bond distance of 3·023 Å. A unique distinction between these would have been impossible without the direct location of the hydrogen atoms.

Table 5. *Non-hydrogen-bonding intermolecular distances less than* 3·3 Å *between the heavier atoms*

Atom i	Atom j	in molecule at:	Distance d_{ij}
C(5)	O(7)	$x,y,z+(0,1,0)$	3·210 Å
N(6)	O(2)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	3·239
N(8)	O(2)	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	3·079
N(8)	O(4)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	3·145
O(4)	O(4)	$\bar{x},\bar{y},\bar{z}+(1,1,0)$	3·233

In addition to the least-squares refinement program referred to previously the following computer programs were used in this analysis: IBM 7070 programs for data processing (McMullan, 1964), Fourier syntheses (Chu & McMullan, 1962), structure factors (Shiono, 1962) and IBM 1620 programs for the direct method of sign determination (Beurskens, 1963) and for the calculation of inter and intra-molecular geometry (Chu, 1963).

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A Theory of the Joint Probability Distribution of Complex-Valued Structure Factors

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The joint probability distribution of complex-valued structure factors, which may be used for the statistical determination of the phase angles in non-centrosymmetric crystals, is derived as an extension of our previous theory for real-valued structure factors (Naya, Nitta & Oda, 1964). The probability distribution function is given in a form of an orthogonal series based upon the associated Laguerre polynomials. The application of the theory is also illustrated in some special examples.

Introduction

In a previous paper (Naya, Nitta & Oda, 1964), the present authors dealt with a theory of the joint probability distribution of signs of structure factors which is applicable to centrosymmetric space groups. A theory of the joint probability distribution of complex-valued structure factors for non-centrosymmetric crystals may similarly be formulated and will be useful for statistical determination of the relevant phase angles. Although studies along this line have been published by Bertaut (1956) and Karle & Hauptman (1956), it seems that much is still left open regarding the complex structure factors. In this paper, we extend our theory of the statistical method of the sign determination in real structure factors to the phase angle determination in complex structure factors.

In §1 is introduced a concept of the joint probability distribution of phase angles. In §2 is given a formulation of the joint probability distribution of complex structure factors, from which the explicit expression of the joint probability of phase angles can be derived.

In §3 are shown some examples of calculation on the basis of our theories in §§ 1 and 2, which may show its practical usefulness in crystallography.

1. Joint probability distribution of phase angles

In the previous paper on the statistical method of sign determination (Naya, Nitta & Oda, 1964) for centrosymmetric crystals, the concept of the joint probability distribution of signs was introduced. The same concept can be easily extended to the phase angles of complex structure factors as described below.

1·1 *A general expression of the joint probability distribution of phase angles*

Let m normalized complex-valued structure factors be denoted by $\mathbf{E}_1,\ldots,\mathbf{E}_m$, their amplitudes by $E_1,\ldots,E_m$ and the corresponding phase angles by $\varphi_1,\ldots,\varphi_m$.

$$\mathbf{E}_1=E_1\exp(i\varphi_1),\ldots,\mathbf{E}_m=E_m\exp(i\varphi_m) \quad (1)$$

Values of the amplitudes $E_1,\ldots,E_m$ are determinable from measurements. Let $P(\varphi_1,\ldots,\varphi_m)$ for the phase angles be the joint probability distribution under the condition that the magnitudes of $E_1,\ldots,E_m$ have already been known. Since the distribution function $P(\varphi_1,\ldots,\varphi_m)$ should naturally have the periodicity of 2π for each φ_i, it may be expanded in a form of multiple Fourier series as

$$P(\varphi_1,\ldots,\varphi_m)=\frac{1}{(2\pi)^m}\sum_{n_1=-\infty}^{\infty}\ldots\sum_{n_m=-\infty}^{\infty}\times\langle\exp\{-i(n_1\varphi_1+\ldots+n_m\varphi_m)\}\rangle\exp\{i(n_1\varphi_1+\ldots+n_m\varphi_m)\}, \quad (2)$$

where the coefficients with angular brackets are the expected values of $\exp\{-i(n_1\varphi_1+\ldots+n_m\varphi_m)\}$, namely,

$$\langle\exp\{-i(n_1\varphi_1+\ldots+n_m\varphi_m)\}\rangle=\int_0^{2\pi}\ldots\int_0^{2\pi}\exp\{-i(n_1\varphi_1+\ldots+n_m\varphi_m)\}\times P(\varphi_1,\ldots,\varphi_m)d\varphi_1\ldots d\varphi_m\,. \quad (3)$$

Because $P(\varphi_1,\ldots,\varphi_m)$ should be invariant with respect to the simultaneous change in signs of the angular variables $\varphi_1,\ldots,\varphi_m$ (Karle & Hauptman, 1956; Bertaut, 1956,) we have

$$P(\varphi_1,\ldots,\varphi_m)=P(-\varphi_1,\ldots,-\varphi_m)\,. \quad (4)$$

Since equation (3) with (4) gives

$$\langle\exp\{-i(n_1\varphi_1+\ldots+n_m\varphi_m)\}\rangle=\langle\exp\{i(n_1\varphi_1+\ldots+n_m\varphi_m)\}\rangle=\langle\cos(n_1\varphi_1+\ldots+n_m\varphi_m)\rangle\,, \quad (5)$$

and

$$\langle\sin(n_1\varphi_1+\ldots+n_m\varphi_m)\rangle=0\,, \quad (6)$$

(2) can be rewritten as

$$P(\varphi_1,\ldots,\varphi_m)=\frac{1}{(2\pi)^m}\sum_{n_1=-\infty}^{\infty}\ldots\sum_{n_m=-\infty}^{\infty}\times\langle\cos(n_1\varphi_1+\ldots+n_m\varphi_m)\rangle\cos(n_1\varphi_1+\ldots+n_m\varphi_m)\,. \quad (7)$$

The equation (2) or (7) is a generalized analogue to the joint probability distribution of signs $P(s_1,\ldots,s_m)$†, which was introduced in the previous paper on the centrosymmetric case.

1·2 *Reduced probabilities of phase angles*

The probability distribution for a single structure invariant which is independent of the choice of permissible origin (*cf.* for example, Karle & Hauptman, 1956) is derived from (2) or (7), as follows. Let Φ_1 be a structure invariant, being a linear combination of several components φ_i's whose indices $\mathbf{h}_i$'s satisfy a necessary condition; for example,

$$\Phi_1=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}\equiv\varphi_1+\varphi_2+\varphi_3\,, \quad (8)$$

with

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

The probability $P(\Phi_1)d\Phi_1$ for Φ_1 to be between Φ_1 and $\Phi_1+d\Phi_1$ is given by the reduction (integral) of $P(\varphi_1,\ldots,\varphi_m)$ concerning $\varphi_1,\ldots,\varphi_m$, assuming that $\varphi_1+\varphi_2+\varphi_3=\Phi_1$ is kept constant.

$$\begin{aligned}P(\Phi_1)&=\underset{(\varphi_1+\varphi_2+\varphi_3=\Phi_1=\text{const.})}{\int_0^{2\pi}\ldots\int_0^{2\pi}}P(\varphi_1,\ldots,\varphi_m)d\varphi_1\ldots d\varphi_m\\&=\frac{1}{2\pi}\sum_{N_1=-\infty}^{\infty}\langle\exp\{-iN_1(\varphi_1+\varphi_2+\varphi_3)\}\rangle\exp\{iN_1(\varphi_1+\varphi_2+\varphi_3)\}\\&=\frac{1}{2\pi}\sum_{N_1=-\infty}^{\infty}\langle\exp(-iN_1\Phi_1)\rangle\exp(iN_1\Phi_1)\\&=\frac{1}{2\pi}\{1+\sum_{\substack{N_1=-\infty\\(N_1\neq0)}}^{\infty}\langle\exp(-iN_1\Phi_1)\rangle\exp(iN_1\Phi_1)\}\,. \quad (9)\end{aligned}$$

With the use of (5), equation (9) is rewritten

$$P(\Phi_1)=\frac{1}{2\pi}\{1+2\sum_{N_1=1}^{\infty}\langle\cos N_1\Phi_1\rangle\cos N_1\Phi_1\}\,, \quad (10)$$

which gives a general form of the probability distribution for a structure invariant.

Similarly, the probability distribution generalized for k structure invariants $\Phi_1,\ldots,\Phi_k$ is obtained by reduction,

$$\begin{aligned}P(\Phi_1,\ldots,\Phi_k)&=\underset{(\Phi_1=\text{const.},\ldots,\,\Phi_k=\text{const.})}{\int_0^{2\pi}\ldots\ldots\int_0^{2\pi}}P(\varphi_1,\ldots,\varphi_m)d\varphi_1\ldots d\varphi_m\\&=\frac{1}{(2\pi)^k}\sum_{N_1=-\infty}^{\infty}\ldots\sum_{N_k=-\infty}^{\infty}\langle\exp\{-i(N_1\Phi_1+\ldots+N_k\Phi_k)\}\rangle\exp\{i(N_1\Phi_1+\ldots+N_k\Phi_k)\}\\&=\frac{1}{(2\pi)^k}\sum_{N_1=-\infty}^{\infty}\ldots\sum_{N_k=-\infty}^{\infty}\langle\cos(N_1\Phi_1+\ldots+N_k\Phi_k)\rangle\cos(N_1\Phi_1+\ldots+N_k\Phi_k)\,. \quad (11)\end{aligned}$$

It is to be noted that the k invariants are linearly independent of each other, namely

$$N_1\Phi_1+N_2\Phi_2+\ldots+N_k\Phi_k\not\equiv0\,,\quad(\text{except for } N_1=N_2=\ldots=N_k=0)\,. \quad (12)$$

---

† $P(s_1,\ldots,s_m)$ can be expanded as

$$P(s_1,\ldots,s_m)=\frac{1}{2^m}\sum_{n_1=0}^{1}\ldots\sum_{n_m=0}^{1}\langle s_1^{n_1}\ldots s_m^{n_m}\rangle s_1^{n_1}\ldots s_m^{n_m}.$$

[See also equation (1) in our paper (Naya, Nitta & Oda, 1964)].

1·3 *Conditional probabilities*

The knowledge of the value of a structure invariant Φ_2 has an influence upon the probability distribution of another invariant Φ_1. Let $P(\Phi_1|\Phi_2)$ be the conditional probability distribution of Φ_1 for a fixed value of Φ_2. It is shown that

$$P(\Phi_1, \Phi_2)=P(\Phi_2)P(\Phi_1|\Phi_2)\,, \tag{13}$$

$$\begin{aligned} P(\Phi_1|\Phi_2) &= \frac{P(\Phi_1, \Phi_2)}{P(\Phi_2)} \\ &= \frac{\frac{1}{(2\pi)^2}\sum_{N_1=-\infty}^{\infty}\sum_{N_2=-\infty}^{\infty}\langle\exp\{-i(N_1\Phi_1+N_2\Phi_2)\}\rangle\exp\{i(N_1\Phi_1+N_2\Phi_2)\}}{\frac{1}{2\pi}\sum_{N_2=-\infty}^{\infty}\langle\exp(-iN_2\Phi_2)\rangle\exp(iN_2\Phi_2)} \\ &= \frac{1}{2\pi}\sum_{N_1=-\infty}^{\infty}\langle\exp(-iN_1\Phi_1)\rangle_{\Phi 2}\exp(iN_1\Phi_1) \\ &= \frac{1}{2\pi}\{1+\sum_{\substack{N_1=-\infty \\ (N_1\neq 0)}}^{\infty}\langle\exp(-iN_1\Phi_1)\rangle_{\Phi 2}\exp(iN_1\Phi_1)\}\,, \end{aligned} \tag{14}$$

where the coefficient

$$\begin{aligned} \langle\exp(-iN_1\Phi_1)\rangle_{\Phi 2} &= \frac{\sum_{N_2=-\infty}^{\infty}\langle\exp\{-i(N_1\Phi_1+N_2\Phi_2)\}\rangle\exp(iN_2\Phi_2)}{\sum_{N_2=-\infty}^{\infty}\langle\exp(-iN_2\Phi_2)\rangle\exp(iN_2\Phi_2)} \\ &= \frac{\langle\exp(-iN_1\Phi_1)\rangle+\sum_{\substack{N_2=-\infty \\ (N_2\neq 0)}}^{\infty}\langle\exp\{-i(N_1\Phi_1+N_2\Phi_2)\}\rangle\exp(iN_2\Phi_2)}{1+\sum_{\substack{N_2=-\infty \\ (N_2\neq 0)}}^{\infty}\langle\exp(-iN_2\Phi_2)\rangle\exp(iN_2\Phi_2)} \end{aligned} \tag{15}$$

represents the conditional expected value. From (14), $P(\Phi_1|\Phi_2)$ becomes

$$\begin{aligned} P(\Phi_1|\Phi_2) = \frac{1}{2\pi}\{1&+2\sum_{N_1=1}^{\infty}\langle\cos N_1\Phi_1\rangle_{\Phi 2}\cos N_1\Phi_1 \\ &+2\sum_{N_1=1}^{\infty}\langle\sin N_1\Phi_1\rangle_{\Phi 2}\sin N_1\Phi_1\}\,, \end{aligned} \tag{16}$$

where the conditional expected values of $\cos N_1\Phi_1$ and $\sin N_1\Phi_1$ are given respectively by

$$\langle\cos N_1\Phi_1\rangle_{\Phi 2} = \frac{\langle\cos N_1\Phi_1\rangle+\sum_{N_2=1}^{\infty}\{\langle\cos(N_1\Phi_1+N_2\Phi_2)\rangle+\langle\cos(N_1\Phi_1-N_2\Phi_2)\rangle\}\cos N_2\Phi_2}{1+2\sum_{N_2=1}^{\infty}\langle\cos N_2\Phi_2\rangle\cos N_2\Phi_2} \tag{17}$$

and

$$\langle\sin N_1\Phi_1\rangle_{\Phi 2} = \frac{-\sum_{N_2=1}^{\infty}\{\langle\cos(N_1\Phi_1+N_2\Phi_2)\rangle-\langle\cos(N_1\Phi_1-N_2\Phi_2)\rangle\}\sin N_2\Phi_2}{1+2\sum_{N_2=1}^{\infty}\langle\cos N_2\Phi_2\rangle\cos N_2\Phi_2}\,. \tag{18}$$

