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# Pairs in $P2_1$: Probability Distributions which Lead to Unique Estimates of the Two-Phase Structure Seminvariants in the Interval $(-\pi,\pi)$

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Conditional probability distributions of the two-phase structure seminvariant $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$ in $P2_1$, given the values of one or more two-phase structure seminvariants, as well as appropriately chosen sets of structure factor magnitudes $|E|$, are derived. These distributions yield unique and reliable estimates, in the whole interval $(-\pi,\pi)$, of the values of these seminvariants. In the case that a given structure seminvariant specifies the enantiomorph, the values of the remaining seminvariants are consistent with this choice of enantiomorph. In any event, the variance of any distribution of the kind described here is much smaller, in favorable cases, than that of a distribution which assumes as known magnitudes $|E|$ alone, reflecting the fact that previously derived phase information severely limits the possible values of other phases.

## 1. Introduction

The linear combination of the two phases

$$\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2} \tag{1.1}$$

is a structure seminvariant if

$$(h_1 - h_2, 0, l_1 - l_2) \equiv 0 \ (\text{mod } \omega_s), \tag{1.2}$$

where $\omega_s$, the seminvariant modulus in $P2_1$, is defined by

$$\omega_s = (2,0,2). \tag{1.3}$$

In two previous papers (Green & Hauptman, 1978; Hauptman & Green 1978), estimates for $\varphi_{12}$ were obtained from conditional probability distributions derived on the basis that selected sets of magnitudes $|E|$, the neighborhoods of $\varphi_{12}$, were known. In the first paper (Green & Hauptman, 1978) it was shown that, given the magnitudes in any neighborhood of the first kind, estimates of $\varphi_{12}$ in the vicinity of 0 or $\pi$ could be reliably determined. In the second paper (Hauptman & Green, 1978) it was demonstrated that, given the magnitudes in any neighborhood of the second kind, reliable, but ambiguous estimates of $\varphi_{12} \simeq \pm\pi/2$ could, in favorable cases, be found; the enantiomorph is then specified by choosing arbitrarily the sign of one such estimate. These two papers leave unanswered two related questions: Can the presumed known values of one or more two-phase seminvariants be used to estimate reliably the value of a related seminvariant, the initial estimate of which, based on known values of magnitudes $|E|$ alone, was unreliable? Secondly, given the value of a single enantiomorph-sensitive two-phase seminvariant, is it possible to resolve, in a way consistent with this choice of enantiomorph, the sign ambiguity of the remaining two-phase enantiomorph-sensitive seminvariants, *i.e.* those whose values differ significantly from 0 or $\pi$? The analogous questions for quartets were recently given an affirmative answer (Hauptman, 1977*b*,*c*), and the present paper is heavily dependent on the methods introduced in this earlier work. In strict analogy with the recently developed theory of quartets, the clue to the answer is found in the third and higher neighborhoods of $\varphi_{12}$ of the first kind (Green & Hauptman, 1978), the 'trio relations' used to define the higher neighborhoods (compare Hauptman, 1977*a*), and related probability distributions.

In $P2_1$ the normalized structure factor $E_{hkl}$ is defined by

$$E_{hkl} = |E_{hkl}| \exp(i\varphi_{hkl}) = \frac{2}{(\varepsilon\sigma_2)^{1/2}} \sum_{j=1}^{N/2} f_j \cos 2\pi\left(\mathbf{h}\cdot\mathbf{r}_j + \frac{k}{4}\right) \exp i2\pi\left(ky_j - \frac{k}{4}\right), \tag{1.4}$$

where $\mathbf{h}$ and $\mathbf{r}_j$ are two-dimensional vectors defined by

$$\mathbf{h} = (h,l), \tag{1.5}$$

$$\mathbf{r}_j = (x_j,z_j) \tag{1.6}$$

and $f_j$ is the zero-angle atomic scattering factor of the atom labeled $j$; in the X-ray diffraction case the $f_j$ are the atomic numbers $Z_j$ and are therefore positive; for neutron diffraction some of the $f_j$ may be negative; the term $\sigma_n$ is defined by

$$\sigma_n = \sum_{j=1}^{N} f_j^n, \tag{1.7}$$

and $\varepsilon = 2$ if $h = l = 0$ and 1 otherwise. Finally, $(x_k,y_j,z_j)$ is the position vector of the $j$th atom. Other definitions and notations used here are in accord with the previous papers in this series (Green & Hauptman, 1978; Hauptman & Green, 1978).

The major results obtained in this paper are (1) $P_{1|1,11}$, the conditional probability distribution of a structure seminvariant, given the value of another structure seminvariant and 11 magnitudes $|E|$, equation (2.5); (2) $P_{1|2,20}$, the conditional probability distribution of a structure seminvariant, given the values of two other structure seminvariants and 20 magnitudes $|E|$, equation (3.5); and (3) $P_{1|1,24}$, the conditional probability distribution of a structure seminvariant, given the value of another structure seminvariant and 24 magnitudes $|E|$, equation (4.3). Important auxiliary distributions needed in the derivation of these three are $P_{15}$, $P_{3|15}$, $P_{2|15}$, $P_{4|28}$, $P_{3|28}$, $P_{2|1,24}$; equations (I.5), (I.15), (I.28), (II.4), (II.16), (II.31), respectively. Among the latter, $P_{2|15}$ and $P_{2|1,24}$ may also prove to be useful in the applications.

## 2. The conditional probability distribution of the structure seminvariant $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$, given the structure seminvariant $\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}$ and 11 magnitudes $|E|$

Suppose that $\Phi_{23}(-\pi < \Phi_{23} \le \pi)$ and the 11 non-negative numbers $R_1$, $R_2$, $R_3$, $R_{1\bar{2}/10}$, $R_{3\bar{1}/30}$, $R_{12/11}$, $R_{12/1\bar{1}}$, $R_{31/31}$, $R_{31/3\bar{1}}$, $R_{1\bar{2}}$, $R_{3\bar{1}}$ are specified and that the ordered triple $[(h_1kl_1), (h_2kl_2), (h_3kl_3)]$ is a random variable which is uniformly distributed over the subset of the threefold Cartesian product $W \times W \times W$ of reciprocal space $W$ defined by (I.1), (I.2), (Appendix I),

$$\varphi_{23} = \Phi_{23}; \tag{2.1}$$

and

$$\begin{aligned}
&|E_{h_1kl_1}| = R_1, \quad |E_{h_2kl_2}| = R_2, \quad |E_{h_3kl_3}| = R_3,\\
&|E_{\frac{1}{2}(h_1-h_2),q,\frac{1}{2}(l_1-l_2)}| = R_{1\bar{2}/10}, \quad |E_{\frac{1}{2}(h_3-h_1),s,\frac{1}{2}(l_3-l_1)}| = R_{3\bar{1}/30},\\
&|E_{\frac{1}{2}(h_1+h_2),q+k,\frac{1}{2}(l_1+l_2)}| = R_{12/11},\\
&|E_{\frac{1}{2}(h_1+h_2),q-k,\frac{1}{2}(l_1-l_2)}| = R_{12/1\bar{1}},\\
&|E_{\frac{1}{2}(h_3+h_1),s+k,\frac{1}{2}(l_3+l_1)}| = R_{31/31},\\
&|E_{\frac{1}{2}(h_3+h_1),s-k,\frac{1}{2}(l_3+l_1)}| = R_{31/3\bar{1}}, \quad |E_{h_1-h_2,0,l_1-l_2}| = R_{1\bar{2}},\\
&|E_{h_3-h_1,0,l_3-l_1}| = R_{3\bar{1}},
\end{aligned} \tag{2.2}$$

where, as usual, $q$ and $s$ are arbitrary non-zero integers. In view of (I.1) and (I.2)

$$\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2} \tag{2.3}$$

and

$$\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3} \tag{2.4}$$

are structure seminvariants. The structure seminvariant $\varphi_{12}$, as a function of the primitive random variable $[(h_1kl_1), (h_2kl_2)]$ is itself a random variable. Denote by

$$P_{1|1,11} = P(\Phi_{12}|\Phi_{23}, R_1, R_2, R_3, R_{1\bar{2}/10}, R_{3\bar{1}/30}, R_{12/11}, R_{12/1\bar{1}}, R_{31/31}, R_{31/3\bar{1}}, R_{1\bar{2}}, R_{3\bar{1}})$$

the conditional probability distribution of $\varphi_{12}$ given the structure seminvariant (2.1) and the eleven magnitudes (2.2). This distribution, correct to terms of order $1/N$, is obtained from $P_{2|15}$, [equation (I.28), Appendix I], by fixing $\Phi_{23}$ and multiplying by a suitable normalization factor:

$$P_{1|1,11} = \frac{1}{K_{1|1,11}} Q_1(\Phi_{12}) Q_2'(\Phi_{12}|\Phi_{23}), \tag{2.5}$$

where $Q_1(\Phi_{12})$ is given by (I.29) and $Q_2'(\Phi_{12}|\Phi_{23})$ is obtained from $Q_2(\Phi_{12},\Phi_{23})$, [(I.30), Appendix I)] by suppressing those factors independent of $\Phi_{12}$, but dependent on the fixed parameter $\Phi_{23}$, so that they are absorbed by the normalizing parameter $K_{1|1,11}$:

$$\begin{aligned}
Q_2'(\Phi_{12}|\Phi_{23}) = \exp\Bigg\{\Bigg[&-2(-1)^s\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)R_3R_1R^2_{3\bar{1}/30}\\
&+\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)(-2(-1)^s(R^2_{31/31}+R^2_{31/3\bar{1}})\\
&+6(-1)^sR_3R_1)\Bigg]\cos(\Phi_{12}+\Phi_{23})\\
&-\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)R_3^2R_1^2\cos 2(\Phi_{12}+\Phi_{23})\Bigg\}\\
&\times\cosh\left\{\frac{\sigma_3}{\sigma_2^{3/2}}R_{3\bar{1}}V_{3\bar{1}}\right\}I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar{1}/30}R_{31/31}U_{3\bar{1}}\right\}\\
&\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar{1}/30}R_{31/3\bar{1}}U_{3\bar{1}}\right\},
\end{aligned} \tag{2.6}$$

with $V_{3\bar{1}}$ and $U_{3\bar{1}}$ defined by (I.33) and (I.36) respectively; the normalizing parameter $K_{1|1,11}$, a function of the 12 parameters (2.1) and (2.2) and independent of $\Phi_{12}$, is best obtained numerically in any given case. It should perhaps be emphasized that $P_{1|1,11}$ is a function of the single variable $\Phi_{12}$ and that $\Phi_{23}$ appears as a parameter; despite the superficial resemblance, $P_{2|15}$, in contrast, is a function of the two variables $\Phi_{12}$ and $\Phi_{23}$.

