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A Theory of Phase Determination for the Four Types of Non-Centrosymmetric Space Groups $1P222$, $2P22$, $3P_12$, $3P_22$

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Joint probability distributions and relevant expected values and variances are obtained for selected (but typical) non-centrosymmetric space groups belonging to the four types $1P222$, $2P22$, $3P_12$, $3P_22$. These lead to formulas for phase determination the analysis and interpretation of which constitute the major goal of this paper. The analysis is strongly dependent on the theory of invariants and seminvariants, and the agreement between this theory and certain consequences of the probability theory is noteworthy.

1. Introduction

In a previous paper (Hauptman & Karle, 1953) it was pointed out that 'the concept of the joint or compound probability distribution forms the basis for a direct attack on the phase problem' since the probability distribution of a phase may thereby be obtained once a set of structure factor magnitudes or phases is known. The details of a program for phase determination based on this idea have been carried out for all centrosymmetric space groups (Hauptman & Karle, 1954, hereafter referred to as Monograph I). The purpose of this paper is to derive relevant probability distributions and to describe possible procedures for phase determination based on them for typical non-centrosymmetric space groups in the four types $1P222$, $2P22$, $3P_12$, $3P_22$ (Hauptman & Karle, 1956). These four types comprise roughly 45% of all the non-centrosymmetric space groups. They are characterized by the property that each component of their invariant and seminvariant moduli is two. The remaining types in which zero, three, or six appear as components of the moduli will be treated at a later date. Detailed computations are not carried out for Category 3, but the methods described for Categories 1 and 2 carry over to Category 3 in a routine way.

Although the joint probability distributions are rigorously derived, their prime purpose here is as a heuristic device. The formulas for phase determination suggested by them are analyzed *ab initio* and their exact significance and limitations critically evaluated. One important conclusion is that the presence of grossly dis-similar atoms (e.g. a small number of relatively heavy atoms) is more likely to prove a serious obstacle to the successful application of these methods than was the case for the centrosymmetric space groups. Even in the case that all atoms are equal, the number of data needed may well exceed the number contained within the copper sphere. No statement concerning the general applicability of these procedures will be made at this time. However, this paper supplies the statistical tools for estimating how reliable the methods are likely to be in any particular application.

2. Invariants and seminvariants

A knowledge of the theory of the invariants and seminvariants (Hauptman & Karle, 1956) was found to be an invaluable aid in gaining a preliminary survey of procedures for phase determination. This theory enables one to decide which phases are determined by the crystal structure and which by the magnitudes of a sufficient number of structure factors. It also enables one to fix an origin by first selecting a functional form for the structure factor and then specifying in a suitable way the values of an appropriate set of phases. Again, it provides a means for distinguishing between the two enantiomorphous structures S and S' (related to each other by reflection through a point) which are permitted by the given set of structure factor magnitudes. Finally, the theory indicates which joint distributions will be of value in determining phases, and in this way motivates the analysis.

In order to illustrate the role played by the invariants we consider in some detail the space group $P222$ belonging to the type $1P222$. The phases which are intensity invariants (and therefore also structure invariants) are all phases φ_{hkl}, where h, k, and l are all even and at least one of h, k, l is zero. These phases are the structure invariants the values of which (either 0 or π) are uniquely determined by the intensities. Only the magnitudes of the remaining phases φ_{hkl} which are structure invariants, i.e. for which h, k, and l are all even and $hkl \neq 0$, are determined by the intensities. The sign of any such phase (the magnitude of which is different from 0 and π, and preferably close to $\frac{1}{2}\pi$) may be specified arbitrarily, thus distinguishing between the enantiomorphous structures S and S' permitted by the intensities. Once this is done then the values (not merely the magnitudes) of all phases which are structure invariants are uniquely determined. Finally, in order to fix the origin, three phases $\varphi_{h_ik_il_i}$, $i = 1, 2, 3$, one index of each of which is zero and constituting a linearly independent set, are chosen. The value of each such phase is either 0 or π. Either one of the two possible values for each such phase may be chosen and then the values of all remaining phases are uniquely determined.

For space group $P2_12_12_1$, also of type $1P222$, the same procedure as that just described may be used. However, it is expedient to alter the procedure somewhat, and this will be described in detail later.

3. The normalized structure factor *E*

The structure factor $F_{\mathbf{h}}$ is defined by means of

$$F_{\mathbf{h}} = |F_{\mathbf{h}}| \exp [i\varphi_{\mathbf{h}}] = X+iY \ , \qquad (3\cdot01)$$

$$X = \sum_{j=1}^{N/n} f_{j\mathbf{h}} \xi(x_j, y_j, z_j, \mathbf{h}) \ , \qquad (3\cdot02)$$

$$Y = \sum_{j=1}^{N/n} f_{j\mathbf{h}} \eta(x_j, y_j, z_j, \mathbf{h}) \ , \qquad (3\cdot03)$$

where N is the number of atoms in the unit cell, n is the order of the space group, $f_{j\mathbf{h}}$ is the atomic scattering factor, x_j, y_j, z_j are the coordinates of the jth atom, and ξ and η are trigonometric functions which depend upon the space group; e.g. for $P1$,

$$\xi = \cos 2\pi(hx+ky+lz) \ , \qquad (3\cdot04)$$

$$\eta = \sin 2\pi(hx+ky+lz) \ . \qquad (3\cdot05)$$

For non-centrosymmetric structures having atoms in general positions only the probability distribution for the magnitude $|F_{\mathbf{h}}|$ of a particular structure factor (neither real nor pure imaginary as a consequence of space group symmetry) as the atoms in the asymmetric unit range uniformly and independently throughout the unit cell is given approximately by (Hauptman & Karle, 1953, equation (24))

$$P_R(x) = \frac{nx \exp(-nx^2/2m_2\sigma_2)}{m_2\sigma_2} \ , \qquad (3\cdot06)$$

where

$$m_2^0 = \int_0^1\int_0^1\int_0^1 \xi^2 dx\,dy\,dz \neq 0 \ , \qquad (3\cdot07)$$

$$m_0^2 = \int_0^1\int_0^1\int_0^1 \eta^2 dx\,dy\,dz \neq 0 \ , \qquad (3\cdot08)$$

$$m_2 = m_2^0 = m_0^2 \ , \qquad (3\cdot09)$$

and

$$\sigma_2 = \sum_{j=1}^{N} f_{j\mathbf{h}}^2 = n \sum_{j=1}^{N/n} f_{j\mathbf{h}}^2 \ . \qquad (3\cdot10)$$

Evidently both m_2 and σ_2, and therefore $P_R(x)$, depend on $\mathbf{h}$. However, it turns out that for each space group the number of different distributions $P_R(x)$ is finite. From (3·06) the average of any power of $|F|$ may be found. In particular,

$$\langle |F|^2 \rangle = 2m_2\sigma_2/n \ . \qquad (3\cdot11)$$

Next we define the normalized structure factor $E_{\mathbf{h}}$ by means of

$$E_{\mathbf{h}} = \frac{F_{\mathbf{h}}}{((m_2^0+m_0^2)\sigma_2/n)^{\frac{1}{2}}} \ . \qquad (3\cdot12)$$

Equation (3·12) is valid also for the centrosymmetric space groups and for those structure factors for non-centrosymmetric space groups which, as a consequence of space-group symmetry, are either real or pure imaginary (cf. Monograph I, p. 34), since in these cases one of m_2^0, m_0^2 is identically zero and equation (3·15) of Monograph I (to which (3·12) now reduces) applies. Evidently, the phase of $E_{\mathbf{h}}$ is equal to $\varphi_{\mathbf{h}}$, the phase of $F_{\mathbf{h}}$. From (3·11) it follows that the average value $\langle |E_{\mathbf{h}}|^2 \rangle_{\mathbf{r}}$ of the square of the magnitude of a particular normalized structure factor as the atoms in the asymmetric unit range uniformly and independently throughout the unit cell is unity, i.e.

$$\langle |E_{\mathbf{h}}|^2 \rangle_{\mathbf{r}} = 1 \ . \qquad (3\cdot13)$$

It is a fact of fundamental importance that, in general, the average of $|E|^2$ over x, y, z is the same as the average of $|E|^2$ over h, k, l (cf. Monograph I, p. 35). In other words, *for a fixed structure*, the average value $\langle |E_{\mathbf{h}}|^2 \rangle_{\mathbf{h}}$ of the squares of the magnitudes of the normalized structure factors as the vectors $\mathbf{h}$ range uniformly over all reciprocal space is unity, i.e.

$$\langle |E_{\mathbf{h}}|^2 \rangle_{\mathbf{h}} = 1 \ . \qquad (3\cdot14)$$

As with centrosymmetric structures, (3·14) is important in that it is the basis, in an obvious way, of a procedure for correcting observed intensities for vibrational motion and for putting them on an absolute scale (cf. Wilson, 1949).

In terms of the normalized structure factor, the probability distributions (3·06) assume a very simple form. Denoting by $P(x)dx$ the probability that $|E|$ lie between x and $x+dx$, where $x \geq 0$, (3·06) implies

$$P(x) = 2x \exp[-x^2] \ . \qquad (3\cdot15)$$

It is seen that $P(x)$ has the same form for all vectors $\mathbf{h}$ and for all the non-centrosymmetric space groups.

4. Joint distribution

As in the case of the centrosymmetric crystal, the joint distribution is useful for deriving the probability distribution of the magnitude and phase of a structure factor when certain magnitudes or phases are specified.

It is convenient to use the abbreviations

$$\xi_\varrho = \xi(x, y, z, \mathbf{h}_\varrho) \ , \qquad (4\cdot01)$$

$$\eta_\sigma = \eta(x, y, z, \mathbf{h}'_\sigma) \ . \qquad (4\cdot02)$$

Denote by $p(\xi_1, \ldots, \xi_r, \eta_1, \ldots, \eta_s)$ the joint probability that ξ_ϱ lie in the interval ξ_ϱ, $\xi_\varrho+d\xi_\varrho$ and that η_σ lie in the interval η_σ, $\eta_\sigma+d\eta_\sigma$, $\varrho = 1, 2, \ldots, r$; $\sigma = 1, 2, \ldots, s$. Let $P_1(A_1, \ldots, A_r, B_1, \ldots, B_s)dA_1\ldots dB_s$ be the joint probability that X_ϱ lie in the interval

A_ϱ, $A_\varrho+dA_\varrho$ and Y_σ lie in the interval B_σ, $B_\sigma+dB_\sigma$, $\varrho = 1, 2, \ldots, r$; $\sigma = 1, 2, \ldots, s$; where X_ϱ and Y_σ are obtained from (3·02) and (3·03) by replacing $\mathbf{h}$ by $\mathbf{h}_\varrho$ and $\mathbf{h}'_\sigma$ respectively. We prove next the fundamental result

$$P_1(A_1, \ldots, A_r, B_1, \ldots, B_s) = \frac{1}{(2\pi)^{r+s}} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left(-i\sum_{\varrho=1}^{r} A_\varrho u_\varrho - i\sum_{\sigma=1}^{s} B_\sigma v_\sigma\right) \times \prod_{j=1}^{N/n} q(f_{j1}u_1, \ldots, f_{jr}u_r, f_{j1}v_1, \ldots f_{js}v_s)\,du_1\ldots dv_s\,, \quad (4\cdot03)$$

where

$$q(f_{j1}u_1, \ldots, f_{jr}u_r, f_{j1}v_1, \ldots, f_{js}v_s) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\xi_1, \ldots, \xi_r, \eta_1, \ldots, \eta_s) \times \exp\left(i\sum_{\varrho=1}^{r} f_{j\varrho}\xi_\varrho u_\varrho + i\sum_{\sigma=1}^{s} f_{j\sigma}\eta_\sigma v_\sigma\right) d\xi_1\ldots d\eta_s\,, \quad (4\cdot04)$$

and

$$\left.\begin{aligned} f_{j\varrho} &= f_j(h_\varrho, k_\varrho, l_\varrho) = f_j(\mathbf{h}_\varrho)\,, \\ f_{j\sigma} &= f_j(h'_\sigma, k'_\sigma, l'_\sigma) = f_j(\mathbf{h}'_\sigma)\,. \end{aligned}\right\} \quad (4\cdot05)$$

The probability, $Q(A_1, \ldots, A_r, B_1, \ldots, B_s)$, that X_ϱ be less than A_ϱ and Y_σ be less than B_σ for every $\varrho = 1, 2, \ldots, r$; $\sigma = 1, 2, \ldots, s$, is

$$Q(A_1, \ldots, A_r, B_1, \ldots, B_s) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \prod_{j=1}^{N/n} p(\xi_{j1}, \ldots, \xi_{jr}, \eta_{j1}, \ldots, \eta_{js}) d\xi_{j1}\ldots d\eta_{js} \times \prod_{\varrho=1}^{r} T(\xi_{1\varrho}, \ldots, \xi_{N/n\varrho}) \prod_{\sigma=1}^{s} T(\eta_{1\sigma}, \ldots, \eta_{N/n\sigma})\,, \quad (4\cdot06)$$

where

$$T(\xi_{1\varrho}, \ldots, \xi_{N/n\varrho}) = \frac{1}{2} - \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\exp[i(X_\varrho - A_\varrho)u_\varrho]du_\varrho}{iu_\varrho} = \begin{cases} 1 & \text{if } X_\varrho < A_\varrho \\ 0 & \text{if } X_\varrho > A_\varrho \end{cases}, \quad (4\cdot07)$$

$$T(\eta_{1\sigma}, \ldots, \eta_{N/n\sigma}) = \frac{1}{2} - \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\exp[i(Y_\sigma - B_\sigma)v_\sigma]dv_\sigma}{iv_\sigma} = \begin{cases} 1 & \text{if } Y_\sigma < B_\sigma \\ 0 & \text{if } Y_\sigma > B_\sigma \end{cases}, \quad (4\cdot08)$$

and

$$\left.\begin{aligned} \xi_{j\varrho} &= \xi(x_j, y_j, z_j, \mathbf{h}_\varrho)\,, \\ \eta_{j\sigma} &= \eta(x_j, y_j, z_j, \mathbf{h}'_\sigma)\,. \end{aligned}\right\} \quad (4\cdot09)$$

By differentiating (4·06) with respect to $A_1, \ldots, A_r, B_1, \ldots, B_s$, we obtain (4·03) and (4·04), since

$$P_1(A_1, \ldots, A_r, B_1, \ldots, B_s) = \frac{\partial^{r+s}Q(A_1, \ldots, A_r, B_1, \ldots, B_s)}{\partial A_1 \ldots \partial B_s}\,. \quad (4\cdot10)$$

Equations (4·03) and (4·04) are the starting point from which the joint probability distributions for the magnitudes and phases of the structure factors may be derived on the basis that certain sets of magnitudes or phases are known. As in the derivation of (4·03), the atoms in the asymmetric unit are assumed to range at random throughout the unit cell. Useful distributions are then obtained by making use of a knowledge of the magnitudes or the phases of a specified set of structure factors. The formulas to be derived are of two types, those requiring a knowledge of intensities only, and others requiring a knowledge of the phases also.

