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A Probabilistic Theory of the Coincidence Method. I. Centrosymmetric Space Groups

BY C. GIACOVAZZO

Institute of Mineralogy and Petrography, University of Bari, Bari, Italy

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A general probabilistic theory of sign coincidences is described which is valid in all the centrosymmetric space groups. The theory makes full use of space-group symmetry by means of suitable joint probability distribution functions. The phase relationships obtained are in some way space-group dependent: their estimation requires an appropriate use of space-group algebra.

1. Introduction

The method of coincidences was described by Grant, Howells & Rogers (1957) for the application of the Sayre relation $S(\mathbf{H}_1)S(\mathbf{H}_2)\simeq S(\mathbf{H}_1+\mathbf{H}_2)$ to projections with symmetry *pgg*, *pmg*, and *p*4*g*. In their terminology, if **A** and **B** are reciprocal vectors, the product $S(\mathbf{A})\times S(\mathbf{B})$ can enter into a relation with several different third terms $S(\mathbf{C}_1)$, $S(\mathbf{C}_2)$, *etc.*, whose signs are said to coincide:

$$[S(\mathbf{C}_1)\simeq S(\mathbf{C}_2)\ldots]_{A,B}.$$

A particular coincidence case is obtained for centrosymmetric space groups when $|E_{\mathbf{H}_1}|$, $|E_{\mathbf{H}_2}|$, $|E_{\mathbf{H}_1+\mathbf{H}_2}|$, $|E_{\mathbf{H}_1-\mathbf{H}_2}|$ are sufficiently large: in fact

$$S(\mathbf{H}_1)S(\mathbf{H}_2)\simeq S(\mathbf{H}_1+\mathbf{H}_2), \qquad (1a)$$

$$S(\mathbf{H}_1)S(\mathbf{H}_2)\simeq S(\mathbf{H}_1-\mathbf{H}_2), \qquad (1b)$$

from which

$$S(\mathbf{H}_1+\mathbf{H}_2)\simeq S(\mathbf{H}_1-\mathbf{H}_2). \qquad (2)$$

Debaerdemaeker & Woolfson (1972) have extended the idea of coincidence to non-centrosymmetric space groups in which there are translational elements of symmetry. According to them, from a $\sum_2$ listing one can deduce the existence of pairs of phase relations of the general form

$$\varphi_p+B_{prs}(\varphi_r+\varphi_s)+b_{prs}\simeq 0, \qquad (3a)$$

$$\varphi_q+B_{qrs}(\varphi_r+\varphi_s)+b_{qrs}\simeq 0, \qquad (3b)$$

where the *b*'s are constant angles arising because of the translational symmetry, and the *B*'s can be ± 1. By a combination of (3*a*) and (3*b*) one obtains a general relation between φ_p and φ_q:

$$\varphi_p\pm\varphi_q\pm(b_{prs}\pm b_{qrs})\simeq 0. \qquad (4)$$

Debaerdemaeker & Woolfson (1972) supplied in their paper a probabilistic theory of the coincidence phase relations. In accordance with them, we refer to $P2_12_12_1$: let us consider the relations

$$\varphi_p\simeq\eta$$
$$\zeta_q=b\varphi_q-m\pi\simeq\eta,$$

where $b=\pm 1$ and $m=0{\cdot}1$. P_1 and P_2 are the probability distributions for φ_p and ζ_q, derivable from the Cochran (1955) theory:

$$P_{1,2}(\varphi)=[2\pi I_0(G)]^{-1}\exp[G\cos(\varphi-\eta)],$$

where (Karle & Karle, 1966) $G=2\sigma_3\sigma_2^{-3/2}|E_1E_2E_3|$.

According to Debaerdemaeker & Woolfson (1972), the strength of a coincidence phase relation depends on the probability distribution P of the quantity $\theta=\varphi_p-\zeta_q$:

$$P=\int_{-\pi}^{\pi}P_1(x)P_2(x+\theta)\mathrm{d}x. \qquad (5)$$

In centrosymmetric space groups (5) is equivalent to the statement: if P_1 and P_2 are respectively the probabilities of the relations (1*a*) and (1*b*), the probability of (2) is given by (Woolfson, 1961)

$$P=P_1P_2+(1-P_1)(1-P_2). \qquad (6)$$

Giacovazzo (1974*a*) showed that (6) is in contrast with the Harker–Kasper inequalities, and that results are misleading when $|E_{\mathbf{H}_1}|$ or $|E_{\mathbf{H}_2}|$ is small. We will show in part II of the present paper that (5) may also lead to wrong phase relations when $|E_{\mathbf{H}_1}|$ and (or) $|E_{\mathbf{H}_2}|$ are small. The phase information deduced from weak reflexions $\mathbf{H}_1$ and (or) $\mathbf{H}_2$ is particularly important in symmorphic space groups because it can lead to relations such as

$$\varphi_p-\zeta_q\simeq\pi. \qquad (7)$$

Debaerdemaeker & Woolfson's (1972) approach implies, on the other hand, that the probability distributions of φ_p in (3*a*) and φ_q in (3*b*) are independent in a statistical sense: it is not then possible in principle to obtain (7).

Formulae for linear combinations of two phases which are structure seminvariant have been derived in some space groups by Hauptman (1972) by means of an algebraic approach. As the method requires knowledge of the algebraic form of the structure factor, the derivation of the phase values in any space group requires an *ad hoc* mathematical treatment.

Although coincidence and seminvariant cosine methods work on the same sets of phases, the conclusive relations are not quite consistent. As far as we know, no attempt has been made at explaining the statistical meaning of the incongruence of the two methods. The chief aim of the present paper is to derive a probabilistic theory which generalizes Debaerdemaeker & Woolfson's (1972) results so as to give improved estimates of the seminvariant cosines.

