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Sextets in $P1$: The Probabilistic Theory of the Six-Phase Structure Invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}$

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It is assumed that a crystal structure $P1$ is fixed and that the 31 non-negative numbers $R_1, R_2, \ldots, R_6$; $R_{12}, R_{13}, \ldots, R_{56}$; $R_{123}, R_{124}, \ldots, R_{156}$ are also specified. The random variables (vectors) **h**, **k**, **l**, **m**, **n**, **p** are assumed to be uniformly and independently distributed in the regions of reciprocal space defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ \ldots,\ |E_{\mathbf{p}}|=R_6\ ; \tag{1}$$

$$|E_{\mathbf{h+k}}|=R_{12},\ |E_{\mathbf{h+l}}|=R_{13},\ \ldots,\ |E_{\mathbf{n+p}}|=R_{56}\ ; \tag{2}$$

$$|E_{\mathbf{h+k+l}}|=R_{123},\ |E_{\mathbf{h+k+m}}|=R_{124},\ \ldots,\ |E_{\mathbf{h+n+p}}|=R_{156}\ ; \tag{3}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}+\mathbf{p}=0\,. \tag{4}$$

Then the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}$, as a function of the primitive random variables **h**, **k**, **l**, **m**, **n**, **p**, is itself a random variable, and its conditional probability distribution, given (1), (2) and (3), is derived from the main result of the previous paper [equation (3.1); Fortier & Hauptman (1977). *Acta Cryst.* A**33**, 694–696.] and compared with the distribution when only (1) is given. The distribution leads to estimates for cos φ in terms of the 31 magnitudes (1), (2) and (3).

1. The probabilistic background

A crystal structure in $P1$ consisting of N atoms (not necessarily identical) per unit cell is assumed to be fixed. The 31 non-negative numbers

$$R_1, R_2, \ldots, R_6 \text{ (6 `main terms')}; \tag{1.1}$$

$$R_{12}, R_{13}, \ldots, R_{56} \text{ (15 `cross-terms')}; \tag{1.2}$$

$$R_{123}, R_{124}, \ldots, R_{156} \text{ (10 `cross-terms')}; \tag{1.3}$$

are also specified. The sixfold Cartesian product $W\times W\times W\times W\times W\times W$ of reciprocal space W is defined to consist of all ordered sextuples (**h**, **k**, **l**, **m**, **n**, **p**) of reciprocal vectors. It is assumed that the ordered sextuple (**h**, **k**, **l**, **m**, **n**, **p**) is a random variable (vector) which is uniformly distributed over the subset of $W\times W\times W\times W\times W\times W$ defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ \ldots,\ |E_{\mathbf{p}}|=R_6; \tag{1.4}$$

$$|E_{\mathbf{h+k}}|=R_{12},\ |E_{\mathbf{h+l}}|=R_{13},\ \ldots,\ |E_{\mathbf{n+p}}|=R_{56}; \tag{1.5}$$

$$|E_{\mathbf{h+k+l}}|=R_{123},|E_{\mathbf{h+k+m}}|=R_{124},\ldots,|E_{\mathbf{h+n+p}}|=R_{156}; \tag{1.6}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}+\mathbf{p}=0\,. \tag{1.7}$$

Note that in order to ensure that the domain of the random variable (**h**, **k**, **l**, **m**, **n**, **p**) be non-vacuous, it is necessary to interpret the strict equality $|E_{\mathbf{h}}|=R_1$ of (1.4), for example, as the inequalities $R_1\le|E_{\mathbf{h}}|\le R_1+\mathrm{d}R_1$, where $\mathrm{d}R_1$ is a small positive quantity, *etc.* In view of (1.7), the sextet

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}} \tag{1.8}$$

is a structure invariant which, as a function of the primitive random variable (**h**, **k**, **l**, **m**, **n**, **p**), is itself a random variable. The major result of this paper is the derivation of the conditional probability distribution of φ, given the 31 magnitudes (1.4)–(1.6) in its second neighborhood. To this end the joint conditional probability distribution of the six phases $\varphi_{\mathbf{h}}$, $\varphi_{\mathbf{k}}$, $\varphi_{\mathbf{l}}$, $\varphi_{\mathbf{m}}$ $\varphi_{\mathbf{n}}$, $\varphi_{\mathbf{p}}$, given the 31 magnitudes (1.4)–(1.6), is derived first.