In order to express (4·03) in a more useful form we first find the Maclaurin expansion of the exponential in (4·04):

$$q(f_{j1}u_1, \ldots, f_{jr}u_r, f_{j1}v_1, \ldots, f_{js}v_s) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\xi_{j1}, \ldots, \xi_{jr}, \eta_{j1}, \ldots, \eta_{js}) \times \left\{1 + i\left(\sum_{\varrho=1}^{r} f_{j\varrho}\xi_\varrho u_\varrho + \sum_{\sigma=1}^{s} f_{j\sigma}\eta_\sigma v_\sigma\right) - \frac{1}{2!}\left(\sum_{\varrho=1}^{r} f_{j\varrho}\xi_\varrho u_\varrho + \sum_{\sigma=1}^{s} f_{j\sigma}\eta_\sigma v_\sigma\right)^2 + \frac{i}{3!}\left(\sum_{\varrho=1}^{r} f_{j\varrho}\xi_\varrho u_\varrho + \sum_{\sigma=1}^{s} f_{j\sigma}\eta_\sigma v_\sigma\right)^3 + \ldots\right\}. \quad (4\cdot11)$$

The terms of (4·11) are all of the form of a mixed moment

$$m_{\lambda_1\ldots\lambda_r}^{\varkappa_1\ldots\varkappa_s} = \int_{-\infty}^{\infty} \cdots \int_{\infty}^{\infty} p(\xi_1, \ldots, \xi_r, \eta_1, \ldots, \eta_s) \times \xi_1^{\lambda_1}\ldots\xi_r^{\lambda_r}\eta_1^{\varkappa_1}\ldots\eta_s^{\varkappa_s}d\xi_1\ldots d\eta_s\,. \quad (4\cdot12)$$

Interpreting (4·12) as an expected value, or average, of $\xi_1^{\lambda_1}\ldots\xi_r^{\lambda_r}\eta_1^{\varkappa_1}\ldots\eta_s^{\varkappa_s}$, we infer that

$$m_{\lambda_1\ldots\lambda_r}^{\varkappa_1\ldots\varkappa_s} = \int_0^1\int_0^1\int_0^1 \xi^{\lambda_1}(x, y, z, \mathbf{h}_1)\ldots\xi^{\lambda_r}(x, y, z, \mathbf{h}_r) \times \eta^{\varkappa_1}(x, y, z, \mathbf{h}'_1)\ldots\eta^{\varkappa_s}(x, y, z, \mathbf{h}'_s)\,dx\,dy\,dz\,. \quad (4\cdot13)$$

It may be seen from (4·13) that the evaluation of q from (4·11) and (4·12) does not require an explicit expression for $p(\xi_1, \ldots, \xi_r, \eta_1 \ldots, \eta_s)$. It is sufficient to evaluate the moments $m_{\lambda_1\ldots\lambda_r}^{\varkappa_1\ldots\varkappa_s}$ from (4·13), a relatively simple (but often tedious) matter, given the functions ξ_ϱ and η_σ, which are known for all the space groups. It is thus seen that the exact nature of the interdependence of the various structure factors is revealed by the values of the mixed moments (4·13). As a general rule these moments vanish. However, for suitable relationships among the vectors $\mathbf{h}_\varrho$, $\mathbf{h}'_\sigma$, $\varrho = 1, \ldots, r$, $\sigma = 1, \ldots, s$, which depend upon the space group (and are easily determined for each space group), these moments differ from zero. In this way those structure factors most intimately related to any given one are determined. Our next task is to derive certain of the significant non-vanishing mixed moments (4·13) and to express the probability distributions in terms of them. It is important to observe that in general not only may r be different from s but the sets $\mathbf{h}_\varrho$, $\varrho = 1, \ldots, r$, and $\mathbf{h}'_\sigma$, $\sigma = 1, \ldots, s$, need have no elements in common. It will be seen that this general formulation will enable us to obtain information concerning three-dimensional phases from one- and two-dimensional data, and vice versa.

5. Type 1P222

Only the space groups $P222$ and $P2_12_12_1$ belonging to Type 1P222 are here considered in detail. The remaining space groups belonging to this type are readily treated in a similar fashion.

5·1. *Space group P222*

For this space group

$$\xi_{\mathbf{h}} = 4 \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz\,, \qquad (5\cdot01)$$

$$\eta_{\mathbf{h}} = -4 \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz\,. \qquad (5\cdot02)$$

5·1·1. *The intensity invariants.*—Since the values of the intensity invariants (either 0 or π) are uniquely determined by the observed intensities, we first seek formulas involving these phases. It is readily verified that the phases φ_{hkl} which are intensity invariants have all indices h, k, l even and at least one index (h or k or l) zero. Hence we are led to consider structure factors $F_{\mathbf{h}_1}$, $F_{\mathbf{h}_2}$, the indices of which satisfy

$$h_1 = 2h_2 \neq 0,\; k_1 = 2k_2 \neq 0,\; l_1 = 0,\; l_2 \neq 0\,. \qquad (5\cdot03)$$

Equations (4·03) and (4·04) become

$$P_1(A_1, A_2, B_2) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\,[-i(A_1u_1+A_2u_2+B_2v_2)] \times \prod_{j=1}^{N/4} q(f_{j1}u_1, f_{j2}u_2, f_{j2}v_2)\,du_1\,du_2\,dv_2\,, \qquad (5\cdot04)$$

$$q(f_{j1}u_1, f_{j2}u_2, f_{j2}v_2) = \int_0^1\int_0^1\int_0^1 \exp\,[i(f_{j1}\xi_1u_1+f_{j2}\xi_2u_2+f_{j2}\eta_2v_2)]\,dx\,dy\,dz\,. \qquad (5\cdot05)$$

Using the Maclaurin expansion of the exponential in (5·05), this becomes

$$q = 1-\tfrac{1}{2}(f_{j1}^2u_1^2m_{20}^{00}+f_{j2}^2u_2^2m_{02}^{00}+f_{j2}^2v_2^2m_{00}^{02}) - (i/2)f_{j1}f_{j2}^2(u_1u_2^2m_{12}^{00}+u_1v_2^2m_{10}^{02})+\ldots\,, \qquad (5\cdot06)$$

where only the non-vanishing mixed moments have been retained in (5·06). It is readily verified from (5·01) and (5·02) that, in view of (5·03), the values of these moments are given by

$$m_{20}^{00} = 4,\; m_{02}^{00} = m_{00}^{02} = m_{12}^{00} = m_{10}^{02} = 2\,. \qquad (5\cdot07).$$

Substituting from (5·07) into (5·06) and using an analysis like that on p. 33 of Monograph I, we find

$$\prod_{j=1}^{N/4} q = \exp\left[-i\left(\sum_{j=1}^{N/4}(2f_{j1}^2u_1^2+f_{j2}^2u_2^2+f_{j2}^2v_2^2)\right)\right] \times \left\{1-i\sum_{j=1}^{N/4}f_{j1}f_{j2}^2(u_1u_2^2+u_1v_2^2)\right\}. \qquad (5\cdot08)$$

Substituting into (5·04) and evaluating the resulting integrals, one obtains

$$P_1(A_1, A_2, B_2) = \frac{2\exp\left(-\dfrac{A_1^2}{2\sum_{j=1}^{N}f_{j1}^2}-\dfrac{A_2^2}{\sum_{j=1}^{N}f_{j2}^2}-\dfrac{B_2^2}{\sum_{j=1}^{N}f_{j2}^2}\right)}{(2\pi)^{3/2}\left(\sum_{j=1}^{N}f_{j1}^2\right)^{\frac{1}{2}}\left(\sum_{j=1}^{N}f_{j2}^2\right)} \times\left\{1+\frac{\sum_{j=1}^{N}f_{j1}f_{j2}^2}{\left(\sum_{j=1}^{N}f_{j1}^2\right)^{\frac{1}{2}}\left(\sum_{j=1}^{N}f_{j2}^2\right)}\left(\frac{A_2^2+B_2^2}{\sum_{j=1}^{N}f_{j2}^2}-1\right)\right\}, \qquad (5\cdot09)$$

where now all indices of summation range from 1 to N. Transforming to polar coordinates and referring the final distribution to the normalized structure factors E rather than the structure factors F, (5·09) finally becomes

$$P(E_1, |E_2|, \varphi_2) = \frac{2|E_2|\exp\,(-\tfrac{1}{2}E_1^2-|E_2|^2)}{(2\pi)^{3/2}} \times\left\{1+\frac{\sum_{j=1}^{N}f_{j1}f_{j2}^2}{\left(\sum_{j=1}^{N}f_{j1}^2\right)^{\frac{1}{2}}\left(\sum_{j=1}^{N}f_{j2}^2\right)}E_1(|E_2|^2-1)\right\}, \qquad (5\cdot10)$$

where P is the joint distribution of E_1, $|E_2|$, and φ_2, and φ_2 is the phase of E_2. Since (5·10) is independent of φ_2, the joint distribution of E_1 and $|E_2|$ is easily obtained. Although our analysis does not require us to do so, in order to simplify the later computations, we make the usual assumption that

$$f_{j\mathbf{h}} = Z_jf_{\mathbf{h}}\,, \qquad (5\cdot11)$$

where Z_j is the atomic number of the jth atom and $f_{\mathbf{h}}$ is independent of j. We finally obtain from (5·10)

$$P(E_1, |E_2|) = \frac{2|E_2|\exp\,(-\tfrac{1}{2}E_1^2-|E_2|^2)}{(2\pi)^{\frac{1}{2}}} \times\left\{1+\frac{S_3}{S_2^{3/2}}E_1(|E_2|^2-1)\right\}, \qquad (5\cdot12)$$

where

$$S_n = \sum_{j=1}^{N} Z_j^n \qquad (5\cdot13)$$

and $P(E_1, |E_2|)\,dE_1\,d|E_2|$ is the probability that E_1 lie between E_1 and E_1+dE_1 and that $|E_2|$ lie between $|E_2|$ and $|E_2|+d|E_2|$.

For a known value of E_1 the expected (or average) value of $(|E_2|^2-1)$ is readily found from (5·12) to be

$$\int_0^\infty (x^2-1) \frac{(2\pi)^{\frac{1}{2}} P(E_1, x)}{\exp(-\frac{1}{2}E_1^2)} dx = \frac{S_3}{S_1^{3/2}} E_1 . \quad (5\cdot14)$$

Equation (5·14) suggests that we consider the distribution of δ_{hk}, where

$$\delta_{hk} = E_{2h,2k,0} - (S_2^{3/2}/S_3) \langle |E_{hkl}|^2 - 1 \rangle_l , \quad (5\cdot15)$$

as h and k range uniformly and independently over the integers. For each fixed h, k the average on the right side of (5·15) is taken over all integers $l \neq 0$. First, from (3·02), (3·03), (5·01), (5·02), and (5·11)

$$X_{\mathbf{h}} = 4f_{\mathbf{h}} \sum_{j=1}^{N/4} Z_j \cos 2\pi hx_j \cos 2\pi ky_j \cos 2\pi lz_j , \quad (5\cdot16)$$

$$Y_{\mathbf{h}} = -4f_{\mathbf{h}} \sum_{j=1}^{N/4} Z_j \sin 2\pi hx_j \sin 2\pi ky_j \sin 2\pi lz_j , \quad (5\cdot17)$$

$$X_{\mathbf{h}}^2 = 16f_{\mathbf{h}}^2 \sum_{j,j'} Z_j Z_{j'} \cos 2\pi hx_j \cos 2\pi hx_{j'} \times \cos 2\pi ky_j \cos 2\pi ky_{j'} \cos 2\pi lz_j \cos 2\pi lz_{j'} , \quad (5\cdot18)$$

$$Y_{\mathbf{h}}^2 = 16f_{\mathbf{h}}^2 \sum_{j,j'} Z_j Z_{j'} \sin 2\pi hx_j \sin 2\pi hx_{j'} \times \sin 2\pi ky_j \sin 2\pi ky_{j'} \sin 2\pi lz_j \sin 2\pi lz_{j'} , \quad (5\cdot19)$$

$$X_{\mathbf{h}}^2 = 16f_{\mathbf{h}}^2 \sum_j Z_j^2 \cos^2 2\pi hx_j \cos^2 2\pi ky_j \times (\tfrac{1}{2} + \tfrac{1}{2}\cos 4\pi lz_j) + R_1 , \quad (5\cdot20)$$

$$Y_{\mathbf{h}}^2 = 16f_{\mathbf{h}}^2 \sum_j Z_j^2 \sin^2 2\pi hx_j \sin^2 2\pi ky_j \times (\tfrac{1}{2} - \tfrac{1}{2}\cos 4\pi lz_j) + R_2 , \quad (5\cdot21)$$

where R_1 and R_2 are obtained from (5·18) and (5·19) by replacing $\sum_{j,j'}$ by $\sum_{j \neq j'}$. Since

$$\cos 2\pi lz_j \cos 2\pi lz_{j'} = \tfrac{1}{2}\cos 2\pi l(z_j + z_{j'}) + \tfrac{1}{2}\cos 2\pi l(z_j - z_{j'}) , \quad (5\cdot22)$$

$$\sin 2\pi lz_j \sin 2\pi lz_{j'} = -\tfrac{1}{2}\cos 2\pi l(z_j + z_{j'}) + \tfrac{1}{2}\cos 2\pi l(z_j - z_{j'}) , \quad (5\cdot23)$$

we conclude that

$$\langle R_1 \rangle_l = \langle R_2 \rangle_l = 0 , \quad (5\cdot24)$$

provided that

$$z_j \pm z_{j'} \neq 0 \quad \text{if} \quad j \neq j' . \quad (5\cdot25)$$

From (3·01), (5·20), (5·21), and (5·24) we find, assuming $h^2+k^2 \neq 0$,

$$\langle |E_{hkl}|^2 \rangle_l = \frac{\langle |F_{hkl}|^2 \rangle_l}{f_{\mathbf{h}}^2 \sum_{j=1}^{N} Z_j^2} = \frac{\langle X_{\mathbf{h}}^2 + Y_{\mathbf{h}}^2 \rangle_l}{f_{\mathbf{h}}^2 \sum_{j=1}^{N} Z_j^2} \quad (5\cdot26)$$

$$= \frac{8 \sum_{j=1}^{N/4} Z_j^2 (\cos^2 2\pi hx_j \cos^2 2\pi ky_j + \sin^2 2\pi hx_j \sin^2 2\pi ky_j)}{S_2} \quad (5\cdot27)$$

$$= \frac{4 \sum_{j=1}^{N/4} Z_j^2 (1 + \cos 4\pi hx_j \cos 4\pi ky_j)}{S_2} , \quad (5\cdot28)$$

$$\langle |E_{hkl}|^2 - 1 \rangle_l = \frac{4 \sum_{j=1}^{N/4} Z_j^2 \cos 4\pi hx_j \cos 4\pi ky_j}{S_2} . \quad (5\cdot29)$$