The probabilistic background employed in the present paper assumes that the reciprocal vectors are fixed and that the atomic coordinates are the primitive random variables. Under this assumption two different mathematical methods will be used. The first involves a Gram–Charlier expansion of the characteristic function in terms of standardized cumulants. The second uses the same cumulants, but directly in the exponential expression of the characteristic function. The resulting formulae obtained by means of the two methods are not quite identical and require different computation times. Both methods require the ability to compute non-vanishing standardized cumulants for every space group. Space-group algebra can provide estimates of these cumulants: in both sections of the paper, therefore, a number of appendices are devoted to carrying out this algebraic analysis. We note explicitly that the mathematical approach stated in this paper enables us to find the expected value of a seminvariant phase from pairs of quartets as well as from pairs of triplets. This theme will be the subject of a future paper.

2. Preliminary remarks

Let the symmetry number of the actual space group be denoted by m, and by $\mathbf{C}_s=(\mathbf{R}_s, \mathbf{T}_s)$, $s=1, \ldots, m$, the m symmetry operators. $\mathbf{R}_s$ represents the rotation matrix involved, $\mathbf{T}_s$ the column matrix of translation. As is well known,

$$\varphi_{\mathbf{H}_1+\mathbf{H}_2} \simeq \varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}, \quad (8a)$$

$$\varphi_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q} \simeq \varphi_{\mathbf{H}_1\mathbf{R}_p}+\varphi_{\mathbf{H}_2\mathbf{R}_q}, \quad (8b)$$

if all the moduli of the normalized structure factors involved in (8) are large enough. As

$$\varphi_{\mathbf{HR}_s}=\varphi_{\mathbf{H}}-2\pi\mathbf{HT}_s,$$

(8*a*) and (8*b*) become

$$\varphi_{\mathbf{H}_1+\mathbf{H}_2} \simeq \varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2},$$

$$\varphi_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q} \simeq \varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}-2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q),$$

from which

$$\varphi_{\mathbf{H}_1+\mathbf{H}_2}-\varphi_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}-2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q) \simeq 0. \quad (9)$$

From now on we will regard $\varphi_{\mathbf{H}_1+\mathbf{H}_2}$ and $\varphi_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}$ as constituting a specially related pair of phases (s.r.p.p.): their difference is a seminvariant phase. The value of $2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)$, in fact, depends on the fixed functional form of the structure factor and is independent of the choice of the cell origin. From (9) one derives that an s.r.p.p. will give rise to a phase coincidence ($\varphi_{\mathbf{H}_1+\mathbf{H}_2} \simeq \varphi_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}$) when all the magnitudes of the normalized structure factors involved in (9) are large enough, and $2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)=0$. From the point of view of direct methods, nevertheless, (9) is equally useful both when a coincidence occurs, and when $2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)$ is not zero. In fact, the knowledge of one phase of the two which constitute an s.r.p.p. always enables us to assign, from (9), a value to the other phase. In conclusion, even if we continue denoting the method as the 'coincidence method', its major goals are: (1) the search of all the s.r.p.p.'s whose phases are, statistically speaking, strongly related; (2) the estimate of the probability and variance values joined with any s.r.p.p.

Some other remarks about the method should be made. In accordance with (5) and (9), Debaerdemaeker & Woolfson's (1972) procedure derives the s.r.p.p.'s from a $\sum_2$ listing made from the largest $|E|$ magnitudes alone. This procedure is unsuitable when one wants to derive phase information from weak reflexions $\mathbf{H}_1$ and (or) $\mathbf{H}_2$. In fact in this case the derivation of the s.r.p.p.'s from a complete $\sum_2$ listing would require too much computer storage. A different procedure may be suggested if one notes that the s.r.p.p.'s in (8) and (9) are defined *via* the rotation matrices. One should then try to exploit the algebraic properties of the rotation matrices in order to derive the parities of the s.r.p.p.'s in each space group and the nature of the vectors which contribute to the value of each s.r.p.p. Based on these principles an automatic procedure has been successfully carried out by Spagna & Giacovazzo (1976) which works in all the space groups.

3. The mathematical approach

Suppose that a crystal structure consists of N identical atoms in the unit cell and that m is the order of the space group: $t=N/m$ is the number of atoms in the asymmetric unit.

The characteristic function $C(u_1, u_2, \ldots, u_n)$ of the multivariate distribution $P(E_1, E_2, \ldots, E_n)$ is given by

$$C(u_1, \ldots, u_n)=\exp\left[\sum_{2\nu}^{\infty} \frac{S_\nu}{t^{\nu/2}}\right], \quad (10)$$

where

$$S_\nu = t \sum_{r+s+\ldots+w=\nu} \frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iu_n)^w.$$

$\lambda_{rs\ldots w}$ are the standardized cumulants of the distribution. In accordance with our preceding papers (Giacovazzo, 1974*a*, 1975, 1976) the Fourier transform of (10) is calculated *via* its Gram–Charlier expansion (Klug, 1958).

$$\exp\left[-\tfrac{1}{2}(u_1^2+\ldots+u_n^2)\right]\left(1+\frac{S_3}{t^{3/2}}+\frac{S_4}{t^2}+\frac{S_3^2}{2t^3}+\ldots\right). \quad (11)$$

The reader will find a detailed account of the method in the quoted papers.

A second method will be used here which calculates the sign relations directly from the Fourier transform of (10). Details of the method are described in Appendix *C*.