As usual, the following definition is made:

$$\sigma_n=\sum_{j=1}^{N} f_j^n\,, \tag{1.9}$$

where the f_j are the zero-angle atomic scattering factors. Since the f_j are not required to be positive, the results obtained are valid for both the X-ray and neutron diffraction cases.

2. The joint conditional probability distribution of the six phases, $\varphi_{\mathbf{h}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{l}}, \varphi_{\mathbf{m}}, \varphi_{\mathbf{n}}, \varphi_{\mathbf{p}}$, given the 31 magnitudes (1.4)–(1.6)

Under the hypotheses of § 1, denote by

$$P_{6|31}=P(\Phi_1, \Phi_2, \Phi_3, \Phi_4, \Phi_5, \Phi_6|R_1, R_2, \ldots, R_6; R_{12}, R_{13}, \ldots, R_{56}; R_{123}, R_{124}, \ldots, R_{156})\,, \tag{2.1}$$

the joint conditional probability distribution of the six phases $\varphi_{\mathbf{h}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{l}}, \varphi_{\mathbf{m}}, \varphi_{\mathbf{n}}, \varphi_{\mathbf{p}}$, given the 31 magnitudes (1.4)–(1.6). Then $P_{6|31}$ is obtained from P_{31} [equation (3.1) of the previous paper (Fortier & Hauptman, 1977)], the joint probability distribution of 31 structure factors, by fixing the 31 magnitudes $R_1, R_2, \ldots, R_6$; $R_{12}, R_{13}, \ldots, R_{56}$; $R_{123}, R_{124}, \ldots, R_{156}$, in accordance with the scheme (1.4)–(1.6), integrating P_{31} from 0 to 2π with respect to the 25 phase variables $\Phi_{12}, \Phi_{13}, \ldots, \Phi_{56}$; $\Phi_{123}, \Phi_{124}, \ldots, \Phi_{156}$ and multiplying the result by a suitable normalizing parameter which is independent of the 31 Φ's. Thus

$$P_{6|31}=\frac{1}{K}\int_0^{2\pi}\ldots\int_0^{2\pi} P_{31}\mathrm{d}\Phi_{12}\ldots\mathrm{d}\Phi_{56}\mathrm{d}\Phi_{123}\ldots\mathrm{d}\Phi_{156}\,. \tag{2.2}$$

Since it has not been possible to evaluate the 25-fold integral (2.2) exactly, an approximation technique has been introduced as follows [see Hauptman & Fortier (1977) for the quintet analogue]: First, the Taylor expansion of P_{31} is found and introduced into (2.2). The 25-fold integral (2.2) is then readily evaluated. Finally, in analogy with earlier work (Hauptman, 1975; Hauptman & Fortier, 1977), an exponential–Bessel function form for $P_{6|31}$ is assumed, the Taylor expansion of which agrees with that of (2.2) up to and including terms of order $1/N^2$. Thus substituting the Taylor expansion of P_{31} (equation 3.1 of Fortier & Hauptman, 1977) into (2.2) and carrying out the 25-fold integration, one readily finds