However, from (5·16)

$$E_{2h,2k,0} = \frac{X_{2h,2k,0}}{f_{2h,2k,0}\left(\sum_{j=1}^{N} Z_j^2\right)^{\frac{1}{2}}} = \frac{4 \sum_{j=1}^{N/4} Z_j \cos 4\pi hx_j \cos 4\pi ky_j}{S_2^{\frac{1}{2}}} , \quad (5\cdot30)$$

since

$$Y_{2h,2k,0} = 0 \quad \text{from} \quad (5\cdot17) .$$

From (5·15), (5·29), and (5·30) we get

$$\delta_{hk} = 4 \sum_{j=1}^{N/4} \left(\frac{Z_j}{S_2^{\frac{1}{2}}} - \frac{S_2^{\frac{1}{2}}}{S_3} Z_j^2 \right) \cos 4\pi hx_j \cos 4\pi ky_j . \quad (5\cdot31)$$

Now (see equation (1·25) and Appendix of Monograph I) it is well known that, as h, k range uniformly and independently over all the integers, δ_{hk} is approximately normally distributed about the mean of zero with a variance σ_1, given by

$$\sigma_1 = \sum_{j=1}^{N} \left(\frac{Z_j}{S_2^{\frac{1}{2}}} - \frac{S_2^{\frac{1}{2}}}{S_3} Z_j^2 \right)^2 = \frac{S_2 S_4}{S_3^2} - 1 . \quad (5\cdot32)$$

Hence (5·15) may be written

$$E_{2h,2k,0} \approx (S_2^{3/2}/S_3) \langle |E_{hkl}|^2 - 1 \rangle_l , \quad (5\cdot33)$$

where the symbol $\approx$ means probably equal. More precisely, the values of $E_{2h,2k,0}$ are normally distributed about the mean value given by the right hand side of (5·33) with the variance σ_1, given by (5·32). The importance of this result is due to the fact that we can now estimate how often the right side of (5·33) can be expected to lead to the correct sign for $E_{2h,2k,0}$. For example, let σ_1, as computed from (5·32), be 0·5, whence $\sigma_1^{1/2} = 0\cdot7$. If $|E_{2h,2k,0}| = 1\cdot4$, then in order for the right side of (5·33) to give the wrong sign for $E_{2h,2k,0}$ it must deviate in one direction from $E_{2h,2k,0}$ by at least two standard deviations. Since the probability of this occurrence is only about 1/43, the right side of (5·33) will give the correct sign for $E_{2h,2k,0}$ about 42 times out of 43. Even if $|E_{2h,2k,0}| = 0\cdot7$, (5·33) will give the correct sign about 5 times out of 6, while if $|E_{2h,2k,0}| = 2\cdot1$, (5·33) will give the correct sign about 769 times out of 770. Of course (5·33) becomes more reliable as σ_1 approaches zero. It may be noted that σ_1 is a rough measure of the dissimilarity of the atoms present, the larger values of σ_1 belonging to those structures with grossly unlike atoms (e.g. the presence of a small number of relatively heavy atoms together with a much larger number of lighter atoms). In particular, if all the atoms are identical then $\sigma_1 = 0$, and (5·33) becomes an exact equality for all $E_{2h,2k,0}$.

It has been assumed in this discussion that the right side of (5·33) can be found exactly. This would be

Table 1. *The phases which are intensity invariants, related probability distributions, expected values, and variances for space group P222*

The phases which head the columns are those phases, φ_{hkl}, for which values are to be determined

$P(E, \lvert E_j\rvert)$ E Variance $\sigma_1 = \frac{S_2S_4}{S_3^2}-1$ Variance σ	φ_{gg0} $h_j=\frac{1}{2}h,\ k_j=\frac{1}{2}k$	φ_{g0g} $h_j=\frac{1}{2}h,\ l_j=\frac{1}{2}l$	φ_{0gg} $k_j=\frac{1}{2}k,\ l_j=\frac{1}{2}l$	φ_{g00} $h_j=\frac{1}{2}h$	φ_{0g0} $h_j=\frac{1}{2}k$	φ_{00g} $l_j=\frac{1}{2}l$
$P(E, \lvert E_j\rvert) = \frac{2\lvert E_j\rvert \exp[-\frac{1}{2}E^2-\lvert E_j\rvert^2]}{\sqrt{(2\pi)}}\left\{1+\frac{S_3}{S_2^{3/2}}E(\lvert E_j\rvert^2-1)\right\}$ $E = \frac{S_2^{3/2}}{S_3}\langle\lvert E_j\rvert^2-1\rangle$ $\sigma = \frac{S_2^3}{S_3^2}$	$l_j \neq 0$	$k_j \neq 0$	$h_j \neq 0$	—	—	—
$P(E, \lvert E_j\rvert) = \frac{\exp[-\frac{1}{2}E^2-\frac{1}{2}E_j^2]}{\pi}\left\{1+\frac{1}{2}\cdot\frac{S_3}{S_2^{3/2}}E(E_j^2-1)\right\}$ $E = \frac{S_2^{3/2}}{S_3}\langle E_j^2-1\rangle$ $\sigma = \frac{S_2^3}{S_3^2}\cdot 2$	$l_j = 0$	$k_j = 0$	$h_j = 0$	—	—	—
$P(E, \lvert E_j\rvert) = \frac{\exp[-\frac{1}{2}E^2-\frac{1}{2}E_j^2]}{\pi}\left\{1+\frac{1}{\sqrt{2}}\cdot\frac{S_3}{S_2^{3/2}}E(E_j^2-1)\right\}$ $E = \frac{1}{\sqrt{2}}\cdot\frac{S_2^{3/2}}{S_3}\langle E_j^2-1\rangle$ $\sigma = \frac{1}{2}\cdot\frac{S_2^3}{S_3^2}\cdot 2$	—	—	—	$k_j=0$ or $l_j=0$	$l_j=0$ or $h_j=0$	$h_j=0$ or $k_j=0$

true only in the case that the infinite number of data were known. In practice the average on the right side of (5·33) must be computed from a finite sample chosen (not even at random) from an infinite population. To obtain a rough estimate of the reliability of the mean so computed we first find the expected value of $(\lvert E_2\rvert^2-1)^2$ from (5·12). We get

$$\int_0^\infty (x^2-1)^2 \frac{(2\pi)^{\frac{1}{2}}P(E_1, x)}{\exp(-\frac{1}{2}E_1^2)}dx = 1\,. \quad (5·34)$$

From (5·34) and (5·14) we find the variance of $(\lvert E_2\rvert^2-1)$ to be

$$1-(S_3^2/S_2^3)E_1^2 \approx 1\,, \quad (5·35)$$

since $(S_3^2/S_2^3)E_1^2$ is small compared to unity. We conclude that if n terms contribute to the mean in (5·33) then the right side of (5·33) is normally distributed about its true value (as computed from the infinite population) with the variance σ' given approximately by

$$\sigma' = \frac{\sigma}{n} = \frac{S_2^3}{S_3^2}\cdot\frac{1}{n}\,. \quad (5·36)$$

If we combine (5·32) and (5·36) it is possible to estimate, in any given case, the probability that (5·33) give the right sign for $E_{2h,2k,0}$ by taking into account the values of σ, σ_1, $\lvert E_{2h,2k,0}\rvert$, and the right side of (5·33). In this way the proportion of signs correctly determined by (5·33) can be estimated and levels of rejection, which must be exceeded by the right side of (5·33) before a sign is considered to be decisively determined, can be specified. It should be noted that in the case that not all atoms are identical the non-zero value of σ_1, as given by (5·32), implies that a certain percentage of signs will be incorrectly determined by (5·33) even if an infinite number of data is available.

The cases that $l_2 = 0$ and one of h_1, k_1 is zero are treated in a similar way. The results are summarized in Table 1 in which h and k replace $2h$ and $2k$ respectively and $\mathbf{h}_j$ replaces $\mathbf{h}_2$. The notation φ_{gg0} means that h and k are both even (but not zero and not necessarily equal) while $l = 0$.

5·1·2. *The relation* $\mathbf{h}_1 = \mathbf{h}_2+\mathbf{h}_3$.—We consider in detail only the case

$$h_i \neq 0,\ k_i \neq 0,\ l_i \neq 0,\ i = 1, 2, 3; \quad (5·37)$$

and find, as in the previous analysis (5·03)–(5·12),

$$P(|E_1|, |E_2|, |E_3|, \varphi_1, \varphi_2, \varphi_3)$$
$$= (|E_1|.|E_2|.|E_3|/\pi^3) \exp(-|E_1|^2-|E_2|^2-|E_3|^2)$$
$$\times \{1+2(S_3/S_2^{3/2})|E_1|.|E_2|.|E_3| \cos(\varphi_1-\varphi_2-\varphi_3)\}. \quad (5\cdot38)$$

For fixed E_1 we find the expected value of

$$|E_2E_3|^p \cos(\varphi_2+\varphi_3),$$

where p is any number, from (5·38) as follows:

$$\langle |E_2E_3|^p \cos(\varphi_2+\varphi_3)\rangle$$
$$= \int_{|E_2|=0}^{\infty}\int_{|E_3|=0}^{\infty}\int_{\varphi_2=0}^{2\pi}\int_{\varphi_3=0}^{2\pi} \frac{\pi|E_2E_3|^p\cos(\varphi_2+\varphi_3)}{|E_1|\exp(-|E_1|^2)}$$
$$\times P(|E_1|, |E_2|, |E_3|, \varphi_1, \varphi_2, \varphi_3)\,d|E_2|\,d|E_3|\,d\varphi_2 d\varphi_3 \quad (5\cdot39)$$
$$= \iiiint 2\frac{S_3}{S_2^{3/2}}|E_1|.|E_2E_3|^{p+1}.\frac{|E_2E_3|\exp(-|E_2|^2-|E_3|^2)}{\pi^2}$$
$$\times \cos\varphi_1 \cos^2(\varphi_2+\varphi_3)\,d|E_2|\,d|E_3|\,d\varphi_2 d\varphi_3 \quad (5\cdot40)$$
$$= \langle |E_2E_3|^{p+1}\rangle (S_3/S_2^{3/2})\,|E_1| \cos\varphi_1. \quad (5\cdot41)$$

Hence

$$\cos\varphi_1 = \frac{S_2^{3/2}}{S_3|E_1|}\cdot\frac{\langle |E_2E_3|^p\cos(\varphi_2+\varphi_3)\rangle}{\langle |E_2E_3|^{p+1}\rangle}. \quad (5\cdot42)$$

In a similar manner we find

$$\sin\varphi_1 = \frac{S_2^{3/2}}{S_3|E_1|}\cdot\frac{\langle |E_2E_3|^p\sin(\varphi_2+\varphi_3)\rangle}{\langle |E_2E_3|^{p+1}\rangle}. \quad (5\cdot43)$$

Replace E_1 by E, E_2 by E_i, E_3 by E_j and write

$$E_iE_j = E_{ij}, \quad \varphi_i+\varphi_j = \varphi_{ij}. \quad (5\cdot44)$$

Then (5·42) and (5·43) suggest that we consider the validity of the following equations:

$$\cos\varphi \approx \frac{S_2^{3/2}}{S_3|E|}\cdot\frac{\sum_{i,j}|E_{ij}|^p\cos\varphi_{ij}}{\sum_{i,j}|E_{ij}|^{p+1}}, \quad (5\cdot45)$$

$$\sin\varphi \approx \frac{S_2^{3/2}}{S_3|E|}\cdot\frac{\sum_{i,j}|E_{ij}|^p\sin\varphi_{ij}}{\sum_{i,j}|E_{ij}|^{p+1}}, \quad (5\cdot46)$$

$$\tan\varphi \approx \frac{\sum_{i,j}|E_{ij}|^p\sin\varphi_{ij}}{\sum_{i,j}|E_{ij}|^p\cos\varphi_{ij}}, \quad (5\cdot47)$$

where the sums in (5·45)–(5·47) are taken over all i, j such that

$$\mathbf{h} = \mathbf{h}_i+\mathbf{h}_j, \quad (5\cdot48)$$

$$hkl \neq 0, \quad h_ik_il_i \neq 0, \quad h_jk_jl_j \neq 0. \quad (5\cdot49)$$

We treat in detail only the case $p = 1$ and, since $\langle |E_{ij}|^2\rangle \approx 1$ (Hauptman & Karle, 1955), consider therefore the distribution of $\delta_{\mathbf{h}}$, where

$$\delta_{\mathbf{h}} = |E|\cos\varphi-(S_2^{3/2}/S_3)\langle |E_{ij}|\cos\varphi_{ij}\rangle_{i,j}$$
$$+\,i(|E|\sin\varphi-(S_2^{3/2}/S_3)\langle |E_{ij}|\sin\varphi_{ij}\rangle_{i,j}), \quad (5\cdot50)$$

as h, k, and l range uniformly and independently over the integers and the supplementary conditions (5·48) and (5·49) are fulfilled. (No confusion should arise over the use of the symbol i both as the imaginary unit and as an index of summation.)