It is to be noted here that although the expected value $\langle\sin N_1\Phi_1\rangle$ is zero as shown by (6), the conditional one $\langle\sin N_1\Phi_1\rangle_{\Phi 2}$ does not always vanish as shown by (18).

In the same way, the conditional probability distribution of Φ_1 under the condition that the values of two structure invariants Φ_2 and Φ_3 are fixed is derivable as follows [equation (19)]:

$$\begin{aligned} &P(\Phi_1|\Phi_2, \Phi_3) \\ &= \frac{1}{2\pi}\{1+\sum_{\substack{N_1=-\infty \\ (N_1\neq 0)}}^{\infty}\langle\exp(-iN_1\Phi_1)\rangle_{\Phi 2,\Phi 3}\exp(iN_1\Phi_1)\}, \end{aligned} \tag{19}$$

where the conditional expected value

$$\langle\exp(-iN_1\Phi_1)\rangle_{\Phi 2,\Phi 3}$$

is [equation (20)]

$$\langle \exp(-iN_1\Phi_1)\rangle_{\Phi_2,\Phi_3} = \frac{\sum_{N_2=-\infty}^{\infty}\sum_{N_3=-\infty}^{\infty} \langle \exp\{-i(N_1\Phi_1+N_2\Phi_2+N_3\Phi_3)\}\rangle \exp\{i(N_2\Phi_2+N_3\Phi_3)\}}{\sum_{N_2=-\infty}^{\infty}\sum_{N_3=-\infty}^{\infty} \langle \exp\{-i(N_2\Phi_2+N_3\Phi_3)\}\rangle \exp\{i(N_2\Phi_2+N_3\Phi_3)\}} . \quad (20)$$

Similarly to the case of the centrosymmetric crystals in the previous paper (Naya, Nitta & Oda, 1964), any conditional probability and expected value can be successively obtained as the number of known values of the structure invariants increases.

2. Joint probability distribution of complex-valued structure factors

Let the explicit form of the joint probability distribution of a set of m complex structure factors be $P(E_1,\ldots, E_m, \varphi_1, \ldots, \varphi_m)$. Then, since the joint probability $P(\varphi_1, \ldots, \varphi_m)$ introduced in 1·1 is taken, by its definition, as the conditional probability obtained from $P(E_1, \ldots, E_m, \varphi_1,\ldots, \varphi_m)$ for a set of fixed values of $E_1,\ldots, E_m$, we have

$$P(\varphi_1,\ldots,\varphi_m) \equiv P(\varphi_1,\ldots,\varphi_m|E_1,\ldots,E_m) = \frac{P(E_1,\ldots,E_m,\varphi_1,\ldots,\varphi_m)}{\int_0^{2\pi}\cdots\int_0^{2\pi} P(E_1,\ldots,E_m,\varphi_1,\ldots,\varphi_m)d\varphi_1\ldots d\varphi_m} . \quad (21)$$

Hence, if the explicit form for $P(E_1,\ldots, E_m, \varphi_1,\ldots, \varphi_m)$ is obtained, the equations introduced in §1 which are useful for phase determination will be explicitly derived.

In this section the explicit form of the joint probability of the complex structure factors is derived, by extending the methods used by Klug (1958) and by us (Naya, Nitta & Oda, 1964) for the real structure factors. The calculation is carried out based upon *a priori* probability of 'uniform distribution' for atoms in a unit cell.

2·1 *Moments of complex-valued trigonometric structure factors*

Starting from the complex-valued trigonometric structure factors as

$$\xi(\mathbf{h}) = \tau \sum_{p=0}^{s-1} \exp(2\pi i \mathbf{hr}\boldsymbol{S}_p) = \tau \sum_{p=0}^{s-1} \exp(2\pi i \boldsymbol{R}_p\mathbf{hr}) \exp(2\pi i \mathbf{ht}_p) , \quad (22)$$

we introduce the mixed moments of $\xi(\mathbf{h}_1),\ldots, \xi(\mathbf{h}_m)$,

$$m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}(\mathbf{h}_1,\ldots,\mathbf{h}_m) = \overline{\xi^\alpha(\mathbf{h}_1)\xi^{*\alpha^*}(\mathbf{h}_1)\ldots\xi^\omega(\mathbf{h}_m)\xi^{*\omega^*}(\mathbf{h}_m)} , \quad (23)†$$

where $\boldsymbol{S}_p$ is the pth operation of the symmetry with the rotational part $\boldsymbol{R}_p$ and the translational part $\mathbf{t}_p$, s is the order of factor group, τ the order of translation group ($\tau=2$ for A, B, C, I; $\tau=3$ for R; $\tau=4$ for F), $\xi^*(\mathbf{h})$ means the complex conjugate of $\xi(\mathbf{h})$, and α, $\alpha^*,\ldots, \omega, \omega^*$ are non-negative integers. The average in (23) means the integration with respect to $\mathbf{r}$ over the unit cell. The integration can be easily carried out (refer to Appendix I of Naya, Nitta & Oda, 1964), and this results in

$$m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}(\mathbf{h}_1,\ldots,\mathbf{h}_m) = \tau^{(\alpha+\alpha^*)+\ldots+(\omega+\omega^*)} \sum_{\substack{\Sigma\alpha_p=\alpha\\p}} \sum_{\substack{\Sigma\alpha_p^*=\alpha^*\\p}}\cdots\sum_{\substack{\Sigma\omega_p=\omega\\p}} \sum_{\substack{\Sigma\omega_p^*=\omega^*\\p}} \times \frac{\alpha!\alpha^*!\ldots\omega!\omega^*!}{\prod_p(\alpha_p!\alpha_p^*!\ldots\omega_p!\omega_p^*!)}$$
$$\times \exp[2\pi i\{\sum_{p=0}^{s-1}[(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m]\mathbf{t}_p\}]$$
$$\times\delta[\sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m\}] , \quad (24)$$

where the ranges of the integers $\alpha_p, \alpha_p^*,\ldots, \omega_p, \omega_p^*$ are $0\le\alpha_p\le\alpha,\ldots, 0\le\omega_p^*\le\omega^*$, respectively; the summation is to be carried out over all possible combinations of $\alpha_p,\ldots, \omega_p^*$ satisfying $\sum_{p=0}^{s-1}\alpha_p=\alpha,\ldots, \sum_{p=0}^{s-1}\omega_p^*=\omega^*$.

The Kronecker symbol δ means

$$\delta[\sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m\}]=1 ,$$
$$\text{if } \sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m\}=0 ,$$
$$\delta[\sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m\}]=0,$$
$$\text{if } \sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p-\alpha_p^*)\mathbf{h}_1+\ldots+(\omega_p-\omega_p^*)\mathbf{h}_m\}\neq0. \quad (25)$$

For the space group $P1$, (24) takes a simple form

$$m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}(\mathbf{h}_1,\ldots,\mathbf{h}_m)=\delta\{(\alpha-\alpha^*)\mathbf{h}_1+\ldots+(\omega-\omega^*)\mathbf{h}_m\}. \quad (26)$$

2·2 *Moment-cumulant transformation*

The cumulants with respect to the moments of (23) can be obtained by an extension of the one-dimensional moment-cumulant transformation

$$\sum_{n=0}^{\infty} k_n \frac{u^n}{n!} = \log\left\{\sum_{n=0}^{\infty} m_n \frac{u^n}{n!}\right\}, m_1=0, \quad (27)$$

where u is a real carrying variable and k_n the cumulant. In the case of many-dimensional transformation with complex carrying variables $\mathbf{u}_i$'s†, we have

$$\sum_{\alpha,\alpha^*,\ldots,\omega,\omega^*=0}^{\infty} k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega} \frac{\mathbf{u}_1^{*\alpha}\mathbf{u}_1^{\alpha^*}\ldots\mathbf{u}_m^{*\omega}\mathbf{u}_m^{\omega^*}}{\alpha!\alpha^*!\ldots\omega!\omega^*!} = \log\left\{\sum_{\alpha,\alpha^*,\ldots,\omega,\omega^*=0}^{\infty} m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega} \frac{\mathbf{u}_1^{*\alpha}\mathbf{u}_1^{\alpha^*}\ldots\mathbf{u}_m^{*\omega}\mathbf{u}_m^{\omega^*}}{\alpha!\alpha^*!\ldots\omega!\omega^*!}\right\}, \quad (28)$$

† Karle & Hauptman (1956) used the mixed moments of another type

$$m^{\mu_1\ldots\mu_m}_{\lambda_1\ldots\lambda_m}(\mathbf{h}_1,\ldots,\mathbf{h}_m) = \overline{\eta^{\lambda_1}(\mathbf{h}_1)\zeta^{\mu_1}(\mathbf{h}_1)\ldots\eta^{\lambda_m}(\mathbf{h}_m)\zeta^{\mu_m}(\mathbf{h}_m)} ,$$

where η and ζ express the real and imaginary parts in $\xi=\eta+i\zeta$ respectively.

† The complex carrying variable can be expressed by $\mathbf{u}=v+iw=ue^{i\theta}$. $\mathbf{u}^*$ is the complex conjugate of $\mathbf{u}$.

where $k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}$ represent the cumulants.

Comparison of the expansion series in both sides of equation (28) gives the following relations:

$$k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}=m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega},\ \text{for } (\alpha+\alpha^*)+\ldots+(\omega+\omega^*)=1,2 \text{ and } 3, \quad (29)$$

$$k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}=m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega} -3\sum_{(\alpha'+\alpha^{*\prime})+\ldots+(\omega'+\omega^{*\prime})=2}\ \sum_{(\alpha''+\alpha^{*\prime\prime})+\ldots+(\omega''+\omega^{*\prime\prime})=2} \times m^{\alpha^{*\prime}\ldots\omega^{*\prime}}_{\alpha'\ldots\omega'} m^{\alpha^{*\prime\prime}\ldots\omega^{*\prime\prime}}_{\alpha''\ldots\omega''}\frac{(2!)^2}{4!} \times \frac{\alpha!\alpha^*!\ldots\omega!\omega^*!}{(\alpha'!\alpha^{*\prime}!\ldots\omega'!\omega^{*\prime}!)(\alpha''!\alpha^{*\prime\prime}!\ldots\omega''!\omega^{*\prime\prime}!)} \times\delta\{\alpha-(\alpha'+\alpha'')\}\delta\{\alpha^*-(\alpha^{*\prime}+\alpha^{*\prime\prime})\}\ldots\delta\{\omega-(\omega'+\omega'')\}\,\delta\{\omega^*-(\omega^{*\prime}+\omega^{*\prime\prime})\}, \quad (30)$$

for $(\alpha+\alpha^*)+\ldots+(\omega+\omega^*)=4$,

$$k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}=m^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega} -10\sum_{(\alpha'+\alpha^{*\prime})+\ldots+(\omega'+\omega^{*\prime})=2}\ \sum_{(\alpha''+\alpha^{*\prime\prime})+\ldots+(\omega''+\omega^{*\prime\prime})=3} \times m^{\alpha^{*\prime}\ldots\omega^{*\prime}}_{\alpha'\ldots\omega'} m^{\alpha^{*\prime\prime}\ldots\omega^{*\prime\prime}}_{\alpha''\ldots\omega''}\frac{2!3!}{5!} \times \frac{\alpha!\alpha^*!\ldots\omega!\omega^*!}{(\alpha'!\alpha^{*\prime}!\ldots\omega'!\omega^{*\prime}!)(\alpha''!\alpha^{*\prime\prime}!\ldots\omega''!\omega^{*\prime\prime}!)} \times\delta\{\alpha-(\alpha'+\alpha'')\}\delta\{\alpha^*-(\alpha^{*\prime}+\alpha^{*\prime\prime})\}\ldots\delta\{\omega-(\omega'+\omega'')\} \times\delta\{\omega^*-(\omega^{*\prime}+\omega^{*\prime\prime})\}, \quad (31)$$

for $(\alpha+\alpha^*)+\ldots+(\omega+\omega^*)=5$,

and so on.