4. The distribution $P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q})$ when the Gram–Charlier expansion of the characteristic function is used

We introduce the abbreviations

$$E_1 = E_{\mathbf{H}_1},\ E_2 = E_{\mathbf{H}_2},\ E_3 = E_{\mathbf{H}_1+\mathbf{H}_2},\ E_4 = E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}.$$

In order to retain terms up to order N^{-1}, we derive (see Appendices *A* and *B*)

$$S_3/t^{3/2} = \frac{1}{\sqrt{N}}\left[(iu_1)(iu_2)(iu_3) + (-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}(iu_1)(iu_2)(iu_4)\right],$$

$$S_4/t^2 = \frac{\beta}{N}\left[(iu_1)^4+\ldots+(iu_4)^4\right] + \frac{\alpha}{N}(iu_3)^2(iu_4)^2 + \frac{(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}}{2N}\gamma\left[(iu_1)^2(iu_3)(iu_4)+(iu_2)^2(iu_3)(iu_4)\right].$$

β is a factor depending on the symmetry class: its lowest value is $-1/8$, assumed, for example, in $P\bar{1}$, but it may be positive in space groups of higher symmetry.

The α and β factors depend on the symmetry class as well as on the actual rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$. For example, $\gamma=1$ and $\alpha=0$ when $\mathbf{R}_p=\mathbf{I}$ and $\mathbf{R}_q=-\mathbf{I}$ or *vice versa*; $\gamma\geq 2$ and $\alpha\geq 0$ in other cases.

After some calculation we derive

$$P_+ \simeq \tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{2N}|E_3E_4| \times \frac{1}{1+2H_2(E_1)H_2(E_2)/N+4\alpha/N} \times \frac{1}{1+\beta[H_4(E_1)+H_4(E_2)]/N} \times \left[2E_1^2E_2^2+(\gamma-2)(E_1^2+E_2^2)-2(\gamma-1)\right](-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}\right\}, \quad (12)$$

where H_ν is the Hermite polynomial of νth order defined by the equation

$$H_\nu(x) = (-1)^\nu \exp\left(\tfrac{1}{2}x^2\right)\frac{d^\nu}{dx^\nu}\exp\left(-\tfrac{1}{2}x^2\right).$$

P_+ represents the probability that $S(\mathbf{H}_1+\mathbf{H}_2)S(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)$ is positive when $|E_{\mathbf{H}_1}|, |E_{\mathbf{H}_2}|, |E_{\mathbf{H}_1+\mathbf{H}_2}|, |E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}|$ are known.

We first make some remarks about the mathematical form of (12). If N is large enough, the β and α factors do not play a critical role: their calculation, nevertheless, may be very time consuming. A useful approximation to (12) is therefore the simpler relation

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{2N}|E_3E_4|\frac{1}{1+2H_2(E_1)H_2(E_2)/N} \times \left[2E_1^2E_2^2+(\gamma-2)(E_1^2+E_2^2)-2(\gamma-1)\right](-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}\right\}, \quad (13)$$

in which we have fixed $\beta\simeq\alpha\simeq 0$. For the sake of simplicity the same approximation will be used in following relations.

It is useful to compare (13) with the corresponding sign relation derived from the use of (6). As

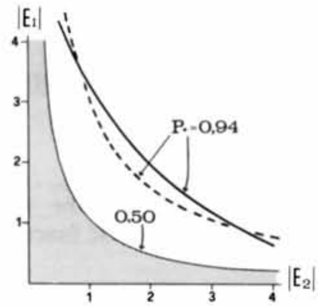

Fig. 1. Two contours of (13) are shown when $\gamma=2$, $\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q\equiv 0$ (mod. 1) and $N=40$. The broken line represents a contour of (14), the shaded area is the region in which (13) is less than $\frac{1}{2}$.

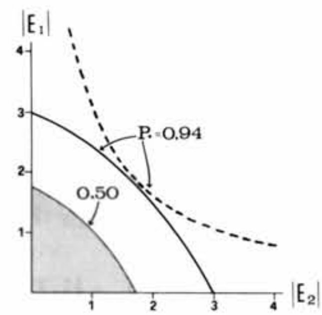

Fig. 2. The broken line represents a contour of (14), the full lines are two contours of (13) when $\gamma=4$, $\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_o\equiv 0$ (mod. 1) and $N=40$. The shaded area is the region in which (13) is less than $\frac{1}{2}$.

$$P_+(E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q})$$
$$\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{\sqrt{N}}|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}p+\mathbf{H}_2\mathbf{R}_q}|(-1)^{2(\mathbf{H}_1\mathbf{T}p+\mathbf{H}_2\mathbf{T}_q)}\right],$$

by expanding tanh as far as the first power, we obtain from (6)

$$P_+=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{|E_3E_4|}{N}E_1^2E_2^2(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}\right]. \quad (14)$$

When $\mathbf{R}_p=\mathbf{I}$ and $\mathbf{R}_q=-\mathbf{I}$, (14) is in contrast with the Harker–Kasper inequalities and gives entirely misleading results when $|E_{\mathbf{H}_1}|$ or $|E_{\mathbf{H}_2}|$ is small (Giacovazzo, 1974*a*). Presumably the same inconvenience should affect any coincidence theory based on (6). The cases $\gamma=2,4$ in (13) are illustrated in Figs. 1 and 2, respectively, when $(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)\equiv 0$ (mod. 1), and are compared with (14). The same figures hold also when $(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)\not\equiv 0$ (mod. 1) if we change P_+ into P_- values. We observe that: (*a*) P_+ values smaller than 1/2 are not possible in (14) when $(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)\equiv 0$ (mod. 1). On the other hand, (13) involves some regions of the $(|E_1|,|E_2|)$ plane in which $P_+<1/2$, in accordance with Harker–Kasper inequalities. These regions are shaded in Figs. 1 and 2. (*b*) When $\gamma=2$, (13) agrees well with (14) solely at high values of $|E_1|$ and $|E_2|$ [broken lines in Figs. 1 and 2 correspond to curves of (14)]. The behaviour of (13) when $\gamma=4$ is, on the other hand, remarkably different from that corresponding to $\gamma=2$ (compare Figs. 1 and 2).

These considerations indicate that, unlike α and β, it could be worth while calculating the γ factor for each pair $(\mathbf{R}_p,\mathbf{R}_q)$ used in the coincidence procedure.