In view of (5·01) and (5·02),

$$E_{\mathbf{h}_i} = \frac{F_{\mathbf{h}_i}}{f_{\mathbf{h}_i}\left(\sum_{j'=1}^{N} Z_{j'}^2\right)^{\frac{1}{2}}} = \frac{X_{\mathbf{h}_i}+iY_{\mathbf{h}_i}}{f_{\mathbf{h}_i}S_2^{\frac{1}{2}}}, \quad (5\cdot51)$$

$$E_{\mathbf{h}_i} = \frac{4}{S_2^{\frac{1}{2}}}\left(\sum_{j'=1}^{N/4} Z_{j'}\cos 2\pi h_ix_{j'}\cos 2\pi k_iy_{j'}\cos 2\pi l_iz_{j'}\right.$$
$$\left.-i\sum_{j'=1}^{N/4} Z_{j'}\sin 2\pi h_ix_{j'}\sin 2\pi k_iy_{j'}\sin 2\pi l_iz_{j'}\right), \quad (5\cdot52)$$

$$E_{\mathbf{h}_i}E_{\mathbf{h}_j} = \frac{16}{S_2}\Big\{\sum_{j',j''\,1}^{N/4} Z_{j'}Z_{j''}(\cos 2\pi h_ix_{j'}\cos 2\pi h_jx_{j''}$$
$$\times\cos 2\pi k_iy_{j'}\cos 2\pi k_jy_{j''}\cos 2\pi l_iz_{j'}\cos 2\pi l_jz_{j''}$$
$$-\sin 2\pi h_ix_{j'}\sin 2\pi h_jx_{j''}\sin 2\pi k_iy_{j'}\sin 2\pi k_jy_{j''}$$
$$\times\sin 2\pi l_iz_{j'}\sin 2\pi l_jz_{j''})$$
$$-i\sum_{j',j''\,1}^{N/4} Z_{j'}Z_{j''}(\cos 2\pi h_ix_{j'}\sin 2\pi h_jx_{j''}$$
$$\times\cos 2\pi k_iy_{j'}\sin 2\pi k_jy_{j''}\cos 2\pi l_iz_{j'}\sin 2\pi l_jz_{j''}$$
$$+\sin 2\pi h_ix_{j'}\cos 2\pi h_jx_{j''}\sin 2\pi k_iy_{j'}\cos 2\pi k_jy_{j''}$$
$$\times\sin 2\pi l_iz_{j'}\cos 2\pi l_jz_{j''})\Big\}, \quad (5\cdot53)$$

$$|E_{ij}|(\cos\varphi_{ij}+i\sin\varphi_{ij}) = \frac{16}{S_2}\Big\{\sum_{j'=1}^{N/4} Z_{j'}^2(\cos 2\pi h_ix_{j'}\cos 2\pi h_jx_{j'}$$
$$\times\cos 2\pi k_iy_{j'}\cos 2\pi k_jy_{j'}\cos 2\pi l_iz_{j'}\cos 2\pi l_jz_{j'}$$
$$-\sin 2\pi h_ix_{j'}\sin 2\pi h_jx_{j'}\sin 2\pi k_iy_{j'}\sin 2\pi k_jy_{j'}$$
$$\times\sin 2\pi l_iz_{j'}\sin 2\pi l_jz_{j'})$$
$$-i\sum_{j'=1}^{N/4} Z_{j'}^2(\cos 2\pi h_ix_{j'}\sin 2\pi h_jx_{j'}$$
$$\times\cos 2\pi k_iy_{j'}\sin 2\pi k_jy_{j'}\cos 2\pi l_iz_{j'}\sin 2\pi l_jz_{j'}$$
$$+\sin 2\pi h_ix_{j'}\cos 2\pi h_jx_{j'}\sin 2\pi k_iy_{j'}\cos 2\pi k_jy_{j'}$$
$$\times\sin 2\pi l_iz_{j'}\cos 2\pi l_jz_{j'})\Big\}+R, \quad (5\cdot54)$$

where R is obtained from (5·53) by replacing

$$\sum_{j',j''} \text{ by } \sum_{j'\neq j''}.$$

We conclude that

$$\langle R\rangle_{\mathbf{h}_i+\mathbf{h}_j} = 0, \quad (5\cdot55)$$

provided that

$$(x_{j'}, y_{j'}, z_{j'}) \neq \pm(x_{j''}, y_{j''}, z_{j''}) \text{ if } j' \neq j''. \quad (5\cdot56)$$

Table 2. *The relation* $\mathbf{h} = \mathbf{h}_i + \mathbf{h}_j$, *related probability distributions, expected values, and variances for space group P222*

The phases which head the columns are those phases, φ_{hkl}, for which values are to be determined

$P(|E|, |E_i|, |E_j|, \varphi, \varphi_i, \varphi_j)$; $\cos\varphi$; $\sin\varphi$

Variance $\sigma_1 = \dfrac{1}{|E|^2}\left(\dfrac{S_2 S_4}{S_3^2} - 1\right)$

Variance σ

	φ_{hkl} $\varphi_{h_ik_il_i}$ $\varphi_{h_jk_jl_j}$	φ_{hkl} $\varphi_{h_ik_i0}$ $\varphi_{h_jk_jl_j}$	φ_{hkl} φ_{h_i00} $\varphi_{h_jk_jl_j}$	φ_{hkl} $\varphi_{h_ik_i0}$ $\varphi_{h_j0l_j}$	φ_{hkl} φ_{h_i00} $\varphi_{0k_jl_j}$	φ_{hk0} $\varphi_{h_ik_i0}$ $\varphi_{h_jk_j0}$	φ_{hk0} $\varphi_{h_i0l_i}$ $\varphi_{0k_jl_j}$	φ_{hk0} $\varphi_{h_ik_i0}$ φ_{h_j00}	φ_{hk0} φ_{h_i00} φ_{0k_j0}	φ_{hk0} $\varphi_{h_ik_il_i}$ $\varphi_{h_jk_jl_j}$	φ_{hk0} $\varphi_{h_ik_il_i}$ $\varphi_{h_j0l_j}$	φ_{h00} φ_{h_i00} φ_{h_j00}	φ_{h00} $\varphi_{h_ik_il_i}$ $\varphi_{h_jk_jl_j}$	φ_{h00} $\varphi_{h_ik_il_i}$ $\varphi_{0k_jl_j}$
$\dfrac{\lvert EE_iE_j\rvert}{\pi^3}\exp[-\lvert E\rvert^2-\lvert E_i\rvert^2-\lvert E_j\rvert^2]\left\{1+t\dfrac{S_3}{S_2^{3/2}}\lvert EE_iE_j\rvert\cos(\varphi-\varphi_i-\varphi_j)\right\}$	$t=2$	—	—	—	—	—	—	—	—	—	—	—	—	—
$\dfrac{\lvert EE_j\rvert}{\pi^2\sqrt{(2\pi)}}\exp[-\lvert E\rvert^2-\frac{1}{2}E_i^2-\lvert E_j\rvert^2]\left\{1+t\dfrac{S_3}{S_2^{3/2}}\lvert EE_iE_j\rvert\cos(\varphi-\varphi_i-\varphi_j)\right\}$	—	$t=2$	$t=2\sqrt{2}$	—	—	—	—	—	—	—	—	—	—	—
$\dfrac{\lvert E\rvert}{2\pi^2}\exp[-\lvert E\rvert^2-\frac{1}{2}E_i^2-\frac{1}{2}E_j^2]\left\{1+t\dfrac{S_3}{S_2^{3/2}}\lvert EE_iE_j\rvert\cos(\varphi-\varphi_i-\varphi_j)\right\}$	—	—	—	$t=2$	$t=2\sqrt{2}$	—	—	—	—	—	—	—	—	—
$\dfrac{\exp[-\frac{1}{2}E^2-\frac{1}{2}E_i^2-\frac{1}{2}E_j^2]}{(2\pi)^{3/2}}\left\{1+t\dfrac{S_3}{S_2^{3/2}}EE_iE_j\right\}$	—	—	—	—	—	$t=1$	$t=2$	$t=\sqrt{2}$	$t=2$	—	—	$t=\sqrt{2}$	—	—
$\dfrac{\lvert E_iE_j\rvert}{\pi^2\sqrt{(2\pi)}}\exp[-\frac{1}{2}E^2-\lvert E_i\rvert^2-\lvert E_j\rvert^2]\left\{1+t\dfrac{S_3}{S_2^{3/2}}\lvert EE_iE_j\rvert\cos(\varphi-\varphi_i-\varphi_j)\right\}$	—	—	—	—	—	—	—	—	—	$t=2$	—	—	$t=2\sqrt{2}$	—
$\dfrac{\lvert E_i\rvert}{2\pi^2}\exp[-\frac{1}{2}E^2-\lvert E_i\rvert^2-\frac{1}{2}E_j^2]\left\{1+t\dfrac{S_3}{S_2^{3/2}}\lvert EE_iE_j\rvert\cos(\varphi-\varphi_i-\varphi_j)\right\}$	—	—	—	—	—	—	—	—	—	—	$t=2$	—	—	$t=2\sqrt{2}$
$\cos\varphi = \varkappa_c\dfrac{S_2^{3/2}}{S_3\lvert E\rvert}\cdot\langle\lvert E_{ij}\rvert\cos\varphi_{ij}\rangle\cdot\langle\lvert E_{ij}\rvert^2\rangle^{-1}$	$\varkappa_c=1$	$\varkappa_c=1$	$\varkappa_c=\frac{1}{\sqrt{2}}$	$\varkappa_c=\frac{1}{2}$	$\varkappa_c=\frac{1}{2\sqrt{2}}$	$\varkappa_c=1$	$\varkappa_c=\frac{1}{2}$	$\varkappa_c=\frac{1}{\sqrt{2}}$	$\varkappa_c=\frac{1}{2}$	$\varkappa_c=1$	$\varkappa_c=1$	$\varkappa_c=\frac{1}{\sqrt{2}}$	$\varkappa_c=\frac{1}{\sqrt{2}}$	$\varkappa_c=\frac{1}{\sqrt{2}}$
$\sin\varphi = \varkappa_s\dfrac{S_2^{3/2}}{S_3\lvert E\rvert}\cdot\langle\lvert E_{ij}\rvert\sin\varphi_{ij}\rangle\cdot\langle\lvert E_{ij}\rvert^2\rangle^{-1}$	$\varkappa_s=1$	$\varkappa_s=1$	$\varkappa_s=\frac{1}{\sqrt{2}}$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$	$\varkappa_s=\infty$
$\sigma = \varkappa_\sigma\dfrac{\varkappa_c^2S_2^3}{S_3^2\lvert E\rvert^2}\cdot\langle\lvert E_{ij}\rvert^2\rangle^{-1}$ or $\varkappa_\sigma\dfrac{\varkappa_s^2S_2^3}{S_3^2\lvert E\rvert^2}\cdot\langle\lvert E_{ij}\rvert^2\rangle^{-1}$*	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=1$	$\varkappa_\sigma=1$	$\varkappa_\sigma=1$	$\varkappa_\sigma=1$	$\varkappa_\sigma=1$	$\varkappa_\sigma=1$	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=1$	$\varkappa_\sigma=\frac{1}{2}$	$\varkappa_\sigma=\frac{1}{2}$

* Infinite variance is consistent with the absence of the corresponding term from both the numerator and denominator of (5·87).

Hence, from (5·54),

$$\langle |E_{ij}| (\cos \varphi_{ij}+i \sin \varphi_{ij})\rangle_{\mathbf{h}_i+\mathbf{h}_j} = \frac{4}{S_2}\left\{\sum_{j'=1}^{N/4} Z_{j'}^2 \cos 2\pi(h_i+h_j)x_{j'} \cos 2\pi(k_i+k_j)y_{j'} \times \cos 2\pi(l_i+l_j)z_{j'} - i\sum_{j'=1}^{N/4} Z_{j'}^2 \sin 2\pi(h_i+h_j)x_{j'} \sin 2\pi(k_i+k_j)y_{j'} \times \sin 2\pi(l_i+l_j)z_{j'}\right\} . \quad (5·57)$$

However

$$E_{\mathbf{h}_i+\mathbf{h}_j} = E_{\mathbf{h}} = |E_{\mathbf{h}}| (\cos \varphi+i \sin \varphi) = \frac{4}{S_2^{\frac{1}{2}}} \sum_{j'=1}^{N/4} Z_{j'} (\cos 2\pi hx_{j'} \cos 2\pi ky_{j'} \cos 2\pi lz_{j'} - i \sin 2\pi hx_{j'} \sin 2\pi ky_{j'} \sin 2\pi lz_{j'}) . \quad (5·58)$$

From (5·50), (5·57), and (5·58),

$$\delta_{\mathbf{h}} = 4\sum_{j'=1}^{N/4}\left(\frac{Z_{j'}}{S_2^{\frac{1}{2}}}-\frac{S_2^{\frac{1}{2}}}{S_3}Z_{j'}^2\right) \times (\cos 2\pi hx_{j'} \cos 2\pi ky_{j'} \cos 2\pi lz_{j'} - i \sin 2\pi hx_{j'} \sin 2\pi ky_{j'} \sin 2\pi lz_{j'}) . \quad (5·59)$$

Now, just as in the derivation of (5·32), we conclude that, as h, k, l range uniformly and independently over all the integers, both the real part and the imaginary part of $\delta_{\mathbf{h}}$ are normally distributed about zero with a variance given by (5·32). In short we may write

$$\cos \varphi \approx \frac{S_2^{3/2}}{S_3|E|} \langle |E_{ij}| \cos \varphi_{ij}\rangle_{i,j} , \quad (5·60)$$

$$\sin \varphi \approx \frac{S_2^{3/2}}{S_3|E|} \langle |E_{ij}| \sin \varphi_{ij}\rangle_{i,j} , \quad (5·61)$$

$$\tan \varphi \approx \frac{\langle |E_{ij}| \sin \varphi_{ij}\rangle_{i,j}}{\langle |E_{ij}| \cos \varphi_{ij}\rangle_{i,j}} , \quad (5·62)$$

where the symbol $\approx$ denotes probable equality. More precisely, $\cos\varphi$ and $\sin\varphi$ are normally distributed about the means (5·60) and (5·61) respectively with the variance σ_1 given by

$$\sigma_1 = \frac{1}{|E|^2}\left(\frac{S_2S_4}{S_3^2}-1\right) . \quad (5·63)$$

The variance σ arising from the use of a finite number n of data to compute a mean is calculated as in § 5·1·1. The various cases which arise when (5·49) is not fulfilled are treated in a similar manner and the results are summarized in Table 2. It should be noted that in order to conserve space, the cases corresponding to the various cyclic permutations on the indices permitted by the space-group symmetries have not been included in Table 2; but these may be easily deduced from the existing entries.