It should be noted that if $\Phi_{23} \ne 0$ or $\pi$, (2.5) is not an even function of $\Phi_{12}$ (*cf.* Figs. 1–5) and has a unique maximum in the whole interval

$$-\pi < \Phi_{12} \le \pi. \tag{2.7}$$

In other words, once the enantiomorph has been fixed by a proper choice of the value for $\Phi_{23}$ ($\ne 0$ or $\pi$), then the most probable value for $\Phi_{12}$, given $\varphi_{23}$ and the 11 magnitudes (2.2), is given by the unique maximum of (2.5). The initial estimate for $\varphi_{23}$, assumed in (2.5), may be found in terms of magnitudes $|E|$ alone from probability distributions associated with the second and higher neighborhoods of the second kind discussed in the previous paper (Hauptman & Green, 1978). Thus, the most probable value of $\varphi_{12}$ corresponds to that value of $\Phi_{12}$ which maximizes $P_{1|1,11}$.

If $\Phi_{23} = 0$ or $\pi$ then $\varphi_{12}$ has the same value for both enantiomorphs. Thus (2.5) is bimodal, one maximum corresponding to one enantiomorph and the second to the other enantiomorph. In this case enantiomorph selection may be made by arbitrarily specifying the sign of $\Phi_{12}$ corresponding to the maxima of $P_{1|1,11}$ in the whole interval $(-\pi,\pi)$. If $\Phi_{23} = 0$ or $\pi$ and the initial estimate of $\varphi_{12}$, as obtained from magnitudes $|E|$ alone, is also 0 or $\pi$, but with a large variance, then (2.5) may yield a more reliable estimate for the value of $\varphi_{12}$.

### 3. The conditional probability distribution of the structure seminvariant $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$, given the two seminvariants $\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}$, $\varphi_{14} = \varphi_{h_1kl_1} - \varphi_{h_4kl_4}$ and 20 magnitudes

Under the usual assumptions suppose that $\Phi_{23}$, $\Phi_{14}$ $(-\pi < \Phi_{23}, \Phi_{14} \le \pi)$ and the 20 non-negative numbers

$$R_1,R_2,R_3,R_{1\bar{2}/10},R_{3\bar{1}/30},R_{12/11},R_{12/1\bar{1}},R_{31/31},R_{31/3\bar{1}},R_{1\bar{2}},R_{3\bar{1}}, \tag{3.1}$$

$$R_4,R_{4\bar{2}/50},R_{4\bar{3}/60},R_{42/51},R_{42/5\bar{1}},R_{43/61},R_{43/6\bar{1}},R_{4\bar{2}},R_{4\bar{3}} \tag{3.2}$$

are specified, and that the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$ is uniformly distributed over the subset of the fourfold Cartesian product $W \times W \times W \times W$ defined by (I.1), (I.2), (II.2), (2.2), (II.27),

$$\varphi_{23} = \Phi_{23}, \tag{3.3}$$

and

$$\varphi_{14} = \Phi_{14}. \tag{3.4}$$

Then the structure seminvariant $\varphi_{12}$, as a function of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$, is itself a random variable whose conditional probability distribution given the 22 parameters (2.2), (II.27), (3.3) and (3.4), $P_{1|2,20} = P(\Phi_{12}|\Phi_{23},\Phi_{14},R_1, \ldots R_{4\bar{3}})$, is found from $P_{2|1,24}$, (II.31), by fixing the value of $\Phi_{23}$ and multiplying by a suitable normalization factor. Thus

$$P_{1|2,20} \simeq \frac{1}{K_{1|2,20}} Q_1(\Phi_{12})\, Q_2'(\Phi_{12}|\Phi_{23}) \times Q_3''(\Phi_{12}|\Phi_{23}, \Phi_{14}) \tag{3.5}$$

where $Q_1(\Phi_{12})$ and $Q_3''(\Phi_{12}|\Phi_{23},\Phi_{14}) = Q_3'(\Phi_{12},\Phi_{23}|\Phi_{14})$ are given by (I.29) and (II.32) respectively, and $Q_2'(\Phi_{12}|\Phi_{23})$ is obtained from $Q_2(\Phi_{12},\Phi_{23})$, (I.30), by suppressing those factors in the latter which are independent of $\Phi_{12}$, but dependent on the fixed parameter $\Phi_{23}$, so that they are absorbed by the normalizing parameter $K_{1|2,20}$:

$$\begin{aligned} Q_2'(\Phi_{12}|\Phi_{23}) = \exp\Bigg\{ & -2(-1)^s \left(\frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) R_3R_1R_{3\bar{1}/30}^2 \\ & \times \cos(\Phi_{12} + \Phi_{23}) - 2(-1)^s \left(\frac{\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) \\ & \times R_3R_1(R_{31/31}^2 + R_{31/3\bar{1}}^2 - 3)\cos(\Phi_{12} + \Phi_{23}) \\ & - \left(\frac{\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) R_3^2R_1^2 \cos 2(\Phi_{12} + \Phi_{23}) \Bigg\} \\ & \times \cosh\left\{\frac{\sigma_3}{\sigma_2^{3/2}} R_{3\bar{1}} V_{3\bar{1}}\right\} \\ & \times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}} R_{3\bar{1}/30} R_{31/31} U_{3\bar{1}}\right\} \\ & \times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}} R_{3\bar{1}/30} R_{31/3\bar{1}} U_{3\bar{1}}\right\}, \end{aligned} \tag{3.6}$$

with $V_{3\bar{1}}$ and $U_{3\bar{1}}$ defined by (I.33) and (I.36) respectively.

### 4. The conditional probability distribution of the structure seminvariant $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$, given the structure seminvariant $\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}$ and 24 magnitudes

Under the usual assumptions suppose that $\Phi_{23}$ $(-\pi < \Phi_{23} \le \pi)$ and the 24 non-negative numbers

$$R_1,R_2,R_3,R_{1\bar{2}/10},R_{3\bar{1}/30},R_{12/11},R_{12/1\bar{1}},R_{31/31},R_{31/3\bar{1}},R_{1\bar{2}},R_{3\bar{1}} \tag{4.1}$$

and

$$R_4,R_{1\bar{4}/40},R_{4\bar{2}/50},R_{4\bar{3}/60},R_{14/41},R_{14/4\bar{1}},R_{42/51},R_{42/5\bar{1}},R_{43/61}, R_{43/6\bar{1}},R_{1\bar{4}},R_{4\bar{2}},R_{4\bar{3}} \tag{4.2}$$

are specified, and that the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$ is uniformly distributed over the subset of the fourfold Cartesian product $W \times W \times W \times W$ defined by (I.1), (I.2), (II.2), (I.7), (II.27) and (3.3). Then $\varphi_{12}$, as a function of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$, is itself a random variable. The conditional probability distribution of $\varphi_{12}$, given the 25 parameters (I.7), (II.27) and (3.3), $P_{1|1,24} = P(\Phi_{12}|\Phi_{23}, R_1,R_2, \ldots, R_{4\bar{3}})$, is obtained from $P_{3|1,28}$, (II.16), by fixing the value of $\Phi_{23}$, integrating (II.16) with respect to $\Phi_{14}$ over the interval $(-\pi,\pi)$ and multiplying the result by a suitable normalization parameter:

$$P_{1|1,24} = \frac{1}{K_{1|1,24}} Q_1(\Phi_{12})\, Q_2'(\Phi_{12}|\Phi_{23}) \times \int_{-\pi}^{\pi} Q_3(\Phi_{12},\Phi_{23},\Phi_{14})\, \mathrm{d}\Phi_{14}, \tag{4.3}$$

where $Q_1(\Phi_{12})$, $Q_2'(\Phi_{12}|\Phi_{23})$ and $Q_3(\Phi_{12},\Phi_{23},\Phi_{14})$ are given by (I.29), (2.6) and (II.17) respectively. The 25 numbers (I.7), (II.27) and (3.3) are parameters of the distribution and $K_{1|1,24}$ is a normalization factor independent of $\Phi_{12}$. The integration of $Q_3(\Phi_{12},\Phi_{23},\Phi_{14})$ is done by numerical techniques since no simple exact analytical expression has been found. The probability distribution $P_{1|1,24}$ is the third major result of this paper and is analogous to $P_{1|1,11}$, (2.5). Its properties are similar to $P_{1|1,11}$ and the reader is referred to the latter for further discussion.

## 5. The applications

The figures accompanying this section show $P_{1|1,11}$, (2.5), and $P_{1|1,24}$, (4.3), as functions of $\Phi_{12}$ in the domain $(-180°, 180°)$ for several representative sets of values of the parameters on which these distributions depend. They illustrate their properties for structures containing $N = 100$ and $N = 300$ identical atoms in the unit cell. The values given for $\Phi_{23}$ and the various magnitudes, $|E|$, have been selected to show optimal behavior of these distributions and thus to illustrate the kinds of estimates which may occur in favorable cases.

### 5.1. $P_{1|1,11}$

In Figs. 1–4 it is assumed that

$$\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3} = 90°, \tag{5.1}$$

thus specifying the enantiomorph. As described in the previous paper (Hauptman & Green, 1978), reliable estimates for $\varphi_{23} \simeq \pm 90°$ are obtainable *via* the neighborhoods of the second kind, and specifying the sign of $\varphi_{23}$ is equivalent to choosing the enantiomorph. Figs. 1 and 2, corresponding to $N = 100$ and 300 atoms respectively, show that, for the values of the parameters listed $P_{1|1,11}$ has a unique maximum in the whole interval $(-180°, +180°)$, *i.e.* the ambiguity of the two-fold estimate, $\varphi_{12} \simeq \pm 90°$, obtainable from magnitudes $|E|$ of the second kind alone (Hauptman & Green, 1978), is decisively broken. In fact, as Figs. 1 and 2 clearly show, there is a single sharp peak at $\varphi_{12} \simeq +90°$ with no evidence of a peak at $\varphi_{12} \simeq -90°$ (which corresponds, as it happens, to the minimum of $P_{1|1,11}$), so that the value $+90°$ for $\varphi_{12}$ is consistent with the enantiomorph chosen by setting $\varphi_{23} = +90°$. Even

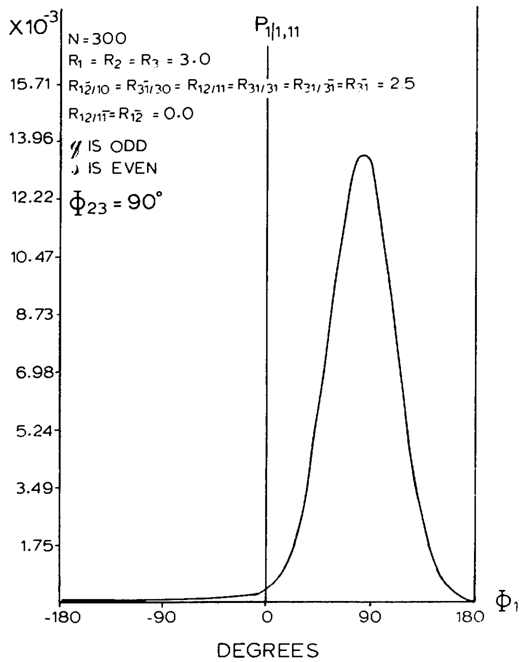


Fig. 2. The probability distribution $P_{1|1,11}$, (2.5), for the values of the parameters shown.