2·3 *Moment-generating function*

The moment-generating function corresponding to the moments defined by (23) can easily be prepared as follows (see Appendix I):

$$\mathfrak{M}(\mathbf{u}_1,\ldots,\mathbf{u}_m) =\exp\{\tfrac{1}{4}(u_1^2+\ldots+u_m^2)\}\exp\left[\sum_{n=3}^{\infty}\frac{Z_n}{S}\mathfrak{L}_n\right], \quad (32)$$

where $\mathfrak{L}_n$ is

$$\mathfrak{L}_n=\sum_{(\alpha+\alpha^*)+\ldots+(\omega+\omega^*)=n}\left(\frac{1}{\sqrt{\tau\varepsilon_1}}\right)^{\alpha+\alpha^*}\ldots\left(\frac{1}{\sqrt{\tau\varepsilon_m}}\right)^{\omega+\omega^*} \times\frac{k^{\alpha^*\ldots\omega^*}_{\alpha\ldots\omega}}{\alpha!\alpha^*!\ldots\omega!\omega^*!}\left(\frac{\mathbf{u}_1^*}{2}\right)^{\alpha}\left(\frac{\mathbf{u}_1}{2}\right)^{\alpha^*}\ldots\left(\frac{\mathbf{u}_m^*}{2}\right)^{\omega}\left(\frac{\mathbf{u}_m}{2}\right)^{\omega^*}, \quad (33)$$

and

$$Z_n=\sum_{j=1}^{N}\psi_j^n,\quad \psi_j=\frac{f_j}{(\sum_{j=1}^{N}f_j^2)^{\frac{1}{2}}}. \quad (34)$$

In these equations, $S=s\tau$ is the symmetry number, f_j the atomic scattering factor and ψ_j is its normalized one, and N is the number of the atoms in the unit cell. $\varepsilon_1,\ldots,\varepsilon_m$ are the statistical weights for special type reflexions (Bertaut, 1960). Expansion of the right hand side of (32) gives

$$\mathfrak{M}(\mathbf{u}_1,\ldots,\mathbf{u}_m)=\exp\{\tfrac{1}{4}(u_1^2+\ldots+u_m^2)\}\left[1+\frac{Z_3}{S}\mathfrak{L}_3 +\left\{\frac{Z_4}{S}\mathfrak{L}_4+\frac{Z_3^2}{2S^2}\mathfrak{L}_3^2\right\} +\left\{\frac{Z_5}{S}\mathfrak{L}_5+\frac{Z_3Z_4}{S^2}\mathfrak{L}_3\mathfrak{L}_4+\frac{Z_3^3}{6S^3}\mathfrak{L}_3^3\right\}+\ldots\right]. \quad (35)$$

It is to be noted that the form of the series (35) is the same as the one in the case of centrosymmetric crystals [1964, equation (39)], although the implication of $\mathfrak{L}_n$'s is modified corresponding to complex-valued quantities.

2·4 *Fundamental inversion transformation*

The inversion transformation of the moment-generating function (35) gives the joint probability distribution of complex structure factors

$$P(\mathbf{E}_1,\ldots,\mathbf{E}_m)=\frac{1}{(2\pi)^{2m}}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\mathfrak{M}(i\mathbf{u}_1,\ldots,i\mathbf{u}_m) \times\exp\left[-i\left\{\left(\frac{\mathbf{u}_1}{2}\mathbf{E}_1^*+\frac{\mathbf{u}_1^*}{2}\mathbf{E}_1\right)+\ldots +\left(\frac{\mathbf{u}_m}{2}\mathbf{E}_m^*+\frac{\mathbf{u}_m^*}{2}\mathbf{E}_m\right)\right\}\right]d\mathbf{u}_1\ldots d\mathbf{u}_m \quad (36)$$

(see Appendix I).

Substituting equation (35) in (36), and taking account of relation (33), it is found that the integration in (36) can be expressed by a series of inversion terms as follows:

$$I\equiv\text{Inversion of}\left\{\exp(\tfrac{1}{4}u^2)\left(\frac{\mathbf{u}^*}{2}\right)^n\left(\frac{\mathbf{u}}{2}\right)^{n^*}\right\} =\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp(-\tfrac{1}{4}u^2)\left(\frac{i\mathbf{u}^*}{2}\right)^n\left(\frac{i\mathbf{u}}{2}\right)^{n^*} \times\exp\left\{-i\,\frac{\mathbf{u}\mathbf{E}^*+\mathbf{u}^*\mathbf{E}}{2}\right\}d\mathbf{u}, \quad (37)$$

where n and n^* are non-negative integers.

By the relations $\mathbf{E}=Ee^{i\varphi}$ and $\mathbf{u}=ue^{i\theta}$, it holds that

$$\tfrac{1}{2}(\mathbf{u}\mathbf{E}^*+\mathbf{u}^*\mathbf{E})=uE\cos(\varphi-\theta),$$

and

$$d\mathbf{u}\equiv dvdw=ududθ.$$

Then

$$I=\frac{1}{(2\pi)^2}\frac{i^{n+n^*}}{2^{n+n^*}}\int_0^{\infty}\int_0^{2\pi}\exp(-\tfrac{1}{4}u^2) \times\exp\{-iuE\cos(\varphi-\theta)\}u^{n+n^*+1}\exp\{i(n^*-n)\theta\}dud\theta. \quad (38)$$

With use of the relations

$$e^{-iuE\cos(\varphi-\theta)}=(-i)^m\sum_{m=-\infty}^{\infty}J_m(uE)e^{-im(\varphi-\theta)} \quad (39)$$

and

$$\int_0^{2\pi}e^{-im(\varphi-\theta)}e^{i(n^*-n)\theta}d\theta=2\pi e^{-im\varphi}\delta_{m,n-n^*}, \quad (40)$$

(38) becomes

$$I=\frac{1}{\pi}e^{-i(n-n^*)\varphi}$$
$$\times\left[\frac{(-1)^{n^*}}{2^{n+n^*+1}}\int_0^\infty \exp(-\tfrac{1}{4}u^2)J_{n-n^*}(uE)u^{n+n^*+1}du\right], \quad (41)$$

where $J_m(uE)$ are the Bessel functions of degree m. The relation (41) is further integrable with respect to u [see Appendix II and Erdélyi (1953)], and its final result is

$$I=\frac{1}{\pi}e^{-E^2}K_{n,n^*}(\boldsymbol{E}), \quad (42)\dagger$$

where

$$K_{n,n^*}(\boldsymbol{E})=R_{n,n^*}(E)e^{-i(n-n^*)\varphi}, \quad (43)$$

and

$$R_{n,n^*}(E)=(-1)^{n^*}n^*!E^{n-n^*}L_{n^*}^{(n-n^*)}(E^2). \quad (44)$$

In (44), $L_\nu^{(\mu)}(x)$ is the associated Laguerre polynomial which is defined by

$$L_\nu^{(\mu)}(x)=\frac{e^x x^{-\mu}}{\nu!}\frac{d^\nu}{dx^\nu}\{e^{-x}x^{\nu+\mu}\}. \quad (45)$$

The function $K_{n,n^*}(\boldsymbol{E})$ satisfies the orthogonal relation with respect to the weight function $1/\pi\exp(-E^2)$ proper to the complex structure factors; namely,

$$\int_0^\infty\int_0^{2\pi}\frac{1}{\pi}\exp(-E^2)K^*_{n,n^*}(\boldsymbol{E})K_{m,m^*}(\boldsymbol{E})EdEd\varphi$$
$$=n!n^*!\delta_{nm}\delta_{n^*m^*}, \quad (46)$$

(see also Appendix III).

Thus, when the probability distribution of a single structure factor is taken as a simple example, it is easily shown by the use of the orthogonal relation (46) that the probability $P(\boldsymbol{E})$ can be expressed as

$$P(\boldsymbol{E})=\frac{1}{\pi}e^{-E^2}\sum_{n=0}^\infty\sum_{n^*=0}^\infty\frac{\langle K^*_{n,n^*}(\boldsymbol{E})\rangle}{n!n^*!}K_{n,n^*}(\boldsymbol{E}), \quad (47)\ddagger$$

where

$$\langle K^*_{n,n^*}(\boldsymbol{E})\rangle=\int_0^\infty\int_0^{2\pi}K^*_{n,n^*}(\boldsymbol{E})P(\boldsymbol{E})EdEd\varphi. \quad (48)$$

From the nature of the Laguerre polynomials, it is also shown that the polynomials $R_{n,n^*}(E)$ possess a symmetric character in n and n^* as follows,

$$R_{n,n^*}(E)=R_{n^*,n}(E). \quad (49)$$

$R_{n,n^*}(E)$ can be expressed by the expansion series

$$R_{n,n^*}(E)=\sum_{m=0}^{n^*}(-1)^m m!\binom{n}{m}\binom{n^*}{m}E^{n+n^*-2m},\ (n\ge n^*), \quad (50)$$

(see Appendix IV).

The particular forms of $R_{n,n^*}(E)$ with their numerical examples are given in Appendix V.

2·5 *General expression for the joint probability distribution of complex-valued structure factors*

By substituting the relations (24), (29), (30), (31), (33) and (35) into the inversion formula (36) and by taking account of (42), the joint probability distribution function of complex structure factors can be derived as follows:

$$P(\boldsymbol{E}_1,\ldots,\boldsymbol{E}_m)$$
$$=\frac{1}{\pi^m}\exp\{-(E_1^2+\ldots+E_m^2)\}$$
$$\times\Big[1+\frac{Z_3}{S}\Sigma_3+\frac{Z_4}{S}\{\Sigma_4-\tfrac{1}{2}\Sigma_{22}\}+\frac{Z_3^2}{2S^2}\Sigma_{33}$$
$$+\frac{Z_5}{S}\{\Sigma_5-\Sigma_{32}\}+\frac{Z_3Z_4}{S^2}\{\Sigma_{43}-\tfrac{1}{2}\Sigma_{322}\}$$
$$+\frac{Z_3^3}{6S^3}\Sigma_{333}+\ldots\Big], \quad (51)$$

where

$$\Sigma_{a\ldots f}\equiv\sum_{\Sigma\{(\alpha_p'+\alpha_p^{*\prime})+\ldots+(\omega_p'+\omega_p^{*\prime})\}=a}\cdot\ \cdot\ \cdot\sum_{\Sigma\{(\alpha_p''^{\cdot\prime}+\alpha_p^{*\prime\prime\cdot\prime})+\ldots+(\omega_p''^{\cdot\prime}+\omega_p^{*\prime\prime\cdot\prime})\}=f}$$
$$\times\frac{\left(\sqrt{\frac{\tau}{\varepsilon_1}}\right)^{\Sigma(\alpha_p'+\ldots+\alpha_p''^{\cdot\prime})+(\alpha_p^{*\prime}+\ldots+\alpha_p^{*\prime\prime\cdot\prime})}\cdots\left(\sqrt{\frac{\tau}{\varepsilon_m}}\right)^{\Sigma(\omega_p'+\ldots+\omega_p''^{\cdot\prime})+(\omega_p^{*\prime}+\ldots+\omega_p^{*\prime\prime\cdot\prime})}}{\prod_p(\alpha_p'!\alpha_p^{*\prime}!\ldots\omega_p'!\omega_p^{*\prime}!)\ldots(\alpha_p''''!\alpha_p^{*''''}!\ldots\omega_p''''!\omega_p^{*''''}!)}$$
$$\times\exp\Big[2\pi i\sum_{p=0}^{s-1}[\{(\alpha_p'-\alpha_p^{*\prime})+\ldots+(\alpha_p''''-\alpha_p^{*''''})\}\mathbf{h}_1+\ldots+\{(\omega_p'-\omega_p^{*\prime})+\ldots+(\omega_p''''-\omega_p^{*''''})\}\mathbf{h}_m]\mathbf{t}_p\Big]$$
$$\times K_{\Sigma(\alpha_p'+\ldots+\alpha_p''''),\Sigma(\alpha_p^{*\prime}+\ldots+\alpha_p^{*''''})}(\boldsymbol{E}_1)\ldots K_{\Sigma(\omega_p'+\ldots+\omega_p''''),\Sigma(\omega_p^{*\prime}+\ldots+\omega_p^{*''''})}(\boldsymbol{E}_m)$$
$$\times\delta\Big[\sum_{p=0}^{s-1}\boldsymbol{R}_p\{(\alpha_p'-\alpha_p^{*\prime})\mathbf{h}_1+\ldots+(\omega_p'-\omega_p^{*\prime})\mathbf{h}_m\}\Big]\ldots\delta\Big[\sum_{p=0}^{s-1}\mathbf{R}_p\{(\alpha_p''''-\alpha_p^{*''''})\mathbf{h}_1+\ldots+(\omega_p''''-\omega_p^{*''''})\mathbf{h}_m\}\Big]. \quad (52)$$