5. The distribution $P(E_{\mathbf{H}_1},E_{\mathbf{H}_2},E_{\mathbf{H}_1+\mathbf{H}_2},E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q},E_{\mathbf{H}_1+\mathbf{K}},E_{\mathbf{H}_2-\mathbf{K}},\ldots)$ when $\mathbf{K}(\mathbf{R}_p-\mathbf{R}_q)=0$ and when the Gram–Charlier expansion of the characteristic function is used

Let us denote

$$\mathbf{H}_1+\mathbf{H}_2=\mathbf{U},\quad \mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q=\mathbf{V}. \quad (15)$$

In §2 we showed that

$$\varphi_\mathbf{U}-\varphi_\mathbf{V}\simeq 2\pi(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)$$

if $|E_{\mathbf{H}_1}|$, $|E_{\mathbf{H}_2}|$, $|E_\mathbf{U}|$, $|E_\mathbf{V}|$ are large enough.

The algebraic properties of the symmetry operators $\mathbf{C}=(\mathbf{R},\mathbf{T})$ can in general allow more pairs $(\mathbf{H}_1,\mathbf{H}_2)$ to give information about the expected value of $\varphi_\mathbf{U}-\varphi_\mathbf{V}$. A general way of obtaining these pairs is to calculate the values

$$\mathbf{H}_1'=\mathbf{H}_1+\mathbf{K},\quad \mathbf{H}_2'=\mathbf{H}_2-\mathbf{K}$$

when $\mathbf{K}(\mathbf{R}_p-\mathbf{R}_q)=0$. In fact the pair $(\mathbf{H}_1',\mathbf{H}_2')$ satisfies (15) and leads to

$$\varphi_\mathbf{U}-\varphi_\mathbf{V}=2\pi(\mathbf{H}_1'\mathbf{T}_p+\mathbf{H}_2'\mathbf{T}_q)$$

if $|E_{\mathbf{H}_1'}|$, $|E_{\mathbf{H}_2'}|$, $|E_\mathbf{U}|$, $|E_\mathbf{V}|$ are large enough.

This result suggests that more exhaustive information on an s.r.p.p. may be given by means of the distribution

$$P(E_{\mathbf{H}_1},\ldots,E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q},\ldots,E_{\mathbf{H}_1+\mathbf{K}_j},E_{\mathbf{H}_2-\mathbf{K}_j},\ldots)$$

when $\mathbf{K}_j(\mathbf{R}_p-\mathbf{R}_q)=0$ for each j.

After lengthy calculations we obtain

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{2N}\,\frac{1}{Q}|E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}|$$
$$\times\{\sum_j[2E^2_{\mathbf{H}_1+\mathbf{K}_j}E^2_{\mathbf{H}_2-\mathbf{K}_j}$$
$$+(E^2_{\mathbf{H}_1+\mathbf{K}_j}+E^2_{\mathbf{H}_2-\mathbf{K}_j})(\gamma-2)-2(\gamma-1)]$$
$$\times(-1)^{2[(\mathbf{H}_1+\mathbf{K}_j)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_j)\mathbf{T}_q]}\}, \quad (16)$$

where

$$Q=1+2[\sum_j(E^2_{\mathbf{H}_1+\mathbf{K}_j}-1)(E^2_{\mathbf{H}_2-\mathbf{K}_j})]/N.$$

In order to obtain some insight into the nature of (16) let us examine its practical application in a given space group, for example $P2_1/c$. By leaving out the trivial case $\mathbf{R}_p=\mathbf{I}$, $\mathbf{R}_q=\pm\mathbf{I}$, we shall devote our attention to the case in which

$$\mathbf{R}_p=\mathbf{I};\quad \mathbf{R}_q=\begin{vmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{vmatrix},\quad \mathbf{T}_q=\begin{vmatrix}0\\\frac{1}{2}\\\frac{1}{2}\end{vmatrix}.$$

As $\gamma=2$, (16) becomes

$$P_+=\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{2N}\,\frac{1}{Q}|E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}|$$
$$\times\{2\sum_j(E^2_{\mathbf{H}_1+\mathbf{K}_j}E^2_{\mathbf{H}_2-\mathbf{K}_j}-1)$$
$$\times(-1)^{2[(\mathbf{H}_1+\mathbf{K}_j)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_j)\mathbf{T}_q]}\}. \quad (17)$$

Let us suppose, now,

$$\mathbf{H}_1+\mathbf{H}_2=(2,3,4),\quad \mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q=(6,3,2).$$

As the vector $\mathbf{K}$ defined by the condition $\mathbf{K}(\mathbf{R}_p-\mathbf{R}_q)=0$ is an $(0,k,0)$ type vector, one obtains

$$\mathbf{H}_1=(4,k,3),\quad \mathbf{H}_2=(-2,3-k,1), \quad (18)$$

where k can assume any value. In Fig. 3 is shown a region of the reciprocal plane which contains the reflexions (18): as the sign probability of $E_{2,3,4}E_{6,3,2}$ depends on the distribution of the $|E|$ values in the rows defined by (18), we have marked this set in the figure by full circles: the radius of any circle is proportional to $|E|$ of the corresponding reflexion. We observe that the vectors $\mathbf{H}_1+\mathbf{K}_j$, $\mathbf{H}_2-\mathbf{K}_j$ are symmetrically related by a centre located at $(\mathbf{H}_1+\mathbf{H}_2)/2$. For large values of probability (P_+ or P_-) the magnitudes $|E_{\mathbf{H}_1+\mathbf{K}_j}E_{\mathbf{H}_2-\mathbf{K}_j}|$ must be alternately large or small according to the parity of $\mathbf{H}_2-\mathbf{K}_j$. In Fig. 3 is shown a situation favourable to large values of P_+.