$$\begin{aligned}
P_{6|31}&=\int_0^{2\pi}\ldots\int_0^{2\pi} P_{31}\mathrm{d}\Phi_{12}\mathrm{d}\Phi_{13}\ldots\mathrm{d}\Phi_{156}\\
&=\frac{1}{K}\left\{1+\left[-\frac{2}{\sigma_2^6}(105\sigma_3^4\right.\right.\\
&\quad-105\sigma_2\sigma_3^2\sigma_4+15\sigma_2^2\sigma_3\sigma_5+10\sigma_2^2\sigma_4^2-\sigma_2^3\sigma_6)\\
&\quad+\frac{2\sigma_3}{\sigma_2^6}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\sum_{15}R_{12}^2\\
&\quad+\frac{2}{\sigma_2^6}(3\sigma_3^2-\sigma_2\sigma_4)^2\sum_{10}R_{123}^2\\
&\quad-\frac{2\sigma_3^2}{\sigma_2^6}(3\sigma_3^2-\sigma_2\sigma_4)\sum_{10}R_{123}^2(R_{45}^2+R_{46}^2+R_{56}^2)\\
&\quad-\frac{2\sigma_3^2}{\sigma_2^6}(3\sigma_3^2-\sigma_2\sigma_4)\sum_{10}R_{123}^2(R_{12}^2+R_{13}^2+R_{23}^2)\\
&\quad-\frac{2\sigma_3^2}{\sigma_2^6}(3\sigma_3^2-\sigma_2\sigma_4)\sum_{45}R_{12}^2R_{34}^2\\
&\quad+\frac{2\sigma_3^4}{\sigma_2^6}\sum_{15}R_{12}^2R_{34}^2R_{56}^2\\
&\quad\left.+\frac{2\sigma_3^4}{\sigma_2^6}\sum_{10}R_{123}^2(R_{12}^2+R_{13}^2+R_{23}^2)(R_{45}^2+R_{46}^2+R_{56}^2)\right]\\
&\quad\times R_1R_2R_3R_4R_5R_6\cos(\Phi_1+\Phi_2+\Phi_3\\
&\quad\left.+\Phi_4+\Phi_5+\Phi_6)\right\}\left\{1+O\left(\frac{1}{N}\right)\right\},
\end{aligned} \tag{2.3}$$

where $O(1/N)$ consists of all terms of order $1/N$ or higher in which the terms of order $1/N$ and $1/N^2$ are independent of the Φ's, so that $O(1/N)$ makes no contribution of order $1/N^2$ or lower to the conditional distribution to be derived. In (2.3) it is to be understood that the term $\sum_{15} R_{12}^2$, for example, is an abbreviation for the sum of fifteen terms

$$R_{12}^2+R_{13}^2+\ldots+R_{56}^2; \tag{2.4}$$

the term $\sum_{10} R_{123}^2$ is an abbreviation for the sum of ten terms

$$R_{123}^2+R_{124}^2+R_{125}^2+\ldots+R_{156}^2; \tag{2.5}$$

the term $\sum_{10} R_{123}^2(R_{45}^2+R_{46}^2+R_{56}^2)$ is an abbreviation for the sum of ten terms

$$\begin{aligned}R_{123}^2(R_{45}^2+R_{46}^2+R_{56}^2)+R_{124}^2(R_{35}^2+R_{36}^2+R_{56}^2)\\+\ldots+R_{156}^2(R_{23}^2+R_{24}^2+R_{34}^2);\end{aligned} \tag{2.6}$$

etc. Thus (2.3), the Taylor expansion of $P_{6|31}$, is a good approximation to $P_{6|31}$ when the values of the 25 parameters $R_{12}, \ldots, R_{56}$; $R_{123}, \ldots, R_{156}$ are all small. However this approximation is clearly unsatisfactory when some of $R_{12}, R_{13}, \ldots$ are large because (2.3) may then become negative, which no probability distribution can do. Employing the formula

$$x=\exp(\log x) \tag{2.7}$$

and expanding the logarithm of the right-hand side of (2.3), one readily transforms (2.3) into pure exponential form:

$$\begin{aligned}P_{6|15}\approx\frac{1}{K}\exp\{\Delta R_1R_2R_3R_4R_5R_6\\ \times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5+\Phi_6)\}\,,\end{aligned} \tag{2.8}$$

correct up to and including terms of order $1/N^2$, where Δ, the 'discriminant' of the structure invariant φ (equation 1.8), is the polynomial of sixth degree in the 25 'cross-terms', $R_{12}, R_{13}, \ldots, R_{156}$, defined by

