) to derive the quartet relationships in $P\bar{1}$ is

$$C(u_1,u_2,\ldots,u_n) = \exp\left[-\tfrac{1}{2}(u_1^2+u_2^2+\ldots+u_n^2)\right] \times \left(1+\frac{S_3}{t^{3/2}}+\frac{S_4}{t^2}+\frac{S_3^2}{2t^3}+\ldots\right), \quad (1)$$

where u_i, $i=1,7$, are carrying variables associated with E_i, $t=N/m$ is the number of independent atoms in the unit cell for a space group of order m, and

$$S_v = t \sum_{(r+s+\ldots+w=v)} \frac{\lambda_{rs\ldots w}}{r!s!\ldots w!} (iu_1)^r (iu_2)^s \ldots (iu_n)^w . \quad (2)$$

$\lambda_{rs\ldots w}$ are the standardized cumulants of the distribution defined by

$$\lambda_{rs\ldots w} = \frac{K_{rs\ldots w}}{K_{20\ldots 0}^{r/2} K_{02\ldots 0}^{s/2} K_{00\ldots 2}^{w/2}} . \quad (3)$$

$K_{rs\ldots w}$ is a multivariate cumulant of order $r+s+\ldots+w$. The Fourier transform of (1) in $P\bar{1}$ gave the fundamental relation

$$P_+ \simeq \tfrac{1}{2} + \tfrac{1}{2} \tanh \left\{ \frac{1}{N} |E_{\mathbf{H}_1} E_{\mathbf{H}_2} E_{\mathbf{H}_3} E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \times \frac{[1 + (E^2_{\mathbf{H}_1+\mathbf{H}_2} - 1) + (E^2_{\mathbf{H}_1+\mathbf{H}_3} - 1) + (E^2_{\mathbf{H}_2+\mathbf{H}_3} - 1)]}{1 + 4(E^2_{\mathbf{H}_1+\mathbf{H}_2} + E^2_{\mathbf{H}_1+\mathbf{H}_3} + E^2_{\mathbf{H}_2+\mathbf{H}_3} - 3)/N} \right\} . \quad (4)$$

In order to derive phase information in $P1$ we have used the Gram–Charlier expansion

$$C(u_1, \ldots, u_7, v_1, \ldots, v_7) \simeq \exp\left[-\tfrac{1}{2} \left(\frac{u_1^2}{2} + \ldots + \frac{u_7^2}{2} + \frac{v_1^2}{2} + \ldots + \frac{v_7^2}{2} \right) \right] \times \left\{ 1 + \frac{S_3}{t^{3/2}} + \left(\frac{S_4}{t^2} + \frac{S_3^2}{2t^3} \right) + \ldots \right\}, \quad (5)$$

where

$$S_v = t \sum_{(r+s+\ldots+w=v)} \frac{1}{2^{v/2}} \frac{\lambda_{rs\ldots w}}{r!s!\ldots w!} (iu_1)^r (iu_2)^s \ldots (iv_7)^w . \quad (6)$$

The Fourier transform of (5) leads to

$$\langle \cos (\varphi_{\mathbf{H}_1} + \varphi_{\mathbf{H}_2} + \varphi_{\mathbf{H}_3} - \varphi_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}) \rangle \simeq \frac{I_1(G)}{I_0(G)}, \quad (7)$$

where

$$G = 2|E_{\mathbf{H}_1} E_{\mathbf{H}_2} E_{\mathbf{H}_3} E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \times [1 + (E^2_{\mathbf{H}_1+\mathbf{H}_2} - 1) + (E^2_{\mathbf{H}_1+\mathbf{H}_3} - 1) + (E^2_{\mathbf{H}_2+\mathbf{H}_3} - 1)]/N . \quad (8)$$

Retaining terms to order $1/t$, the probability distribution function is

$$P(E_1, E_2, E_3, E_4) = \frac{1}{(2\pi)^2} \exp \{ -\tfrac{1}{2}(E_1^2 + E_2^2 + E_3^2 + E_4^2) \} \times \left\{ 1 + \frac{1}{t} \left[\frac{\lambda_{4000}}{4!0!0!0!} H_4(E_1) + \ldots + \frac{\lambda_{0004}}{0!0!0!4!} H_4(E_4) + \frac{\lambda_{1111}}{1!1!1!1!} E_1 E_2 E_3 E_4 \right] \right\}, \quad (9)$$

where

$$E_1 = E_{\mathbf{H}_1}, E_2 = E_{\mathbf{H}_2}, \ldots,$$

and $H_v(x)$ is a Hermite polynomial defined by

$$H_v(x) = (-1)^v \exp (\tfrac{1}{2}x^2) \frac{\mathrm{d}^v}{\mathrm{d}x^v} \exp (-\tfrac{1}{2}x^2) .$$

From Appendix A

$$\langle E_{\mathbf{H}_1} E_{\mathbf{H}_2} E_{\mathbf{H}_3} E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \rangle = \frac{1}{tm^2} \left\langle \frac{\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)}{\sqrt{(p_{\mathbf{H}_1} p_{\mathbf{H}_2} p_{\mathbf{H}_3} p_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})}} \right\rangle = W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} N^{-1},$$

where

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} = \frac{1}{m} \left\langle \frac{\sum_{p,s,q}^{m} \xi[\mathbf{H}_1(\mathbf{R}_p - \mathbf{I}) + \mathbf{H}_2(\mathbf{R}_s - \mathbf{I}) + \mathbf{H}_3(\mathbf{R}_q - \mathbf{I})] \exp 2\pi i(\mathbf{H}_1\mathbf{T}_p + \mathbf{H}_2\mathbf{T}_s + \mathbf{H}_3\mathbf{T}_q)}{\sqrt{(p_{\mathbf{H}_1} p_{\mathbf{H}_2} p_{\mathbf{H}_3} p_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})}} \right\rangle .$$

In order to obtain general phase relationships, the more relevant standardized cumulants $\lambda_{rs\ldots w}$ will be estimated by Bertaut (1959*a*, *b*) algebra. For the sake of simplicity the analysis will be made for centrosymmetric space groups alone. Most of the conclusions derived however are valid in non-centrosymmetric space groups. Relevant differences will be explicitly mentioned.