5·1·3. *Miscellaneous relations.*—Some of the higher-order terms in the Maclaurin expansion of the exponential in (5·05) lead ultimately to useful relations. We list only five of the most useful such distributions:

$$P(E, E_i, |E_j|) = \frac{|E_j|}{\pi} \exp(-\tfrac{1}{2}E^2-\tfrac{1}{2}E_i^2-|E_j|^2) \times \left\{1+t\frac{S_4}{S_2^2}EE_i(|E_j|^2-1)\right\} , \quad (5·64)$$

where

$$h = h_i+2h_j,\ k = k_i+2k_j , \quad (5·65)$$

$$l = l_i = 0,\ t = \tfrac{1}{2} \text{ if } l_j = 0,\ t = 1 \text{ if } l_j \neq 0; \quad (5·66)$$

or where

$$h = h_i+2h_j,\ k_i = 0,\ k = 2k_j , \quad (5·67)$$

$$l = l_i = 0,\ t = \tfrac{1}{2}\sqrt{2} \text{ if } l_j = 0,\ t = \sqrt{2} \text{ if } l_j \neq 0 . \quad (5·68)$$

$$P(E, E_i, E_j) = \frac{\exp(-\tfrac{1}{2}E^2-\tfrac{1}{2}E_i^2-\tfrac{1}{2}E_j^2)}{(2\pi)^{3/2}} \times \left\{1+t\frac{S_4}{S_2^2}EE_i(E_j^2-1)\right\} , \quad (5·69)$$

where

$$h = h_i+2h_j,\ k = k_i = l = l_i = 0,\ t = 1; \quad (5·70)$$

or where

$$h = 2h_j,\ k_i = 2k_j,\ l = l_i,\ k = h_i = l_j = 0,\ t = 1; \quad (5·71)$$

or where

$$h=h_i+2h_j,\ k=k_i+2k_j,\ l=l_i=l_j=0,\ t=\tfrac{1}{2} . \quad (5·72)$$

5·1·4. *A procedure for phase determination.*—We start with a set of observed structure-factor magnitudes containing all the usual corrections except those for vibrational motion and absolute scale. Define

$$\sigma_2 = \sigma_2(s) = \sigma_2(h, k, l) = \sum_{j=1}^{N} f_j^2(h, k, l) , \quad (5·73)$$

where $s = \sin\theta/\lambda$. Also define

$$\varepsilon = \varepsilon(s) = \varepsilon(h, k, l) = 2 \quad \text{if } h = k = 0 \text{ or if } k = l = 0 \text{ or if } l = h = 0 , \quad (5·74)$$

$$\varepsilon = \varepsilon(s) = \varepsilon(h, k, l) = 1 \text{ otherwise}, \quad (5·75)$$

since, in view of (5·01) and (5·02), these are the values of $(m_2^0+m_0^2)/n$ appearing in (3·12). Arrange the s values in increasing order and divide the s range into intervals in such a way that each interval contains approximately 200 $|F|^2_{\text{obs.}}$ values. For each such interval compute

$$K = \Sigma\varepsilon\sigma_2/\Sigma|F|^2_{\text{obs.}} , \quad (5·76)$$

where the sums are extended over the corresponding s (or h, k, l) values appearing in the interval. Label each interval by the s value at its center so that K

appears as a function of s. Draw a smooth monotonically increasing curve $K(s)$ among these points. Finally, by means of

$$|F_{hkl}|^2 = |F|^2_{\text{obs.}} K(s) \tag{5·77}$$

we obtain the values of the $|F_{hkl}|^2$ corrected for vibrational motion and placed on an absolute scale which are needed to compute the $|E_{hkl}|^2$.

In view of (3·12), the normalized structure-factor magnitudes $|E_{hkl}|^2$ are computed by means of

$$|E_{hkl}|^2 = |F_{hkl}|^2/\varepsilon\sigma_2 \,. \tag{5·78}$$

At this point it is well to verify the following averages which are easily obtained from the distributions for $|E|$ given by us (Hauptman & Karle, 1953; Karle & Hauptman, 1953):

$$\left.\begin{array}{l}\langle|E|\rangle=0·798,\ \langle|E|^2\rangle=1·000,\ \langle|E|^3\rangle=1·596\,,\\ \langle|E|^4\rangle=3·000,\ \langle||E|^2-1|\rangle=0·968\,,\end{array}\right\} hkl=0; \tag{5·79}$$

$$\left.\begin{array}{l}\langle|E|\rangle=0·886,\ \langle|E|^2\rangle=1·000,\ \langle|E|^3\rangle=1·329\,,\\ \langle|E|^4\rangle=2·000,\ \langle||E|^2-1|\rangle=0·736\,,\end{array}\right\} hkl\neq0. \tag{5·80}$$

The averages given in (5·79) and (5·80) are sufficiently accurate for large N. The more accurate formulas needed when N is small (e.g. < 10) are readily obtained from the distributions cited above.

Next, three summary tables are constructed. In the first table the entries, for each fixed k_j and l_j, are

$$\sum_{h_j} (|E_{h_jk_jl_j}|^2-1) \,. \tag{5·81}$$

In the second table the entries, for each fixed l_j and h_j, are

$$\sum_{k_j} (|E_{h_jk_jl_j}|^2-1) \,. \tag{5·82}$$

In the third table the entries, for each fixed h_j and k_j, are

$$\sum_{l_j} (|E_{h_jk_jl_j}|^2-1) \,. \tag{5·83}$$

Step 1.—Tentative phases φ_{hkl} (either 0 or π) for the normalized structure factors E_{hkl} are first obtained for h, k, and l all even and $hkl = 0$. These phases are the intensity invariants, i.e. their values are uniquely determined by the magnitudes of the structure factors. For example, in view of Table 1, the tentative phase of φ_{hk0}, where h and k are both even and $hk \neq 0$, is either 0 or π depending on whether (5·83), with $h_j = \frac{1}{2}h$, $k_j = \frac{1}{2}k$, is positive or negative. In view of Table 1, to determine a phase φ_{h00}, where h is even, we add (5·83) with $h_j = \frac{1}{2}h$, $k_j = 0$ to (5·82) with $h_j = \frac{1}{2}h$, $l = 0$, and, according as this sum is positive or negative, the value of φ_{h00} is 0 or π. It is thus seen that tentative values for the phases which are intensity invariants are immediately obtainable by inspection of the three summary tables. Of course only those phases φ_{hkl} will be reliably determined for which the corresponding $|E_{hkl}|$ is large and the corresponding entry in the summary table is large, as measured by the variances σ and σ_1 (Table 1). The exact number of phases so determined will depend of course on the amount of data available relative to the complexity of the crystal structure.

Making use of the phases tentatively determined, we use columns 7–10, 13 of Table 2 and find final values for the phases $\varphi_{\mathbf{h}}$ by means of

$$\cos\varphi_{\mathbf{h}} = \frac{S_2^{3/2}}{S_3|E_{\mathbf{h}}|}\cdot\frac{\sum\limits_{i,j}\frac{1}{\varkappa_{\sigma ij}^{\frac{1}{2}}}|E_{ij}|\cos\varphi_{ij}}{\sum\limits_{i,j}\frac{|E_{ij}|^2}{\varkappa_{\sigma ij}^{\frac{1}{2}}\varkappa_{cij}}}\,, \tag{5·84}$$

$$\mathbf{h} = \mathbf{h}_i+\mathbf{h}_j,\ E_{ij} = E_{\mathbf{h}_i}E_{\mathbf{h}_j},\ \varphi_{ij} = \varphi_{\mathbf{h}_i}+\varphi_{\mathbf{h}_j}\,. \tag{5·85}$$

Equation (5·84) is implied by (5·45). The contribution of each term, however, is weighted by means of the reciprocal of its standard deviation obtained from Table 2.

We assign to $\varphi_{\mathbf{h}}$ the value 0 or π according as the right side of (5·84) is positive or negative. In conjunction with (5·84) use may be made of (5·64)–(5·72), especially if the number of phases assigned tentatively is so small that (5·84) is not statistically reliable. We conclude that $\varphi_{\mathbf{h}}$ is probably 0 or π according as

$$\sum_{i,j}\frac{1}{\varkappa^{\frac{1}{2}}}E_{\mathbf{h}_i}(|E_{\mathbf{h}_j}|^2-1) \tag{5·86}$$

is positive or negative, where $x = 1/t$ if (5·64) is used while $x = 2/t$ if (5·69) is used. Occasionally discrepancies between (5·84) and (5·86) will be observed. These are to be resolved in an obvious manner depending on the relative statistical weights of (5·84) and (5·86).

Step 2.—Next, the largest $|E_{\mathbf{h}_1}|$, with $h_1k_1l_1 = 0$ and for which $\varphi_{\mathbf{h}_1}$ is linearly independent, is selected. The value, either 0 or π, of the phase $\varphi_{\mathbf{h}_1}$ may be specified arbitrarily. Then the values of all remaining phases $\varphi_{\mathbf{h}}$, which are linearly dependent on $\varphi_{\mathbf{h}_1}$ and for which $hkl = 0$, are uniquely determined by the magnitudes of the structure factors. To find these use is made of (5·84)–(5·86), in the manner described in Step 1, together with the phases already determined.

For example, the phase $\varphi_{\mathbf{h}_1}$ may be chosen to be a phase φ_{ug0}, i.e. h_1 is odd (*ungerade*), k_1 is even (*gerade*), and $l_1 = 0$. Then the values of all other phases φ_{ug0} and φ_{u0g} are uniquely determined.

Step 3.—The largest $|E_{\mathbf{h}_2}|$, with $h_2k_2l_2 = 0$, for which $\varphi_{\mathbf{h}_2}$ is linearly independent of $\varphi_{\mathbf{h}_1}$ is next selected. We then proceed as in Step 2 but replace $\mathbf{h}_1$ by $\mathbf{h}_2$. Now however, in addition to the phases $\varphi_{\mathbf{h}}$, with $hkl = 0$, which are linearly dependent on $\varphi_{\mathbf{h}_2}$, those phases which are linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ are also uniquely determined. Again, use is made of (5·84) and all phases the values of which have been previously determined.

For example, if $\varphi_{\mathbf{h}_1}$ is chosen to be φ_{ug0}, then the phase $\varphi_{\mathbf{h}_2}$ may be chosen to be φ_{0ug}. Then the values of all phases φ_{0ug} and φ_{gu0}, linearly dependent on $\varphi_{\mathbf{h}_2}$, as well as those of all phases φ_{uu0}, linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$, are uniquely determined.

Step 4.—The largest $|E_{\mathbf{h}_3}|$, with $h_3k_3l_3 = 0$, for which $\varphi_{\mathbf{h}_3}$ is linearly independent of the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ is selected. We then proceed as in Step 2 but replace $\mathbf{h}_1$ by $\mathbf{h}_3$. In addition to the phases $\varphi_{\mathbf{h}}$, with $hkl = 0$, which are linearly dependent on $\varphi_{\mathbf{h}_3}$, those which are linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_3}$ or on the pair $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$ are also uniquely determined. The values of all phases which have been previously determined are used in conjunction with (5·84).

For example, if $\varphi_{\mathbf{h}_1} = \varphi_{ug0}$ and $\varphi_{\mathbf{h}_2} = \varphi_{0ug}$, then $\varphi_{\mathbf{h}_3}$ may be chosen to be φ_{g0u}. Then the values of all phases φ_{g0u} and φ_{0gu}, linearly dependent on $\varphi_{\mathbf{h}_3}$, as well as those of all phases φ_{u0u}, linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_3}$, and those of all phases φ_{0uu}, linearly dependent on the pair $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$, are uniquely determined.

Step 5.—Making use of the phases already determined and columns 5 and 6 of Table 2 we find tentative values for the magnitudes of all phases $\varphi_{\mathbf{h}}$ which are structure invariants (i.e. h, k, and l are all even) by means of (5·84) and (5·85). Improved values for the magnitudes of these phases are obtained from columns 2–6 of Table 2 by using (5·84) and (5·85) until several cycles of refinement yield no further changes in these values.

Step 6.—We specify arbitrarily the sign of a phase $\varphi_{\mathbf{h}}$ which is a structure invariant (whence its magnitude is known from Step 5). The corresponding $|E_{\mathbf{h}}|$ should be large while the value of $|\varphi_{\mathbf{h}}|$ should be close to $\frac{1}{2}\pi$. In this way we distinguish between the two enantiomorphous structures S and S' permitted by the known magnitudes of the structure factors. Final values for the phases which are structure invariants are obtained by repeated use of (5·84), (5·85),

$$\sin \varphi_{\mathbf{h}} = \frac{S_2^{3/2}}{S_3|E_{\mathbf{h}}|} \cdot \frac{\sum_{i,j} \frac{1}{\varkappa_{\sigma ij}^{1/2}} |E_{ij}| \sin \varphi_{ij}}{\sum_{i,j} \frac{|E_{ij}|^2}{\varkappa_{\sigma ij}^{1/2} \varkappa_{sij}}}, \qquad (5\cdot87)$$

and

$$\tan \varphi_{\mathbf{h}} = \sin \varphi_{\mathbf{h}} / \cos \varphi_{\mathbf{h}} . \qquad (5\cdot88)$$

Equation (5·87) is implied by (5·46). The contribution of each term, however, is weighted by means of the reciprocal of its standard deviation obtained from Table 2. Although the values of $\cos \varphi_{\mathbf{h}}$ and $\sin \varphi_{\mathbf{h}}$, as obtained from (5·84) and (5·87), may be inaccurate (and even exceed unity) owing to inadequate or faulty sampling, these errors tend to compensate in (5·88). Hence, (5·88) should be used to compute $\varphi_{\mathbf{h}}$ whenever possible, instead of (5·84) and (5·87) separately.