---

† Equations (37) and (42) are to be compared with the inversion transformation formula given by Klug [1958, equation (1·16)] for the case of centrosymmetry as follows

$$I=\text{Inversion of }\{\exp(\tfrac{1}{2}u^2)u^n\}$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-\tfrac{1}{2}u^2)\,(iu)^n\exp(-iu\boldsymbol{E})\,du$$
$$=(1/\sqrt{2\pi})\exp(-\tfrac{1}{2}E^2)\,H_n(\boldsymbol{E}),$$

where $H_n(\mathbf{E})$ is the Hermite polynomial of degree n.

‡ This formula corresponds to the following one as given for the case of centrosymmetry

$$P(\boldsymbol{E})=\frac{1}{\sqrt{2\pi}}\exp(-\tfrac{1}{2}E^2)\sum_{n=0}^\infty\frac{\langle H_n(\boldsymbol{E})\rangle}{n!}H_n(\boldsymbol{E}),$$

where

$$\langle H_n(\boldsymbol{E})\rangle=\int_{-\infty}^\infty H_n(\boldsymbol{E})P(\boldsymbol{E})d\boldsymbol{E}.$$

It is again noted that the series on the right hand side of equation (51) has the same form as given by us (1964) for the case of centrosymmetric crystals except for a difference in the definition of $\Sigma_{ab\ldots f}$. The higher order terms such as $O(N^{-5/2})$ and $O(N^{-2})$ are omitted in (51), since they can be looked for in our previous paper. $K_{n,n^*}(\mathbf{E})$† in (52) are the orthogonal functions given by (43) and (44); the other notations in (51) and (52) have the same meaning as in the preceding §§ 2·1 and 2·3.

Equation (51), with (52), is a general expression for the joint probability distribution of complex structure factors with the form of a series based on orthogonal polynomials, and is applicable to any non-centrosymmetric space group.

3. Some examples of calculations of joint probabilities

In this section are shown some examples of calculations of the joint probabilities for the space group $P1$. First let us start from a particular example of calculation of the quantities $\Sigma_{ab\ldots f}$ in the joint probability distribution (51).

3·1 *Examples of deriving $\Sigma_{ab\ldots f}$*

It has been shown in the earlier paper (Naya, Nitta & Oda, 1964) that $\Sigma_{ab\ldots f}$'s are successively constructed from those of lower degree to higher ones in the case of centrosymmetry. The same holds also in the present case of non-centrosymmetric groups. Thus, let us put forward an example of calculation of $\Sigma_{ab\ldots f}$ for three structure factors $\mathbf{E}_1=\mathbf{E}_{\mathbf{h}_1}$, $\mathbf{E}_2=\mathbf{E}_{\mathbf{h}_2}$, $\mathbf{E}_3=\mathbf{E}_{\mathbf{h}_3}$ with indices which are related to each other by $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$.

In this example, relation (52) gives Σ_a in the form

$$\Sigma_a=\sum_{\alpha+\alpha^*+\beta+\beta^*+\gamma+\gamma^*=a}\frac{1}{\alpha!\alpha^*!\beta!\beta^*!\gamma!\gamma^*!}\times K_{\alpha,\alpha^*}(\mathbf{E}_1)K_{\beta,\beta^*}(\mathbf{E}_2)K_{\gamma,\gamma^*}(\mathbf{E}_3)\delta\{(\alpha-\alpha^*)\mathbf{h}_1+(\beta-\beta^*)\mathbf{h}_2+(\gamma-\gamma^*)\mathbf{h}_3\}\,. \quad (53)$$

The non-vanishing condition of $\delta\{\ldots\}$ is written

$$(\alpha-\alpha^*)\mathbf{h}_1+(\beta-\beta^*)\mathbf{h}_2+(\gamma-\gamma^*)\mathbf{h}_3=0\,, \quad (54)$$

or

$$\alpha-\alpha^*=\beta-\beta^*=\gamma-\gamma^*\,. \quad (55)$$

There is another condition for the summation

$$\alpha+\alpha^*+\beta+\beta^*+\gamma+\gamma^*=a\,. \quad (56)$$

The particular partitions of the non-negative values of α, α^*, β, β^*, γ, γ^* are allowed by (55) and (56), as shown in Table 1.

Table 1. *Possible partitions of α, α^*, β, β^*, γ and γ^* satisfying equations* (55) *and* (56)

The last column gives the values of $1/(\alpha!\,\alpha^*!\,\beta!\,\beta^*!\,\gamma!\,\gamma^*!)$.

a	α	α^*	β	β^*	γ	γ^*	
2	1	1	0	0	0	0	1
	0	0	1	1	0	0	1
	0	0	0	0	1	1	1
3	1	0	1	0	1	0	1
	0	1	0	1	0	1	1
4	2	2	0	0	0	0	$\frac{1}{4}$
	0	0	2	2	0	0	$\frac{1}{4}$
	0	0	0	0	2	2	$\frac{1}{4}$
	1	1	1	1	0	0	1
	0	0	1	1	1	1	1
	1	1	0	0	1	1	1
5	2	1	1	0	1	0	$\frac{1}{2}$
	1	0	2	1	1	0	$\frac{1}{2}$
	1	0	1	0	2	1	$\frac{1}{2}$
	1	2	0	1	0	1	$\frac{1}{2}$
	0	1	1	2	0	1	$\frac{1}{2}$
	0	1	0	1	1	2	$\frac{1}{2}$
6	3	3	0	0	0	0	$\frac{1}{36}$
	0	0	3	3	0	0	$\frac{1}{36}$
	0	0	0	0	3	3	$\frac{1}{36}$
	2	2	1	1	0	0	$\frac{1}{4}$
	0	0	2	2	1	1	$\frac{1}{4}$
	1	1	0	0	2	2	$\frac{1}{4}$
	2	2	0	0	1	1	$\frac{1}{4}$
	1	1	2	2	0	0	$\frac{1}{4}$
	0	0	1	1	2	2	$\frac{1}{4}$
	2	0	2	0	2	0	$\frac{1}{8}$
	0	2	0	2	0	2	$\frac{1}{8}$
	1	1	1	1	1	1	1
7	3	2	1	0	1	0	$\frac{1}{12}$
	1	0	3	2	1	0	$\frac{1}{12}$
	1	0	1	0	3	2	$\frac{1}{12}$
	2	3	0	1	0	1	$\frac{1}{12}$
	0	1	2	3	0	1	$\frac{1}{12}$
	0	1	0	1	2	3	$\frac{1}{12}$
	2	1	2	1	1	0	$\frac{1}{4}$
	1	0	2	1	2	1	$\frac{1}{4}$
	2	1	1	0	2	1	$\frac{1}{4}$
	1	2	1	2	0	1	$\frac{1}{4}$
	0	1	1	2	1	2	$\frac{1}{4}$
	1	2	0	1	1	2	$\frac{1}{4}$

From (53) with Table 1, we have

$$\begin{aligned}\Sigma_3&=K_{10}(\mathbf{E}_1)K_{10}(\mathbf{E}_2)K_{10}(\mathbf{E}_3)+K_{01}(\mathbf{E}_1)K_{01}(\mathbf{E}_2)K_{01}(\mathbf{E}_3)\\&=2R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)\cos(\varphi_1+\varphi_2+\varphi_3)\\&=2E_1E_2E_3\cos(\varphi_1+\varphi_2+\varphi_3)\,,\end{aligned} \quad (57)$$

$$\begin{aligned}\Sigma_4&=\tfrac{1}{4}[K_{22}(\mathbf{E}_1)+\text{cyc.}]+[K_{11}(\mathbf{E}_1)K_{11}(\mathbf{E}_2)+\text{cyc.}]\\&=\tfrac{1}{4}[R_{22}(E_1)+\text{cyc.}]+[R_{11}(E_1)R_{11}(E_2)+\text{cyc.}]\,,\end{aligned} \quad (58)$$

$$\begin{aligned}\Sigma_5&=\tfrac{1}{2}[K_{21}(\mathbf{E}_1)K_{10}(\mathbf{E}_2)K_{10}(\mathbf{E}_3)+\text{cyc.}]\\&\quad+\tfrac{1}{2}[K_{12}(\mathbf{E}_1)K_{01}(\mathbf{E}_2)K_{01}(\mathbf{E}_3)+\text{cyc.}]\\&=[R_{21}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3),\end{aligned} \quad (59)$$

and so on. $K_{nn^*}(\mathbf{E})$ and $R_{nn^*}(E)$ stand for $K_{n,n^*}(\mathbf{E})$ and $R_{n,n^*}(E)$ respectively for the sake of simplicity.

$\Sigma_{ab}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)$ or, more generally, $\Sigma_{ab\ldots f}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)$ can be constructed from those obtained as above, if the following relationships are used. The definition (52) gives Σ_{ab} the form

$$\begin{aligned}\Sigma_{ab}=&\sum_{\alpha+\alpha^*+\beta+\beta^*+\gamma+\gamma^*=a}\ \sum_{\alpha'+\alpha^{*\prime}+\beta'+\beta^{*\prime}+\gamma'+\gamma^{*\prime}=b}\\&\times\frac{1}{\alpha!\alpha^*!\beta!\beta^*!\gamma!\gamma^*!\alpha'!\alpha^{*\prime}!\beta'!\beta^{*\prime}!\gamma'!\gamma^{*\prime}!}\\&\times K_{\alpha+\alpha',\alpha^*+\alpha^{*\prime}}(\mathbf{E}_1)K_{\beta+\beta',\beta^*+\beta^{*\prime}}(\mathbf{E}_2)K_{\gamma+\gamma',\gamma^*+\gamma^{*\prime}}(\mathbf{E}_3)\\&\times\delta\{(\alpha-\alpha^*)\mathbf{h}_1+(\beta-\beta^*)\mathbf{h}_2+(\gamma-\gamma^*)\mathbf{h}_3\}\\&\times\delta\{(\alpha'-\alpha^{*\prime})\mathbf{h}_1+(\beta'-\beta^{*\prime})\mathbf{h}_2+(\gamma'-\gamma^{*\prime})\mathbf{h}_3\}\,.\end{aligned} \quad (60)$$

The product of Σ_a and Σ_b gives

† Though $K_{n,n^*}(\mathbf{E})$ can be also rewritten

$$\begin{aligned}K_{n,n^*}(\mathbf{E})=K^*_{n^*,n}(\mathbf{E})&=(-1)^n n!\,L_n^{(n^*-n)}(E^2)\mathbf{E}^{n^*-n}\\&=(-1)^{n^*}n^*!\,L_{n^*}^{(n-n^*)}(E^2)\mathbf{E}^{*n-n^*}\,,\end{aligned}$$

the form (43) with (44) will be more convenient.