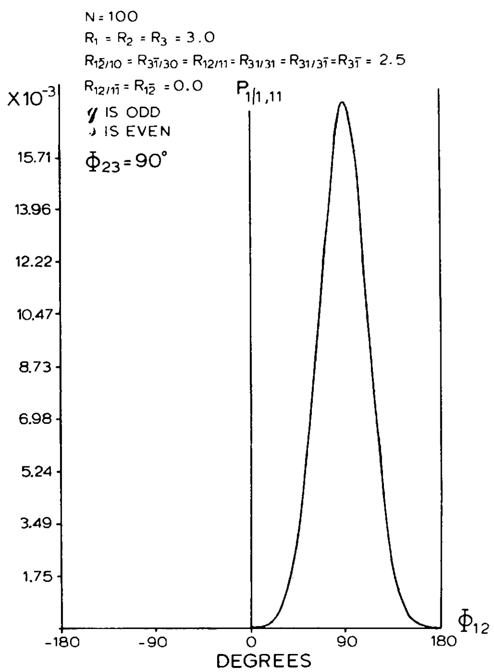


Fig. 1. The probability distribution $P_{1|1,11}$, (2.5), for the values of the parameters shown.

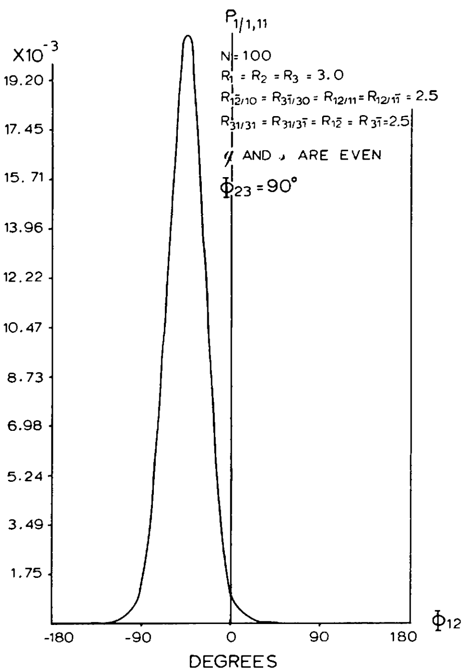


Fig. 3. The probability distribution $P_{1|1,11}$, (2.5), for the values of the parameters shown.

when $N$ is as large as 300, the estimate is extremely reliable in the favorable case shown in Fig. 2.

Figs. 3 and 4 show that reliable estimates for $\varphi_{12} \simeq -45°$ (as distinct from cardinal point estimates 0, 180, $\pm 90°$) are obtainable with suitable choice of parameters. As before, it is particularly noteworthy that the symmetry about $\Phi_{12} = 0$ is destroyed and the unique maximum in the whole interval $(-180°,+180°)$ is consistent with the chosen enantiomorph.

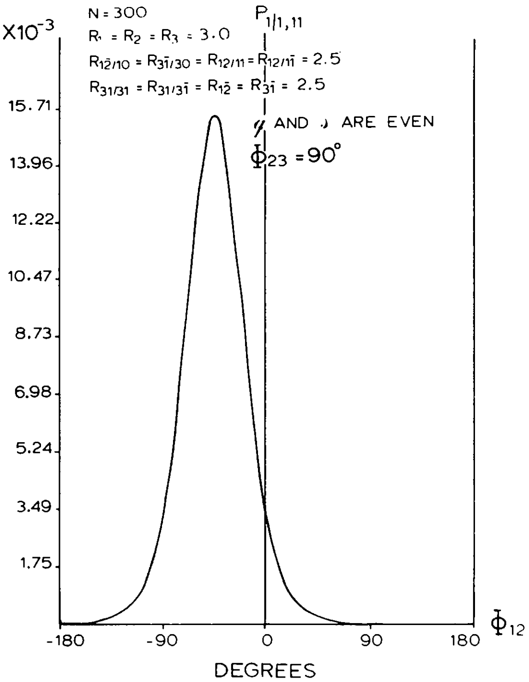


Fig. 4. The probability distribution $P_{1|1,11}$, (2.5), for the values of the parameters shown.

Fig. 5 shows how the 15-magnitude estimate (broken line ---) of $\varphi_{12} \simeq 180°$ may be sharpened when the additional information, $\varphi_{23} = 0$, is available (solid line ——).

## 5.2. $P_{1|1,24}$

In Figs. 6 and 7 it is assumed that $\varphi_{23} = 90°$. Comparison with Figs. 1 and 2 shows that, when the 13 additional magnitudes derived from the fourth neighborhood are presumed to be known, a somewhat more reliable estimate of $\varphi_{12}$ may be obtained *via* $P_{1|1,24}$ than from the analogous distribution $P_{1|1,11}$. However, the gain in going from $P_{1|1,11}$ to $P_{1|1,24}$ appears to be only marginal, possibly a consequence of the fact that our $P_{1|1,24}$ contains some, but not all, terms of order $1/N^2$. It may well be that $P_{1|1,24}$, correct to order $1/N^2$, a time-consuming but not impossible task to derive, would yield a greater improvement.

In view of the discussion in this and the two preceding papers, it is clear that the two-phase structure seminvariants may well prove to be an important tool in phase determination, not only in $P2_1$, but even more so in those space groups containing more varied

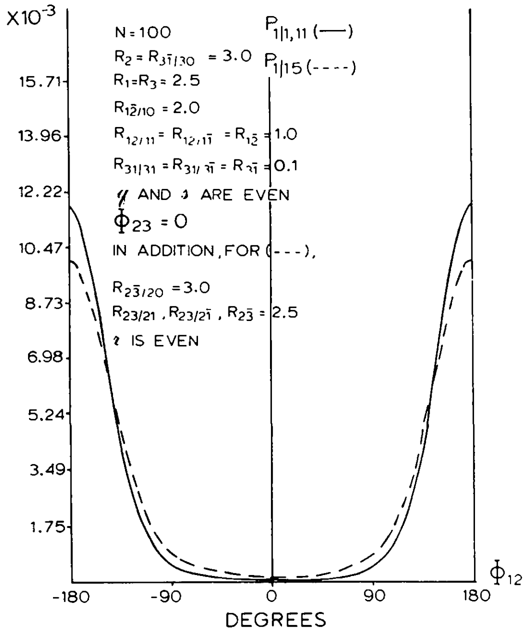


Fig. 5.(*a*) Solid line (——): the probability distribution $P_{1|1,11}$, for the values of the parameters shown. (*b*) Broken line (---): the probability distribution $P_{1|15}$ [equation (6.1), Green & Hauptman, 1978] for the values of the parameters shown.

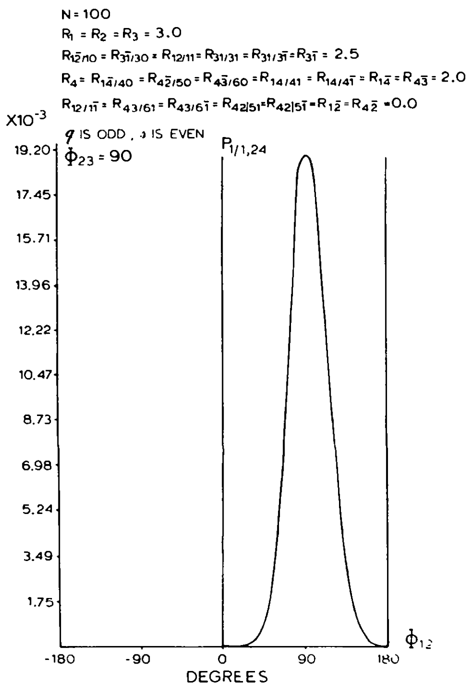


Fig. 6. The probability distribution $P_{1|1,24}$ [Eq. (4.3)] for the values of the parameters shown.

symmetry operators. However, owing to the limited number of two-phase structure seminvariants which may be reliably estimated in any given case, it is anticipated that they will find their greatest use in conjunction with more general seminvariants and invariants, particularly in the applications to very complex structures.

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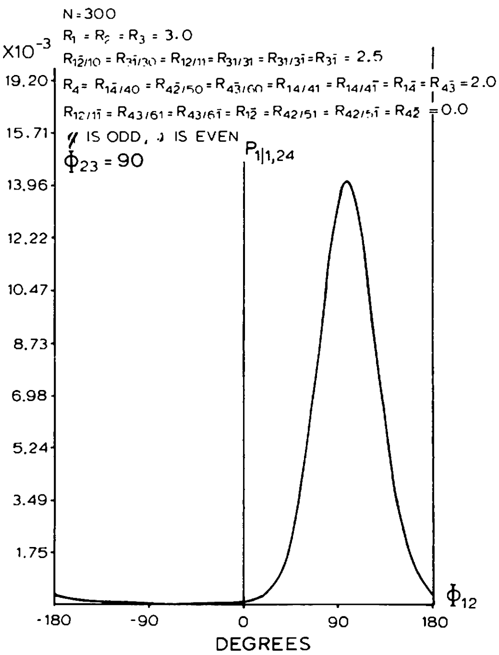


Fig. 7. The probability distribution $P_{1|1,24}$ [Eq. (4.3)] for the values of the parameters shown.