Step 7.—The values of all remaining phases $\varphi_{\mathbf{h}}$ are obtained by repeated use of (5·84), (5·85), (5·87), and (5·88), as many iterations being used as necessary.

Table 3. *The relation* $\mathbf{h} = \mathbf{h}_i + \mathbf{h}_j$ *and the values* $\varkappa_c$, $\varkappa_s$ *and* $\varkappa_\sigma$ *for space group* $P2_12_12_1$

hkl of φ_{hkl} desired	Reference $h_ik_il_i$	Reference $h_jk_jl_j$	Condition	$\varkappa_{cij}$	$\varkappa_{sij}$	$\varkappa_{\sigma ij}$
hkl	$h_ik_il_i$	$h_jk_jl_j$	None	1	1	$\frac{1}{2}$
hkl	h_ik_i0	$h_jk_jl_j$	None	1	1	$\frac{1}{2}$
hkl	h_i00	$h_jk_jl_j$	None	$1/\sqrt{2}$	$1/\sqrt{2}$	$\frac{1}{2}$
hkl	h_ik_i0	h_j0l_j	h_il_j even	$\frac{1}{2}$	∞	1
			h_il_j odd	∞	$\frac{1}{2}$	1
hkl	h_ik_i0	$0k_jl_j$	h_ik_j even	$\frac{1}{2}$	∞	1
			h_ik_j odd	∞	$\frac{1}{2}$	1
hkl	$0k_il_i$	h_j0l_j	k_il_j even	$\frac{1}{2}$	∞	1
			k_il_j odd	∞	$\frac{1}{2}$	1
hkl	h_i00	$0k_jl_j$	k_j even	$1/2\sqrt{2}$	∞	1
			k_j odd	∞	$1/2\sqrt{2}$	1
hkl	$0k_i0$	h_j0l_j	l_j even	$1/2\sqrt{2}$	∞	1
			l_j odd	∞	$1/2\sqrt{2}$	1
hkl	$00l_i$	h_jk_j0	h_j even	$1/2\sqrt{2}$	∞	1
			h_j odd	∞	$1/2\sqrt{2}$	1
$hk0$	h_ik_i0	h_jk_j0	h_ih_j even	1	∞	1
			h_ih_j odd	∞	1	1
$0kl$	$0k_il_i$	$0k_jl_j$	k_ik_j even	1	∞	1
			k_ik_j odd	∞	1	1
$h0l$	h_i0l_i	h_j0l_j	l_il_j even	1	∞	1
			l_il_j odd	∞	1	1
$hk0$	h_i0l_i	$0k_jl_j$	l_ik_j even	$\frac{1}{2}$	∞	1
			l_ik_j odd	∞	$\frac{1}{2}$	1
$h0l$	h_ik_i0	$0k_jl_j$	h_ik_j even	$\frac{1}{2}$	∞	1
			h_ik_j odd	∞	$\frac{1}{2}$	1
$0kl$	h_ik_i0	h_j0l_j	h_il_j even	$\frac{1}{2}$	∞	1
			h_il_j odd	∞	$\frac{1}{2}$	1
$hk0$	h_ik_i0	h_j00	h_i even	$1/\sqrt{2}$	∞	1
			h_i odd	∞	$1/\sqrt{2}$	1
$0kl$	$0k_il_i$	$0k_j0$	k_i even	$1/\sqrt{2}$	∞	1
			k_i odd	∞	$1/\sqrt{2}$	1
$h0l$	h_i0l_i	h_j00	l_i even	$1/\sqrt{2}$	∞	1
			l_i odd	∞	$1/\sqrt{2}$	1
$hk0$	h_i00	$0k_j0$	None	$\frac{1}{2}$	∞	1
$h00$	h_i00	h_j00	None	$1/\sqrt{2}$	∞	1
$hk0$	$h_ik_il_i$	$h_jk_jl_j$	h even	1	∞	$\frac{1}{2}$
			h odd	∞	1	$\frac{1}{2}$
$0kl$	$h_ik_il_i$	$h_jk_jl_j$	k even	1	∞	$\frac{1}{2}$
			k odd	∞	1	$\frac{1}{2}$
$h0l$	$h_ik_il_i$	$h_jk_jl_j$	l even	1	∞	$\frac{1}{2}$
			l odd	∞	1	$\frac{1}{2}$
$h00$	$h_ik_il_i$	$h_jk_jl_j$	None	$1/\sqrt{2}$	∞	$\frac{1}{2}$
$hk0$	$h_ik_il_i$	h_j0l_j	h even	1	∞	$\frac{1}{2}$
			h odd	∞	1	$\frac{1}{2}$
$0kl$	$h_ik_il_i$	h_j0l_j	k even	1	∞	$\frac{1}{2}$
			k odd	∞	1	$\frac{1}{2}$
$h0l$	$h_ik_il_i$	h_jk_j0	l even	1	∞	$\frac{1}{2}$
			l odd	∞	1	$\frac{1}{2}$
$h00$	$h_ik_il_i$	$0k_jl_j$	None	$1/\sqrt{2}$	∞	$\frac{1}{2}$

5·2. *Space group* $P2_12_12_1$

Since the formulas for this space group are similar to those for $P222$, it will suffice only to sketch briefly the procedures for space group $P2_12_12_1$, pointing out in particular where these differ from those for $P222$.

5·2·1. *Procedure for phase determination.*—The normalized structure-factor magnitudes are computed as

Table 4. *The phases which are intensity seminvariants, related probability distributions, expected values, and variances for space group P422*

The phases which head the columns are those phases, φ_{hkl}, for which values are to be determined.

	φ_{hhg} $h = h_j \pm k_j$ $l_j = \frac{1}{2}l$	φ_{gg0} $h_j = \frac{1}{2}h$ $k_j = \frac{1}{2}k$	φ_{gg0} or φ_{uu0} $h \neq \pm k$	φ_{g0g} $h_j = \frac{1}{2}h$ $l_j = \frac{1}{2}l$	φ_{g00} $h_j = \frac{1}{2}h$	φ_{00g} $l_j = \frac{1}{2}l$
$P(E, \lvert E_j\rvert) = \frac{2}{\sqrt{(2\pi)}} \lvert E_j\rvert \exp[-\frac{1}{2}E^2 - \lvert E_j\rvert^2]\left\{1 + \frac{S_3}{S_2^{3/2}} E(\lvert E_j\rvert^2 - 1)\right\}$ $E = \frac{S_2^{3/2}}{S_3}\langle \lvert E_j\rvert^2 - 1\rangle$ $\sigma = \frac{S_2^3}{S_3^2},\ \sigma_1 = \frac{S_2S_4}{S_3^2} - 1$	$l \neq 0$ $h_j \neq \pm k_j$	—	—	$h_j \neq \pm k_j$ $k_j \neq 0$	—	—
$P(E, \lvert E_j\rvert) = \frac{\exp[-\frac{1}{2}E^2 - \frac{1}{2}E_j^2]}{\pi}\left\{1 + \frac{1}{2}\cdot\frac{S_3}{S_2^{3/2}} E(E_j^2 - 1)\right\}$ $E = \frac{S_2^{3/2}}{S_3}\langle E_j^2 - 1\rangle$ $\sigma = \frac{S_2^3}{S_3^2}\cdot 2,\ \sigma_1 = \frac{S_2S_4}{S_3^2} - 1$	$l \neq 0$ $h_j = \pm k_j$	—	—	$h_j = \pm k_j$ $k_j = 0$	—	$h_j = \pm k_j = 0$
$P(E, \lvert E_j\rvert) = \frac{\exp[-\frac{1}{2}E^2 - \frac{1}{2}E_j^2]}{\pi}\left\{1 + \frac{S_3}{S_2^{3/2}} E(E_j^2 - 1)\right\}$ $E = \frac{1}{2}\cdot\frac{S_2^{3/2}}{S_3}\langle E_j^2 - 1\rangle$ $\sigma = \frac{1}{4}\cdot\frac{S_2^3}{S_3^2}\cdot 2,\ \sigma_1 = \frac{S_2S_4}{S_3^2} - 1$	$l = 0$ $h_j \neq \pm k_j$	$h = \pm k$ $l_j \neq 0$	—	$h_j = \pm k_j \neq 0$	$k_j = l_j = 0$	$h_j = 0, k_j \neq 0$ or $h_j \neq 0, k_j = 0$
$P(E, \lvert E_j\rvert) = \frac{\exp[-\frac{1}{2}E^2 - \frac{1}{2}E_j^2]}{\pi}\left\{1 + 2\frac{S_3}{S_2^{3/2}} E(E_j^2 - 1)\right\}$ $E = \frac{1}{4}\cdot\frac{S_2^{3/2}}{S_3}\langle E_j^2 - 1\rangle$ $\sigma = \frac{1}{16}\cdot\frac{S_2^3}{S_3^2}\cdot 2,\ \sigma_1 = \frac{S_2S_4}{S_3^2} - 1$	$l = 0$ $h_j = \pm k_j$	$h = \pm k$ $l_j = 0$	—	—	$k_j = 0, l_j \neq 0$ or $k_j \neq 0, l_j = 0$	$h_j = \pm k_j \neq 0$
$P(E, E', \lvert E_j\rvert) = \frac{\lvert E_j\rvert}{\pi}\exp[-\frac{1}{2}E^2 - \frac{1}{2}E'^2 - \lvert E_j\rvert^2]\left\{1 + \frac{S_3}{S_2^{3/2}}(E + 2E')(\lvert E_j\rvert^2 - 1)\right\}$ $E + 2E' = \frac{S_2^{3/2}}{S_3}\langle \lvert E_j\rvert^2 - 1\rangle,\ E = E_{hk0},\ E' = E_{\frac{1}{2}(h+k), \frac{1}{2}(h-k), 0}$ $\sigma = \frac{S_2^3}{S_3^2},\ \sigma_1 = 5\left(\frac{S_2S_4}{S_3^2} - 1\right)$	—	$h \neq \pm k$ $l_j \neq 0$	—	—	—	—

$P(E, E', \lvert E_j \rvert) = \frac{\sqrt{2}}{\pi^{3/2}} \exp\left[-\tfrac{1}{2}E^2 - \tfrac{1}{2}E'^2 - \tfrac{1}{2}E_j^2\right]\left\{1 + \tfrac{1}{2}\cdot\frac{S_3}{S_2^{3/2}}(E+2E')(E_j^2-1)\right\}$; $E+2E' = \frac{S_2^{3/2}}{S_3}\langle E_j^2-1\rangle$, $E = E_{hk0}$, $E' = E_{\frac{1}{2}(h+k), \frac{1}{2}(h-k), 0}$; $\sigma = \frac{S_2^3}{S_3^2}\cdot 2$, $\sigma_1 = 5\left(\frac{S_2S_4}{S_3^2}-1\right)$	—	$h \neq \pm k$, $l_j = 0$	—	—	—	—
$P(E, E'', \lvert E_j \rvert) = \frac{\lvert E_j \rvert}{\pi} \exp\left[-\tfrac{1}{2}E^2 - \tfrac{1}{2}E''^2 - \lvert E_j \rvert^2\right]\left\{1 + \frac{S_3}{S_2^{3/2}}(2E+E'')(\lvert E_j \rvert^2-1)\right\}$; $2E+E'' = \frac{S_2^{3/2}}{S_3}\langle \lvert E_j \rvert^2-1\rangle$, $E = E_{hk0}$, $E'' = E_{h+k, h-k, 0}$; $\sigma = \frac{S_2^3}{S_3^2}$, $\sigma_1 = 5\left(\frac{S_2S_4}{S_3^2}-1\right)$	—	—	$h_j = \tfrac{1}{2}(h+k)$, $k_j = \tfrac{1}{2}(h-k)$, $l_j \neq 0$	—	—	—
$P(E, E'', \lvert E_j \rvert) = \frac{\sqrt{2}}{\pi^{3/2}} \exp\left[-\tfrac{1}{2}E^2 - \tfrac{1}{2}E''^2 - \tfrac{1}{2}E_j^2\right]\left\{1 + \tfrac{1}{2}\cdot\frac{S_3}{S_2^{3/2}}(2E+E'')(E_j^2-1)\right\}$; $2E+E'' = \frac{S_2^{3/2}}{S_3}\langle E_j^2-1\rangle$, $E = E_{hk0}$, $E'' = E_{h+k, h-k, 0}$; $\sigma = \frac{S_2^3}{S_3^2}\cdot 2$, $\sigma_1 = 5\left(\frac{S_2S_4}{S_3^2}-1\right)$	—	—	$h_j = \tfrac{1}{2}(h+k)$, $k_j = \tfrac{1}{2}(h-k)$, $l_j = 0$	—	—	—

in § 5·1·4 with the exception that now the extinctions, i.e. those reflections E_{hkl} with $h = k = 0$, l odd, or $k = l = 0$, h odd, or $l = h = 0$, k odd, are omitted from consideration.

Next, three summary tables are constructed. In the first table the entries, for each fixed k_j and l_j, are

$$\sum_{h_j} (-1)^{h_j+k_j}(\lvert E_{h_jk_jl_j}\rvert^2-1)\,. \tag{5·89}$$

In the second table the entries, for each fixed l_j and h_j, are

$$\sum_{k_j} (-1)^{k_j+l_j}(\lvert E_{h_jk_jl_j}\rvert^2-1)\,. \tag{5·90}$$

In the third table the entries, for each fixed h_j and k_j, are

$$\sum_{l_j} (-1)^{l_j+h_j}(\lvert E_{h_jk_jl_j}\rvert^2-1)\,. \tag{5·91}$$

In the procedure to be described we naturally make use of these new summary tables rather than the ones outlined in § 5·14 which were appropriate for the space group $P222$.

Step 1.—Tentative values, either 0 or π, for the phases φ_{hkl} which are intensity invariants, i.e. such that $h \equiv k \equiv l \equiv 0 \pmod 2$ and $hkl = 0$, are obtained as in Step 1 of § 5·14 except that we now use the new summary tables with the entries (5·89)–(5·91). Final values for these phases are obtained as before making use of (5·84)–(5·86) but with values of $\varkappa_c$, $\varkappa_s$ and $\varkappa_\sigma$ as obtained from Table 3. However, the separate terms of (5·86) are now multiplied by $(-1)^{h_j+k_j}$ or $(-1)^{k_j+l_j}$ or $(-1)^{l_j+h_j}$ according as $\mathbf{h}_j$ is of the form $0gg$, $g0g$, or $gg0$ respectively. In this way (5·86) is replaced by a new expression hereafter referred to as (5·86′).