Furthermore, it could be useful to note that if the actual space group was $P2/m$, a situation favourable to large values of P_+ would require large magnitudes $|E_{\mathbf{H}_1+\mathbf{K}_j}E_{\mathbf{H}_2-\mathbf{K}_j}|$ irrespective of the parity of $\mathbf{H}_2-\mathbf{K}_j$. On the other hand, small $|E_{\mathbf{H}_1+\mathbf{K}_j}E_{\mathbf{H}_2-\mathbf{K}_j}|$ magnitudes,

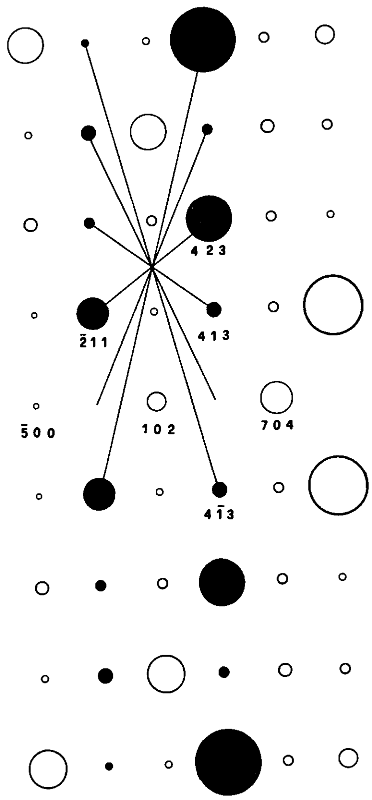

Fig. 3. Region of the reciprocal space defined by the reflexions $(4, k, 3)$ and $(-2, 3-k, 1)$.

irrespective of the parity of $\mathbf{H}_2-\mathbf{K}_j$, indicate in $P2/m$ the sign relation

$$S(\mathbf{H}_1+\mathbf{H}_2)S(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)=-1.$$

This explains the effects of the translation components of the symmetry operations in the coincidence method.

6. The coincidence probability when the exponential form of the characteristic function is used

Appendix C shows that

$$\begin{aligned}P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}) &\simeq \frac{1}{(2\pi)^2}\exp\{-\tfrac{1}{2}(E^2_{\mathbf{H}_1}+\ldots+E^2_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q})\\ &+\frac{1}{\sqrt{N}}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}+\frac{1}{\sqrt{N}}E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}\\ &\times(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}\\ &+\frac{1}{N}\left[(1-\gamma)+\frac{(\gamma-2)}{2}(E^2_{\mathbf{H}_1}+E^2_{\mathbf{H}_2})\right]\\ &\times E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}\}. \qquad (19)\end{aligned}$$

Denoting by $R_{\mathbf{H}}$ the absolute value of $E_{\mathbf{H}}$, from (19) we obtain

$$P_{\pm}\simeq\frac{1}{L}\exp(\pm B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1}R_{\mathbf{H}_2}Z^{\pm}\right), \qquad (20)$$

where

$$B=\frac{1}{N}\left[(1-\gamma)+\left(\frac{\gamma-2}{2}\right)(R^2_{\mathbf{H}_1}+R^2_{\mathbf{H}_2})\right]\times R_{\mathbf{H}_1+\mathbf{H}_2}R_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)},$$

$$Z^{\pm}=[R_{\mathbf{H}_1+\mathbf{H}_2}\pm(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}R_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}],$$

$$L=\exp(+B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1}R_{\mathbf{H}_2}Z^{+}\right)+\exp(-B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1}R_{\mathbf{H}_2}Z^{-}\right).$$

We note explicitly that the value of γ seems able strongly to affect the probability values provided by (20).

When the more general probability density

$$P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}, \ldots, E_{\mathbf{H}_1+\mathbf{K}_j}, E_{\mathbf{H}_2-\mathbf{K}_j}, \ldots)$$

is explored provided $\mathbf{K}_j(\mathbf{R}_p-\mathbf{R}_q)=0$ for each value of j, the more exhaustive sign relation is found:

$$P_{\pm}\simeq\frac{1}{L}\exp(\pm B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_1}R_{\mathbf{H}_2-\mathbf{K}_1}Z^{\pm}_1\right)\ldots\times\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_j}R_{\mathbf{H}_2-\mathbf{K}_j}Z^{\pm}_j\right)\ldots, \qquad (21)$$

where

$$\begin{aligned}B=\Big\{&\left(\frac{1-\gamma}{N}\right)[(-1)^{2[(\mathbf{H}_1+\mathbf{K}_1)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_1)\mathbf{T}_q]}+\ldots\\ &+(-1)^{2[(\mathbf{H}_1+\mathbf{K}_j)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_j)\mathbf{T}_q]}]\\ &+\left(\frac{\gamma-2}{2N}\right)[(-1)^{2[(\mathbf{H}_1+\mathbf{K}_1)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_1)\mathbf{T}_q]}\\ &\times(R^2_{\mathbf{H}_1+\mathbf{K}_1}+R^2_{\mathbf{H}_2-\mathbf{K}_1})+\ldots\\ &+(-1)^{2[(\mathbf{H}_1+\mathbf{K}_j)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_j)\mathbf{T}_q]}(R^2_{\mathbf{H}_1+\mathbf{K}_j}+R^2_{\mathbf{H}_2-\mathbf{K}_j})+\ldots]\Big\}\\ &\times R_{\mathbf{H}_1+\mathbf{H}_2}R_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q},\end{aligned}$$

$$\begin{aligned}L=&\exp(+B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_1}R_{\mathbf{H}_2-\mathbf{K}_1}Z^{+}_1\right)\ldots\\ &\times\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_j}R_{\mathbf{H}_2-\mathbf{K}_j}Z^{+}_j\right)\ldots\\ &+\exp(-B)\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_1}R_{\mathbf{H}_2-\mathbf{K}_1}Z^{-}_1\right)\ldots\\ &\times\cosh\left(\frac{1}{\sqrt{N}}R_{\mathbf{H}_1+\mathbf{K}_j}R_{\mathbf{H}_2-\mathbf{K}_j}Z^{-}_j\right)\ldots,\end{aligned}$$

$$Z^{\pm}_j=[R_{\mathbf{H}_1+\mathbf{H}_2}\pm(-1)^{2[(\mathbf{H}_1+\mathbf{K}_j)\mathbf{T}_p+(\mathbf{H}_2-\mathbf{K}_j)\mathbf{T}_q]}\times R_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}].$$

Details about the practical use of (21) and connexions with (16) would make this paper dull reading and will be described in a future paper.