## APPENDIX I

### Probability distributions derived from the third (15-magnitude) neighborhood of $\varphi_{12}$ of the first kind

I.1. *The joint probability distribution of the* 15 *structure factors whose magnitudes constitute the third neighborhood of* $\varphi_{12}$

Suppose that a crystal structure in $P2_1$ consisting of $N$ atoms, not necessarily identical, in the unit cell is fixed and that the ordered triple $[(h_1kl_1), (h_2kl_2), (h_3kl_3)]$ of reciprocal lattice vectors is a random variable which is uniformly distributed over the subset of the threefold Cartesian product $W \times W \times W$ of reciprocal space $W$ defined by

$$(h_1 - h_2, 0, l_1 - l_2) \equiv 0 \pmod{\omega_s} \qquad \text{(I.1)}$$

and

$$(h_2 - h_3, 0, l_2 - l_3) \equiv 0 \pmod{\omega_s}. \qquad \text{(I.2)}$$

Let $q$, $r$ and $s$ be arbitrary non-zero integers. Then the 15 normalized structure factors

$$\begin{aligned}
&E_{h_1kl_1},\ E_{h_2kl_2},\ E_{h_3kl_3},\ E_{\frac{1}{2}(h_1-h_2),q,\frac{1}{2}(l_1-l_2)},\\
&E_{\frac{1}{2}(h_2-h_3),r,\frac{1}{2}(l_2-l_3)},\quad E_{\frac{1}{2}(h_3-h_1),s,\frac{1}{2}(l_3-l_1)},\\
&E_{\frac{1}{2}(h_1+h_2),q+k,\frac{1}{2}(l_1+l_2)},\quad E_{\frac{1}{2}(h_1+h_2),q-k,\frac{1}{2}(l_1+l_2)},\\
&E_{\frac{1}{2}(h_2+h_3),r+k,\frac{1}{2}(l_2+l_3)},\quad E_{\frac{1}{2}(h_2+h_3),r-k,\frac{1}{2}(l_2+l_3)},\\
&E_{\frac{1}{2}(h_3+h_1),s+k,\frac{1}{2}(l_3+l_1)},\quad E_{\frac{1}{2}(h_3+h_1,s-k,\frac{1}{2}(l_3-l_1)},\\
&E_{h_1-h_2,0,l_1-l_2},\quad E_{h_2-h_3,0,l_2-l_3},\quad E_{h_3-h_1,0,l_3-l_1},
\end{aligned} \qquad \text{(I.3)}$$

as functions of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3)]$, are themselves random variables. Denote by

$$\begin{aligned}
P_{15} = P(&R_1,R_2,R_3,R_{1\bar{2}/10},R_{2\bar{3}/20},R_{3\bar{1}/30},R_{12/11},R_{12/1\bar{1}},R_{23/21},\\
&R_{23/2\bar{1}},R_{31/31},R_{31/3\bar{1}};\ \Phi_1,\Phi_2,\Phi_3,\Phi_{1\bar{2}/10},\Phi_{2\bar{3}/20},\Phi_{3\bar{1}/30},\Phi_{12/11},\\
&\Phi_{12/1\bar{1}},\Phi_{23/21},\Phi_{23/2\bar{1}},\Phi_{31/31},\Phi_{31/3\bar{1}};\ S_{1\bar{2}},S_{2\bar{3}},S_{3\bar{1}})
\end{aligned} \qquad \text{(I.4)}$$

the joint probability distribution of, respectively, the magnitudes and phases of the first 12, complex-valued, and the last three, real-valued, structure factors (I.3). Then following the pattern of the result in Appendix I of the first paper in this series (Green & Hauptman, 1978), it is clear that

$$\begin{aligned}
P_{15} = {}& \frac{R_1R_2R_3R_{1\bar{2}/10}R_{2\bar{3}/20}R_{3\bar{1}/30}R_{12/11}R_{12/1\bar{1}}R_{23/21}R_{23/2\bar{1}}R_{31/31}R_{31/3\bar{1}}}{(2\pi)^{3/2}\pi^{12}}\\
&\times \exp\Bigg\{-\Bigg(R_1^2+R_2^2+R_3^2+R_{1\bar{2}/10}^2+R_{2\bar{3}/20}^2+R_{3\bar{1}/30}^2+R_{12/11}^2+R_{12/1\bar{1}}^2+R_{23/21}^2+R_{23/2\bar{1}}^2+R_{31/31}^2+R_{31/3\bar{1}}^2\\
&+\frac{S_{1\bar{2}}^2}{2}+\frac{S_{2\bar{3}}^2}{2}+\frac{S_{3\bar{1}}^2}{2}\Bigg)+\frac{2\sigma_3}{\sigma_2^{3/2}}\Big[R_1R_2S_{1\bar{2}}\cos(\Phi_1-\Phi_2)+R_2R_3S_{2\bar{3}}\cos(\Phi_2-\Phi_3)+R_3R_1S_{3\bar{1}}\cos(\Phi_3-\Phi_1)\\
&+(-1)^qR_1R_{1\bar{2}/10}R_{12/11}\cos(\Phi_1+\Phi_{1\bar{2}/10}-\Phi_{12/11})+(-1)^{k+q}R_1R_{1\bar{2}/10}R_{12/1\bar{1}}\cos(\Phi_1-\Phi_{1\bar{2}/10}+\Phi_{12/1\bar{1}})\\
&+(-1)^rR_2R_{2\bar{3}/20}R_{23/21}\cos(\Phi_2+\Phi_{2\bar{3}/20}-\Phi_{23/21})+(-1)^{k+r}R_2R_{2\bar{3}/20}R_{23/2\bar{1}}\cos(\Phi_2-\Phi_{2\bar{3}/20}+\Phi_{23/2\bar{1}})\\
&+(-1)^sR_3R_{3\bar{1}/30}R_{31/31}\cos(\Phi_3+\Phi_{3\bar{1}/30}-\Phi_{31/31})+(-1)^{k+s}R_3R_{3\bar{1}/30}R_{31/3\bar{1}}\cos(\Phi_3-\Phi_{31/30}+\Phi_{31/3\bar{1}})\\
&+R_2R_{1\bar{2}/10}R_{12/11}\cos(\Phi_2+\Phi_{1\bar{2}/10}-\Phi_{12/11})+(-1)^kR_2R_{1\bar{2}/10}R_{12/1\bar{1}}\cos(\Phi_2-\Phi_{1\bar{2}/10}+\Phi_{12/1\bar{1}})\\
&+R_3R_{2\bar{3}/20}R_{23/21}\cos(\Phi_3+\Phi_{2\bar{3}/20}-\Phi_{23/21})+(-1)^kR_3R_{2\bar{3}/20}R_{23/2\bar{1}}\cos(\Phi_2-\Phi_{2\bar{3}/20}+\Phi_{23/2\bar{1}})\\
&+R_1R_{3\bar{1}/30}R_{31/31}\cos(\Phi_1+\Phi_{3\bar{1}/30}-\Phi_{31/31})+(-1)^kR_1R_{3\bar{1}/30}R_{31/3\bar{1}}\cos(\Phi_3-\Phi_{3\bar{1}/30}+\Phi_{31/3\bar{1}})
\end{aligned}$$

$$+ \frac{(-1)^q}{2} S_{1\bar{2}}(R^2_{1\bar{2}/10} - 1) + \frac{(-1)^r}{2} S_{2\bar{3}}(R^2_{2\bar{3}/20} - 1) + \frac{(-1)^s}{2} S_{3\bar{1}}(R^2_{3\bar{1}/30} - 1)\Big] - 2\left(\frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right)$$
$$\times [(-1)^q R_1 R_2 R^2_{1\bar{2}/10} \cos(\Phi_1 - \Phi_2) + (-1)^r R_2 R_3 R^2_{2\bar{3}/20} \cos(\Phi_2 - \Phi_3) + (-1)^s R_3 R_1 R^2_{3\bar{1}/30} \cos(\Phi_3 - \Phi_1)]$$
$$- 2\left(\frac{\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) [(-1)^q R_1 R_2 (R^2_{12/11} + R^2_{12/1\bar{1}}) \cos(\Phi_1 - \Phi_2) + (-1)^r R_2 R_3 (R^2_{23/21} + R^2_{23/2\bar{1}}) \cos(\Phi_2 - \Phi_3)$$
$$+ (-1)^s R_3 R_1 (R^2_{31/31} + R^2_{31/3\bar{1}}) \cos(\Phi_3 - \Phi_1)] + 6\left(\frac{\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) [(-1)^q R_1 R_2 \cos(\Phi_1 - \Phi_2) + (-1)^r R_2 R_3$$
$$\times \cos(\Phi_2 - \Phi_3) + (-1)^s R_3 R_1 \cos(\Phi_3 - \Phi_1)] - \left(\frac{\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) R_1^2 R_2^2 \cos(2\Phi_1 - 2\Phi_2) + R_2^2 R_3^2 \cos(2\Phi_2 - 2\Phi_3)$$
$$+ R_3^2 R_1^2 \cos(2\Phi_3 - 2\Phi_1)] + O\left(\frac{1}{N^{1/2}}\right)\Bigg\}\Bigg\{1 + O\left(\frac{1}{N}\right),\Bigg\} \qquad \text{(I.5)}$$

where $O(1/N^{1/2})$ consists of those terms of order $1/N^{1/2}$ or higher which will make no contribution of order $1/N$ or lower to the desired conditional probability distributions to be derived. The term $O(1/N)$ consists of those terms of order $1/N$ or higher in which the terms of order $1/N$ are independent of the $\Phi$'s or contain only even powers of the $S$'s.

I.2. *The joint conditional probability distribution of the three phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, given the fifteen magnitudes in the third neighborhood of $\varphi_{12}$*

In the first paper of this series (Green & Hauptman, 1978), the third neighborhood of the first kind of $\varphi_{12}$ was defined to be the magnitudes of the set of 15 structure factors (I.3) where $q$, $r$ and $s$ are arbitrary non-zero integers. Associated with this set of magnitudes are three phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, having indices satisfying (I.1) and (I.2).