$$\Sigma_a\Sigma_b = \sum_{\alpha+\alpha^*+\beta+\beta^*+\gamma+\gamma^*=a}\ \sum_{\alpha'+\alpha^{*\prime}+\beta'+\beta^{*\prime}+\gamma'+\gamma^{*\prime}=b} \times \frac{1}{\alpha!\alpha^*!\beta!\beta^*!\gamma!\gamma^*!\alpha'!\alpha^{*\prime}!\beta'!\beta^{*\prime}!\gamma'!\gamma^{*\prime}!}$$
$$\times K_{\alpha,\alpha^*}(E_1)K_{\alpha',\alpha^{*\prime}}(E_1)K_{\beta,\beta^*}(E_2)$$
$$\times K_{\beta',\beta^{*\prime}}(E_2)K_{\gamma,\gamma^*}(E_3)K_{\gamma',\gamma^{*\prime}}(E_3)$$
$$\times \delta\{(\alpha-\alpha^*)\mathbf{h}_1+(\beta-\beta^*)\mathbf{h}_2+(\gamma-\gamma^*)\mathbf{h}_3\}$$
$$\times \delta\{(\alpha'-\alpha^{*\prime})\mathbf{h}_1+(\beta'-\beta^{*\prime})\mathbf{h}_2+(\gamma'-\gamma^{*\prime})\mathbf{h}_3\}\,. \quad (61)$$

Comparison of (60) with (61) reveals that (60) is obtainable from (61) only by replacing $K_{\alpha,\alpha^*}(E_1)K_{\alpha',\alpha^{*\prime}}(E_1)$ of (61) with $K_{\alpha+\alpha',\alpha^*+\alpha^{*\prime}}(E_1)$, *etc.* Thus, if we define a formal product

$$K_{\alpha,\alpha^*}(E_1) * K_{\alpha',\alpha^{*\prime}}(E_1) \equiv K_{\alpha+\alpha',\alpha^*+\alpha^{*\prime}}(E_1)\,, \quad (62)$$

we can obtain Σ_{ab} by

$$\Sigma_{ab} = \Sigma_a * \Sigma_b\,. \quad (63)$$

For example, Σ_{33} is given by

$$\begin{aligned}\Sigma_{33} &= \Sigma_3 * \Sigma_3 = \{K_{10}(E_1)K_{10}(E_2)K_{10}(E_3)\\ &\quad + K_{01}(E_1)K_{01}(E_2)K_{01}(E_3)\} * \{K_{10}(E_1)K_{10}(E_2)K_{10}(E_3)\\ &\quad + K_{01}(E_1)K_{01}(E_2)K_{01}(E_3)\}\\ &= K_{20}(E_1)K_{20}(E_2)K_{20}(E_3) + K_{02}(E_1)K_{02}(E_2)K_{02}(E_3)\\ &\quad + 2K_{11}(E_1)K_{11}(E_2)K_{11}(E_3)\\ &= 2R_{20}(E_1)R_{20}(E_2)R_{20}(E_3)\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}\\ &\quad + 2R_{11}(E_1)R_{11}(E_2)R_{11}(E_3)\,, \qquad (64)\end{aligned}$$

and

$$\begin{aligned}\Sigma_{43} &= \Sigma_4 * \Sigma_3 = \{\tfrac{1}{4}[K_{22}(E_1)+\text{cyc.}] + [K_{11}(E_1)K_{11}(E_2)\\ &\quad + \text{cyc.}]\} * \{K_{10}(E_1)K_{10}(E_2)K_{10}(E_3)\\ &\quad + K_{01}(E_1)K_{01}(E_2)K_{01}(E_3)\}\\ &= \tfrac{1}{4}\{[K_{32}(E_1)K_{10}(E_2)K_{10}(E_3)+\text{cyc.}]\\ &\quad + [K_{23}(E_1)K_{01}(E_2)K_{01}(E_3)+\text{cyc.}]\}\\ &\quad + [K_{21}(E_1)K_{21}(E_2)K_{10}(E_3)+\text{cyc.}]\\ &\quad + [K_{12}(E_1)K_{12}(E_2)K_{01}(E_3)+\text{cyc.}]\\ &= \tfrac{1}{2}[R_{32}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\\ &\quad + 2[R_{21}(E_1)R_{21}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\,, \qquad (65)\end{aligned}$$

etc. In general, it can be proved that

$$\Sigma_{ab\ldots f} = \Sigma_a * \Sigma_b * \ldots * \Sigma_f\,. \quad (66)$$

Therefore, when the necessary $\Sigma_{ab\ldots f}$'s for the expansion terms up to $O(N^{-5/2})$ in (51) are to be derived, it is sufficient that the partitions of α, α^*, β, β^*, γ, γ^* are sought for Σ_2, Σ_3, Σ_4, Σ_5, Σ_6, Σ_7 and then $\Sigma_{ab\ldots f}$'s are step by step constructed therefrom by the use of (66). This procedure is useful in the calculation up to the higher orders for any other combinations of structure factors $E_1,\ldots, E_m$. [Refer to equation (40) in our paper (Naya, Nitta & Oda, 1964)].

3·2 *Joint probability distribution of the complex-valued structure factors* $\mathbf{E}_1=\mathbf{E}_{\mathbf{h}_1}$, $\mathbf{E}_2=\mathbf{E}_{\mathbf{h}_2}$, $\mathbf{E}_3=\mathbf{E}_{\mathbf{h}_3}$ *under* $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$.

Introducing $\Sigma_{ab\ldots f}$ of §3·1 into the general expression of joint probability distribution (51), the joint probability distribution of $\mathbf{E}_1$, $\mathbf{E}_2$, $\mathbf{E}_3$ is given as

$$\begin{aligned}P(\mathbf{E}_1,\mathbf{E}_2,\mathbf{E}_3) &= \frac{1}{\pi^3}\exp\{-(E_1^2+E_2^2+E_3^2)\}\\ &\times\Big[1+2Z_3R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)\cos(\varphi_1+\varphi_2+\varphi_3)\\ &-\frac{Z_4}{4}[R_{22}(E_1)+\text{cyc.}]+Z_3^2[R_{20}(E_1)R_{20}(E_2)R_{20}(E_3)\\ &\times\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}+R_{11}(E_1)R_{11}(E_2)R_{11}(E_3)]\\ &-Z_5[R_{21}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\\ &-\frac{Z_3Z_4}{2}[R_{32}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)+Z_3^3[\tfrac{1}{3}R_{30}(E_1)R_{30}(E_2)R_{30}(E_3)\\ &\times\cos\{3(\varphi_1+\varphi_2+\varphi_3)\}+R_{21}(E_1)R_{21}(E_2)R_{21}(E_3)\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)]+Z_6\{\tfrac{1}{9}[R_{33}(E_1)+\text{cyc.}]\\ &-R_{11}(E_1)R_{11}(E_2)R_{11}(E_3)-\tfrac{3}{4}R_{20}(E_1)R_{20}(E_2)R_{20}(E_3)\\ &\times\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}\}-Z_3Z_5\{[R_{31}(E_1)R_{20}(E_2)R_{20}(E_3)\\ &+\text{cyc.}]\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}+[R_{22}(E_1)R_{11}(E_2)R_{11}(E_3)\\ &+\text{cyc.}]\}+Z_4^2\{\tfrac{1}{32}[R_{44}(E_1)+\text{cyc.}]\\ &+\tfrac{1}{16}[R_{22}(E_1)R_{22}(E_2)+\text{cyc.}]\}\\ &-\frac{Z_3^2Z_4}{4}\{[R_{42}(E_1)R_{20}(E_2)R_{20}(E_3)+\text{cyc.}]\\ &\times\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}\\ &+[R_{33}(E_1)R_{11}(E_2)R_{11}(E_3)+\text{cyc.}]\}\\ &+Z_3^4\{\tfrac{1}{12}R_{40}(E_1)R_{40}(E_2)R_{40}(E_3)\cos\{4(\varphi_1+\varphi_2+\varphi_3)\}\\ &+\tfrac{1}{3}R_{31}(E_1)R_{31}(E_2)R_{31}(E_3)\cos\{2(\varphi_1+\varphi_2+\varphi_3)\}\\ &+\tfrac{1}{4}R_{22}(E_1)R_{22}(E_2)R_{22}(E_3)\}\\ &+Z_7\{\tfrac{2}{3}[R_{32}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\\ &+\tfrac{1}{2}[R_{21}(E_1)R_{21}(E_2)R_{10}(E_3)+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\}\\ &+Z_3Z_6\{\tfrac{2}{9}[R_{43}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)-\tfrac{11}{4}R_{21}(E_1)R_{21}(E_2)R_{21}(E_3)\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)-\tfrac{3}{4}R_{30}(E_1)R_{30}(E_2)R_{30}(E_3)\\ &\times\cos\{3(\varphi_1+\varphi_2+\varphi_3)\}\}\\ &+Z_4Z_5\{\tfrac{1}{4}[R_{43}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}]\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)+2[R_{32}(E_1)R_{21}(E_2)R_{10}(E_3)\\ &+\text{perm.}]\cos(\varphi_1+\varphi_2+\varphi_3)\}\\ &-Z_3^2Z_5\{\tfrac{1}{2}[R_{41}(E_1)R_{30}(E_2)R_{30}(E_3)+\text{cyc.}]\cos\{3(\varphi_1\\ &+\varphi_2+\varphi_3)\}+[R_{32}(E_1)R_{21}(E_2)R_{21}(E_3)+\text{cyc.}]\\ &\times\cos(\varphi_1+\varphi_2+\varphi_3)\}+Z_3Z_4^2\{\tfrac{1}{16}[R_{54}(E_1)R_{10}(E_2)R_{10}(E_3)\\ &+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)+\tfrac{1}{8}[R_{32}(E_1)R_{32}(E_2)R_{10}(E_3)\end{aligned}$$

$$+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\}$$
$$-Z_3^3 Z_4\{\tfrac{1}{12}[R_{52}(E_1)R_{30}(E_2)R_{30}(E_3)+\text{cyc.}]$$
$$\times\cos\{3(\varphi_1+\varphi_2+\varphi_3)\}+\tfrac{1}{4}[R_{43}(E_1)R_{21}(E_2)R_{21}(E_3)$$
$$+\text{cyc.}]\cos(\varphi_1+\varphi_2+\varphi_3)\}$$
$$+Z_3^5\{\tfrac{1}{60}R_{50}(E_1)R_{50}(E_2)R_{50}(E_3)\cos\{5(\varphi_1+\varphi_2+\varphi_3)\}$$
$$+\tfrac{1}{12}R_{41}(E_1)R_{41}(E_2)R_{41}(E_3)\cos\{3(\varphi_1+\varphi_2+\varphi_3)\}$$
$$+\tfrac{1}{6}R_{32}(E_1)R_{32}(E_2)R_{32}(E_3)\cos(\varphi_1+\varphi_2+\varphi_3)\}$$
$$+\ldots\ldots\Big]. \quad (67)$$

This result is to be compared with equation (III-2) in the previous paper (Naya, Nitta & Oda, 1964), which dealt with an example on $P\bar{1}$ with three real structure factors $E_1=E_1s_1$, $E_2=E_2s_2$, $E_3=E_3s_3$ under the condition $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$. Both results are in a complete correspondence to each other.

Bertaut (1956) and Karle & Hauptman (1956) carried out also the calculation of the joint probability distribution of the complex structure factors on the same example as the present one. However, their results were only to the approximation $O(N^{-\frac{1}{2}})$, namely up to the second term in (67).

3·3 *Probability distribution of magnitude of a single complex structure factor: P(E)*

In this section, it is shown that the probability distribution of magnitude of a single complex structure factor, or Wilson's probability distribution, can be treated as a simple case of the general relation (51). If an expansion series up to $O(N^{-2})$ is considered, the probability distribution of a complex structure factor $P(\mathbf{E})$ has the form

$$P(\mathbf{E})=\frac{1}{\pi}\exp(-E^2)\Big[1+Z_4\{\Sigma_4-\tfrac{1}{2}\Sigma_{22}\}$$
$$+Z_6\{\Sigma_6-\Sigma_{42}+\tfrac{1}{3}\Sigma_{222}\}$$
$$+\frac{Z_4^2}{2}\{\Sigma_{44}-\Sigma_{422}+\tfrac{1}{4}\Sigma_{2222}\}+\ \ldots\ldots\Big], \quad (68)$$

in which $\Sigma_{ab\ldots f}$'s with the subscripts of odd values are not included. It is easily shown that there are relations

$$\Sigma_4-\tfrac{1}{2}\Sigma_{22}=-\tfrac{1}{4}R_{22}(E)\,,\quad \Sigma_6-\Sigma_{42}+\tfrac{1}{3}\Sigma_{222}=\tfrac{1}{9}R_{33}(E)\,,$$
$$\Sigma_{44}-\Sigma_{422}+\tfrac{1}{4}\Sigma_{2222}=\tfrac{1}{16}R_{44}(E)\,. \quad (69)$$

Substituting (69) in (68) and integrating (68) multiplied by E with regard to φ, the probability distribution of the magnitude of a single complex structure factor is given as

$$P(E)\equiv\int_0^{2\pi}P(\mathbf{E})Ed\varphi=2E\exp(-E^2)$$
$$\times\Big[1-\frac{Z_4}{4}R_{22}(E)+\frac{Z_6}{9}R_{33}(E)+\frac{Z_4^2}{32}R_{44}(E)+\ldots\Big]. \quad (70)$$

This result is the explicit form of the formal expression

$$P(E)=\int_0^{2\pi}P(\mathbf{E})Ed\varphi$$
$$=2E\exp(-E^2)\sum_{n=0}^{\infty}\frac{\langle R_{n,n}(E)\rangle}{(n!)^2}R_{n,n}(E)\,, \quad (71)$$

which can be derived by the integration of (47) with regard to φ. Here it may be noted that the expression shown by Bertaut [1956, equation (28)] is nothing but the non-vanishing first two terms of (71).