$$\begin{aligned}
\Delta=&\frac{2\sigma_3^4}{\sigma_2^6}[\sum_{15}R_{12}^2R_{34}^2R_{56}^2\\
&+\sum_{10}R_{123}^2(R_{12}^2+R_{13}^2+R_{23}^2)(R_{45}^2+R_{46}^2+R_{56}^2)]\\
&-\frac{2\sigma_3^2}{\sigma_2^6}(3\sigma_3^2-\sigma_2\sigma_4)[\sum_{45}R_{12}^2R_{34}^2\\
&+\sum_{10}R_{123}^2(R_{12}^2+R_{13}^2+R_{23}^2)
\end{aligned}$$

$$+\sum_{10} R_{123}^2(R_{45}^2+R_{46}^2+R_{56}^2)]$$
$$+\frac{2}{\sigma_2^6}[\sigma_3(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\sum_{15} R_{12}^2$$
$$+(3\sigma_3^2-\sigma_2\sigma_4)^2\sum_{10} R_{123}^2]$$
$$-\frac{2}{\sigma_2^6}[105\sigma_3^4-105\sigma_2\sigma_3^2\sigma_4$$
$$+15\sigma_2^2\sigma_3\sigma_5+10\sigma_2^2\sigma_4^2-\sigma_2^3\sigma_6]\,. \quad (2.9)$$

Although (2.8) is always positive and is therefore almost surely a better approximation to $P_{6|31}$ than is (2.3) for all values of the 31 parameters $R_1, R_2, \ldots, R_{156}$, presumably a still better approximation is available as reference to the analogous distribution for quartets suggests (Hauptman, 1975, equation 2.5). The earlier (quartet) distribution is in the exponential–Bessel form. It is therefore plausible to assume that the correct functional form for $P_{6|31}$ is an exponential multiplied by 25 Bessel Functions (*cf.* Hauptman & Fortier, 1977, equations 2.9, 2.11). Under this assumption, and employing the relationship,

$$I_0(z)\simeq\exp\left(\frac{z^2}{4}\right) \text{ if } z \text{ is small}, \quad (2.10)$$

the pure exponential form (2.8) is readily transformed into the exponential–Bessel form:

$$P_{6|31}\simeq\frac{1}{K}\exp\left\{-\frac{2}{\sigma_2^6}[105\sigma_3^4-105\sigma_2\sigma_3^2\sigma_4\right.$$
$$+15\sigma_2^2\sigma_3\sigma_5+10\sigma_2^2\sigma_4^2-\sigma_2^3\sigma_6]R_1R_2R_3R_4R_5R_6$$
$$\left.\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5+\Phi_6)\right\}$$
$$\times\prod_{15} I_0\left(\frac{2\sigma_3^2}{\sigma_2^3}R_{12}X_{12}\right)\prod_{10} I_0\left(\frac{2\sigma_3^2}{\sigma_2^3}R_{123}X_{123}\right), \quad (2.11)$$

where

$$X_{12}=\{R_1^2R_2^2x_{12}^2+2x_{12}R_1R_2R_3R_4R_5R_6$$
$$\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5+\Phi_6)$$
$$+R_3^2R_4^2R_5^2R_6^2\}^{1/2}, \quad (2.12)$$

$$x_{12}=\tfrac{1}{3}(R_{34}^2R_{56}^2+R_{35}^2R_{46}^2+R_{36}^2R_{45}^2)$$
$$-\frac{3\sigma_3^2-\sigma_2\sigma_4}{2\sigma_3^2}(R_{34}^2+R_{35}^2+R_{36}^2+R_{45}^2+R_{46}^2+R_{56}^2)$$
$$+\frac{1}{\sigma_3^3}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5), \quad (2.13)$$

etc.,

$$X_{123}=\{R_1^2R_2^2R_3^2x_{456}^2+2x_{123}x_{456}R_1R_2R_3R_4R_5R_6$$
$$\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5+\Phi_6)$$
$$+R_4^2R_5^2R_6^2x_{123}^2\}^{1/2}, \quad (2.14)$$