Assume that a crystal structure in $P2_1$ consisting of $N$ atoms, not necessarily identical, in the unit cell is fixed and specify the 15 non-negative numbers

$$R_1, R_2, R_3, R_{1\bar{2}/10}, R_{2\bar{3}/20}, R_{3\bar{1}/30}, R_{12/11}, R_{12/1\bar{1}}, R_{23/21}, R_{23/2\bar{1}}, R_{31/31}, R_{31/3\bar{1}}, R_{1\bar{2}}, R_{2\bar{3}}, R_{3\bar{1}}. \qquad \text{(I.6)}$$

Suppose finally that the ordered triple $[(h_1kl_1), (h_2kl_2), (h_3kl_3)]$ of reciprocal lattice vectors $(h_1kl_1)$, $(h_2kl_2)$, $(h_3kl_3)$ is a random variable which is uniformly distributed over the subset of the threefold Cartesian product $W \times W \times W$ of reciprocal space $W$ defined by (I.1), (I.2) and

$$|E_{h_1kl_1}| = R_1, \quad |E_{h_2kl_2}| = R_2, \quad |E_{h_3kl_3}| = R_3,$$
$$|E_{\frac{1}{2}(h_1-h_2),q,\frac{1}{2}(l_1-l_2)}| = R_{1\bar{2}/10}, \quad |E_{\frac{1}{2}(h_2-h_3),r,\frac{1}{2}(l_2-l_3)}| = R_{2\bar{3}/20},$$
$$|E_{\frac{1}{2}(h_3-h_1),s,\frac{1}{2}(l_3-l_1)}| = R_{3\bar{1}/30}, \quad |E_{\frac{1}{2}(h_1+h_2),q+k,\frac{1}{2}(l_1+l_2)}| = R_{12/11},$$
$$|E_{\frac{1}{2}(h_1+h_2),q-k,\frac{1}{2}(l_1+l_2)}| = R_{12/1\bar{1}},$$
$$|E_{\frac{1}{2}(h_2+h_3),r+k,\frac{1}{2}(l_1+l_2)}| = R_{23/21},$$
$$|E_{\frac{1}{2}(h_2+h_3),r-k,\frac{1}{2}(l_2+l_3)}| = R_{23/2\bar{1}},$$
$$|E_{\frac{1}{2}(h_3+h_1),s+k,\frac{1}{2}(l_3+l_1)}| = R_{31/31},$$
$$|E_{\frac{1}{2}(h_3+h_1),s-k,\frac{1}{2}(l_3+l_1)}| = R_{31/3\bar{1}}, \quad |E_{h_1-h_2,0,l_1-l_2}| = R_{1\bar{2}},$$
$$|E_{h_2-h_3,0,l_2-l_3}| = R_{2\bar{3}}, \quad |E_{h_3-h_1,0,l_3-l_1}| = R_{3\bar{1}}. \qquad \text{(I.7)}$$

The three phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$ are then functions of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3)]$. Denote by $P_{3|15} = P(\Phi_1,\Phi_2,\Phi_3|R_1,R_2,\ldots,R_{3\bar{1}})$ the joint conditional probability distribution of the three phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, given the 15 magnitudes (I.7). The three real structure factors $S_{1\bar{2}}$, $S_{2\bar{3}}$, $S_{3\bar{1}}$ are related to their respective magnitudes and phases $R_{1\bar{2}}, R_{2\bar{3}}, R_{3\bar{1}}$ and $\Phi_{1\bar{2}}, \Phi_{2\bar{3}}, \Phi_{3\bar{1}}$ by means of

$$S_{1\bar{2}} = R_{1\bar{2}} \cos \Phi_{1\bar{2}}, \quad S_{2\bar{3}} = R_{2\bar{3}} \cos \Phi_{2\bar{3}},$$
$$S_{3\bar{1}} = R_{3\bar{1}} \cos \Phi_{3\bar{1}}, \qquad \text{(I.8)}$$

where $\Phi_{1\bar{2}} = 0$ or $\pi$ according as $S_{1\bar{2}}$ is positive or negative, $\Phi_{2\bar{3}} = 0$ or $\pi$ according as $S_{2\bar{3}}$ is positive or negative, *etc*. In short, the three phase variables $\Phi_{1\bar{2}}, \Phi_{2\bar{3}}, \Phi_{3\bar{1}}$ are discrete, each one taking on only the two values 0 or $\pi$. Then $P_{3|15}$ is obtained from $P_{15}$ by fixing the values of the 15 magnitudes (I.7), integrating $P_{15}$ with respect to the nine continuous phase variables $\Phi$ with multiple subscripts, summing over the two possible values, 0 or $\pi$, of the three discrete phases, $\Phi_{1\bar{2}}$, $\Phi_{2\bar{3}}$, $\Phi_{3\bar{1}}$, and multiplying by a suitable normalization factor:

$$P_{3|15} = \frac{1}{K_{3|15}} \sum_{\Phi_{1\bar{2}},\Phi_{2\bar{3}},\Phi_{3\bar{1}}=0}^{\pi} \int_{\Phi_{1\bar{2}/10},\ldots,\Phi_{31/3\bar{1}}=0}^{2\pi} P_{15}\, d\Phi_{1\bar{2}/10} \ldots d\Phi_{31/3\bar{1}}. \qquad \text{(I.9)}$$

Using techniques which are by now standard (Hauptman, 1975*a*,*b*, 1976; Green & Hauptman, 1976) and employing

$$\sum_i A_i \cos(\Phi + \alpha_i) = X \cos(\Phi + \xi), \qquad \text{(I.10)}$$

$$X = \left[\sum_{i,j} A_i A_j \cos(\alpha_i - \alpha_j)\right]^{1/2},$$

$$X \exp(i\xi) = \sum_j A_j \exp(i\alpha_j), \qquad \text{(I.11)}$$

$P_{3|15}$ is found to be

$$P_{3|15}=\frac{1}{K_{3|15}}\exp\left\{-2\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[(-1)^q R_1R_2R_{1\bar{2}/10}^2\cos(\Phi_1-\Phi_2)+(-1)^r R_2R_3R_{2\bar{3}/20}^2\cos(\Phi_2-\Phi_3)\right.$$

$$+(-1)^s R_3R_1R_{3\bar{1}/30}^2\cos(\Phi_3-\Phi_1)]-2\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[(-1)^q R_1R_2(R_{12/11}^2+R_{12/1\bar{1}}^2)\cos(\Phi_1-\Phi_2)$$

$$+(-1)^r R_2R_3(R_{23/21}^2+R_{23/2\bar{1}}^2)\cos(\Phi_2-\Phi_3)+(-1)^s R_3R_1(R_{31/31}^2+R_{31/3\bar{1}}^2)\cos(\Phi_3-\Phi_1)]$$

$$+6\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[(-1)^q R_1R_2\cos(\Phi_1-\Phi_2)+(-1)^r R_2R_3\cos(\Phi_2-\Phi_3)+(-1)^s R_3R_1\cos(\Phi_3-\Phi_1)]$$

$$\left.-\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[R_1^2R_2^2\cos(2\Phi_1-2\Phi_2)+R_2^2R_3^2\cos(2\Phi_2-2\Phi_3)+R_3^2R_1^2\cos(2\Phi_3-2\Phi_1)]\right\}$$

$$\times\sum_{\Phi_{1\bar{2}}=0}^{\pi}\exp\left\{\frac{\sigma_3R_{1\bar{2}}}{\sigma_2^{3/2}}[(-1)^q(R_{1\bar{2}/10}^2-1)+2R_1R_2\cos(\Phi_1-\Phi_2)]\cos\Phi_{1\bar{2}}\right\}$$

$$\times\sum_{\Phi_{2\bar{3}}=0}^{\pi}\exp\left\{\frac{\sigma_3R_{2\bar{3}}}{\sigma_2^{3/2}}[(-1)^r(R_{2\bar{3}/20}^2-1)+2R_2R_3\cos(\Phi_2-\Phi_3)]\cos\Phi_{2\bar{3}}\right\}$$

$$\times\sum_{\Phi_{3\bar{1}}=0}^{\pi}\exp\left\{\frac{\sigma_3R_{3\bar{1}}}{\sigma_2^{3/2}}[(-1)^s(R_{3\bar{1}/30}^2-1)+2R_3R_1\cos(\Phi_3-\Phi_1)]\cos\Phi_{3\bar{1}}\right\}$$

$$\times\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{2}/10}R_{12/11}X_{1\bar{2}}\cos(\Phi_{12/11}+\xi_{12/11})\right\}d\Phi_{12/11}\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{2}/10}R_{12/1\bar{1}}X_{1\bar{2}}\cos(\Phi_{12/1\bar{1}}+\xi_{12/1\bar{1}})\right\}d\Phi_{12/1\bar{1}}$$

$$\times\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar{3}/20}R_{23/21}X_{2\bar{3}}\cos(\Phi_{23/21}+\xi_{23/21})\right\}d\Phi_{23/21}\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar{3}/20}R_{23/2\bar{1}}X_{2\bar{3}}\cos(\Phi_{23/2\bar{1}}+\xi_{23/2\bar{1}})\right\}d\Phi_{23/2\bar{1}}$$

$$\times\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar{1}/30}R_{31/31}X_{3\bar{1}}\cos(\Phi_{31/31}+\xi_{31/31})\right\}d\Phi_{31/31}\int_0^{2\pi}\exp\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar{1}/30}R_{31/3\bar{1}}X_{3\bar{1}}\cos(\Phi_{31/3\bar{1}}+\xi_{31/3\bar{1}})\right\}d\Phi_{31/3\bar{1}}. \quad (I.12)$$

In view of the integral formula

$$\int_0^{2\pi}\exp[A\cos(\theta+\xi)]d\theta=2\pi I_0(A) \quad (I.13)$$

and

$$\sum_{\varphi=0}^{\pi}\exp(A\cos\varphi)=2\cosh A, \quad (I.14)$$

the desired joint conditional probability distribution of $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$ given the 15 magnitudes (I.7) of the third neighborhood, is found to be correct to terms of order $1/N$,

$$P_{3|15}=\frac{1}{K_{3|15}}Q_1(\Phi_1,\Phi_2)\,Q_2(\Phi_1,\Phi_2,\Phi_3) \quad (I.15)$$

where

$$Q_1(\Phi_1,\Phi_2)=\exp\left\{\frac{-2(-1)^qR_1R_2}{\sigma_2^3}[(3\sigma_3^2-\sigma_2\sigma_4)R_{1\bar{2}/10}^2\right.$$

$$+(\sigma_3^2-\sigma_2\sigma_4)(R_{12/11}^2+R_{12/1\bar{1}}^2)-3(\sigma_3^2-\sigma_2\sigma_4)]$$

$$\left.\times\cos(\Phi_1-\Phi_2)-\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)R_1^2R_2^2\cos2(\Phi_1-\Phi_2)\right\}$$

$$\times\cosh\left\{\frac{\sigma_3R_{1\bar{2}}}{\sigma_2^{3/2}}Y_{1\bar{2}}\right\}I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{2}/10}R_{12/11}X_{1\bar{2}}\right\}$$