Step 2.—Next, the largest $\lvert E_{\mathbf{h}_1}\rvert$, with $h_1k_1l_1 = 0$ and for which $\varphi_{\mathbf{h}_1}$ is linearly independent, is selected. The value of the phase $\varphi_{\mathbf{h}_1}$, of necessity chosen from one of the pairs 0, π or $\pm\frac{1}{2}\pi$ depending on the nature of $\mathbf{h}_1$, may be specified arbitrarily. Then the values of all remaining phases $\varphi_{\mathbf{h}}$, which are linearly dependent on $\varphi_{\mathbf{h}_1}$ and for which $h = 0$ or $k = 0$ or $l = 0$ depending on whether $h_1 = 0$ or $k_1 = 0$ or $l_1 = 0$, are uniquely determined by the magnitudes of the structure factors. To find these, use is made of (5·84) or (5·87), (5·85), and (5·86′) in the manner described in Step 1, together with the phases already determined. It should be emphasized at this point that, contrary to the situation for space group $P222$, it is not sufficient that $\varphi_{\mathbf{h}}$ merely be linearly dependent on $\varphi_{\mathbf{h}_1}$. It is further required of $\varphi_{\mathbf{h}}$ that a certain one of its indices be zero. This is not a contradiction of Theorem 8·02·2 of Hauptman & Karle (1956) since Hypothesis B of this theorem is not fulfilled. In fact we have not yet distinguished between the enantiomorphous structures S and S' permitted by the structure-factor magnitudes. For space group $P222$ this does not matter since a phase $\varphi_{\mathbf{h}}$ with $hkl = 0$ has the same value for both enantiomorphs. For $P2_12_12_1$, on the other hand, the value of such a phase may depend on the choice of enantiomorph, S or S'.

For example, the phase $\varphi_{\mathbf{h}_1}$ may be chosen to be a phase φ_{0uu} whence its value is chosen arbitrarily to be one of $\pm\frac{1}{2}\pi$. Then the values of all other phases φ_{0uu} are uniquely determined.

Step 3.—The largest $|E_{\mathbf{h}_2}|$, with $h_2k_2l_2 = 0$, for which $\varphi_{\mathbf{h}_2}$ is linearly independent of $\varphi_{\mathbf{h}_1}$, is next selected. We then continue as in Step 2 but replace $\mathbf{h}_1$ by $\mathbf{h}_2$. We need to proceed now with utmost caution. Are all phases $\varphi_{\mathbf{h}}$, with one index 0, which are linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ uniquely determined by the structure-factor magnitudes, as was the case with $P222$? The answer is 'yes' if the structure invariant $\varphi_{\mathbf{h}}-\varphi_{\mathbf{h}_1}-\varphi_{\mathbf{h}_2}$ is an intensity invariant, i.e. has the value 0 or π, for the value of such an invariant is the same for both enantiomorphous structures S, S'. The answer is 'no' if the value of this invariant is $\pm\frac{1}{2}\pi$, for such an invariant has the value $+\frac{1}{2}\pi$ for S and the value $-\frac{1}{2}\pi$ for S'. In the latter case we are free to choose arbitrarily one of the two possible values of $\varphi_{\mathbf{h}}$ (i.e. of $\varphi_{\mathbf{h}}-\varphi_{\mathbf{h}_1}-\varphi_{\mathbf{h}_2}$), and in fact must do so if we are to distinguish the two structures S, S'.

Let us assume that it is the former case which applies, and postpone for a while the choice of enantiomorphous structure S, S'. To this end, take $\varphi_{\mathbf{h}_1}=\varphi_{0uu}$, $\varphi_{\mathbf{h}_2} = \varphi_{uu0}$. Then the values of all phases φ_{0uu} and φ_{uu0} are uniquely determined. To find these, use is naturally made of (5·87) in the manner already described.

It is interesting and easy to verify that, in the case that the invariant $\varphi_{\mathbf{h}}-\varphi_{\mathbf{h}_1}-\varphi_{\mathbf{h}_2} = \pm\frac{1}{2}\pi$, (5·84) actually does yield no information concerning the value of $\varphi_{\mathbf{h}}$. This is an instance in which the joint distribution bears out in a rather striking fashion the results of the invariant theory.

Step 4.—The largest $|E_{\mathbf{h}_3}|$, with $h_3k_3l_3 = 0$, for which $\varphi_{\mathbf{h}_3}$ is linearly independent of the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ is selected. We then proceed as in Step 2 but replace $\mathbf{h}_1$ by $\mathbf{h}_3$. The remarks of Step 3 are relevant here too.

For example, let us take $\varphi_{\mathbf{h}_1} = \varphi_{0uu}$, $\varphi_{\mathbf{h}_2} = \varphi_{uu0}$, $\varphi_{\mathbf{h}_3} = \varphi_{0ug}$. Not only are the values of all phases φ_{0uu}, φ_{uu0}, φ_{0ug} which are linearly dependent on $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$ respectively, uniquely determined by the magnitudes of the structure factors, but so are the values of all phases φ_{0gu} and φ_{u0g}, linearly dependent on the pairs $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_3}$ and $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$ respectively. This is a consequence of the fact that the value of each of the structure invariants $\varphi_{0gu}-\varphi_{\mathbf{h}_1}-\varphi_{\mathbf{h}_3}$ and $\varphi_{u0g}-\varphi_{\mathbf{h}_2}-\varphi_{\mathbf{h}_3}$ is 0 or π, hence the same for the two enantiomorphous structures S, S'. The phases φ_{u0u}, which are linearly dependent on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ are, on the other hand, not uniquely determined by the magnitudes of the structures factors since the values of the structure invariants $\varphi_{u0u}-\varphi_{\mathbf{h}_1}-\varphi_{\mathbf{h}_2}$ are $\pm\frac{1}{2}\pi$, hence different for the two enantiomorphous structures S, S'. The phases φ_{gu0} also are not uniquely determined by the structure-factor magnitudes despite the fact that these phases are linearly dependent on $\varphi_{\mathbf{h}_3}$. Again the reason is the fact that the values of the structure invariants $\varphi_{gu0}-\varphi_{\mathbf{h}_3}$ are $\pm\frac{1}{2}\pi$.

Step 5.—Any phase $\varphi_{\mathbf{h}_4}$, with $h_4k_4l_4 = 0$, is of necessity linearly dependent on the triple $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$ already chosen. For example, taking, as in Step 4, $\varphi_{\mathbf{h}_1} = \varphi_{0uu}$, $\varphi_{\mathbf{h}_2} = \varphi_{uu0}$, $\varphi_{\mathbf{h}_3} = \varphi_{0ug}$ we may take $\varphi_{\mathbf{h}_4} = \varphi_{gu0}$, where $|E_{\mathbf{h}_4}|$ is maximal. Since the value of the structure invariant $\varphi_{\mathbf{h}_4}-\varphi_{\mathbf{h}_3}$ is $\pm\frac{1}{2}\pi$, we may choose either one of these values, i.e. either of the values 0 or π for $\varphi_{\mathbf{h}_4}$, and thus, finally, distinguish between the two enantiomorphous structures S, S'. Now the phases φ_{g0u} and φ_{ug0} linearly dependent on the pairs $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_4}$ and $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_4}$ respectively, are uniquely determined. Finally the phases φ_{u0u} linearly dependent on the set $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$, $\varphi_{\mathbf{h}_4}$ are also uniquely determined. These phases are all to be found by means of (5·84) and (5·87) in conjunction with the values of all previously determined phases.

Step 6.—All remaining phases are obtained as in Step 7, § 5·1·4, by repeated use of (5·84), (5·85), (5·87), and (5·88), referring to Table 3 for values of $\varkappa_c$, $\varkappa_s$ and $\varkappa_\sigma$.

It should be pointed out that, from the point of view of phase determination, space group $P2_12_12_1$ is more favorable than $P222$. In order to determine the value of the structure invariant φ_{hkl} with $hkl \neq 0$, both (5·84) and (5·87) are available to yield independent estimates of cos φ_{hkl} and sin φ_{hkl} for space group $P2_12_12_1$. For $P222$, however, only (5·84) is available in the initial stages, and (5·87) may be used only after the values of a sufficient number of phases have been determined.

6. Type 2*P*22

Only the space group $P422$ belonging to Type $2P22$ is here considered in any detail. Since the methods are similar to those described in § 5, only a brief sketch of the procedures used will suffice. The remaining space groups belonging to this type are easily treated in a similar way.

6·1. *Space group P*422

We choose one of the two possible functional forms for the structure factor as follows:

$$\xi_{\mathbf{h}}=4\cos 2\pi lz\,[\cos 2\pi hx \cos 2\pi ky+\cos 2\pi kx \cos 2\pi hy], \tag{6·01}$$

$$\eta_{\mathbf{h}}=-4\sin 2\pi lz\,[\sin 2\pi hx \sin 2\pi ky-\sin 2\pi kx \sin 2\pi hy]. \tag{6·02}$$

6·1·1. *The intensity seminvariants.*—Since the values of the intensity seminvariants (those structure seminvariants whose values, as a consequence of the space-group symmetry, are either 0 or π) are uniquely determined, for each fixed functional form for the structure factor, by the magnitudes of the structure factors, we first seek formulas involving these phases.

Table 5. *The relation* $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$ *and related probability distributions for space group P*422

$P(\lvert E_1\rvert, \lvert E_2\rvert, \lvert E_3\rvert, \varphi_1, \varphi_2, \varphi_3)$	Relation	t
$8\lvert E_1\rvert\lvert E_2\rvert\lvert E_3\rvert \exp[-\lvert E_1\rvert^2-\lvert E_2\rvert^2-\lvert E_3\rvert^2] \times\left\{1+t\frac{S_3}{S_2^{3/2}}\lvert E_1\rvert\lvert E_2\rvert\lvert E_3\rvert\cos(\varphi_1+\varphi_2+\varphi_3)\right\}$	$h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0$	2
$\frac{4\lvert E_2\rvert\lvert E_3\rvert \exp[-\frac{1}{2}\lvert E_1\rvert^2-\lvert E_2\rvert^2-\lvert E_3\rvert^2]}{\sqrt{(2\pi)}} \times\left\{1+t\frac{S_3}{S_2^{3/2}}\lvert E_1\rvert\lvert E_2\rvert\lvert E_3\rvert\cos(\varphi_1+\varphi_2+\varphi_3)\right\}$	$h_1=\pm k_1,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0$	2
	$h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	2
	$h_1=\pm k_1,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	$2\sqrt{2}$
	$h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_2+l_3=0,\ k_1=0$	2
	$h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=0$	2
	$h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=k_1=0$	4
	$h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_2+l_3=0,\ k_1=l_1=0$	$2\sqrt{2}$
	$h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ h_1=l_1=0$	$2\sqrt{2}$
$\frac{2\lvert E_3\rvert \exp[-\frac{1}{2}\lvert E_1\rvert^2-\frac{1}{2}\lvert E_2\rvert^2-\lvert E_3\rvert^2]}{2\pi} \times\left\{1+t\frac{S_3}{S_2^{3/2}}\lvert E_1\rvert\lvert E_2\rvert\lvert E_3\rvert\cos(\varphi_1+\varphi_2+\varphi_3)\right\}$	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_1-k_2+k_3=0,\ l_1+l_2+l_3=0$	2
	$h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	2
	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_1-k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	$2\sqrt{2}$
	$h_1+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=h_2=0$	2
	$h_1=\pm k_1,\ h_1+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=h_2=0$	$2\sqrt{2}$
	$h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_2+l_3=0,\ k_1=0$	2
	$h_2=\pm k_2,\ h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=0$	2
	$h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_3=0,\ h_1=k_1=l_2=0$	4
	$h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_2+l_3=0,\ k_1=l_1=0$	$2\sqrt{2}$
	$h_2=\pm k_2,\ h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ h_1=l_1=0$	$2\sqrt{2}$
	$h_1+h_3=0,\ k_2+k_3=0,\ l_2+l_3=0,\ k_1=l_1=h_2=0$	$2\sqrt{2}$
	$h_2+h_3=0,\ k_1+k_3=0,\ l_2+l_3=0,\ h_1=l_1=k_2=0$	$2\sqrt{2}$
$\frac{\exp[-\frac{1}{2}\lvert E_1\rvert^2-\frac{1}{2}\lvert E_2\rvert^2-\frac{1}{2}\lvert E_3\rvert^2]}{(2\pi)^{3/2}} \times\left\{1+t\frac{S_3}{S_2^{3/2}}\lvert E_1\rvert\lvert E_2\rvert\lvert E_3\rvert\cos(\varphi_1+\varphi_2+\varphi_3)\right\}$	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0$	1
	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	$\sqrt{2}$
	$h_1=\pm k_1,\ h_3=\pm k_3,\ h_1+h_3=0,\ k_1+k_2-k_3=0,\ l_2+l_3=0,\ l_1=h_2=0$	$2\sqrt{2}$
	$h_3=\pm k_3,\ h_1+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0,\ l_1=h_2=0$	2
	$h_1+h_2+h_3=0,\ k_1+k_2+k_3=0$	1
	$h_1=\pm k_1,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0$	$\sqrt{2}$
	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_1+h_2+h_3=0,\ k_1-k_2+k_3=0$	2
	$h_1=\pm k_1,\ h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_1+k_2+k_3=0$	$\sqrt{2}$
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_1-k_2+k_3=0,\ l_2+l_3=0,\ l_1=0$	2
	$h_1+h_2=0,\ k_1+k_3=0,\ l_2+l_3=0,\ l_1=k_2=h_3=0$	2
	$h_1=\pm k_1,\ h_1+h_2=0,\ k_1+k_3=0,\ l_2+l_3=0,\ l_1=k_2=h_3=0$	$2\sqrt{2}$
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_2+l_3=0,\ k_1=0$	2
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=0$	2
	$h_1+h_2+h_3=0,\ l_1+l_2+l_3=0,\ k_1=k_2=k_3=0$	1
	$k_1+k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=h_2=h_3=0$	1
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_2+l_3=0,\ h_1=k_1=0$	2
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_2+h_3=0,\ k_2+k_3=0,\ l_1+l_3=0,\ h_1=k_1=l_2=0$	$2\sqrt{2}$
	$k_2+k_3=0,\ l_1+l_3=0,\ h_1=k_1=h_2=l_2=h_3=0$	$2\sqrt{2}$
	$l_1+l_2+l_3=0,\ h_1=k_1=h_2=k_2=h_3=k_3=0$	2
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_1+h_2+h_3=0,\ k_2+k_3=0,\ l_2+l_3=0$	$\sqrt{2}$
	$h_2=\pm k_2,\ h_3=\pm k_3,\ h_2+h_3=0,\ k_1+k_2+k_3=0,\ l_2+l_3=0$	$\sqrt{2}$
	$h_3=\pm k_3,\ h_1+h_3=0,\ k_2+k_3=0,\ l_2+l_3=0,\ k_1=l_1=h_2=0$	$2\sqrt{2}$
	$h_3=\pm k_3,\ h_2+h_3=0,\ k_1+k_3=0,\ l_2+l_3=0,\ h_1=l_1=k_2=0$	$2\sqrt{2}$
	$h_1+h_3=0,\ k_2+k_3=0,\ k_1=l_1=h_2=l_2=l_3=0$	2
	$h_3=\pm k_3,\ h_1+h_3=0,\ k_2+k_3=0,\ k_1=l_1=h_2=l_2=l_3=0$	2
	$h_1+h_2+h_3=0,\ k_1=l_1=k_2=l_2=k_3=l_3=0$	$\sqrt{2}$
	$k_1+k_2+k_3=0,\ h_1=l_1=h_2=l_2=h_3=l_3=0$	$\sqrt{2}$