7. Conclusions

A theory has been described which, from the knowledge of $|E|$'s, derives a probabilistic value for the sign of the product $E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}$. In particular, the theory is able to give in symmorphic space groups relations of the type

$$S(\mathbf{H}_1+\mathbf{H}_2)S(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)\simeq -1,$$

which are of great interest in direct procedures for phase determination [see Schenk & de Jong (1973) for the case $\mathbf{R}_p=\mathbf{I}$, $\mathbf{R}_q=-\mathbf{I}$ or *vice versa*].

The formulae which yield the sign of $E_{\mathbf{H}_1+\mathbf{H}_2}E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q}$ are expressed, as well as those corresponding to triplets $E_\mathbf{h}$, $E_\mathbf{k}$, $E_{\mathbf{h}+\mathbf{k}}$, in terms of the hyperbolic tangent if the Gram–Charlier expansion of the characteristic function is used. The sign relations obtained *via* the Fourier transform of the original expression of the characteristic function are more complex than the preceding, but seem able to give more accurate values of the coincidence probability.

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APPENDIX *A*

In the study of the multivariate distribution $P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q})$ some standardized cumulants of low order have been used. With a view to deriving them, the linearization theory of Bertaut (1959) will be utilized. We consider here the vectors $\mathbf{H}_1$, $\mathbf{H}_2$, $\mathbf{H}_1+\mathbf{H}_2$, $\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q$ whose statistical weights equal unity. In order to deal with special vector covariances, algebraic considerations as in Giacovazzo (1974*b*,*c*) are necessary

As is well known

$$\lambda_{1110}=\frac{m_{1110}}{m^{3/2}}=\frac{\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1+\mathbf{H}_2)\rangle}{m^{3/2}}=\frac{1}{\sqrt{m}},$$

where ξ is the trigonometric factor for the centrosymmetric space group involved, m is the order of the group. In an analogous way

$$\lambda_{1101}=\frac{\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)\rangle}{m^{3/2}}=\frac{(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}}{\sqrt{m}}.$$

In fact, as

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)\rangle =\left\langle\sum_{1s,n}^{m}\xi[\mathbf{H}_1(\mathbf{R}_p-\mathbf{R}_s)+\mathbf{H}_2(\mathbf{R}_q-\mathbf{R}_n)] \times\exp\left[2\pi i(\mathbf{H}_1\mathbf{T}_s+\mathbf{H}_2\mathbf{T}_n)\right]\right\rangle, \qquad (A.1)$$

$(A.1)$ is not zero for $\mathbf{R}_s=\mathbf{R}_p$ and $\mathbf{R}_n=\mathbf{R}_q$. Finally

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)\rangle =\xi(0)(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}=m(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}.$$

In order to derive the relation

$$\lambda_{2011}=\frac{m_{2011}}{m^2}=\frac{\gamma_{p,q}}{m}(-1)^{2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q)}, \qquad (A.2)$$

($\gamma_{p,q}=1$ if $\mathbf{R}_p=\mathbf{I}$ and $\mathbf{R}_q=-\mathbf{I}$ or *vice versa*; $\gamma_{p,q}\geq 2$ in the other cases), we observe that

$$m_{2011}=\langle\xi(\mathbf{H}_1)\xi(-\mathbf{H}_1)\xi(\mathbf{H}_1+\mathbf{H}_2)\xi(\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q)\rangle =\left\langle\sum_{1\ s,n,v}^{m}\xi[\mathbf{H}_1(\mathbf{R}_p+\mathbf{R}_s+\mathbf{R}_n+\mathbf{R}_v)+\mathbf{H}_2(\mathbf{R}_q+\mathbf{R}_s)] \times\exp\{2\pi i[\mathbf{H}_1(\mathbf{T}_s+\mathbf{T}_n-\mathbf{T}_v)+\mathbf{H}_2\mathbf{T}_s]\}\right\rangle. \qquad (A.3)$$

m_{2011} is not zero when

(*a*) $\mathbf{R}_s=-\mathbf{R}_q$, $\mathbf{R}_n=\mathbf{R}_q$, $\mathbf{R}_v=\mathbf{R}_p$;

(*b*) $\mathbf{R}_s=-\mathbf{R}_q$, $\mathbf{R}_n=-\mathbf{R}_p$, $\mathbf{R}_v=-\mathbf{R}_q$.

The two cases coincide when $\mathbf{R}_p=\mathbf{I}$ and $\mathbf{R}_q=-\mathbf{I}$ or *vice versa*: the statement $\gamma=1$ is thus justified in this case.