3. The probability distribution $P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})$ in the centrosymmetric space groups

The aim of this section is to investigate the influence of the space group symmetry on the standardized cumulants λ_{1111} in the distribution $P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})$. For this distribution the characteristic function (1) has values

$$S_3 = 0 ,$$

$$S_4 = t \left[\frac{\lambda_{4000}}{4!0!0!0!} (iu_1)^4 + \ldots + \frac{\lambda_{0004}}{0!0!0!4!} (iu_4)^4 + \frac{\lambda_{1111}}{1!1!1!1!} (iu_1)(iu_2)(iu_3)(iu_4) \right] .$$

Thus, from (9) the probability that $E_{\mathbf{H}_1} E_{\mathbf{H}_2} E_{\mathbf{H}_3} E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$ is positive is given by

$$P_+ \simeq \tfrac{1}{2} + \tfrac{1}{2} \tanh \left(\frac{1}{N} W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} |E_{\mathbf{H}_1} E_{\mathbf{H}_2} E_{\mathbf{H}_3} E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \right) . \quad (10)$$

$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}$ takes the statistical nature of the reflexions into account: its value may be notably different from unity. When $W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} > 1$ the positivity of the quartet is strengthened. As an example, numerical values of $W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}$ for different reflexion types are shown in Table 1 for space group *Pmmm*. The table holds on condition that, when not demanded by the chosen types of $\mathbf{H}_j$ vectors, all the cross-vectors $\mathbf{H}_{ij} = \mathbf{H}_i + \mathbf{H}_j$ do not satisfy the relation $\mathbf{H}_{ij}(\mathbf{R}_s - \mathbf{I}) = 0$ for $\mathbf{R}_s \neq \mathbf{I}$.

For example, if the reflexions in the first column of the Table 1 have indices $(h_1k_1l_1)$, $(h_2k_2l_2)$, $h_2k_3l_3)$, $(h_1k_4l_4)$, H_{23} is a special reflexion: we obtain $W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} = 2$. Hence, the absolute value of $W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}$ may be notably different from unity even when all the $E_{\mathbf{H}_j}$ reflexions are general. The condition is that one or more cross-vectors lie on a symmetry element of the point group. In particular (Appendix A), the probability that the product $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$ is positive equals $\frac{1}{2}$ when one of the cross-reflexions is systematically absent, whatever the moduli $|E_{\mathbf{H}i}|$ may be. This is the chief result of this section.

For example, the reader will be able to show, from the expression of the trigonometric structure factor in $P2_1$, that

$$\langle\xi(257)\xi(31\bar{4})\xi(\bar{2}2\bar{7})\xi(\bar{3}\bar{8}4)\rangle=0\ .$$

In accordance with our conclusions, $\mathbf{H}_1+\mathbf{H}_3=(070)$ is a systematic absence. As will be shown in § 4, however, it is possible to obtain information about $\cos(\varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}+\varphi_{\mathbf{H}_3}-\varphi_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})$ even when some cross-reflexions correspond to space-group extinctions.

One needs to consider the more general probability distribution

$$P(E_{\mathbf{H}_1},E_{\mathbf{H}_2},E_{\mathbf{H}_3},E_{\mathbf{H}_1+\mathbf{H}_2},E_{\mathbf{H}_1+\mathbf{H}_3},E_{\mathbf{H}_2+\mathbf{H}_3},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\ .$$

This distribution in fact enables us to calculate (Giacovazzo, 1975) the products

$$\begin{aligned}&\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle\\ &\quad\times\langle\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle\ ,\\ &\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3)\rangle\\ &\quad\times\langle\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3)\rangle\ ,\\ &\langle\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_2+\mathbf{H}_3)\rangle\\ &\quad\times\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_2+\mathbf{H}_3)\rangle\ ,\end{aligned}$$

which, together with

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle\ ,$$

define the positivity or negativity of a quartet (Appendix *B*).

4. The probability distribution $P(E_{\mathbf{H}_1},E_{\mathbf{H}_2},E_{\mathbf{H}_3},E_{\mathbf{H}_1+\mathbf{H}_2},E_{\mathbf{H}_1+\mathbf{H}_3},E_{\mathbf{H}_2+\mathbf{H}_3},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})$ in the centrosymmetric space groups

In any centrosymmetric space group

$$\begin{aligned}S_3=t[&\lambda_{1101000}(iu_1)\,(iu_2)\,(iu_4)+\lambda_{1010100}(iu_1)\,(iu_3)\,(iu_5)\\ &+\lambda_{0110010}(iu_2)\,(iu_3)\,(iu_6)+\lambda_{100011}(iu_1)\,(iu_6)\,(iu_7)\\ &+\lambda_{0100101}(iu_2)\,(iu_5)\,(iu_7)+\lambda_{0011001}(iu_3)\,(iu_4)\,(iu_7)]\ ,\\ S_4=t[&\ldots+\lambda_{1110001}(iu_1)\,(iu_2)\,(iu_3)\,(iu_7)+\ldots\ .\end{aligned}$$

We omit in the expression of S_4 all non-zero standardized cumulants which do not affect the conclusive sign relation. From Appendices *A, B, C* we obtain

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{1}{N}\,|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|\times\frac{W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}+A}{1+B}\right)\ ,\quad(11)$$

where

$$\begin{aligned}A=&\,W_{\mathbf{H}_1,\mathbf{H}_2}W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)\\ &+W_{\mathbf{H}_1,\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1)\\ &+W_{\mathbf{H}_2,\mathbf{H}_3}W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)\ ,\\ B=&\,\frac{2}{N}\,[(W^2_{\mathbf{H}_1,\mathbf{H}_2}+W^2_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)\\ &+(W^2_{\mathbf{H}_1,\mathbf{H}_3}+W^2_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1)\\ &+(W^2_{\mathbf{H}_2,\mathbf{H}_3}+W^2_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]\ ,\\ W_{\mathbf{H}_1,\mathbf{H}_2}=&\,\frac{1}{m}\left\langle\frac{\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2)}{\sqrt{(p_{\mathbf{H}_1}p_{\mathbf{H}_2}p_{\mathbf{H}_1+\mathbf{H}_2})}}\right\rangle\ ,\end{aligned}$$

(11) reduces to (4) both in $P\bar{1}$ and in any space group when all the reflexions are general. When special reflexions are involved, the estimates of P_+ by (4) and by (11) can have different values. As an example, in *Pbca*, let

$$\mathbf{H}_1=(0k_1l_1)\ ,\quad\mathbf{H}_2=(0k_2l_2)\ ,\quad\mathbf{H}_3=(h_30-l_1)\ .$$

Then

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{N}\,|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|\times\frac{2\sqrt{2}E^2_{\mathbf{H}_1+\mathbf{H}_2}+4\sqrt{2}E^2_{\mathbf{H}_1+\mathbf{H}_2}+4\sqrt{2}E^2_{\mathbf{H}_2+\mathbf{H}_3}-6\sqrt{2}}{1+4(3E^2_{\mathbf{H}_1+\mathbf{H}_2}+6E^2_{\mathbf{H}_1+\mathbf{H}_3}+9E^2_{\mathbf{H}_2+\mathbf{H}_3}-18)/N}\right].\quad(12)$$

If $N=50$, $|E_{\mathbf{H}_1}|=|E_{\mathbf{H}_2}|=|E_{\mathbf{H}_3}|=|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|=2$, $|E_{\mathbf{H}_1+\mathbf{H}_2}|=0{\cdot}80$, $|E_{\mathbf{H}_1+\mathbf{H}_3}|=|E_{\mathbf{H}_2+\mathbf{H}_3}|=1{\cdot}2$, we obtain $P_+\simeq0{\cdot}72$ by (4) and $P_+\simeq0{\cdot}98$ by (12).