Now let us calculate the expected value for $|\mathbf{E}|^p=E^p$ by the use of (70). Using a relation

$$\int_0^{\infty}2E^{p+1}\exp(-E^2)R_{n,n}(E)dE$$
$$=\Gamma\left(\frac{p+2}{2}\right)2^{-n}p(p-2)(p-4)\ldots[p-(2n-2)] \quad (72)$$

(Appendix VI), we obtain

$$\langle E^p\rangle=\int_0^{\infty}E^pP(E)dE=\Gamma\left(\frac{p+2}{2}\right)\Big[1-\frac{Z_4}{16}p(p-2)$$
$$+\frac{Z_6}{72}p(p-2)(p-4)$$
$$+\frac{Z_4^2}{512}p(p-2)(p-4)(p-6)+\ldots\Big]. \quad (73)$$

In a particular case of equal atoms, for which $Z_4=N^{-1}$, $Z_6=Z_4^2=N^{-2}$,

$$\langle E^p\rangle=\Gamma\left(\frac{p+2}{2}\right)\Big[1-\frac{1}{16N}p(p-2)$$
$$+\frac{1}{4608N^2}p(p-2)(p-4)(9p+10)+\ldots\Big]. \quad (74)$$

The formula (74) agrees with that calculated by Karle & Hauptman (1958) from their new joint probability distribution method.

3·4 *Joint probability distribution of two structure invariants: P(Φ₁, Φ₂)*

Consider five complex structure factors $\mathbf{E}_1$, $\mathbf{E}_2$, $\mathbf{E}_3$, $\mathbf{E}_4$, $\mathbf{E}_5$ related by $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$ and $\mathbf{h}_1+\mathbf{h}_4+\mathbf{h}_5=0$. Then,

$$\Phi_1\equiv\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}\equiv\varphi_1+\varphi_2+\varphi_3$$

and

$$\Phi_2\equiv\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_4}+\varphi_{\mathbf{h}_5}\equiv\varphi_1+\varphi_4+\varphi_5 \quad (75)$$

are the two structure invariants. As was suggested by Karle & Hauptman (1956), these two structure invariants possess a sort of interaction not only between their magnitude but also between their signs.

To study more explicitly the nature of the interaction, calculation of the joint probability of these two structure invariants is carried out as follows. $P(\mathbf{E}_1, \mathbf{E}_2, \mathbf{E}_3, \mathbf{E}_4, \mathbf{E}_5)$ is set up by using the fundamental equation (51), and then, following the relation (21), the joint probabilities of phase angles given in §1 are obtained. The calculation up to $O(N^{-3/2})$ shows that the joint probability distribution for the two phases Φ_1, Φ_2 corresponding to (11) is given by

$$P(\Phi_1, \Phi_2)=\frac{1}{(2\pi)^2}[1+2\langle\cos\Phi_1\rangle\cos\Phi_1+2\langle\cos\Phi_2\rangle \times\cos\Phi_2+2\langle\cos 2\Phi_1\rangle\cos 2\Phi_1+2\langle\cos 2\Phi_2\rangle\cos 2\Phi_2 +2\langle\cos(\Phi_1+\Phi_2)\rangle\cos(\Phi_1+\Phi_2)+2\langle\cos(\Phi_1-\Phi_2)\rangle \times\cos(\Phi_1-\Phi_2)+2\langle\cos 3\Phi_1\rangle\cos 3\Phi_1+2\langle\cos 3\Phi_2\rangle \times\cos 3\Phi_2+2\langle\cos(2\Phi_1+\Phi_2)\rangle\cos(2\Phi_1+\Phi_2) +2\langle\cos(\Phi_1+2\Phi_2)\rangle\cos(\Phi_1+2\Phi_2)+2\langle\cos(2\Phi_1 -\Phi_2)\rangle\cos(2\Phi_1-\Phi_2)+2\langle\cos(\Phi_1-2\Phi_2)\rangle\cos(\Phi_1 -2\Phi_2)+\ldots\ldots], \qquad (76)$$

where the expected values are given by

$$\langle\cos\Phi_1\rangle=Z_3R_{10}(E_1)R_{10}(E_2)R_{10}(E_3) -\frac{Z_5}{2}[R_{21}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}] -\frac{Z_3Z_4}{4}[R_{32}(E_1)R_{10}(E_2)R_{10}(E_3)+\text{cyc.}] +\frac{Z_3Z_4}{4}R_{10}(E_1)R_{10}(E_2)(R_{10})(E_3)[R_{22}(E_1)+\text{cyc.}] +\frac{Z_3^3}{2}R_{21}(E_1)R_{21}(E_2)R_{21}(E_3) -Z_3^3R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)R_{11}(E_1)R_{11}(E_2)R_{11}(E_3) -Z_5R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)[R_{11}(E_4)+R_{11}(E_5)] +Z_3Z_4R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)R_{11}(E_4)R_{11}(E_5) +Z_3^3R_{21}(E_1)R_{10}(E_2)R_{10}(E_3)R_{11}(E_4)R_{11}(E_5) -Z_3^3R_{10}(E_1)R_{10}(E_2)R_{10}(E_3)R_{11}(E_1)R_{11}(E_4)R_{11}(E_5), \qquad (77)$$

and

$$\langle\cos\Phi_2\rangle=\text{✡}, \qquad (78)$$

(The symbol ✡ means that the set $\boldsymbol{E}_1$, $\boldsymbol{E}_2$, $\boldsymbol{E}_3$ and the set $\boldsymbol{E}_1$, $\boldsymbol{E}_4$, $\boldsymbol{E}_5$ in the former equation are interchanged with each other).

$$\langle\cos 2\Phi_1\rangle=\frac{Z_3^2}{2}R_{20}(E_1)R_{20}(E_2)R_{20}(E_3), \qquad (79)$$

$$\langle\cos 2\Phi_2\rangle=\text{✡}, \qquad (80)$$

$$\langle\cos(\Phi_1+\Phi_2)\rangle =Z_3^2R_{20}(E_1)R_{10}(E_2)R_{10}(E_3)R_{10}(E_4)R_{10}(E_5), \qquad (81)$$

$$\langle\cos(\Phi_1-\Phi_2)\rangle=Z_4R_{10}(E_2)R_{10}(E_3)R_{10}(E_4)R_{10}(E_5) +Z_3^2R_{11}(E_1)R_{10}(E_2)R_{10}(E_3)R_{10}(E_4)R_{10}(E_5), \qquad (82)$$

$$\langle\cos 3\Phi_1\rangle=\frac{Z_3^3}{6}R_{30}(E_1)R_{30}(E_2)R_{30}(E_3), \qquad (83)$$

$$\langle\cos 3\Phi_2\rangle=\text{✡}, \qquad (84)$$

$$\langle\cos(2\Phi_1+\Phi_2)\rangle =\frac{Z_3^3}{2}R_{30}(E_1)R_{20}(E_2)R_{20}(E_3)R_{10}(E_4)R_{10}(E_5), \qquad (85)$$

$$\langle\cos(\Phi_1+2\Phi_2)\rangle=\text{✡}, \qquad (86)$$

$$\langle\cos(2\Phi_1-\Phi_2)\rangle =Z_3Z_4R_{10}(E_1)R_{20}(E_2)R_{20}(E_3)R_{10}(E_4)R_{10}(E_5) +\frac{Z_3^3}{2}R_{21}(E_1)R_{20}(E_2)R_{20}(E_3)R_{10}(E_4)R_{10}(E_5), \qquad (87)$$

$$\langle\cos(\Phi_1-2\Phi_2)\rangle=\text{✡}. \qquad (88)$$

In the case of equal atoms for which $Z_3^2=Z_4=N^{-1}$, it proves that relations (81) and (85) become equal to (82) and (87), respectively. However, these equalities do not hold for non-equal atoms. Thus, the calculation of (76) in the approximation to $O(N^{-3/2})$ shows, with (16), (17) and (18), that the correlation between the invariants Φ_1 and Φ_2 appears only in their magnitudes in the case of the equal atoms, while the correlation is quite appreciable not only in their magnitudes but also in their signs in the case of non-equal atoms.

Conclusion

We have presented a systematic theory to derive probability formulae which may be used for determination of the phase angles in non-centrosymmetric structure factors; that is, from the joint probability distribution $P(\varphi_1,\ldots,\varphi_m)$ for a set of the related phase angles, we derive the corresponding expected values *via* reduced probabilities, and, finally, the various conditional probabilities for structure invariants. The functional form of $P(\varphi_1,\ldots,\varphi_m)$ in equation (2) or (7) has an orthogonal expansion form, corresponding to the similar form of the sign joint probability distribution $P(s_1,\ldots,s_m)$ given in our previous paper for the centrosymmetric case. The results obtained seem to be of significance in the practical procedure for determining angles of structure invariants and their individual phase angles.

By making use of general space-group-symmetry operators, our calculation of the joint probability distribution of noncentrosymmetric structure factors $P(\boldsymbol{E}_1,\ldots,\boldsymbol{E}_m)$ has been carried out in a more general form than in other works. As results, we obtained the general expressions (51) and (52) for the joint probability distribution of complex structure factors. This probability distribution can, in principle, be applied to the case with a greater number of structure factors in any non-centrosymmetric space group.

These equations have the form of an expansion series of the orthogonal terms with the weighting function $(1/\pi^m)\exp\{-(E_1^2+\ldots+E_m^2)\}$. This expansion has not been found in the results given by Bertaut (1956) and Karle & Hauptman (1956). The Laguerre polynomials found in this paper correspond to the Hermite type ones found by Bertaut (1955) in the case of centrosymmetry.

APPENDIX I
Moment generating function

The method of the moment generating function was used by Klug (1958) for deriving the joint probability distribution of the real structure factors of centrosymmetric crystals. In this Appendix it is shown how to extend the method to the case of complex-valued structure factors.

We write the trigonometric structure factor ξ_j and the normalized structure factor $E_{\mathbf{h}}$ in the following forms,

$$\xi_j(\mathbf{h})=\eta_j(\mathbf{h})+i\zeta_j(\mathbf{h})\,,\quad E_{\mathbf{h}}=R_{\mathbf{h}}+iI_{\mathbf{h}}\,. \qquad \text{(I–1)}$$

These functions are related by

$$E_{\mathbf{h}}=\sum_{j=1}^{t}\psi_j\xi_j(\mathbf{h})\,, \qquad \text{(I–2)}$$

where ψ_j is the normalized atomic structure factor of the jth atom, $t(=N/S)$ the total number of atoms in the asymmetric unit. (I-2) with (I-1) gives

$$R_{\mathbf{h}}=\sum_{j=1}^{t}\psi_j\eta_j(\mathbf{h})\,,\quad I_{\mathbf{h}}=\sum_{j=1}^{t}\psi_j\zeta_j(\mathbf{h})\,. \qquad \text{(I-3)}$$