Nevertheless γ may be larger than 2. In symmetry classes *mmm*, for example, in which the rotation components of the symmetry operations are

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

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

$\gamma=4$ if $p=1$, $q=2,3,4$; $\gamma=1$ if $p=1$, $q=5$; $\gamma=2$ if $p=1$, $q=6,7,8$. In fact, when $p=1$ and $q=2$, for example, $(A.3)$ does not vanish when

$$\begin{aligned}&\mathbf{R}_s=-\mathbf{R}_2,\quad \mathbf{R}_n=\mathbf{R}_2,\quad \mathbf{R}_v=\mathbf{R}_1,\\ &\mathbf{R}_s=-\mathbf{R}_2,\quad \mathbf{R}_n=\mathbf{R}_5,\quad \mathbf{R}_v=\mathbf{R}_6,\\ &\mathbf{R}_s=-\mathbf{R}_2,\quad \mathbf{R}_n=\mathbf{R}_8,\quad \mathbf{R}_v=\mathbf{R}_3,\\ &\mathbf{R}_s=-\mathbf{R}_2,\quad \mathbf{R}_n=\mathbf{R}_7,\quad \mathbf{R}_v=\mathbf{R}_4.\end{aligned}$$

Some multivariate distributions studied in this paper involve a vector $\mathbf{K}$ which satisfies the condition $\mathbf{K}(\mathbf{R}_p-\mathbf{R}_q)=0$. On the basis of the linearization theory it is a straightforward task to verify the relation

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

In a similar way we derive the relation

$$\langle\xi(\mathbf{H}_1+\mathbf{K})\xi(\mathbf{H}_2-\mathbf{K})\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\rangle$$
$$=\left\langle\sum_{1\ p,q,v}^{m}\xi[\mathbf{H}_1(\mathbf{I}+\mathbf{R}_n)+\mathbf{H}_2(\mathbf{R}_q+\mathbf{R}_v)+\mathbf{K}(\mathbf{I}-\mathbf{R}_q)] \times\exp\{2\pi i[\mathbf{H}_1\mathbf{T}_n+\mathbf{H}_2(\mathbf{T}_q+\mathbf{T}_v)-\mathbf{K}\mathbf{T}_q]\}\right\rangle. \quad (A.4)$$

If $\mathbf{R}_n=-\mathbf{I}$ and $\mathbf{R}_v=-\mathbf{R}_q$, the value of $(A.4)$ equals

$$\left\langle\sum_{1\ q}^{m}\xi[\mathbf{K}(\mathbf{I}-\mathbf{R}_q)\exp(-2\pi i\mathbf{K}\mathbf{T}_q)]\right\rangle=\xi^2(\mathbf{K})=p_{\mathbf{K}}m. \quad (A.5)$$

If $\mathbf{K}$ is a zero reflexion ($p_{\mathbf{K}}=0$), $(A.5)$ vanishes.

APPENDIX *B*

In this Appendix the values of some standardized cumulants are calculated whose estimate is not critical in order to define the coincidence conditions for an s.r.p.p. Their estimates however may be of some interest from an algebraic point of view. From the S_4 definition in §4,

$$\alpha=m\frac{\lambda_{0022}}{2!2!},$$

where

$$\lambda_{0022}=\frac{m_{0022}-m_{0020}m_{0002}}{m^2}. \quad (B.1)$$

If we limit ourselves to the simple case in which $\mathbf{R}_p=\mathbf{I}$, $\mathbf{R}_q=\mathbf{R}_s$. Then

$$m_{0022}=\langle\xi^2(\mathbf{H}_1+\mathbf{H}_2)\xi^2(\mathbf{H}_1+\mathbf{H}_2\mathbf{R}_s)\rangle$$
$$=\left\langle\sum_{1\ p,n,q}^{m}\xi[\mathbf{H}_1(\mathbf{I}+\mathbf{R}_p+\mathbf{R}_n+\mathbf{R}_q)+\mathbf{H}_2(\mathbf{R}_s+\mathbf{R}_p+\mathbf{R}_s\mathbf{R}_n+\mathbf{R}_q)] \times\exp\{2\pi i[\mathbf{H}_1(\mathbf{T}_p+\mathbf{T}_n+\mathbf{T}_q)+\mathbf{H}_2(\mathbf{T}_p+\mathbf{R}_s\mathbf{T}_n+\mathbf{T}_q)]\}\right\rangle. \quad (B.2)$$

$(B.2)$ does not vanish when

$$\mathbf{R}_q=-\mathbf{R}_p,\quad \mathbf{R}_n=-\mathbf{I}. \quad (B.3)$$

The combinations in $(B.3)$ give a contribution equal to m^2, which, substituted in $(B.1)$, make $(B.1)$ zero. If $\mathbf{R}_s$ is a proper or improper rotation matrix of a symmetry element of order two, additional combinations exist besides those described by $(B.3)$. In fact $(B.2)$ does not vanish also when

$$-\mathbf{R}_p-\mathbf{R}_q=\mathbf{I}+\mathbf{R}_n=\mathbf{R}_s(\mathbf{I}+\mathbf{R}_n),\quad \mathbf{R}_n\neq-\mathbf{I}. \quad (B.4)$$

$(B.4)$ is verified when

$$\mathbf{R}_n=\mathbf{R}_s,\quad \mathbf{R}_n\mathbf{R}_s=\mathbf{I},$$

which involves in its turn the condition

$$\mathbf{R}_s^2=\mathbf{I}. \quad (B.5)$$

$(B.5)$ is just the condition which denotes the symmetry elements of order two.

So, in symmetry class $2/m$ we have, when $s=3,4$,

$$m_{0022}=24,\quad \lambda_{0022}=1/2;$$

in *mmm*

$$\lambda_{0022}=5/4 \quad \text{when} \quad s=2,3,4$$
$$\lambda_{0022}=0 \quad \text{when} \quad s=5$$
$$\lambda_{0022}=1/2 \quad \text{when} \quad s=6,7,8.$$

It is worth while spending some time on the factor β which appears in the S_4 definition. We find

$$\beta=\frac{1}{t}\,\frac{\lambda_{400\ldots}}{4!0!0!\ldots},$$

where

$$\lambda_{400\ldots}=\frac{m_{400\ldots}-3m_{200\ldots}^2}{m_{200}^2}.$$

The moment $m_{400\ldots}$, in its turn, is defined in any space group by

$$\langle\xi^4(\mathbf{H})\rangle=\left\langle\sum_{1\ p,q,v}^{m}\xi[\mathbf{H}(\mathbf{I}+\mathbf{R}_p+\mathbf{R}_q+\mathbf{R}_v)] \times\exp\{2\pi i[\mathbf{H}(\mathbf{T}_p+\mathbf{T}_q+\mathbf{T}_v)]\}\right\rangle. \quad (B.6)$$

Expression $(B.6)$ is non-zero for all combinations of the rotation matrices for which

$$\mathbf{I}+\mathbf{R}_p+\mathbf{R}_q+\mathbf{R}_v=0. \quad (B.7)$$

Condition $(B.7)$ is valid, for example, when

(*a*) $\mathbf{R}_p=-\mathbf{I},\quad \mathbf{R}_q=-\mathbf{R}_v$

(*b*) $\mathbf{R}_q=-\mathbf{I},\quad \mathbf{R}_p=-\mathbf{R}_v$

(*c*) $\mathbf{R}_v=-\mathbf{I},\quad \mathbf{R}_p=-\mathbf{R}_q$.