If $|E_{\mathbf{H}_1+\mathbf{H}_2}|\simeq|E_{\mathbf{H}_1+\mathbf{H}_3}|\simeq|E_{\mathbf{H}_2+\mathbf{H}_3}|\simeq0{\cdot}6$, we obtain $P_+\simeq0{\cdot}33$ by (4) and $P_+\simeq0{\cdot}01$ by (12).

Thus, the positivity (negativity) of strong positive (negative) quartets with special reflexions seems enhanced by the space-group symmetry. The phase assignment in this special type of quartet seems then more reliable than in quartets in which all the involved reflexions are of general type. Of considerable interest are the quartets in which some of the cross-reflexions corresponds to a space-group extinction. For example, let us consider in *Pbca* the case in which

$$\mathbf{H}_1=(0k_1l_1)\ ,\quad\mathbf{H}_2=(0k_2l_2)\ ,\quad\mathbf{H}_3=(hk_1l_1)\ ,$$

Table 1. *Values of $W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}$ in Pmmm for some types of reflexions*

	$h_1k_1l_1$ $h_2k_2l_2$ $h_3k_3l_3$ $h_4k_4l_4$	$0k_1l_1$ $h_2k_2l_2$ $h_3k_3l_3$ $h_4k_4l_4$	$00l_1$ $h_2k_2l_2$ $h_3k_3l_3$ $h_4k_4l_4$	$0k_1l_1$ $0k_2l_2$ $h_3k_3l_3$ $h_4k_4l_4$	$0k_1l_1$ $0k_2l_2$ $0k_3l_3$ $0k_4l_4$	$0k_1l_1$ h_200 $h_3k_3l_3$ $h_4k_4l_4$	$0k_1l_1$ h_20l_2 h_3k_30 $h_4k_4l_4$	$00l_1$ h_200 $h_3k_3l_3$ $h_4k_4l_4$	$00l_1$ h_200 h_3k_30 $h_4k_4l_4$	$00l_1$ h_200 $0k_30$ $h_4k_4l_4$	$00l_1$ $00l_2$ $00l_3$ $00l_4$
$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle$	8	16	32	32	64	64	64	128	256	512	512
$\left\langle\frac{\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)}{p_{\mathbf{H}_1}p_{\mathbf{H}_2}p_{\mathbf{H}_3}p_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}}\right\rangle$	8	$8\sqrt{2}$	16	16	16	$16\sqrt{2}$	$16\sqrt{2}$	32	$32\sqrt{2}$	64	32
$W_{\mathbf{H}1,\mathbf{H}2,\mathbf{H}3}$	1	$\sqrt{2}$	2	2	2	$2\sqrt{2}$	$2\sqrt{2}$	4	$4\sqrt{2}$	8	4

with h odd. (11) gives then

$$P_+ \simeq \tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{N}|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \times \frac{2(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)+2(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)}{1+4[2(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)+2(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]/N}\right\}. \quad (13)$$

$E_{\mathbf{H}_1+\mathbf{H}_3}$ in fact is a systematically absent reflexion, so that (see Appendices)

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_3}=W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=0\,.$$

If all the E's are general and $E_{\mathbf{H}_1+\mathbf{H}_3}$ corresponds to a space group extinction, (11) reduces to

$$P_+ \simeq \tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{N}|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \times \frac{E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_2+\mathbf{H}_3}-2}{1+4(E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_2+\mathbf{H}_3}-2)/N}\right]. \quad (14)$$

(13) and (14) suggest that, when $\mathbf{H}_1, \mathbf{H}_2, \mathbf{H}_3$ range over all reciprocal space on condition that one of the cross-vectors corresponds to a space-group extinction, the percentage of negative quartets equals 0·50. From (13) furthermore

$$\langle E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}\rangle=0\,,$$

in strong contrast with the overall positivity of the quartets. The anomalous character of these quartets, therefore, requires an appropriate use in the procedures for phase determination.

5. Strengthening of some quartet relationships

In a centrosymmetric space group of order $m>2$ let

$$E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \quad (15)$$

be a quartet whose reflexions are of general type. If $E_{\mathbf{H}_2+\mathbf{H}_3}$ is a special reflexion

$$E_{\mathbf{H}_1}, E_{\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_3\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \quad (16)$$

is a quartet too, provided that $(\mathbf{H}_2+\mathbf{H}_3)\,(\mathbf{R}_s-\mathbf{I})=0$.

(15) and (16) are symmetry-equivalent quartets, but the first depends on the cross-reflexions

$$E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_3}, E_{\mathbf{H}_2+\mathbf{H}_3}\,, \quad (17)$$

the second on

$$E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}, E_{\mathbf{H}_2+\mathbf{H}_3}\,. \quad (18)$$

The pairs $(E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_3})$ and $(E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s})$ are not symmetry equivalent: so two different sign relations are then available for the same quartet. If we denote by P_{1+} and P_{2+} the probabilities of a positive sign for (15) arising respectively from (17) and (18), a measure of the overall probability should be (Woolfson, 1961)

$$P_+ = \left(1+\frac{P_{1-}P_{2-}}{P_{1+}P_{2+}}\right)^{-1}.$$

However, as the two sign relations are not independent, a better procedure should be to study the joint probability distribution

$$P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_3}, E_{\mathbf{H}_2+\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s})\,.^*$$