Let $\mathfrak{M}(v_1,\ldots,v_m,w_1,\ldots,w_m)$ be the moment generating function. By the use of the mathematical expectation operator $\mathfrak{E}$ (Klug, 1958) and taking into account of relation (I-3), this function is expressed as

$$\begin{aligned}
&\mathfrak{M}(v_1,\ldots,v_m,w_1,\ldots,w_m)\equiv\mathfrak{M}(\mathbf{u}_1,\ldots,\mathbf{u}_m)\\
&=\mathfrak{E}\exp\,[v_1R_{\mathbf{h}_1}+v_2R_{\mathbf{h}_2}+\ldots+v_mR_{\mathbf{h}_m}]\\
&\times\exp\,[w_1I_{\mathbf{h}_1}+w_2I_{\mathbf{h}_2}+\ldots+w_mI_{\mathbf{h}_m}]\\
&=\mathfrak{E}\exp\,[\{v_1\sum_{j=1}^{t}\psi_j\eta_j(\mathbf{h}_1)\}+\{v_2\sum_{j=1}^{t}\psi_j\eta_j(\mathbf{h}_2)\}\\
&+\ldots+\{v_m\sum_{j=1}^{t}\psi_j\eta_j(\mathbf{h}_m)\}]\\
&\times\exp\,[\{w_1\sum_{j=1}^{t}\psi_j\zeta_j(\mathbf{h}_1)\}+\{w_2\sum_{j=1}^{t}\psi_j\zeta_j(\mathbf{h}_2)\}\\
&+\ldots+\{w_m\sum_{j=1}^{t}\psi_j\zeta_j(\mathbf{h}_m)\}]\\
&=\mathfrak{E}\exp\,[\psi_1\{v_1\eta_1(\mathbf{h}_1)+w_1\zeta_1(\mathbf{h}_1)\}+\psi_1\{v_2\eta_1(\mathbf{h}_2)\\
&+w_2\zeta_1(\mathbf{h}_2)\}+\ldots+\psi_1\{v_m\eta_1(\mathbf{h}_m)+w_m\zeta_1(\mathbf{h}_m)\}]\\
&\times\mathfrak{E}\exp\,[\psi_2\{v_1\eta_2(\mathbf{h}_1)+w_1\zeta_2(\mathbf{h}_1)\}+\psi_2\{v_2\eta_2(\mathbf{h}_2)\\
&+w_2\zeta_2(\mathbf{h}_2)\}+\ldots+\psi_2\{v_m\eta_2(\mathbf{h}_m)+w_m\zeta_2(\mathbf{h}_m)\}]\\
&\times\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\\
&\times\mathfrak{E}\exp\,[\psi_t\{v_1\eta_t(\mathbf{h}_1)+w_1\zeta_t(\mathbf{h}_1)\}+\psi_t\{v_2\eta_t(\mathbf{h}_2)\\
&+w_2\zeta_t(\mathbf{h}_2)\}+\ldots+\psi_t\{v_m\eta_t(\mathbf{h}_m)+w_m\zeta_t(\mathbf{h}_m)\}]\,.
\end{aligned} \qquad \text{(I-4)}$$

Noting that

$$\mathbf{u}=v+iw\,,\quad \xi=\eta+i\zeta\,,$$

we have

$$v\eta+w\zeta=\tfrac{1}{2}(\mathbf{u}^*\xi+\mathbf{u}\xi^*)\,.$$

Then

$$\begin{aligned}
\mathfrak{M}(\mathbf{u}_1,\ldots,\mathbf{u}_m)&=\mathfrak{E}\exp\Big[\psi_1\Big\{\frac{\mathbf{u}_1^*}{2}\xi_1(\mathbf{h}_1)+\frac{\mathbf{u}_1}{2}\xi_1^*(\mathbf{h}_1)\Big\}\\
&+\ldots+\psi_1\Big\{\frac{\mathbf{u}_m^*}{2}\xi_1(\mathbf{h}_m)+\frac{\mathbf{u}_m}{2}\xi_1^*(\mathbf{h}_m)\Big\}\Big]\\
&\times\mathfrak{E}\exp\Big[\psi_2\Big\{\frac{\mathbf{u}_1^*}{2}\xi_2(\mathbf{h}_1)+\frac{\mathbf{u}_1}{2}\xi_2^*(\mathbf{h}_1)\Big\}\\
&+\ldots+\psi_2\Big\{\frac{\mathbf{u}_m^*}{2}\xi_2(\mathbf{h}_m)+\frac{\mathbf{u}_m}{2}\xi_2^*(\mathbf{h}_m)\Big\}\Big]\\
&\times\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\\
&\times\mathfrak{E}\exp\Big[\psi_t\Big\{\frac{\mathbf{u}_1^*}{2}\xi_t(\mathbf{h}_1)+\frac{\mathbf{u}_1}{2}\xi_t^*(\mathbf{h}_1)\Big\}\\
&+\ldots+\psi_t\Big\{\frac{\mathbf{u}_m^*}{2}\xi_t(\mathbf{h}_m)+\frac{\mathbf{u}_m}{2}\xi_t^*(\mathbf{h}_m)\Big\}\Big]\,.
\end{aligned} \qquad \text{(I-5)}$$

Comparison of this expression with Klug's formula [1958, equation (2·2)] indicates that our moment generating function is also similar to Klug's (C·6); namely,

$$\mathfrak{M}(\mathbf{u}_1,\ldots,\mathbf{u}_m)=\exp\Big[\sum_{n=2}^{\infty}\frac{Z_n}{S}\mathfrak{L}_n\Big]\,. \qquad \text{(I-6)}$$

$\mathfrak{L}_n$ is given, in the present case, by

$$\begin{aligned}
\mathfrak{L}_n=&\sum_{\alpha+\alpha^*)+\ldots+(\omega+\omega^*)=n}\left(\frac{1}{\sqrt{\tau\varepsilon_1}}\right)^{\alpha+\alpha^*}\\
&\times\ldots\times\left(\frac{1}{\sqrt{\tau\varepsilon_m}}\right)^{\omega+\omega^*}\times\frac{k_{\alpha\ldots\omega}^{\alpha^*\ldots\omega^*}}{\alpha!\alpha^*!\ldots\omega!\omega^*!}\left(\frac{\mathbf{u}_1^*}{2}\right)^{\alpha}\\
&\times\left(\frac{\mathbf{u}_1}{2}\right)^{\alpha^*}\ldots\left(\frac{\mathbf{u}_m^*}{2}\right)^{\omega}\left(\frac{\mathbf{u}_m}{2}\right)^{\omega^*},
\end{aligned} \qquad \text{(I-7)}$$

in accordance with the moments defined by (23). The coefficients $\left(\frac{1}{\sqrt{\tau\varepsilon_1}}\right)^{\alpha+\alpha^*},\ldots,\left(\frac{1}{\sqrt{\tau\varepsilon_m}}\right)^{\omega+\omega^*}$ in (I-7) have been so introduced that the normalization condition $\langle|E|^2\rangle=1$ can be kept in cases of τ, $\varepsilon\neq1$ (*cf.* Bertaut, 1960). In the particular case that the degree $n=(\alpha+\alpha^*)+\ldots+(\omega+\omega^*)$ is equal to 2, the relations (24) and (29) give

$$k_{10\ldots0}^{10\ldots0}=\tau^2s\varepsilon_1\,,\qquad k_{010\ldots0}^{010\ldots0}=\tau^2s\varepsilon_2,\ldots,\qquad k_{0\ldots01}^{0\ldots01}=\tau^2s\varepsilon_m\,, \qquad \text{(I-8)}$$

and for all the other cumulants of the degree 2

$$k_{\alpha\ldots\omega}^{\alpha^*\ldots\omega^*}=0\,. \qquad \text{(I-9)}$$

From (34), (I-7), (I-8) and (I-9), the first term in (I-6) corresponding to $n=2$ is given by

$$\begin{aligned}
\exp\Big[\frac{Z_2}{S}\mathfrak{L}_2\Big]&=\exp\,[\tfrac{1}{4}\mathbf{u}_1^*\mathbf{u}_1+\ldots+\tfrac{1}{4}\mathbf{u}_m^*\mathbf{u}_m]\\
&=\exp\,\{\tfrac{1}{4}(u_1^2+\ldots+u_m^2)\}\,.
\end{aligned} \qquad \text{(I-10)}$$

This relation and (I-6) lead to the formula (32).

Inversion transformation of the moment generating function (I-6) is also easily obtained by an extension of Klug's method, as follows

$$P(\mathbf{E}_1,\ldots,\mathbf{E}_m)\equiv P(R_1,\ldots,R_m,I_1,\ldots,I_m)$$
$$=\frac{1}{(2\pi)^{2m}}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\mathfrak{M}(iv_1,\ldots,iv_m,iw_1,\ldots,iw_m)$$
$$\times\exp\left[-i\{(v_1R_1+w_1I_1)+\ldots+(v_mR_m+w_mI_m)\}\right]$$
$$\times dv_1\ldots dv_m dw_1\ldots dw_m$$
$$=\frac{1}{(2\pi)^{2m}}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\mathfrak{M}(i\mathbf{u}_1,\ldots,i\mathbf{u}_m)$$
$$\times\exp\left[-i\left\{\left(\frac{\mathbf{u}_1}{2}\mathbf{E}_1^*+\frac{\mathbf{u}_1^*}{2}\mathbf{E}_1\right)\right.\right.$$
$$\left.\left.+\ldots+\left(\frac{\mathbf{u}_m}{2}\mathbf{E}_m^*+\frac{\mathbf{u}_m^*}{2}\mathbf{E}_m\right)\right\}\right]d\mathbf{u}_1\ldots d\mathbf{u}_m\,. \quad \text{(I-11)}$$

APPENDIX II

The Weber–Sonine integral formula is given by

$$\int_0^{\infty}J_\nu(at)\,e^{-p^2t^2}\,t^{\mu-1}\,dt=\frac{\left(\frac{a}{2p}\right)^{\nu}\Gamma\left(\frac{\nu+\mu}{2}\right)}{2p^{\mu}\,\Gamma(\nu+1)}$$
$${}_1F_1\left(\frac{\nu+\mu}{2};\,\nu+1;\,-\frac{a^2}{4p^2}\right), \quad \text{(II-1)}$$
$$\left[\Re(\nu+\mu)>0,\ |\arg p|<\frac{\pi}{4},\ a>0\right].$$

When $p=\frac{1}{2}$, $\nu=n-n^*$, $\mu=n+n^*+2$, $a=E$ and $t=u$ are introduced in (II-1), we obtain

$$\frac{(-1)^{n^*}}{2^{n+n^*+1}}\int_0^{\infty}\exp\left(-\tfrac{1}{4}u^2\right)J_{n-n^*}(Eu)\,u^{n+n^*+1}\,du$$
$$=(-1)^{n^*}\frac{\Gamma(n+1)}{\Gamma(n-n^*+1)}E^{n-n^*}$$
$$\times{}_1F_1(n+1;\,n-n^*+1;\,-E^2)\,, \quad \text{(II-2)}$$

where the Kummer function

$${}_1F_1(a;b;x)\equiv\sum_{m=0}^{\infty}\frac{\Gamma(a+m)}{\Gamma(a)}\,\frac{\Gamma(b)}{\Gamma(b+m)}\,\frac{x^m}{m!} \quad \text{(II-3)}$$

has the following property:

$${}_1F_1(a;b;x)=e^x{}_1F_1(b-a;b;-x)\,. \quad \text{(II-4)}$$

If we substitute $a=n+1$, $b=n-n^*+1$ and $x=-E^2$ in (II-4), the following relation is obtained

$${}_1F_1(n+1;n-n^*+1;-E^2)$$
$$=\exp(-E^2){}_1F_1(-n^*;n-n^*+1;E^2)\,. \quad \text{(II-5)}$$

The Kummer function ${}_1F_1$ and the Laguerre polynomial $L_\nu^{(\mu)}(x)$ are related by

$$L_\nu^{(\mu)}(x)=\frac{\Gamma(\nu+\mu+1)}{\Gamma(\nu+1)\,\Gamma(\mu+1)}\,{}_1F_1(-\nu;\mu+1;x)\,. \quad \text{(II-6)}\dagger$$

If we substitute $\nu=n^*$, $\mu=n-n^*$, $x=E^2$ in this relation, then the following relation holds:

$${}_1F_1(-n^*;n-n^*+1;E^2)$$
$$=\frac{\Gamma(n-n^*+1)\,\Gamma(n^*+1)}{\Gamma(n+1)}\,L_{n^*}^{(n-n^*)}(E^2)\,. \quad \text{(II-7)}$$

Substitution of these relations (II-2), (II-5) and (II-7) into (41) leads to the expressions (42), (43) and (44).