Excluding equivalent combinations, we obtain a total of $3(m-1)$ solutions to $(B.7)$. In accordance with this result, in symmetry classes $\bar{1}$ and $2/m$, $(B.6)$ equals 6 and 36 respectively. Further combinations, nevertheless, add to the combinations in (*a*), (*b*), (*c*) for space groups with higher symmetry. For example, in class *mmm*

$$\langle\xi^4\rangle=27m>3(m-1)m:$$

the additional combinations are

$\mathbf{R}_p=\mathbf{R}_6, \mathbf{R}_q=\mathbf{R}_7, \mathbf{R}_v=\mathbf{R}_8;\quad \mathbf{R}_p=\mathbf{R}_6, \mathbf{R}_q=\mathbf{R}_8, \mathbf{R}_v=\mathbf{R}_7$

$\mathbf{R}_p=\mathbf{R}_7, \mathbf{R}_q=\mathbf{R}_6, \mathbf{R}_v=\mathbf{R}_8;\quad \mathbf{R}_p=\mathbf{R}_7, \mathbf{R}_q=\mathbf{R}_8, \mathbf{R}_v=\mathbf{R}_6$

$\mathbf{R}_p=\mathbf{R}_8, \mathbf{R}_q=\mathbf{R}_6, \mathbf{R}_v=\mathbf{R}_7;\quad \mathbf{R}_p=\mathbf{R}_8, \mathbf{R}_q=\mathbf{R}_7, \mathbf{R}_v=\mathbf{R}_6.$

For a space group of order m, therefore, $\beta\geq-1/8N$. We indicate explicitly that one may have $\beta>0$: in symmetry class *mmm*, in fact, $\beta=+1/8N$.

APPENDIX *C*

Denoting

$$E_1=E_{\mathbf{H}_1},\quad E_2=E_{\mathbf{H}_2},\quad E_3=E_{\mathbf{H}_1+\mathbf{H}_2},$$
$$E_4=E_{\mathbf{H}_1\mathbf{R}_p+\mathbf{H}_2\mathbf{R}_q},\quad f=2(\mathbf{H}_1\mathbf{T}_p+\mathbf{H}_2\mathbf{T}_q),$$

their probability density function may be written

$$P(E_1,\ldots,E_4)\simeq\frac{1}{(2\pi)^4}\int_{-\infty}^{+\infty}\ldots\int\exp\left[-\tfrac{1}{2}(u_1^2+\ldots+u_4^2)\right.$$
$$-i(E_1u_1+\ldots+E_4u_4)$$
$$-\frac{i}{\sqrt{N}}u_1u_2u_3-\frac{i}{\sqrt{N}}(-1)^f u_1u_2u_4$$
$$\left.+\frac{\gamma}{2N}(-1)^f(u_1^2u_3u_4+u_2^2u_3u_4)\right]du_1du_2du_3du_4. \quad (C.1)$$

The integration of $(C.1)$ with respect to u_3 and u_4 is readily carried out:

$$P\simeq\frac{1}{(2\pi)^3}\exp\left[-\tfrac{1}{2}(E_3^2+E_4^2)\right]$$
$$\times\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\exp\left[-\tfrac{1}{2}(u_1^2+u_2^2)-i(E_1u_1+E_2u_2)\right.$$
$$-\frac{1}{\sqrt{N}}u_1u_2E_3-\frac{1}{\sqrt{N}}(-1)^f u_1u_2E_4$$
$$\left.-\frac{\gamma}{2N}(-1)^f(u_1^2+u_2^2)E_3E_4\right]. \quad (C.2)$$

The integrations of $(C.2)$ with respect to u_1 and u_2 are carried out by means of the expansion

$$\exp\left[-\frac{\gamma}{2N}(-1)^f E_3E_4u_j^2\right]\simeq 1-\frac{\gamma}{2N}(-1)^f E_3E_4u_j^2+\ldots, \quad (C.3)$$

and by means of the integral relation

$$\int_{-\infty}^{+\infty}x^2\exp(-\mu x^2+2vx)dx=\frac{1}{2\mu}\sqrt{\frac{\pi}{\mu}}\left(1+2\frac{v^2}{\mu}\right)\exp(v^2/\mu).$$

Finally, we obtain

$$P\simeq\frac{1}{(2\pi)^2}\left[1+(-1)^f\left(\frac{1-\gamma}{N}\right)E_3E_4\right.$$
$$\left.+(-1)^f\frac{\gamma}{2N}E_2^2E_3E_4-(-1)^f\left(\frac{2-\gamma}{2N}\right)E_1^2E_3E_4\right]$$
$$\times\exp\left[-\tfrac{1}{2}(E_1^2+\ldots+E_4^2)+\frac{1}{\sqrt{N}}E_1E_2E_3\right.$$
$$\left.+\frac{1}{\sqrt{N}}(-1)^f(E_1E_2E_4-\frac{1}{N}(-1)^f E_2^2E_3E_4\right],$$

which, by means of $(C.3)$, reduces to (19).

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