From Appendix D we derive (11) again, but this time

$$\begin{aligned} A \simeq\ & W_{\mathbf{H}_1,\mathbf{H}_2}W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1) \\ &+ W_{\mathbf{H}_1,\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1) \\ &+ W_{\mathbf{H}_2,\mathbf{H}_3}W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1) \\ &+ W'_{\mathbf{H}_1,\mathbf{H}_2}W'_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}-1) \\ &\times(-1)^{2(\mathbf{H}_2+\mathbf{H}_3)\mathbf{T}_s} + W'_{\mathbf{H}_1,\mathbf{H}_3}W'_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\ &\times(E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-1)\,(-1)^{2(\mathbf{H}_2+\mathbf{H}_3)\mathbf{T}_s}\,, \end{aligned} \quad (19)$$

$$\begin{aligned} B \simeq \frac{2}{N}\,[& (W^2_{\mathbf{H}_1,\mathbf{H}_2}+W^2_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1) \\ &+(W^2_{\mathbf{H}_1,\mathbf{H}_3}+W^2_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1) \\ &+(W^2_{\mathbf{H}_2,\mathbf{H}_3}+W^2_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1) \\ &+(W'^2_{\mathbf{H}_1,\mathbf{H}_2}+W'^2_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}-1) \\ &+(W'^2_{\mathbf{H}_1,\mathbf{H}_2}+W'^2_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,(E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-1)]\,, \end{aligned} \quad (20)$$

where

$$W'_{\mathbf{H}_1,\mathbf{H}_2}=\frac{1}{m}\left\langle\frac{\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)}{\sqrt{(p_{\mathbf{H}_1}p_{\mathbf{H}_2}p_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s})}}\right\rangle,$$

$$W'_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=\frac{1}{m}\left\langle\frac{\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)}{\sqrt{(p_{\mathbf{H}_1}p_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}p_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s})}}\right\rangle.$$

The reader will be able to generalize the above considerations to the case in which more than one of the reflexions

$$E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, \ldots, E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}, E_{\mathbf{H}_2+\mathbf{H}_3\mathbf{R}_s}, \ldots$$

are of special type. We limit ourselves to some considerations about the role of the weights W in the direct procedures for phase determination.

When the space-group symmetry is involved in the probabilistic approach, the positive or negative character of the quartets is generally enhanced in comparison with the direct use in any space group of the formulae valid in $P\bar{1}$. So, if one does not wish to spend calculation time in the evaluation of the W's, the use of the approximation $W=1$ seems in accordance with the principles usually adopted for proper weighting. What seems important, however, is to recognize if some of the cross-vectors are of special type: if possible, a larger number of cross-vectors should be tested in order to define the sign of a quartet. In order to save computing time a simple procedure should be that

* Lessinger (1976) has recently suggested that $\mathbf{R}_s$ may in general be a rotation matrix of the Laue group of the crystal. Thus, in accordance with Lessinger's geometrical considerations, one may conclude that more than three cross-vectors exist when one of the cross-vectors lies on a symmetry element of the Laue group of the crystal.

of assuming $W=1$ always, except when $W=0$. This last case is easily recognizable as it involves a cross-reflexion which corresponds to a space-group extinction. For an example, in $P2_1/c$, let

$$\mathbf{H}_1=(222)\,,\quad \mathbf{H}_2=(111)\,,\quad \mathbf{H}_3=(2\bar{1}0)\,.$$

$\mathbf{H}_2+\mathbf{H}_3=(301)$ corresponds to a space-group extinction. In accordance with the previous assumptions all the W's will be unity, whereas

$$W_{\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=0\,.$$

So we obtain

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{N}|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|\times\frac{E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_3}-2-(E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}+E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-2)}{1+4(E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_3}+E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}+E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-4)/N}\right].\quad(21)$$

$\mathbf{R}_s$ is defined by the condition $(\mathbf{H}_2+\mathbf{H}_3)(\mathbf{R}_s-\mathbf{I})=0$; so in (21)

$$\mathbf{R}_s=\begin{vmatrix}1&0&0\\0&\bar{1}&0\\0&0&1\end{vmatrix}.$$

If $|E_{\mathbf{H}_1+\mathbf{H}_2}|,|E_{\mathbf{H}_1+\mathbf{H}_3}|$ are large and $|E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}|$, $|E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}|$ are small, (21) indicates a strongly positive quartet: on the other hand a strong negative quartet is suggested if $|E_{\mathbf{H}_1+\mathbf{H}_2}|,|E_{\mathbf{H}_1+\mathbf{H}_3}|$ are small and $|E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}|,|E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}|$ are large. Let us note furthermore: (*a*) it is possible to derive a negative character for a quartet from large $|E|$ values, (*b*) if all the cross-vectors in (21) are large, the value of P_+ nears 0·50.

As a further example, in $P2_1/c$, let

$$\mathbf{H}_1=(222)\,,\quad \mathbf{H}_2=(111)\,,\quad \mathbf{H}_3=(2\bar{1}3)\,.$$

As $\mathbf{H}_2+\mathbf{H}_3=(304)$ is a special reflexion which does not correspond to a space-group extinction ($p_{\mathbf{H}_2+\mathbf{H}_3}=2$), we obtain

If we denote the point group operators by

$$\mathbf{R}_1=\begin{vmatrix}1&0&0\\0&1&0\\0&0&1\end{vmatrix};\ \mathbf{R}_2=\begin{vmatrix}\bar{1}&0&0\\0&1&0\\0&0&1\end{vmatrix};\ \mathbf{R}_3=\begin{vmatrix}1&0&0\\0&\bar{1}&0\\0&0&1\end{vmatrix};\ \mathbf{R}_4=\begin{vmatrix}1&0&0\\0&1&0\\0&0&\bar{1}\end{vmatrix};$$

$$\mathbf{R}_5=\begin{vmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{vmatrix};\ \mathbf{R}_6=\begin{vmatrix}1&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{vmatrix};\ \mathbf{R}_7=\begin{vmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{vmatrix};\ \mathbf{R}_8=\begin{vmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{vmatrix},$$

the following quartets, symmetry related to each other, may be constructed:

$$\begin{array}{llll}
\mathbf{H}_1, & \mathbf{H}_2, & \mathbf{H}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_2, & \mathbf{H}_2\mathbf{R}_2, & \mathbf{H}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_4, & \mathbf{H}_2\mathbf{R}_4, & \mathbf{H}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_7, & \mathbf{H}_2\mathbf{R}_7, & \mathbf{H}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_2, & \mathbf{H}_2, & \mathbf{H}_3\mathbf{R}_2, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1, & \mathbf{H}_2\mathbf{R}_3, & \mathbf{H}_3\mathbf{R}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,
\end{array}$$

with their cross-relations (of quartet type)

$$\begin{array}{llll}
\mathbf{H}_1\mathbf{R}_2, & \mathbf{H}_2\mathbf{R}_2\mathbf{R}_3, & \mathbf{H}_3\mathbf{R}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_4\mathbf{R}_2, & \mathbf{H}_2\mathbf{R}_4, & \mathbf{H}_3\mathbf{R}_2, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_4, & \mathbf{H}_2\mathbf{R}_4\mathbf{R}_3, & \mathbf{H}_3\mathbf{R}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_7, & \mathbf{H}_2\mathbf{R}_7\mathbf{R}_3, & \mathbf{H}_3\mathbf{R}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\\
\mathbf{H}_1\mathbf{R}_2, & \mathbf{H}_2\mathbf{R}_3, & \mathbf{H}_3\mathbf{R}_2\mathbf{R}_3, & \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3.
\end{array}$$

From the considerations developed above, the sign of the quartet depends in this case on 16 cross-vectors: *i.e.* (070), (0,3,11), (205), (2,3,11), (005), (035), (2,0,11), (235), (0,0,11), (270), (030), (0,7,11), (2,7,11), (075), (275), (230).