APPENDIX III

Let us prove the orthogonality relation

$$\frac{1}{\pi}\int_0^{\infty}\int_0^{2\pi}\exp(-E^2)\,K^*_{n,n^*}(\mathbf{E})\,K_{m,m^*}(\mathbf{E})\,E\,dE\,d\varphi$$
$$=n!\,n^*!\,\delta_{nm}\,\delta_{n^*m^*}\,, \quad \text{(III-1)}$$

found among the functions $K_{n,n^*}(\mathbf{E})$. If we substitute $K_{n,n^*}(\mathbf{E})=R_{n,n^*}(E)\exp\{-i(n-n^*)\varphi\}$ in the integrand of the left hand side of (III-1), then the following relation is obtained;

$$\int_0^{\infty}\exp(-E^2)\,R_{n,n^*}(E)\,R_{m,m^*}(E)\,E\,dE$$
$$\times\frac{1}{\pi}\int_0^{2\pi}\exp\{i(n-n^*)\varphi\}\exp\{-i(m-m^*)\varphi\}\,d\varphi$$
$$=\int_0^{\infty}\exp(-E^2)\,R_{n,n^*}(E)\,R_{m,m^*}(E)2E\,dE.\delta_{n-n^*,m-m^*}\,. \quad \text{(III-2)}$$

When $n-n^*$ is not equal to $m-m^*$, (III-2) becomes zero. If $n-n^*$ is equal to $m-m^*$, (III-2) is written as

$$\int_0^{\infty}\exp(-E^2)\,R_{n,n^*}(E)\,R_{m,m^*}(E)\,2\,E\,dE$$
$$=(-1)^{n^*+m^*}\,n^*!\,m^*!\int_0^{\infty}\exp(-E^2)\,E^{2\mu}\,L_{n^*}^{(\mu)}(E^2)\,L_{m^*}^{(\mu)}(E^2)$$
$$\times 2\,E\,dE\,, \quad \text{(III-3)}$$

where

$$\mu\equiv n-n^*=m-m^*\,.$$

With the orthogonality relations for the Laguerre polynomials

$$\int_0^{\infty}e^{-x}x^{\mu}\,L_\nu^{(\mu)}(x)\,L_\lambda^{(\mu)}(x)\,dx=\delta_{\nu\lambda}\frac{(\nu+\mu)!}{\nu!}, \quad \text{(III-4)}$$

(III-3) is expressed as

$$\int_0^{\infty}\exp(-E^2)\,R_{n,n^*}(E)\,R_{m,m^*}(E)\,2E\,dE$$
$$=(-1)^{n^*+m^*}\,n^*!\,m^*!\,\delta_{n^*m^*}\frac{(n^*+\mu)!}{n^*!}=n!\,n^*!\,\delta_{n^*m^*}\,. \quad \text{(III-5)}$$

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† It is of interest that the Kummer function is related to the Hermite polynomials as

$$H_{2\nu}(x)=(-2)^{\nu}\,\nu!\,L_\nu^{(-\frac{1}{2})}(x^2)=(-1)^{\nu}(2\nu-1)!!\,{}_1F_1(-\nu;\,\tfrac{1}{2};\,x^2)\,,$$
$$H_{2\nu+1}(x)=(-2)^{\nu}\,\nu!\,\sqrt{2}x\,L_\nu^{(\frac{1}{2})}(x^2)$$
$$=(-1)^{\nu}(2\nu+1)!!\,\sqrt{2}x\,{}_1F_1(-\nu;\,\tfrac{3}{2};\,x^2)$$

As the summary of these results, we can obtain the orthogonal relation (III-1).

APPENDIX IV

The associated Laguerre polynomials satisfy the relation

$$L_{\nu+\mu}^{(-\mu)}(x) = \frac{(-1)^{\mu}\,\nu!}{(\nu+\mu)!}\,x^{\mu}\,L_{\nu}^{(\mu)}(x)\,. \qquad \text{(IV-1)}$$

Substitution of relations such as $x=E^2$, $-\mu=n-n^*$, $\nu=n$ into (IV-1) gives the following relation:

$$L_{n^*}^{(n-n^*)}(E^2) = \frac{n!}{n^*!}\,(-1)^{n^*-n}\,E^{2(n^*-n)}\,L_{n}^{(n^*-n)}(E^2). \qquad \text{(IV-2)}$$

Then

$$\begin{aligned} R_{n,n^*}(E) &= (-1)^{n^*}\,n^*!\,E^{n-n^*}\,L_{n^*}^{(n-n^*)}(E^2) \\ &= (-1)^{n}\,n!\,E^{n^*-n}\,L_{n}^{(n^*-n)}(E^2) = R_{n^*,n}(E)\,, \end{aligned} \qquad \text{(IV-3)}$$

which proves the symmetrical property of $R_{n,n^*}(E)$ in n and n^*.

As well known, the associated Laguerre polynomials are given by

$$L_{\nu}^{(\mu)}(x) = \sum_{j=0}^{\nu} \binom{\nu+\mu}{\nu-j}\frac{(-x)^j}{j!}\,, \quad (\nu,\mu=0,1,2,\ldots)\,. \qquad \text{(IV-4)}$$

This formula is rewritten with $j=\nu-m$ as

$$L_{\nu}^{(\mu)}(x) = \sum_{m=0}^{\nu} \binom{\nu+\mu}{m}\frac{(-x)^{\nu-m}}{(\nu-m)!}\,. \qquad \text{(IV-5)}$$

Substitution of $\nu=n^*$, $\mu=n-n^*$, $x=E^2$ in this formula gives

$$L_{n^*}^{(n-n^*)}(E^2) = \sum_{m=0}^{n^*} \binom{n}{m}\frac{(-E^2)^{n^*-m}}{(n^*-m)!}\,. \qquad \text{(IV-6)}$$

Thus we obtain an explicit form of the polynomical $R_{n,n^*}(E)$ as follows

$$\begin{aligned} R_{n,n^*}(E) &= (-1)^{n^*}\,n^*!\,E^{n-n^*}\,L_{n^*}^{(n-n^*)}(E^2) \\ &= \sum_{m=0}^{n^*} (-1)^m\,m!\binom{n}{m}\binom{n^*}{m}E^{n+n^*-2m}\,, \quad (n\geq n^*)\,. \end{aligned} \qquad \text{(IV-7)}$$

APPENDIX V

Table 2. *Particular forms of $R_{n,n^*}(E)$*

Order	$R_{n,n^*}(E)$	Order	$R_{n,n^*}(E)$
1	$R_{1,0}(E)=E$	6	$R_{6,0}(E)=E^6$
			$R_{5,1}(E)=E^6-5E^4$
2	$R_{2,0}(E)=E^2$		$R_{4,2}(E)=E^6-8E^4+12E^2$
	$R_{1,1}(E)=E^2-1$		$R_{3,3}(E)=E^6-9E^4+18E^2-6$
3	$R_{3,0}(E)=E^3$	7	$R_{7,0}(E)=E^7$
	$R_{2,1}(E)=E^3-2E$		$R_{6,1}(E)=E^7-6E^5$
			$R_{5,2}(E)=E^7-10E^5+20E^3$
4	$R_{4,0}(E)=E^4$		$R_{4,3}(E)=E^7-12E^5+36E^3-24E$
	$R_{3,1}(E)=E^4-3E^2$		
	$R_{2,2}(E)=E^4-4E^2+2$	8	$R_{8,0}(E)=E^8$
			$R_{7,1}(E)=E^8-7E^6$
5	$R_{5,0}(E)=E^5$		$R_{6,2}(E)=E^8-12E^6+30E^4$
	$R_{4,1}(E)=E^5-4E^3$		$R_{5,3}(E)=E^8-15E^6+60E^4-60E^2$
	$R_{3,2}(E)=E^5-6E^3+6E$		$R_{4,4}(E)=E^8-16E^6+72E^4-96E^2+24$

Table 3. *Numerical values of polynomials $R_{n,n^*}(E)$*

E	0·6	0·8	1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4
$R_{1,0}$	+0·600	+0·800	+1·000	+1·200	+1·400	+1·600	+1·800	+2·000	+2·200	+2·400
$R_{2,0}$	+0·360	+0·640	+1·000	+1·440	+1·960	+2·560	+3·240	+4·000	+4·840	+5·760
$R_{1,1}$	−0·640	−0·360	0·000	+0·440	+0·960	+1·560	+2·240	+3·000	+3·840	+4·760
$R_{3,0}$	+0·216	+0·512	+1·000	+1·728	+2·744	+4·096	+5·832	+8·000	+10·648	+13·824
$R_{2,1}$	−0·984	−1·088	−1·000	−0·672	−0·056	+0·896	+2·232	+4·000	+6·248	+9·024
$R_{4,0}$	+0·130	+0·410	+1·000	+2·074	+3·842	+6·554	+10·498	+16·000	+23·426	+33·178
$R_{3,1}$	−0·950	−1·510	−2·000	−2·246	−2·038	−1·126	+0·778	+4·000	+8·906	+15·898
$R_{2,2}$	+0·690	−0·150	−1·000	−1·686	−1·998	−1·686	−0·462	+2·000	+6·066	+12·138
$R_{5,0}$	+0·078	+0·328	+1·000	+2·488	+5·378	+10·486	+18·896	+32·000	+51·537	+79·627
$R_{4,1}$	−0·786	−1·720	−3·000	−4·424	−5·598	−5·898	−4·432	0·000	+8·945	+24·331
$R_{3,2}$	+2·382	+2·056	+1·000	−0·680	−2·686	−4·490	−5·296	−4·000	+0·849	+11·083
$R_{6,0}$	+0·047	+0·262	+1·000	+2·986	+7·529	+16·778	+34·013	+64·000	+113·381	+191·105
$R_{5,1}$	−0·603	−1·788	−4·000	−7·384	−11·681	−15·992	−18·477	−16·000	−3·749	+25·215
$R_{4,2}$	+3·327	+4·662	+5·000	+3·674	+0·313	−4·934	−11·091	−16·000	−15·947	−5·199
$R_{3,3}$	−0·643	+2·092	+4·000	+4·240	+2·231	−2·128	−8·149	−14·000	−16·333	−9·817

APPENDIX VI

Derivation of formula (72)

Let the integration of the left hand side of equation (72) be denoted by Q_n,

$$Q_n = \int_0^\infty 2\,E^{p+1} \exp(-E^2)\, R_{n,n}(E)\, dE\,. \quad \text{(VI-1)}$$

Substituting the polynomial

$$R_{n,n}(E) = (-1)^n n! L_n^{(o)}(E^2) \quad \text{(VI-2)}$$

into (VI-1), and then putting $E^2 = x$, Q_n is rewritten

$$Q_n = (-1)^n\, n! \int_0^\infty e^{-x} x^{p/2} L_n^{(o)}(x)\, dx\,, \quad \text{(VI-3)}$$

where $L_n^{(o)}(x)$ is the Laguerre polynomial $L_n(x)$.

In order to carry out the integration of (VI-3), it is convenient to make use of the generating function of $L_n(x)$; namely,

$$\sum_{n=0}^{\infty} L_n(x)\, t^n = \frac{1}{(1-t)} \exp\left(-\frac{x\,t}{1-t}\right). \quad \text{(VI-4)}$$

Then, it follows from (VI-3) and (VI-4) that

$$\sum_{n=0}^{\infty} Q_n (-t)^n/n! = \int_0^\infty \exp\left(-\frac{x}{1-t}\right) x^{p/2} \frac{dx}{(1-t)}$$

$$= (1-t)^{p/2} \int_0^\infty e^{-X} X^{P/2} dX, \quad \text{(VI-5)}$$

where

$$\frac{x}{(1-t)} = X\,.$$

With the use of the well known relation

$$\int_0^\infty e^{-X} X^{P/2} dX = \Gamma\left(\frac{p+2}{2}\right), \quad \text{(VI-6)}$$

we obtain

$$\sum_{n=0}^{\infty} Q_n (-t)^n/n! = \Gamma\left(\frac{p+2}{2}\right) (1-t)^{p/2}\,. \quad \text{(VI-7)}$$

Comparison of the coefficients of the terms t^n on both sides of equation (VI-7) gives

$$Q_n = \Gamma\left(\frac{p+2}{2}\right) n! \binom{p/2}{n}$$

$$= \Gamma\left(\frac{p+2}{2}\right) \frac{p(p-2)(p-4)\ldots[p-(2n-2)]}{2^n}. \quad \text{(VI-8)}$$

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Application of a System of Linear Structure-Factor Equations to the Structure Determination of $LiB(OH)_4$*

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If the atomic parameters are known in two dimensions, it is possible to determine the atomic parameters in the third direction with the help of a system (or systems) of linear structure-factor equations. The method has been used to determine the approximate structure of $LiB(OH)_4$.

Introduction

Ott (1927) and Avrami (1938) proposed a method for the direct determination of atomic parameters from the observed $F_{\text{obs}}(hkl)$ by means of a non-linear system of equations. This method has hitherto not been applied.

Assuming a knowledge of the atomic parameters in one projection (*e.g.* x_j, y_j), the determination of the third atomic parameters (z_j) is possible with the help of a system of linear structure-factor equations if the structure factors of one particular higher level of the reciprocal lattice [$F(hkL)$ with L constant] are used (Kutschabsky, 1965).

Theory

We shall limit our consideration to centrosymmetric structures. For the space group $P\bar{1}$ the following structure-factor equations hold (x_j, y_j known; L=const.):

* Forming part of the doctorate thesis of L. Kutschabsky.