$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{2}/10}R_{12/1\bar{1}}X_{1\bar{2}}\right\}, \quad (I.16)$$

$$Q_2(\Phi_1,\Phi_2,\Phi_3)=\exp\left\{-2\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)\right.$$

$$\times[(-1)^rR_2R_3R_{2\bar{3}/20}^2\cos(\Phi_2-\Phi_3)$$

$$+(-1)^sR_3R_1R_{3\bar{1}/30}^2\cos(\Phi_3-\Phi_1)]-2\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)$$

$$\times[(-1)^rR_2R_3(R_{23/21}^2+R_{23/2\bar{1}}^2)\cos(\Phi_2-\Phi_3)$$

$$+(-1)^sR_3R_1(R_{31/31}^2+R_{31/3\bar{1}}^2)\cos(\Phi_3-\Phi_1)]$$

$$+ 6\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[(-1)^r R_2R_3\cos(\Phi_2-\Phi_3)$$
$$+ (-1)^s R_3R_1\cos(\Phi_3-\Phi_1)] - \left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)$$
$$\times [R_2^2R_3^2\cos 2(\Phi_2-\Phi_3) + R_3^2R_1^2\cos 2(\Phi_3-\Phi_1)]\Bigg\}$$
$$\times \cosh\left\{\frac{\sigma_3R_{2\bar3}}{\sigma_2^{3/2}}Y_{2\bar3}\right\}\cosh\left\{\frac{\sigma_3R_{3\bar1}}{\sigma_2^{3/2}}Y_{3\bar1}\right\}$$
$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar3/20}R_{23/21}X_{2\bar3}\right\} I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar3/20}R_{23/2\bar1}X_{2\bar3}\right\}$$
$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar1/30}R_{31/31}X_{3\bar1}\right\} I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar1/30}R_{31/3\bar1}X_{3\bar1}\right\}, \quad (I.17)$$

$$Y_{1\bar2} = [(-1)^q(R^2_{1\bar2/10}-1) + 2R_1R_2\cos(\Phi_1-\Phi_2)], \quad (I.18)$$
$$Y_{2\bar3} = [(-1)^r(R^2_{2\bar3/20}-) + 2R_2R_3\cos(\Phi_2-\Phi_3)], \quad (I.19)$$
$$Y_{3\bar1} = [(-1)^s(R^2_{3\bar1/30}-1) + 2R_3R_1\cos(\Phi_3-\Phi_1)], \quad (I.20)$$
$$X_{1\bar2} = [R_1^2+R_2^2+2(-1)^qR_1R_2\cos(\Phi_1-\Phi_2)]^{1/2}, \quad (I.21)$$
$$X_{2\bar3} = [R_2^2+R_3^2+2(-1)^rR_2R_3\cos(\Phi_2-\Phi_3)]^{1/2}, \quad (I.22)$$
$$X_{3\bar1} = [R_3^2+R_1^2+2(-1)^sR_3R_1\cos(\Phi_3-\Phi_1)]^{1/2}, \quad (I.23)$$

and where $K_{3|15}$ is a suitable normalization factor independent of $\Phi_1$, $\Phi_2$, $\Phi_3$. Since $P_{3|15}$ is a function of the structure seminvariants $\Phi_1-\Phi_2$, $\Phi_2-\Phi_3$, $\Phi_3-\Phi_1$ and since $\Phi_3-\Phi_1 \equiv -(\Phi_1-\Phi_2)-(\Phi_2-\Phi_3)$, the distribution $P_{3|15}$ leads directly to the joint conditional probability distribution $P_{2|15}$ of the pair of structure seminvariants $\varphi_{12}$, $\varphi_{23}$, given 15 magnitudes, as shown next.

### I.3. *The joint conditional probability distribution of the pair of structure seminvariants $\varphi_{12}=\varphi_{h_1kl_1}-\varphi_{h_2kl_2}$; $\varphi_{23}=\varphi_{h_2kl_2}-\varphi_{h_3kl_3}$, given the 15 magnitudes in the third neighborhood of $\varphi_{12}$*

Assume that the ordered triple $[(h_1kl_1),(h_2kl_2),(h_3kl_3)]$ of reciprocal lattice vectors is uniformly distributed over the subset of the threefold Cartesian product $W\times W\times W$ of reciprocal space $W$ defined by (I.1), (I.2) and (I.7). Then the two structure seminvariants

$$\varphi_{12}=\varphi_{h_1kl_1}-\varphi_{h_2kl_2},\quad \varphi_{23}=\varphi_{h_2kl_2}-\varphi_{h_3kl_3}, \quad (I.24)$$

as functions of the primitive random variable $[(h_1kl_1),(h_2kl_2),(h_3kl_3)]$, are themselves random variables. Denote by $P_{2|15}=P(\Phi_{12},\Phi_{23}|R_1,R_2,\ldots,R_{3\bar1})$ the joint conditional probability distribution of the pair $\varphi_{12}$, $\varphi_{23}$, given the 15 magnitudes (I.7). Then $P_{2|15}$ is obtained from $P_{3|15}$, (I.15), *via* the transformations

$$\Phi_{12}=\Phi_1-\Phi_2, \quad (I.25)$$
$$\Phi_{23}=\Phi_2-\Phi_3, \quad (I.26)$$
$$-\Phi_{12}-\Phi_{23}=\Phi_3-\Phi_1, \quad (I.27)$$

and is found to be

$$P_{2|15}=\frac{1}{K_{2|15}}Q_1(\Phi_{12})\,Q_2(\Phi_{12},\Phi_{23}) \quad (I.28)$$

where $Q_1(\Phi_{12})$ is obtained from $Q_1(\Phi_1,\Phi_2)$, (I.16), by replacing $\Phi_1-\Phi_2$ in the latter by $\Phi_{12}$; and $Q_2(\Phi_{12},\Phi_{23})$ is obtained from $Q_2(\Phi_1,\Phi_2,\Phi_3)$ (I.17), by replacing $\Phi_2-\Phi_3$ and $\Phi_3-\Phi_1$ in the latter by $\Phi_{23}$ and $-\Phi_{12}-\Phi_{23}$ respectively. Thus

$$Q_1(\Phi_{12})=\exp\Bigg\{\frac{-2(-1)^qR_1R_2}{\sigma_2^3}[(3\sigma_3^2-\sigma_2\sigma_4)R^2_{1\bar2/10}$$
$$+(\sigma_3^2-\sigma_2\sigma_4)(R^2_{12/11}+R^2_{12/1\bar1})-3(\sigma_3^2-\sigma_2\sigma_4)]$$
$$\times\cos\Phi_{12}-\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}R_1^2R_2^2\cos 2\Phi_{12}\Bigg\}$$
$$\times\cosh\left\{\frac{\sigma_3}{\sigma_2^{3/2}}R_{1\bar2}V_{1\bar2}\right\} I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar2/10}R_{12/11}U_{1\bar2}\right\}$$
$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar2/10}R_{12/1\bar1}U_{1\bar2}\right\}, \quad (I.29)$$

$$Q_2(\Phi_{12},\Phi_{23})=\exp\Bigg\{-2\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)$$
$$\times[(-1)^rR_2R_3R^2_{2\bar3/20}\cos\Phi_{23}+(-1)^sR_3R_1R^2_{3\bar1/30}$$
$$\times\cos(\Phi_{12}+\Phi_{23})]-2\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[(-1)^rR_2R_3(R^2_{23/21}$$
$$+R^2_{23/2\bar1})\cos\Phi_{23}+(-1)^sR_3R_1(R^2_{31/31}+R^2_{31/3\bar1})$$
$$\times\cos(\Phi_{12}+\Phi_{23})]+6\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)$$
$$\times[(-1)^rR_2R_3\cos\Phi_{23}+(-1)^sR_3R_1\cos(\Phi_{12}+\Phi_{23})]$$
$$-\left(\frac{\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)[R_2^2R_3^2\cos 2\Phi_{23}+R_3^2R_1^2$$
$$\times\cos 2(\Phi_{12}+\Phi_{23})]\Bigg\}\cosh\left\{\frac{\sigma_3}{\sigma_2^{3/2}}R_{2\bar3}V_{2\bar3}\right\}$$
$$\times\cosh\left\{\frac{\sigma_3}{\sigma_2^{3/2}}R_{3\bar1}V_{3\bar1}\right\} I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar3/20}R_{23/21}U_{2\bar3}\right\}$$
$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{2\bar3/20}R_{23/2\bar1}U_{2\bar3}\right\} I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar1/30}R_{31/31}U_{3\bar1}\right\}$$
$$\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{3\bar1/30}R_{31/3\bar1}U_{3\bar1}\right\}, \quad (I.30)$$

$$V_{1\bar2}=[(-1)^q(R^2_{1\bar2/10}-1)+2R_1R_2\cos\Phi_{12}], \quad (I.31)$$
$$V_{2\bar3}=[(-1)^r(R^2_{2\bar3/20}-1)+2R_2R_3\cos\Phi_{23}], \quad (I.32)$$
$$V_{3\bar1}=[(-1)^s(R^2_{3\bar1/30}-1)+2R_3R_1\cos(\Phi_{12}+\Phi_{23})], \quad (I.33)$$

$$U_{1\bar2}=[R_1^2+R_2^2+2(-1)^qR_1R_2\cos\Phi_{12}]^{1/2}, \quad (I.34)$$
$$U_{2\bar3}=[R_2^2+R_3^2+2(-1)^rR_2R_3\cos\Phi_{23}]^{1/2}, \quad (I.35)$$
$$U_{3\bar1}=[R_3^2+R_1^2+2(-1)^sR_3R_1\cos(\Phi_{12}+\Phi_{23})], \quad (I.36)$$

and $K_{2|15}$ is a suitable normalizing parameter independent of $\Phi_{12}$ and $\Phi_{23}$.

In general, (I.28) has two maxima in the domain

$$-\pi < \Phi_{12} \le \pi \quad \text{(I.37)}$$

$$-\pi = \Phi_{23} \le \pi \quad \text{(I.38)}$$

related to each other by reflection through the origin, since (I.28) is unchanged when $\Phi_{12}$ and $\Phi_{23}$ are both replaced by their negatives. One maximum identifies the most probable values of the pair $\varphi_{12}$, $\varphi_{23}$ corresponding to one enantiomorph; the other the most probable values of $\varphi_{12}$, $\varphi_{23}$ corresponding to the other enantiomorph. The reader is referred to Hauptman (1977*b*), equation (2.13), for further discussion.