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{N}|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|\times\left[\frac{E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_3}+E^2_{\mathbf{H}_2+\mathbf{H}_3}-2+E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}+E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-2}{1+4(E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_3}+E^2_{\mathbf{H}_2+\mathbf{H}_3}+E^2_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}+E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}-5)/N}\right]\right\}.\quad(22)$$

The advantages of (22) in comparison with (4) are evident. The probable sign of the quartet is in fact derived from five cross-vectors. It is natural to expect that this type of quartet will, on average, be more reliable than quartets which depend on three cross-vectors alone. More favourable cases are easily given. For example, in *Pmmm*, the four vectors

$$\mathbf{H}_1=(123)\,,\quad \mathbf{H}_2=(\bar{1}5\bar{3})\,,\quad \mathbf{H}_3=(\bar{1}\bar{5}8)\,,\quad \mathbf{H}_4=(1\bar{2}\bar{8})$$

give rise to a quartet whose cross-vectors are all of special type: $\mathbf{H}_{12}=(070)$ with statistical weight $p=4$, $\mathbf{H}_{13}=(0\bar{3}11)$ with $p=2$, $\mathbf{H}_{23}=(\bar{2}05)$ with $p=2$.

6. Non-centrosymmetric space groups: further remarks

The conclusions about the role played by the statistical nature of the cross-reflexions in defining the sign of a quartet are valid in non-centrosymmetric groups too. Some further remarks however may be useful.

(1) In centrosymmetric as well as non-centrosymmetric space groups the term $(|E_{\mathbf{H}_1+\mathbf{H}_2}|^2-1)$ occurs in (4) or in (8) if (Appendix *B*)

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle\times\langle\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle\neq0\,.\quad(23)$$

Whereas in centrosymmetric space groups (23) is violated solely when $\mathbf{H}_1+\mathbf{H}_2$ corresponds to a space-group extinction, in certain non-centrosymmetric space groups (23) is transgressed in other circumstances too (Giacovazzo, 1974*b*). For example, in $P2_12_12_1$ (23) is violated (see § 1) when

$$\mathbf{H}_1=(0gu)\,,\quad \mathbf{H}_2=(g0u)\,.$$

Our algebraic considerations tell us that (7) is once more valid, but (8) becomes

$$G=\frac{2}{N}\,|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}| \times[(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1)+(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]\,.$$

In conclusion, the magnitude $E_{\mathbf{H}_1+\mathbf{H}_2}$ does not affect in this case the expected value of the cosine invariant.

(2) In centrosymmetric as well as non-centrosymmetric space groups

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=0 \tag{24}$$

when one of the cross-reflexions corresponds to a space-group extinction. In some non-centrosymmetric space groups (24) may occur in other circumstances. For example, in $P2_12_12_1$, let

$$\mathbf{H}_1=(0gu)\,,\quad \mathbf{H}_2=(u0g)\,,\quad \mathbf{H}_3=(ug0)\,,\quad \mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3=(0gu)\,.$$

As the crystallographic symmetry restrains the values of the phases to

$$\varphi_{\mathbf{H}_1},\varphi_{\mathbf{H}_2},\varphi_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=0\,,\quad \varphi_{\mathbf{H}_3}=\pm\pi/2$$

the knowledge of the phase $\varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}+\varphi_{\mathbf{H}_3}$ does not give information on $\varphi_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$, whatever $|E_{\mathbf{H}_1}|,|E_{\mathbf{H}_2}|,|E_{\mathbf{H}_3}|,|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}|$ may be. From an algebraic point of view this situation is marked by

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle=0\,.$$

7. A generalization of the Hauptman formulation

The algebraic considerations which allowed in the preceding sections a generalization of Giacovazzo's quartet phase relationships, enable us also to generalize Hauptman's formulation. We will refer in this section to the centrosymmetric space groups: the reader will be able to deal with the non-centrosymmetric ones by means of the considerations made in § 6.

The general form of the probability density function for seven reflexions is given by ($E1$). When all seven vectors are general, the quartet sign relation

$$P_\pm\simeq\frac{1}{L}\,\exp\,(\mp B)\cosh\frac{R_{12}Z^\pm_{12}}{\sqrt{N}} \times\cosh\frac{R_{23}Z^\pm_{23}}{\sqrt{N}}\cosh\frac{R_{31}Z^\pm_{31}}{\sqrt{N}} \tag{25}$$

holds [Hauptman & Green (1976), equation (3.13): see this paper for the notation]. ($E1$) enables us to derive directly the sign relations when one or more cross-vectors are special or are not in the set of measurements. So, if one (*i.e.* $\mathbf{H}_1+\mathbf{H}_2$) or two (*i.e.* $\mathbf{H}_1+\mathbf{H}_2$ and $\mathbf{H}_1+\mathbf{H}_3$) cross-reflexions are not in the measurements,

$$P_\pm\simeq\frac{1}{L'}\exp\,(\mp B/2)\cosh\frac{R_{23}Z^\pm_{23}}{\sqrt{N}}\cosh\frac{R_{31}Z^\pm_{31}}{\sqrt{N}}\,, \tag{26}$$

or

$$P_\pm\simeq\frac{1}{L''}\cosh\frac{R_{23}Z^\pm_{23}}{\sqrt{N}}\,, \tag{27}$$

hold respectively, where

$$L'=\exp\,(-B/2)\cosh\frac{R_{23}Z^+_{23}}{\sqrt{N}}\cosh\frac{R_{31}Z^+_{31}}{\sqrt{N}} +\exp\,(+B/2)\cosh\frac{R_{23}Z^-_{23}}{\sqrt{N}}\cosh\frac{R_{31}Z^-_{31}}{\sqrt{N}}\,,$$

$$L''=\cosh\frac{R_{23}Z^+_{23}}{\sqrt{N}}+\cosh\frac{R_{23}Z^-_{23}}{\sqrt{N}}\,.$$

(26) and (27) are not explicitly given by Hauptman & Green (1976). As to the occurrence of special reflexions, in accordance with the assumption made in § 5, W is always equal to 1, except when W equals 0. Therefore, if one cross-vector (*i.e.* $\mathbf{H}_1+\mathbf{H}_2$) is a systematic absence,

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_2}=W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=0:$$

then

$$P_\pm=\frac{1}{L^{\rm III}}\exp\,(\mp B)\cosh\frac{R_{23}Z^\pm_{23}}{\sqrt{N}}\cosh\frac{R_{31}Z^\pm_{31}}{\sqrt{N}}\,. \tag{28}$$

If two cross-reflexions are systematic absences (*i.e.* $\mathbf{H}_1+\mathbf{H}_2$ and $\mathbf{H}_1+\mathbf{H}_3$)

$$P_\pm=\frac{1}{L^{\rm IV}}\exp\,(\mp B/2)\cosh\frac{R_{23}Z^\pm_{23}}{\sqrt{N}}\,. \tag{29}$$

$L^{\rm III}$ and $L^{\rm IV}$ are suitable functions that the reader will easily derive.