Table 6. *The relation* $\mathbf{h} = \mathbf{h}_i + \mathbf{h}_j$ *and, together with* (5·84) *and* (5·87), *related expected values and variances for space group* $P422$

hkl of φ_{hkl} desired and conditions	Reference $h_ik_il_i$ and conditions	Reference $h_jk_jl_j$ and conditions	$\varkappa_{\sigma ij}$	$\varkappa_{cij}$	$\varkappa_{sij}$
hkl*	$h_ik_il_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	1
$hkl; h=\pm k$	$h_ik_il_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	∞
hkl	$h_ik_il_i; h_i=\pm k_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	1
$hkl; h=\pm k$	$h_ik_il_i; h_i=\pm k_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	∞
hkl	$h_ik_il_i; h_i=\mp k_i$	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
$hkl; h=\pm k$	$h_ik_il_i; h_i=\pm k_i$	$h_jk_jl_j; h_j=\pm k_j$	1	1	∞
hkl	h_ik_i0	$h_jk_jl_j$	$\frac{1}{2}$	1	1
hkl	$h_ik_i0; h_i=\pm k_i$	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	$1/\sqrt{2}$
$hkl; h=\pm k$	h_ik_i0	$h_jk_jl_j$	$\frac{1}{2}$	1	∞
$hkl; h=\pm k$	$h_ik_i0; h_i=\mp k_i$	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	∞
$hkl; h=\pm k$	h_ik_i0	$h_jk_jl_j; h_j=\mp k_j$	1	$\frac{1}{2}$	∞
$hkl; h=\pm k$	$h_ik_i0; h_i=\pm k_i$	$h_jk_jl_j; h_j=\pm k_j$	1	$1/\sqrt{2}$	∞
hkl	h_i0l_i	$h_jk_jl_j$	$\frac{1}{2}$	1	1
$hkl; h=\pm k$	h_i0l_i	$h_jk_jl_j$	$\frac{1}{2}$	1	∞
hkl	h_i0l_i	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
$hkl; h=\pm k$	h_i0l_i	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
hkl	$0k_il_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	1
$hkl; h=\pm k$	$0k_il_i$	$h_jk_jl_j$	$\frac{1}{2}$	1	∞
hkl	$0k_il_i$	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
$hkl; h=\pm k$	$0k_il_i$	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
hkl	h_ik_i0	$0k_jl_j$	1	$\frac{1}{2}$	∞
hkl	$h_ik_i0; h_i=\pm k_i$	$0k_jl_j$	1	$1/2\sqrt{2}$	∞
$hkl; h=\pm k$	h_ik_i0	$0k_jl_j$	1	$\frac{1}{2}$	∞
$hkl; h=\pm k$	$h_ik_i0; h_i=\mp k_i$	$0k_jl_j$	1	$1/2\sqrt{2}$	∞
hkl	$00l_i$	$h_jk_jl_j$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$hkl; h=\pm k$	$00l_i$	$h_jk_jl_j; h_j=\pm k_j$	1	$\frac{1}{2}$	∞
hkl	$00l_i$	h_jk_j0	1	$\frac{1}{4}$	∞
$hkl; h=\pm k$	$00l_i$	$h_jk_j0; h_j=\pm k_j$	1	$1/2\sqrt{2}$	∞
hkl	h_i00	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	$1/\sqrt{2}$
hkl	h_i00	$h_jk_jl_j; h_j=\pm k_j$	1	$1/2\sqrt{2}$	∞
$hkl; h=\pm k$	h_i00	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	∞
$hkl; h=\pm k$	h_i00	$h_jk_jl_j; h_j=\pm k_j$	1	$1/\sqrt{2}$	∞
hkl	$0k_i0$	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	$1/\sqrt{2}$
hkl	$0k_i0$	$h_jk_jl_j; h_j=\pm k_j$	1	$1/2\sqrt{2}$	∞
$hkl; h=\pm k$	$0k_i0$	$h_jk_jl_j$	$\frac{1}{2}$	$1/\sqrt{2}$	∞
$hkl; h=\pm k$	$0k_i0$	$h_jk_jl_j; h_j\pm k_j$	1	$1/\sqrt{2}$	∞
hkl	h_i00	$0k_jl_j$	1	$1/2\sqrt{2}$	∞
$hkl; h=\pm k$	h_i00	$0k_jl_j$	1	$1/2\sqrt{2}$	∞
hkl	$0k_i0$	h_j0l_j	1	$1/2\sqrt{2}$	∞
$hkl; h=\pm k$	$0k_i0$	h_j0l_j	1	$1/2\sqrt{2}$	∞

* $h \neq \pm k$ unless specified.

The phases which are structure seminvariants are the φ_{hkl} where $h+k$ and l are both even. It is then readily verified that the phases which are intensity seminvariants are the φ_{0gg}, φ_{g0g}, φ_{gg0}, φ_{uu0}, φ_{hhg}, and $\varphi_{h\bar{h}g}$.* (In this notation φ_{0gg}, for example, refers to those phases whose first index is zero and whose second and third indices are both even but not necessarily equal. However, in φ_{hhg} the first two indices are equal and the third is even.)

* The phases which are structure invariants are the φ_{ggg} while those which are intensity invariants are the φ_{0gg}, φ_{g0g}, φ_{gg0}, φ_{hhg}, and $\varphi_{h\bar{h}g}$ where h is even.

We are thus led to consider first normalized structure factors $E_{\mathbf{h}}$, $E_{\mathbf{h}_j}$, where $\varphi_{\mathbf{h}}$ is an intensity seminvariant. We obtain by the usual methods the relevant joint probability distributions shown in Table 4. Two additional columns, not listed in Table 4 in order to save space, are obtained by symmetry. One, headed φ_{0gg}, is obtained from that headed φ_{g0g} by interchanging h and k and by interchanging h_j and k_j. The other, headed φ_{0g0}, is obtained from that headed φ_{g00} by the same substitutions.

6·1·2. *The relation* $\mathbf{h} = \mathbf{h}_i + \mathbf{h}_j$.—We use the methods of § 5·1·2 to obtain relevant joint probability distributions, expected values, and variances. Our results are summarized in Tables 5 and 6, where the notation of Table 2 is used. Equations (5·84), (5·87) and (5·88) are then valid for space group $P422$ also. Table 6 is an immediate consequence of Table 5. Table 6 may be supplemented by entries yielding the values of phases φ_{hkl} with $hkl = 0$. If $\mathbf{h}_i$ is $h_ih_il_i$ or satisfies $h_ik_il_i = 0$ and $\mathbf{h}_j$ is $h_jh_jl_j$ or satisfies $h_jk_jl_j = 0$, then it is found that $\varkappa_{\sigma ij} = 1$, $\varkappa_{cij} = 1/t$; otherwise $\varkappa_{\sigma ij} = \frac{1}{2}$, $\varkappa_{cij} = 2/t$. Note that $\varkappa_{sij} = \varkappa_{cij}$, except when, as a consequence of space-group symmetry, the values of the reference phases $\varphi_{\mathbf{h}_i}$ and $\varphi_{\mathbf{h}_j}$ are either 0 or π or when the value of the phase of interest $\varphi_{\mathbf{h}}$ is either 0 or π; then $\varkappa_{sij} = \infty$.

Although miscellaneous relations analogous to those given in § 5·1·3 are valid here too, we do not list these explicitly.

6·1·3. *Procedure for phase determination.*—We obtain a set of $|E|^2$ values exactly as in § 5·1·4 except that $\varepsilon = (m_2^0 + m_0^2)/n$ is now defined by means of Table 7 instead of (5·74) and (5·75).

Table 7. *The values of* $\varepsilon = (m_2^0 + m_0^2)/n$ *for space group* $P422$

Index	ε
$hkl \neq 0$	1
$hk0$, $h0l$, $0kl$ } $h \neq \pm k$	1
$hk0, h = \pm k$	2
$h00$, $0k0$	2
$00l$	4

If $hkl = 0$ or $h = \pm k$ the averages in (5·79) obtain. If $hkl \neq 0$ and $h \neq \pm k$ the averages in (5·80) obtain.

Next, in view of Table 4, four summary tables are constructed. In the first table, the entries, for each fixed k_j and l_j, are

$$\sum_{h_j \neq k_j} (|E_{h_jk_jl_j}|^2 - 1) \,. \qquad (6·03)$$

In the second table, the entries, for each fixed l_j and h_j, are

$$\sum_{k_j \neq h_j} (|E_{h_jk_jl_j}|^2 - 1) \,. \qquad (6·04)$$

In the third table, the entries, for each fixed h_j and k_j, are

$$\sum_{l_j \neq 0} (|E_{h_j k_j l_j}|^2 - 1) \,. \tag{6·05}$$

In the fourth table, the entries, for each fixed m and l_j, are

$$\sum_{h_j \pm k_j = m \neq 0} (|E_{h_j k_j l_j}|^2 - 1) \,. \tag{6·06}$$

Next, to find the value of a phase $\varphi_{hkl} = \varphi_{hhg}$, where the corresponding $|E|$ is maximal, we employ (6·06) with $m = h$. If h is odd and $l \neq 0$ then, in view of Table 4, $\varphi_{hkl} = 0$ or π according as (6·06) is positive or negative. If h is even and $l \neq 0$ we need to add the term $(1/\sqrt{2})(|E_{\frac{1}{2}h, \frac{1}{2}h, \frac{1}{2}l}|^2 - 1)$ to (6·06) and then, again because of Table 4, $\varphi_{hkl} = 0$ or π according as the sum is positive or negative. Similar remarks hold if $l = 0$.

Again, to find the value of a phase $\varphi_{hkl} = \varphi_{gg0}$ where $|E|$ is maximal, we employ (6·05). Assume $h \neq \pm k$. We first use (6·05) with $h_j = \frac{1}{2}h$, $k_j = \frac{1}{2}k$ and then use (6·05) with $h_j = \frac{1}{2}(h+k)$, $k_j = \frac{1}{2}(h-k)$ in order to compute the approximate values of $E+2E'$ and $2E+E''$ (Table 4). Since $|E|$, $|E'|$, and $|E''|$ are in general all known and $|E|$ is large, the sign of E can ordinarily be deduced from the computed values of $E+2E'$ and $2E+E''$. Similar remarks apply if $h = \pm k$. In this way the values of many of the φ_{gg0}, with large corresponding $|E|$, may be found.

Next, to find the value of a phase $\varphi_{hkl} = \varphi_{uu0}$, where $|E|$ is large, we again employ (6·05) with $h_j = \frac{1}{2}(h+k)$, $k_j = \frac{1}{2}(h-k)$ in order to compute $2E+E''$ (Table 4). If $|E''|$ is small the sign of E is immediately deduced. If $|E''|$ is large, the sign of E'' will probably already be known from the previous paragraph and the sign of E can again be inferred.

The remarks of the previous paragraphs illustrate how Table 4 is to be used in conjunction with the four summary tables given by (6·03)–(6·06). It is apparent that the effective use of Table 4 will enable one to determine tentative values of many phases φ_{hkl}, with large corresponding $|E|$, which are intensity seminvariants.

From this point on the procedure parallels very closely that for $P222$, with one important difference. In order to fix the origin we specify the values of only two phases $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ constituting a linearly semi-independent pair (rather than three as for $P222$). For example, we may specify that the values of $\varphi_{\mathbf{h}_1} = \varphi_{hhu}$ and of $\varphi_{\mathbf{h}_2} = \varphi_{ug0}$, be zero, where naturally $|E_{\mathbf{h}_1}|$ and $|E_{\mathbf{h}_2}|$ are large. Furthermore, the magnitudes of all phases which are structure seminvariants are determined (as for $P222$). Choosing one, say $\varphi_{\mathbf{h}_3}$, which is not an intensity seminvariant and such that $|\varphi_{\mathbf{h}_3}| \approx \frac{1}{2}\pi$ and $|E_{\mathbf{h}_3}|$ is large, we specify its sign arbitrarily, thus distinguishing between the enantiomorphs S, S' permitted by the given set of structure-factor magnitudes. Then the values of all remaining phases are determined as for $P222$, using Tables 5 and 6, with additional entries in Table 6 corresponding to $hkl = 0$, and easily derivable from Table 5.

7. Types $3P_12$ and $3P_22$

The foregoing detailed discussion for Types $1P222$ and $2P22$ reduces to routine the problem for the remaining types. The seminvariant theory shows that for these types only one phase is to be suitably specified in order to fix the origin uniquely, provided, of course, that the functional form for the structure factor has been chosen. As already appeared in Type $2P22$, some of the average values yield the values of certain linear combinations of the structure factors rather than that of a single structure factor. Care should be exercised in identifying the linear combinations which arise. Although the computations for each space group are routine, they will in general be quite tedious.

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