$$x_{123}=(R_{12}^2+R_{13}^2+R_{23}^2)-\frac{1}{\sigma_3^2}(3\sigma_3^2-\sigma_2\sigma_4), \quad (2.15)$$

$$x_{456}=(R_{45}^2+R_{46}^2+R_{56}^2)-\frac{1}{\sigma_3^2}(3\sigma_3^2-\sigma_2\sigma_4), \quad (2.16)$$

etc., K is a suitable normalizing parameter independent of $\Phi_1, \ldots, \Phi_6$, and I_0 is the modified Bessel Function. It is readily verified that the Taylor expansion of (2.11) agrees with that of (2.8) up to and including terms of order $1/N^2$, except for terms which are independent of the Φ's and which are therefore absorbed by the scaling parameter K. Since $P_{6|31}$ is a function of the sum $\Phi=\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5+\Phi_6$, the conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}$, given the 31 magnitudes (1.4)–(1.6) in its second neighborhood, is immediately obtained, as shown next.

3. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}$, given the 31 magnitudes (1.4)–(1.6)

Under the hypotheses of § 1, denote by

$$P_{1|31}=P(\Phi|R_1, \ldots, R_6; R_{12}, \ldots, R_{56}; R_{123}, \ldots, R_{156}) \quad (3.1)$$

the conditional probability distribution of the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}, \quad (3.2)$$

given the 31 magnitudes (1.4)–(1.6) in the second neighborhood of φ. Then $P_{1|31}$ is obtained directly from (2.11). Thus, correct up to and including terms of order $1/N^2$, the major result of this paper is given by

$$P_{1|31}\simeq\frac{1}{K}\exp\left\{-\frac{2}{\sigma_2^6}[105\sigma_3^4-105\sigma_2\sigma_3^2\sigma_4+15\sigma_2^2\sigma_3\sigma_5\right.$$
$$\left.+10\sigma_2^2\sigma_4^2-\sigma_2^3\sigma_6]R_1R_2R_3R_4R_5R_6\cos\Phi\right\}$$
$$\times\prod_{15} I_0\left(\frac{2\sigma_3^2}{\sigma_2^3}R_{12}Y_{12}\right)\prod_{10} I_0\left(\frac{2\sigma_3^2}{\sigma_2^3}R_{123}Y_{123}\right), \quad (3.3)$$

where

$$Y_{12}=\{R_1^2R_2^2x_{12}^2+2x_{12}R_1R_2R_3R_4R_5R_6$$
$$\times\cos\Phi+R_3^2R_4^2R_5^2R_6^2\}^{1/2}, \quad (3.4)$$

etc.,

$$Y_{123}=\{R_1^2R_2^2R_3^2x_{456}^2+2x_{123}x_{456}R_1R_2R_3R_4R_5R_6$$
$$\times\cos\Phi+R_4^2R_5^2R_6^2x_{123}^2\}^{1/2}, \quad (3.5)$$

etc., $x_{12}, x_{13}, \ldots; x_{123}, x_{456}, x_{124}, x_{356}, \ldots$ are defined by (2.13), …; (2.15), (2.16), …; and K is a suitable normalizing parameter independent of Φ.

3.1. *Exponential form of the distribution*

Although, as described earlier, the pure exponential form of the distribution is not expected to be as accurate as the exponential–Bessel form, it is nevertheless worthwhile to give the exponential form because of its simplicity, ease of calculation, and ability to yield results which appear to be at least qualitatively correct. Thus, from (2.8),

$$P_{1|31} \simeq \frac{1}{K} \exp\left(\Delta R_1 R_2 R_3 R_4 R_5 R_6 \cos \Phi\right) \qquad (3.6)$$

where the normalizing parameter K is given by

$$K = 2\pi I_0(\Delta R_1 R_2 R_3 R_4 R_5 R_6), \qquad (3.7)$$

and the discriminant Δ is the sextic polynomial (2.9). Clearly (3.6) has a unique maximum at $\Phi=0$ or $\Phi=\pi$ according as $\Delta>0$ or $\Delta<0$ respectively. A disadvantage of (3.6) is that it is incapable of giving a maximum between 0 and π whereas (3.3) may have a maximum anywhere in the interval $(0,\pi)$.