## APPENDIX II

### Probability distributions derived from the fourth (28-magnitude) neighborhood of $\varphi_{12}$ of the first kind

II.1. *The joint conditional probability distribution of the four phases* $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, $\varphi_{h_4kl_4}$ *given 28 magnitudes*

Using the probabilistic background described previously, the derivation of the joint conditional probability distribution of the four phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, $\varphi_{h_4kl_4}$ given the 28 magnitudes in the fourth neighborhood of $\varphi_{12}$ of the first kind follows the lines already given in Appendices I.1 and I.2. In addition to the 15 non-negative numbers (I.6), the 13 non-negative numbers

$$R_4, R_{1\bar{4}/40}, R_{4\bar{2}/50}, R_{4\bar{3}/60}, R_{14/41}, R_{14/4\bar{1}}, R_{42/51}, R_{42/5\bar{1}}, R_{43/61}, R_{43/6\bar{1}}, R_{1\bar{4}}, R_{4\bar{2}}, R_{4\bar{3}} \quad \text{(II.1)}$$

are also specified. The primitive random variable is the ordered quartet $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$ of reciprocal vectors which is assumed to be uniformly distributed over the subset of the fourfold Cartesian product $W \times W \times W \times W$ defined by (I.1), (I.2),

$$(h_1 - h_4, 0, l_1 - l_4) \equiv 0 \ (\text{mod}\ \omega_s), \quad \text{(II.2)}$$

(I.7) and

$$\begin{aligned}
&|E_{h_4kl_4}| = R_4, \quad |E_{\frac{1}{2}(h_1-h_4),t,\frac{1}{2}(l_4-l_4)}| = R_{1\bar{4}/40},\\
&|E_{\frac{1}{2}(h_4-h_2),u,\frac{1}{2}(l_4-l_2)}| = R_{4\bar{2}/50}, \quad |E_{\frac{1}{2}(h_4-h_3),v,\frac{1}{2}(l_4-l_3)}| = R_{4\bar{3}/60},\\
&|E_{\frac{1}{2}(h_1+h_4),t+k,\frac{1}{2}(l_1+l_4)}| = R_{14/41},\\
&|E_{\frac{1}{2}(h_1+h_4),t-k,\frac{1}{2}(l_1+l_+)}| = R_{14/4\bar{1}},\\
&|E_{\frac{1}{2}(h_4+h_2),u+k,\frac{1}{2}(l_4+l_2)}| = R_{42/51},\\
&|E_{\frac{1}{2}(h_4+h_2),u-k,\frac{1}{2}(l_4+l_2)}| = R_{42/5\bar{1}},\\
&|E_{\frac{1}{2}(h_4+h_3),v+k,\frac{1}{2}(l_4+l_3)}| = R_{43/61},\\
&|E_{\frac{1}{2}(h_4+h_3),v-k,\frac{1}{2}(l_4+l_3)}| = R_{43/6\bar{1}},\\
&|E_{h_1-h_4,0,l_1-l_4}| = R_{14}, \quad |E_{h_4-h_2,0,l_4-l_2}| = R_{4\bar{2}},\\
&|E_{h_4-h_3,0,l_4-l_3}| = R_{4\bar{3}}. \qquad \text{(II.3)}
\end{aligned}$$

Denote by $P_{4|28} = P(\Phi_1,\Phi_2,\Phi_3,\Phi_4|R_1,\ldots,R_{4\bar{3}})$ the joint conditional probability distribution of the four phases $\varphi_{h_1kl_1}$, $\varphi_{h_2kl_2}$, $\varphi_{h_3kl_3}$, $\varphi_{h_4kl_4}$ given the 28 magnitudes (I.7) and (II.3). The distribution, correct to terms of order $1/N$, turns out to be

$$P_{4|28} = \frac{1}{K_{4|28}}\, Q_1(\Phi_1,\Phi_2)\, Q_2(\Phi_1,\Phi_2,\Phi_3)\, Q_3(\Phi_1,\Phi_2,\Phi_3,\Phi_4), \quad \text{(II.4)}$$

where $Q_1(\Phi_1,\Phi_2)$ and $Q_2(\Phi_1,\Phi_2,\Phi_3)$ are defined by (I.16) and (I.17) and

$$\begin{aligned}
Q_3(\Phi_1,\Phi_2,\Phi_3,\Phi_4) \simeq \exp\Bigg\{&-\frac{2}{\sigma_2^3}(3\sigma_3^2-\sigma_2\sigma_4)\\
&\times[(-1)^t R_1R_4R^2_{1\bar{4}/40}\cos(\Phi_1-\Phi_4)\\
&+(-1)^u R_4R_2R^2_{4\bar{2}/50}\cos(\Phi_4-\Phi_2)\\
&+(-1)^v R_4R_3R^2_{4\bar{3}/60}\cos(\Phi_4-\Phi_3)] - \frac{2}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)\\
&\times[(-1)^t R_1R_4R^2_{14/41} + R^2_{14/4\bar{1}})\cos(\Phi_1-\Phi_4)\\
&+(-1)^u R_4R_2(R^2_{42/51}+R^2_{42/5\bar{1}})\cos(\Phi_4-\Phi_2)\\
&+(-1)^v R_4R_3(R^2_{43/61}+R^2_{43/6\bar{1}})\cos(\Phi_4-\Phi_3)]\\
&+\frac{6}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)[(-1)^t R_1R_4\cos(\Phi_1-\Phi_4)\\
&+(-1)^u R_4R_2\cos(\Phi_4-\Phi_2)\\
&+(-1)^v R_4R_3\cos(\Phi_4-\Phi_3)] - \frac{1}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)\\
&\times[R_1^2R_4^2\cos 2(\Phi_1-\Phi_4)+R_4^2R_2^2\cos 2(\Phi_4-\Phi_2)\\
&+R_4^2R_3^2\cos 2(\Phi_4-\Phi_3)]\Bigg\}\\
&\times\cosh\left\{\frac{\sigma_3R_{1\bar{4}}}{\sigma_2^{3/2}}Y_{1\bar{4}}\right\}\cosh\left\{\frac{\sigma_3R_{4\bar{2}}}{\sigma_2^{3/2}}Y_{4\bar{2}}\right\}\cosh\left\{\frac{\sigma_3R_{4\bar{3}}}{\sigma_2^{3/2}}Y_{4\bar{3}}\right\}\\
&\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{4}/40}R_{14/41}X_{1\bar{4}}\right\}\ I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar{4}/40}R_{14/4\bar{1}}X_{1\bar{4}}\right\}\\
&\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{2}/50}R_{42/51}X_{4\bar{2}}\right\}\ I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{2}/50}R_{42/5\bar{1}}X_{4\bar{2}}\right\}\\
&\times I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{3}/60}R_{43/61}X_{4\bar{3}}\right\}\ I_0\left\{\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{3}/60}R_{43/6\bar{1}}X_{4\bar{3}}\right\},
\end{aligned} \quad \text{(II.5)}$$

$$Y_{1\bar{4}} = [(-1)^t(R^2_{1\bar{4}/40}-1) + 2R_1R_4\cos(\Phi_1-\Phi_4)], \quad \text{(II.6)}$$

$$Y_{4\bar{2}} = [(-1)^u(R^2_{4\bar{2}/50}-1) + 2R_4R_2\cos(\Phi_4-\Phi_2)], \quad \text{(II.7)}$$

$$Y_{4\bar{3}} = [(-1)^v(R^2_{4\bar{3}/60}-1) + 2R_4R_3\cos(\Phi_4-\Phi_3)], \quad \text{(II.8)}$$

$$X_{1\bar{4}} = [R_1^2 + R_4^2 + 2(-1)^t R_1R_4\cos(\Phi_1-\Phi_4)]^{1/2}, \quad \text{(II.9)}$$

$$X_{4\bar{2}} = [R_4^2 + R_2^2 + 2(-1)^u R_4R_2\cos(\Phi_4-\Phi_2)]^{1/2}, \quad \text{(II.10)}$$

$$X_{4\bar{3}} = [R_4^2 + R_3^2 + 2(-1)^v R_4R_3\cos(\Phi_4-\Phi_3)]^{1/2}, \quad \text{(II.11)}$$

where $t$, $u$ and $v$ are arbitrary non-zero integers and $K_{4|28}$ is the appropriate normalization factor. Since $P_{4|28}$ is a function of $\Phi_1-\Phi_2$, $\Phi_2-\Phi_3$ and $\Phi_1-\Phi_4$, (II.4) leads directly to the conditional probability distribution of the three structure seminvariants $\varphi_{12}$, $\varphi_{23}$ and $\varphi_{14}$, as shown next.

II.2. *The joint conditional probability distribution of the three structure seminvariants* $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$, $\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}$, *and* $\varphi_{14} = \varphi_{h_1kl_1} - \varphi_{h_4kl_4}$, *given the 28 magnitudes in the fourth neighborhood of* $\varphi_{12}$

Employing the usual probabilistic background as described previously, the three structure seminvariants $\varphi_{12}$, $\varphi_{23}$, (I.24), and,

$$\varphi_{14} = \varphi_{h_1kl_1} - \varphi_{h_4kl_4}, \qquad \text{(II.12)}$$

as functions of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$, are themselves random variables. Denote by

$$P_{3|28} = P(\Phi_{12},\Phi_{23},\Phi_{14}|R_1,R_2,\ldots,R_{4\bar3})$$

the joint conditional probability distribution of $\varphi_{12}$, $\varphi_{23}$, $\varphi_{14}$ given the 28 magnitudes (I.7) and (II.3). Then $P_{3|28}$ is obtained from $P_{4|28}$, (II.4), by means of the transformations (I.25)–(I.27) and

$$\Phi_{14} = \Phi_1 - \Phi_4, \qquad \text{(II.13)}$$

$$\Phi_{12} - \Phi_{14} = \Phi_4 - \Phi_2, \qquad \text{(II.14)}$$

$$\Phi_{12} + \Phi_{23} - \Phi_{14} = \Phi_4 - \Phi_3. \qquad \text{(II.15)}$$

Hence, the joint conditional probability distribution of $\varphi_{12}$, $\varphi_{23}$, $\varphi_{14}$, given the 28 magnitudes (I.7) and (II.3), is found to be

$$P_{3|28} = \frac{1}{K_{3|28}}\, Q_1(\Phi_{12})\, Q_2(\Phi_{12},\Phi_{23})\, Q_3(\Phi_{12},\Phi_{23},\Phi_{14}), \qquad \text{(II.16)}$$

where $Q_1(\Phi_{12})$ and $Q_2(\Phi_{12},\Phi_{23})$ are given by (I.29) and (I.30) respectively, and $Q_3(\Phi_{12},\Phi_{23},\Phi_{14})$ is obtained from $Q_3(\Phi_1,\Phi_2,\Phi_3,\Phi_4)$, (II.5), employing the transformations (II.13)–(II.15):