The quartet sign relation, given only the four magnitudes $R_{\mathbf{H}_1},R_{\mathbf{H}_2},R_{\mathbf{H}_3},R_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$, is

$$P_\pm\simeq\tfrac{1}{2}\,, \tag{30}$$

if one cross-vector is a systematic absence, in strong contrast with the relation (4.1) in Hauptman & Green (1976). Particularly noteworthy is a comparison of (28), (29) and (30) with (25), (26) and (27) which illustrates the change which may take place when some of the seven reflexions are of special type. We deal now with the case in which more than three cross-vectors are explicitly taken into account: *i.e.*, provided $(\mathbf{H}_2+\mathbf{H}_3)\times(\mathbf{R}_s-\mathbf{I})=0$, they are $\mathbf{H}_1+\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_3,\mathbf{H}_2+\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s,\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s$. The general expression of this distribution is given by ($E2$).

If $\mathbf{H}_2+\mathbf{H}_3$ is not a systematic absence,

$$2(\mathbf{H}_2+\mathbf{H}_3)\mathbf{T}_s=2n\,,$$

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_2}=\ldots=W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=1\,, \tag{31a}$$

$$W'_{\mathbf{H}_1+\mathbf{H}_2}=W'_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=(-1)^{2\mathbf{H}_2\mathbf{T}_s};$$
$$W'_{\mathbf{H}_1,\mathbf{H}_3}=W'_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=(-1)^{2\mathbf{H}_3\mathbf{T}_s}. \quad (31b)$$

Denoting

$$R_8=R_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, \quad R_9=R_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s},$$

then

$$P_\pm=\frac{1}{L}\exp(\mp 4R_1R_2R_3R_4)\cosh\frac{R_{12}Z_{12}^\pm}{\sqrt{N}} \times\cosh\frac{R_{31}Z_{31}^\pm}{\sqrt{N}}\cosh\frac{R_{23}Z_{23}^\pm}{\sqrt{N}} \times\cosh\frac{R_8Z_{12}^\pm}{\sqrt{N}}\cosh\frac{R_9Z_{31}^\pm}{\sqrt{N}}, \quad (32)$$

where L is a suitable normalizing function.

If $\mathbf{H}_2+\mathbf{H}_3$ is a systematic absence, (31b) is still valid, but (31a) becomes

$$W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_2,\mathbf{H}_3}=W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}=0;$$
$$W_{\mathbf{H}_1,\mathbf{H}_2}=\ldots=1.$$

As $2(\mathbf{H}_2+\mathbf{H}_3)\mathbf{T}_s=2n+1$, then

$$P_\pm=\frac{1}{L}\cosh\frac{R_{12}Z_{12}^\pm}{\sqrt{N}}\cosh\frac{R_{31}Z_{31}^\pm}{\sqrt{N}} \times\cosh\frac{R_8Z_{12}^\mp}{\sqrt{N}}\cosh\frac{R_9Z_{31}^\mp}{\sqrt{N}}.$$

These equations emphasize the importance of the space-group symmetry in the direct procedures which use quartet relationships.

8. Conclusions

The theory described in the present paper allows us to modify the phase relationships (4), (7) and (25) so as to take the space-group symmetry into account. The more relevant changes occur when one or more cross-reflexions are of special type. In this case the theory recognizes the additional cross-reflexions whose magnitudes should be tested in order to strengthen the phase relationship.

In certain space groups the quartets having special cross-vectors should be a non-negligible percentage of the total. The results of the present investigation, therefore, should improve the overall reliability of the quartet relationships.

APPENDIX *A*

By the definition of normalized structure factors (Hauptman & Karle, 1953) in a centrosymmetric space group of order m,

$$E_{\mathbf{h}}=\frac{1}{\sqrt{p_{\mathbf{h}}}}\sum_{1}^{t}{}_j\, v_j\xi_j(\mathbf{h}),$$

where

$$v_j=f_j/(\sum_1^N{}_j f_j^2)^{1/2}, \quad p_{\mathbf{h}}=\langle\xi^2(\mathbf{h})\rangle/m.$$

Let us denote by $\mathbf{C}_s=(\mathbf{R}_s,\mathbf{T}_s)$ the s-symmetry operator ($\mathbf{R}_s$ rotation component, $\mathbf{T}_s$ translation component). From the theory of linearization (Bertaut, 1959a, b)

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle =\langle\sum_1^m{}_{p,v,s}\,\xi[\mathbf{H}_1(\mathbf{R}_p-\mathbf{I})+\mathbf{H}_2(\mathbf{R}_s-\mathbf{I})+\mathbf{H}_3(\mathbf{R}_v-\mathbf{I})] \times\exp 2\pi i(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_s+\mathbf{H}_3\mathbf{T}_v)\rangle. \quad (A1)$$

The value of (A1) is different from zero for all $\mathbf{R}_p$, $\mathbf{R}_s$, $\mathbf{R}_v$ operators for which

$$\mathbf{H}_1(\mathbf{R}_p-\mathbf{I})+\mathbf{H}_2(\mathbf{R}_s-\mathbf{I})+\mathbf{H}_3(\mathbf{R}_v-\mathbf{I})=0. \quad (A2)$$

As

$$\langle\xi^2(\mathbf{H})\rangle=\langle\sum_1^m{}_s\,\xi[\mathbf{H}(\mathbf{R}_s-\mathbf{I})]\exp 2\pi i\mathbf{H}\mathbf{T}_s\rangle=p_{\mathbf{H}}m,$$

the statistical nature of $\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3$, must be taken into account in order to estimate (A1).