Clearly, if the 25 cross-terms $R_{12}, \ldots, R_{156}$ are mostly large, then $P_{1|31}$, whether given by (3.3) or (3.6), has a unique maximum at $\Phi=0$ so that in this case the most probable value of φ is zero. If, on the other hand, certain of the cross-terms are large and others are small, then the most probable value of φ may well be π, as the reader may easily verify. These several special cases, which were spelled out in some detail for quartets and quintets (Hauptman, 1975; Hauptman & Fortier, 1977) are not further described here.

3.2. *Expected values*

Although the conditional expected value of $\cos \varphi$ may be obtained from (3.3), the analytic form of the result is too complicated to be useful in the applications. Both the expected value and the normalizing parameter K are more readily found numerically from the distribution (3.3) in any given case. If one uses the exponential form (3.6) instead, the following simple formula having at least approximate validity is obtained:

$$\varepsilon(\cos \varphi | R_1, \ldots, R_6; R_{12}, \ldots, R_{56}; R_{123}, \ldots, R_{156}) \approx \frac{I_1(\Delta R_1 R_2 R_3 R_4 R_5 R_6)}{I_0(\Delta R_1 R_2 R_3 R_4 R_5 R_6)} \qquad (3.8)$$

which is positive or negative according as $\Delta>0$ or $\Delta<0$.

3.3. *A conjecture*

It is clear that, according as

$$\Delta \gg 0 \qquad (3.9)$$

or

$$\Delta \ll 0, \qquad (3.10)$$

then

$$\varphi \simeq 0 \qquad (3.11)$$

or

$$\varphi \simeq \pi \qquad (3.12)$$

respectively. In analogy with earlier work on quintets (Hauptman & Fortier, 1977), it is therefore plausible to conjecture that if

$$\Delta \simeq 0 \qquad (3.13)$$

then

$$\varphi \simeq \pm \frac{\pi}{2}, \qquad (3.14)$$

although one would not expect the reliability of the estimate (3.14) to be as high as that of (3.11) or (3.12). It is in fact tempting to go further and to suggest that, at least for each fixed value of

$$D = \frac{2\sigma_6}{\sigma_2^3} R_1 R_2 R_3 R_4 R_5 R_6, \qquad (3.15)$$

the value of $|\varphi|$ is correlated with that of Δ in the sense that as Δ decreases from large positive values to large negative values then $|\varphi|$ tends to increase monotonically from 0 to π. It should however be stressed that this statement is only a plausible conjecture at this point and should be the subject of further testing.

4. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}+\varphi_{\mathbf{p}}$, given the six magnitudes $|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{n}}|, |E_{\mathbf{p}}|$

If, instead of being given all 31 magnitudes (1.4)–(1.6) in the second neighborhood of φ, one is given only the six magnitudes (1.4) in the first neighborhood, then the conditional probability distribution of φ, given (1.4), is readily found to be, correct up to and including terms of order $1/N^2$,

$$P(\Phi | R_1, R_2, R_3, R_4, R_5, R_6) \simeq \frac{1}{K} \exp\left(D \cos \Phi\right), \qquad (4.1)$$

where D is defined by (3.15) and the normalizing parameter K is given by

$$K = 2\pi I_0(D). \qquad (4.2)$$

In contrast to (3.3) and (3.6), (4.1) always has a unique maximum at $\Phi=0$. Finally the conditional expected value of $\cos \varphi$, given the six magnitudes (1.4) of the first neighborhood, is given by

$$\varepsilon(\cos \varphi | R_1, R_2, R_3, R_4, R_5, R_6) \simeq \frac{I_1(D)}{I_0(D)} \qquad (4.3)$$

which should be compared with (3.8). In contrast to (3.8), which may lie anywhere in the interval $(-1,1)$, (4.3) is always positive.