$$\begin{aligned}
Q_3(\Phi_{12},\Phi_{23},\Phi_{14}) \simeq \exp\Big\{ &-\frac{2}{\sigma_2^3}(3\sigma_3^2 - \sigma_2\sigma_4) \\
&\times [(-1)^t R_1R_4R_{1\bar4/40}^2 \cos\Phi_{14} + (-1)^u R_4R_2R_{4\bar2/50}^2 \\
&\times \cos(\Phi_{12}-\Phi_{14}) + (-1)^v R_4R_3R_{4\bar3/60}^2 \\
&\times \cos(\Phi_{12}+\Phi_{23}-\Phi_{14})] - \frac{2}{\sigma_2^3}(\sigma_3^2 - \sigma_2\sigma_4) \\
&\times [(-1)^t R_1R_4(R_{14/41}^2 + R_{14/4\bar1}^2)\cos\Phi_{14} \\
&+ (-1)^u R_4R_2(R_{42/51}^2 + R_{42/5\bar1}^2)\cos(\Phi_{12}-\Phi_{14}) \\
&+ (-1)^v R_4R_3(R_{43/61}^2 + R_{43/6\bar1}^2)\cos(\Phi_{12}+\Phi_{23}-\Phi_{14})] \\
&+ \frac{6}{\sigma_2^3}(\sigma_3^2 - \sigma_2\sigma_4)[(-1)^t R_1R_4\cos\Phi_{14} \\
&+ (-1)^u R_4R_2\cos(\Phi_{12}-\Phi_{14}) \\
&+ (-1)^v R_4R_3\cos(\Phi_{12}+\Phi_{23}-\Phi_{14})] - \frac{1}{\sigma_2^3}(\sigma_3^2 - \sigma_2\sigma_4) \\
&\times [R_1^2R_4^2\cos 2\Phi_{14} + R_4^2R_2^2\cos 2(\Phi_{12}-\Phi_{14}) \\
&+ R_4^2R_3^2\cos 2(\Phi_{12}+\Phi_{23}-\Phi_{14})]\Big\} \\
&\times \cosh\left(\frac{\sigma_3R_{1\bar4}}{\sigma_2^{3/2}}V_{1\bar4}\right)\cosh\left(\frac{\sigma_3R_{4\bar2}}{\sigma_2^{3/2}}V_{4\bar2}\right)\cosh\left(\frac{\sigma_3R_{4\bar3}}{\sigma_2^{3/2}}V_{4\bar3}\right) \\
&\times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar4/40}R_{14/41}U_{1\bar4}\right) I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{1\bar4/40}R_{14/4\bar1}U_{1\bar4}\right) \\
&\times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar2/50}R_{42/51}U_{4\bar2}\right) I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar2/50}R_{42/5\bar1}U_{4\bar2}\right) \\
&\times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar3/60}R_{43/61}U_{4\bar3}\right) I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar3/60}R_{43/6\bar1}U_{4\bar3}\right),
\end{aligned} \qquad \text{(II.17)}$$

where

$$V_{1\bar4} = [(-1)^t(R_{1\bar4/40}^2 - 1) + 2R_1R_4\cos\Phi_{14}], \qquad \text{(II.18)}$$

$$V_{4\bar2} = [(-1)^u(R_{4\bar2/50}^2 - 1) + 2R_4R_2\cos(\Phi_{12}-\Phi_{14})], \qquad \text{(II.19)}$$

$$V_{4\bar3} = [(-1)^v(R_{4\bar3/60}^2 - 1) + 2R_4R_3\cos(\Phi_{12}+\Phi_{23} - \Phi_{14})], \qquad \text{(II.20)}$$

$$U_{1\bar4} = [R_1^2 + R_4^2 + 2(-1)^t R_1R_4\cos\Phi_{14}]^{1/2}, \qquad \text{(II.21)}$$

$$U_{4\bar2} = [R_4^2 + R_2^2 + 2(-1)^u R_4R_2\cos(\Phi_{12}-\Phi_{14})]^{1/2}, \qquad \text{(II.22)}$$

$$U_{4\bar3} = [R_4^2 + R_3^2 + 2(-1)^v R_4R_3\cos(\Phi_{12}+\Phi_{23}-\Phi_{14})]^{1/2}. \qquad \text{(II.23)}$$

II.3. *The joint conditional probability distribution of the two structure seminvariants* $\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}$, $\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}$, *given the structure seminvariant* $\varphi_{14} = \varphi_{h_1kl_1} - \varphi_{h_4kl_4}$ *and 24 magnitudes*

Suppose that $\Phi_{14}(-\pi < \Phi_{14} \le \pi)$, the 24 non-negative numbers

$$R_1,R_2,R_3,R_{1\bar2/10},R_{2\bar3/20},R_{3\bar1/30},R_{12/11},R_{12/1\bar1},R_{23/21},R_{23/2\bar1}, R_{31/31},R_{31/3\bar1},R_{1\bar2},R_{2\bar3},R_{3\bar1} \qquad \text{(II.24)}$$

and

$$R_4,R_{4\bar2/50},R_{4\bar3/60},R_{42/51},R_{42/5\bar1},R_{43/61},R_{43/6\bar1},R_{4\bar2},R_{4\bar3} \qquad \text{(II.25)}$$

are specified and that the ordered quartet $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$ is a random variable which is uniformly distributed over the subset of the fourfold Cartesian product $W \times W \times W \times W$ of reciprocal space $W$ defined by (I.1), (I.2), (II.2),

$$\varphi_{14} = \Phi_{14}, \qquad \text{(II.26)}$$

(I.7) and

$$\begin{aligned}
&|E_{h_4kl_4}| = R_4, \quad |E_{\frac12(h_4-h_2),u,\frac12(l_4-l_2)}| = R_{4\bar2/50}, \\
&|E_{\frac12(h_4-h_3),v,\frac12(l_4-l_3)}| = R_{4\bar3/60}, \\
&|E_{\frac12(h_4+h_2),u+k,\frac12(l_4+l_2)}| = R_{42/51}, \\
&|E_{\frac12(h_4+h_2),u-k,\frac12(l_4+l_2)}| = R_{42/5\bar1}, \\
&|E_{\frac12(h_4+h_3),v+k,\frac12(l_4+l_3)}| = R_{43/61}, \\
&|E_{\frac12(h_4+h_3),v-k,\frac12(l_4+l_3)}| = R_{43/6\bar1}, \\
&|E_{h_4-h_2,0,l_4-l_2}| = R_{4\bar2}, \quad |E_{h_4-h_3,0,l_4-l_3}| = R_{4\bar3}.
\end{aligned} \qquad \text{(II.27)}$$

In view of (I.1), (I.2) and (II.2),

$$\varphi_{12} = \varphi_{h_1kl_1} - \varphi_{h_2kl_2}, \qquad \text{(II.28)}$$

$$\varphi_{23} = \varphi_{h_2kl_2} - \varphi_{h_3kl_3}, \qquad \text{(II.29)}$$

and

$$\varphi_{14} = \varphi_{h_1kl_1} - \varphi_{h_4kl_4} \quad \text{(II.30)}$$

are structure seminvariants. Then $\varphi_{12}$ and $\varphi_{23}$, as functions of the primitive random variable $[(h_1kl_1), (h_2kl_2), (h_3kl_3), (h_4kl_4)]$, are themselves random variables. Denote by

$$P_{2|1,24} = P(\Phi_{12},\Phi_{23}|\Phi_{14},R_1,R_2,\ldots,R_{4\bar{3}})$$

the joint conditional probability distribution of the pair $\varphi_{12}$, $\varphi_{23}$, given $\varphi_{14}$, (II.26), and the 24 magnitudes (I.7) and (II.27). Then $P_{2|1,24}$ is found from $P_{3|28}$, (II.16), by fixing $\Phi_{14}$ and multiplying by a suitable normalizing parameter:

$$P_{2|1,24} = \frac{1}{K_{2|1,24}} Q_1(\Phi_{12}) Q_2(\Phi_{12},\Phi_{23}) Q_3'(\Phi_{12},\Phi_{23}|\Phi_{14}), \quad \text{(II.31)}$$

where $Q_1(\Phi_{12})$ and $Q_2(\Phi_{12},\Phi_{23})$ are given by (I.29) and (I.30) respectively, $Q_3'(\Phi_{12},\Phi_{23}|\Phi_{14})$, obtained from $Q_3(\Phi_{12},\Phi_{23},\Phi_{14})$, (II.17), by suppressing those factors independent of $\Phi_{12}$ or $\Phi_{23}$, but dependent on the fixed parameter $\Phi_{14}$, so that they are absorbed by the normalizing parameter $K_{2|1,24}$, is given by

$$\begin{aligned} Q_3'(\Phi_{12},\Phi_{23}|\Phi_{14}) = \exp\Bigg\{ & -\frac{2}{\sigma_2^3}(3\sigma_3^2-\sigma_2\sigma_4) \\ & \times [(-1)^u R_4R_2R^2_{4\bar{2}/50}\cos(\Phi_{12}-\Phi_{14}) \\ & + (-1)^v R_4R_3R^2_{4\bar{3}/60}\cos(\Phi_{12}+\Phi_{23}-\Phi_{14})] \\ & -\frac{2}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)\,[(-1)^u R_4R_2(R^2_{42/51}+R^2_{42/5\bar{1}}) \\ & \qquad \times\cos(\Phi_{12}-\Phi_{14}) \\ & + (-1)^v R_4R_3(R^2_{43/61}+R^2_{43/6\bar{1}})\cos(\Phi_{12}+\Phi_{23}-\Phi_{14})] \\ & +\frac{6}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)[(-1)^u R_4R_2\cos(\Phi_{12}-\Phi_{14}) \\ & + (-1)^v R_4R_3\cos(\Phi_{12}+\Phi_{23}+\Phi_{14})] \\ & -\frac{1}{\sigma_2^3}(\sigma_3^2-\sigma_2\sigma_4)\,[R_4^2R_2^2\cos 2(\Phi_{12}-\Phi_{14}) \\ & + R_4^2R_3^2\cos 2(\Phi_{12}+\Phi_{23}-\Phi_{14})]\Bigg\} \\ & \times\cosh\left(\frac{\sigma_3R_{4\bar{2}}}{\sigma_2^{3/2}}V_{4\bar{2}}\right)\cosh\left(\frac{\sigma_3R_{4\bar{3}}}{\sigma_2^{3/2}}V_{4\bar{3}}\right) \\ & \times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{2}/50}R_{42/51}U_{4\bar{2}}\right)I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{2}/50}R_{42/5\bar{1}}U_{4\bar{2}}\right) \\ & \times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{3}/60}R_{43/61}U_{4\bar{3}}\right)I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{4\bar{3}/60}R_{43/61}U_{4\bar{3}}\right), \end{aligned} \quad \text{(II.32)}$$

with $V_{4\bar{2}}$, $V_{4\bar{3}}$, $U_{4\bar{2}}$, $U_{4\bar{3}}$ defined by (II.19), (II.20), (II.22), (II.23) respectively, and the normalizing parameter $K_{2|1,24}$, a function of the 25 parameters (II.24)–(II.26) and independent of $\Phi_{12}$ and $\Phi_{23}$, is best obtained numerically in any given case. It should be noted that $P_{2|1,24}$ is a function of the two variables $\Phi_{12}$ and $\Phi_{23}$ and that $\Phi_{14}$ is a parameter of the distribution. Despite the superficial resemblance, $P_{3|28}$ is, in contrast, a function of the three variables $\Phi_{12}$, $\Phi_{23}$ and $\Phi_{14}$.

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