What is particularly noteworthy is that the statistical nature of the cross-reflexions $E_{\mathbf{H}_i+\mathbf{H}_j}$ can affect the value of (A1). Let us suppose, for example, that $E_{\mathbf{H}_1},E_{\mathbf{H}2},E_{\mathbf{H}_3},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$ are all general reflexions and $E_{\mathbf{H}_1+\mathbf{H}_2}$ is a special one. The condition (A2) is satisfied when

$$(\mathbf{H}_1+\mathbf{H}_2)(\mathbf{R}_n-\mathbf{I})=0, \quad \mathbf{H}_3(R_v-\mathbf{I})=0. \quad (A3)$$

If $E_{\mathbf{H}_1+\mathbf{H}_2}$ has the statistical weight $p_{\mathbf{H}_1+\mathbf{H}_2}\neq 1$, $p_{\mathbf{H}_1+\mathbf{H}_2}$ distinct point group operators $\mathbf{R}_n$ will exist for which (A3) is satisfied. In conclusion

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle=p_{\mathbf{H}_1+\mathbf{H}_2}m.$$

Particularly noteworthy is the case when one or more cross-reflexions are systematically absent. Then

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle=0. \quad (A4)$$

In order to show (A4), suppose that $\mathbf{H}_1+\mathbf{H}_2$ is a systematic absence. (A1) reduces then ($p=s$, $v=1$) to

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\rangle =\langle\sum_1^m{}_n\,\xi[(\mathbf{H}_1+\mathbf{H}_2)(\mathbf{R}_n-\mathbf{I})]\exp[2\pi i(\mathbf{H}_1+\mathbf{H}_2)\mathbf{T}_n]\rangle =\langle\xi^2(\mathbf{H}_1+\mathbf{H}_2)\rangle=0.$$

Similar considerations may be used in order to deal with more complicated cases.

APPENDIX *B*

In $P\bar{1}$ (Giacovazzo, 1975)

$$\langle E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}\rangle \simeq\frac{1}{N}[E^2_{\mathbf{H}_1+\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_3}+E^2_{\mathbf{H}_2+\mathbf{H}_3}-2]. \quad (B1)$$

(B1) is derived from the Fourier transform in $P\bar{1}$ of S_4/t^2 as well as of $S_3^2/2t^3$. The transform of the most relevant term in S_4/t^2 for any centrosymmetric space group has been discussed in Appendix A. We derive here the general Fourier transform of the three terms in $S_3^2/2t^3$ which contribute to ($B1$).

These terms are the mixed products

$$\frac{1}{t}[\lambda_{1101000}(iu_1)(iu_2)(iu_4)\,.\,\lambda_{0011001}(iu_3)(iu_4)(iu_7)]\,, \quad (B2)$$

$$\frac{1}{t}[\lambda_{1010100}(iu_1)(iu_3)(iu_5)\,.\,\lambda_{0100101}(iu_2)(iu_5)(iu_7)]\,, \quad (B3)$$

$$\frac{1}{t}[\lambda_{0110010}(iu_2)(iu_3)(iu_6)\,.\,\lambda_{1000011}(iu_1)(iu_6)(iu_7)]\,. \quad (B4)$$

In $P\bar{1}$, or in any space group when all the reflexions are general, the Fourier transform of ($B2$)–($B4$) gives

$$\frac{1}{N}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \times[(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)+(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1)+(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]\,,$$

from which ($B1$) follows.

The general expression of the Fourier transform is

$$\frac{1}{N}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}[W_{\mathbf{H}_1,\mathbf{H}_2}W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \times(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)+W_{\mathbf{H}_1,\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1) + W_{\mathbf{H}_2,\mathbf{H}_3}W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]\,,$$

where

$$W_{\mathbf{H}_1,\mathbf{H}_2}=\frac{1}{m}\left\langle\frac{\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle}{\sqrt{(p_{\mathbf{H}_1}p_{\mathbf{H}2}p_{\mathbf{H}_1+\mathbf{H}_2})}}\right\rangle,\quad etc.$$

APPENDIX C

In $P\bar{1}$ the variance of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$ is given by

$$\sigma^2\simeq\langle E^2_{\mathbf{H}_1}E^2_{\mathbf{H}_2}E^2_{\mathbf{H}_3}E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}\rangle \simeq 1+4[(E^2_{\mathbf{H}_1+\mathbf{H}_2}-1)+(E^2_{\mathbf{H}_1+\mathbf{H}_3}-1)+(E^2_{\mathbf{H}_2+\mathbf{H}_3}-1)]/N\,. \quad (C1)$$

($C1$) is derived from the Fourier transform in $P\bar{1}$ of $S_3^2/2t^3$. The general expression for any centrosymmetric space group of the terms in $S_3^2/2t^3$ which contribute to σ^2 is

$$\frac{1}{2t}[\lambda^2_{1101000}(iu_1)^2(iu_2)^2(iu_4)^2+\lambda^2_{1010100}(iu_1)^2(iu_3)^2(iu_5)^2 +\lambda^2_{0110010}(iu_2)^2(iu_3)^2(iu_6)^2+\lambda^2_{1000011}(iu_1)^2(iu_6)^2(iu_7)^2 +\lambda^2_{0100101}(iu_2)^2(iu_5)^2(iu_7)^2+\lambda^2_{0011001}(iu_3)^2(iu_4)^2(iu_7)^2]\,. \quad (C2)$$

In $P\bar{1}$, or in any space group when all the reflexions are general, the Fourier transform of ($C2$) is

$$\frac{1}{2N}[H_2(E_1)H_2(E_2)H_2(E_4)+H_2(E_1)H_2(E_3)H_2(E_5) +H_2(E_2)H_2(E_3)H_2(E_6)+H_2(E_1)H_2(E_6)H_2(E_7) +H_2(E_2)H_2(E_5)H_2(E_7)+H_2(E_3)H_2(E_4)H_2(E_7)]\,. \quad (C3)$$

The general expression of the Fourier transform of ($C2$) is

$$\frac{1}{2N}[W^2_{\mathbf{H}_1,\mathbf{H}_2}H_2(E_{\mathbf{H}_1})H_2(E_{\mathbf{H}_2})H_2(E_{\mathbf{H}_1+\mathbf{H}_2}) + W^2_{\mathbf{H}_1,\mathbf{H}_3}H_2(E_{\mathbf{H}_1})H_2(E_{\mathbf{H}_3})H_2(E_{\mathbf{H}_1+\mathbf{H}_3})+\ldots]\,, \quad (C4)$$

where $W_{\mathbf{H}_1,\mathbf{H}_2}$, $W_{\mathbf{H}_1,\mathbf{H}_3},\ldots$, have been defined in Appendix B.