5. Concluding remarks

The conditional probability distribution of the sextet (1.8), given, in the first instance, the six magnitudes (1.4) in its first neighborhood and, in the second instance, the 31 magnitudes in its second neighborhood, have been found. Just as the analogous distributions for quartets have already proven to be useful in the applications, and the recently secured quintet distributions are sure to be useful as well, it is anticipated that the distributions derived here, in particular (3.3), will play an important role in the applications. If it should turn out that the discriminant Δ is strongly correlated with the value of the structure invariant φ, as conjectured, then the usefulness of the sextets will surely be enhanced.

It should be observed finally that in the presence of one or a few heavy atoms the distributions derived here are sharpened, thus leading to more reliable estimates of φ, as anticipated. It had been observed earlier (Hauptman, 1976; Hauptman & Fortier, 1977) that in the extreme case that $\sigma_3=0$ (possible only in the neutron diffraction case when some of the f_j may be negative) the distributions of quartets and quintets corresponding to the second neighborhood degenerated to the first-neighborhood distributions, so that nothing was gained in going to the second neighborhood. It is therefore a matter of some interest to observe that this phenomenon does not occur with sextets. Specifically, even in the extreme case that $\sigma_3=0$, the distribution (3.3) [or (3.6)] does not reduce to the distribution (4.1) so that it is still possible to use the information contained in the second neighborhood. In particular, if $\sigma_3=0$ then the dependence on the 15 cross-terms $R_{12}, \ldots, R_{56}$ is indeed lost but, as is easily verified, $\varphi\simeq 0$ or $\varphi\simeq\pi$ according as the ten cross-terms $R_{123}, \ldots, R_{156}$ are mostly large or mostly very small, respectively.

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Structure Determination of a Mixed-Layer Bismuth Titanate, $Bi_7Ti_4NbO_{21}$, by Super-High-Resolution Electron Microscopy

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The crystal structure of a bismuth titanate, $Bi_7Ti_4NbO_{21}$, was determined on the basis of super-high-resolution images, taken by a recently constructed 1000 kV electron microscope, in which each cation site was approximately defined. It was found that the crystal has a mixed-layer structure, *i.e.* $Bi_4Ti_3O_{12}$ and Bi_3TiNbO_9-like layers are alternately intergrown. The symmetry is orthorhombic with space group *I2cm*. The lattice parameters are $a=5{\cdot}45$, $b=5{\cdot}42$ and $c=58{\cdot}1$ Å. That the periodicity along **c** is twice that expected from a simple intergrowth can be accounted for by the rotation of octahedra. The lattice defects found are discussed in terms of twinning of the crystal.

Introduction

Since the work of Aurivillius (1949) it has been known that the ferroelectric bismuth titanates belonging to the $Bi_4Ti_3O_{12}$ family consist of Bi_2O_2 sheets interleaved with perovskite-like $A_{n-1}B_nO_{3n+1}$ layers, where n is an integer between 1 and 5. The cubo-octahedral A site accepts Bi, Ba, Sr, K, Ca, Na, Pb and several rare-earth ions, while the smaller Ti, Nb, Ta, Fe, W, Mo, Ga and Cr ions go into the octahedral B sites. The lattice distortions in the room-temperature phase are understood in fair detail in connexion with the ferroelectricity (Newnham, Wolfe & Dorrian, 1971).

One of the present authors (Kikuchi, 1976) recently prepared a new compound $Bi_7Ti_4NbO_{21}$ by heating mixtures of $Bi_4Ti_3O_{12}$ ($n=3$) and Bi_3TiNbO_9 ($n=2$). X-ray powder diffraction data suggested that the compound is built up by a regular intergrowth of the two starting constituents along **c**. Because of difficulty in preparing large crystals the structure analysis has not been performed.

The contrast of recent electron-microscope images roughly represents the projection of potential distributions of a crystal, when the incident beam is parallel not only to the optical axis but also to a zone axis of the crystal (Cowley & Iijima, 1972). In order to obtain good 'structure images' the resolution limit of the objective lens should be lowered so that as many