APPENDIX D

Let $E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}$ be general reflexions and $E_{\mathbf{H}_2+\mathbf{H}_3}$ a special reflexion for which $(\mathbf{H}_2+\mathbf{H}_3)(\mathbf{R}_s-\mathbf{I})=0$. When the joint probability distribution

$$P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_3}, E_{\mathbf{H}_2+\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s})$$

is considered, a number of non-vanishing cumulants should be added to those which arise from the distribution

$$P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2},\ldots, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3})\,.$$

Of the additional moments those which affect the conclusive phase relationships are

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)\rangle=m(-1)^{2\mathbf{H}_2\mathbf{T}_s}\,, \quad (D1)$$

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s)\rangle=m(-1)^{2\mathbf{H}_3\mathbf{T}_s}\,, \quad (D2)$$

$$\langle\xi^2(\mathbf{H}_1)\xi(\mathbf{H}_1+\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)\rangle=m\gamma_s(-1)^{2\mathbf{H}_2\mathbf{T}_s}\,, \quad (D3)$$

$$\langle\xi^2(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s)\rangle=m\gamma_s(-1)^{2\mathbf{H}_3\mathbf{T}_s}\,, \quad (D4)$$

$$\langle\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s)\rangle=m(-1)^{2\mathbf{H}_2\mathbf{T}_s}\,, \quad (D5)$$

$$\langle\xi(\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)\rangle=m(-1)^{2\mathbf{H}_3\mathbf{T}_s}\,, \quad (D6)$$

($D1$)–($D4$) have been recently stated (Giacovazzo, 1977). γ_s is a factor which depends on the symmetry class and on the actual point group operator R_s.

($D5$) and ($D6$) may be proved from the identity

$$\langle\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3)\xi(\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s)\rangle =\langle\sum_{p,q=1}^{m}\xi[\mathbf{H}_1(\mathbf{R}_q-\mathbf{I})+\mathbf{H}_2(\mathbf{R}_q-\mathbf{I})+\mathbf{H}_3(\mathbf{R}_s\mathbf{R}_q-\mathbf{I})] \times\exp 2\pi i(\mathbf{H}_1\mathbf{T}_q+\mathbf{H}_2\mathbf{T}_p+\mathbf{H}_3\mathbf{R}_s\mathbf{T}_q)\rangle\,. \quad (D7)$$

($D7$) does not vanish when $\mathbf{R}_q=\mathbf{I}$ and $\mathbf{R}_p=\mathbf{R}_s$. In that case ($D7$) coincides with

$$\langle\xi[(\mathbf{H}_2+\mathbf{H}_3)(\mathbf{R}_s-\mathbf{I})]\exp 2\pi i(\mathbf{H}_2\mathbf{T}_s+\mathbf{H}_3\mathbf{R}_s)\rangle =m\exp 2\pi i\mathbf{H}_2\mathbf{T}_s\,,$$

which, as $(\mathbf{H}_2+\mathbf{H}_3)(\mathbf{R}_s-\mathbf{I})=0$, gives ($D5$).

Cumulants which arise from ($D3$) and ($D4$) are not relevant to defining the sign of a quartet (see Giacovazzo, 1975, when $\mathbf{R}_s=-\mathbf{I}$) and have been neglected in §§ 4 and 5.

APPENDIX *E*

In any centrosymmetric space group the probability density function, given the seven magnitudes $R_{\mathbf{H}_1}, R_{\mathbf{H}_2}, \ldots, R_{\mathbf{H}_2+\mathbf{H}_3}$, is

$$
\begin{aligned}
P \simeq \frac{1}{(2\pi)^{7/2}} & \exp\left[-\tfrac{1}{2}(E^2_{\mathbf{H}_1}+\ldots+E^2_{\mathbf{H}_2+\mathbf{H}_3})\right. \\
& + \frac{1}{\sqrt{N}}(W_{\mathbf{H}_1,\mathbf{H}_2}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2} \\
& + W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2} \\
& + W_{\mathbf{H}_2,\mathbf{H}_3}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_1,\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3} \\
& + W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3}) \\
& - \frac{1}{N}(W_{\mathbf{H}_1,\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2} \\
& \times E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3} \\
& + W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& \times E_{\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3} + W_{\mathbf{H}_2,\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_3} \\
& \times E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2} \\
& + W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& \times E_{\mathbf{H}_1+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2}) \\
& + \frac{1}{N}(W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} - W_{\mathbf{H}_1,\mathbf{H}_2}W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& - W_{\mathbf{H}_1,\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& \left. - W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_3})E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}\right].
\end{aligned} \quad (E1)
$$

The generalized expression of the probability density function in any centrosymmetric space group when $\mathbf{H}_2+\mathbf{H}_3$ is a special vector [*i.e.* $(\mathbf{H}_2+\mathbf{H}_3)(\mathbf{R}_s-\mathbf{I})=0$] is

$$
\begin{aligned}
& P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, \ldots, E_{\mathbf{H}_1+\mathbf{H}_3}, E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s}, E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}) \\
& \simeq \frac{1}{(2\pi)^{9/2}}\exp\left[-\tfrac{1}{2}(E^2_{\mathbf{H}_1}+E^2_{\mathbf{H}_2}+\ldots+E^2_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s})\right. \\
& + \frac{1}{\sqrt{N}}(W_{\mathbf{H}_1,\mathbf{H}_2}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2} \\
& + W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2} \\
& + W_{\mathbf{H}_2,\mathbf{H}_3}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_1,\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3} \\
& + W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3} \\
& + W'_{\mathbf{H}_1,\mathbf{H}_2}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s} \\
& + W'_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s} \\
& + W'_{\mathbf{H}_1,\mathbf{H}_3}E_{\mathbf{H}_1}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s} \\
& + W'_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_3\mathbf{R}_s}) \\
& + \frac{1}{N}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& \times (W_{\mathbf{H}_1,\mathbf{H}_2,\mathbf{H}_3} - W_{\mathbf{H}_1,\mathbf{H}_2}W_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& - W_{\mathbf{H}_2,\mathbf{H}_3}W_{\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} - W_{\mathbf{H}_1,\mathbf{H}_3}W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} \\
& - W'_{\mathbf{H}_1,\mathbf{H}_2}W'_{\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3} - W'_{\mathbf{H}_1,\mathbf{H}_3}W'_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}) \\
& - \frac{1}{N}(W_{\mathbf{H}_1,\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1}E_{\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_2+\mathbf{H}_3} \\
& + W_{\mathbf{H}_2,\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3,\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_2} \\
& \left. \times E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3}E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_2+\mathbf{H}_3}+\ldots)\right].
\end{aligned} \quad (E2)
$$

The corresponding distributions in non-centrosymmetric space groups are strongly suggested by (*E*1) and (*E*2).

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