Part IV

Dedicated effort for success

TEST FOR ISOMORPHISM USING HIGH MOMENTS OF INTENSITIES

1. INTRODUCTION

In the preceding chapters we applied statistical methods to study random variables defined in terms of the intensity data from a single crystal. In this chapter and in the next one, we shall apply statistical methods to study random variables defined in terms of the intensity data from a pair of crystals. The aim of the study such as this is to obtain suitable statistical tests for the isomorphism of a pair of crystals.

In the present chapter we shall be mainly interested in exploiting the possibility of using the higher moments of normalised intensities from a pair of crystals for testing the isomorphism of the pair. We shall consider the cases $P = 1, 2$ and $M$ for a pair of centrosymmetric crystals and the cases $P = 1, 2, M_C$ and $M_A$ for a pair of non-centrosymmetric crystals.
2. PRINCIPLE OF THE METHOD

Consider a pair of crystals (both centrosymmetric or both non-centrosymmetric) each of which contains a replaceable group of atoms (\(i\)-group), and a non-replaceable group of atoms (\(Q\)-group) and let \(N(=P+Q)\) be the total number of atoms in the unit cell of each crystal.

We shall use here and in the next chapter superscripts 1 and 2 in parentheses with any variable to denote that the variable corresponds to crystal 1 and crystal 2 of the given pair of crystals. We shall assume that the two crystals have a geometrical similarity (i.e.) they must have the same cell parameters and the same space group. The given pair of crystals is said to be perfectly isomorphous (simply called, isomorphous) if the co-ordinates of all the atoms in the two crystals of the given pair are identical except that the atoms in the \(P\)-groups in the two crystals differ in their scattering powers. The pair is said to be perfectly non-isomorphous (simply called, non-isomorphous) if all the atoms in the two crystals have no correlation at all. The relevant quantities in the two crystals may be symbolically written as follows:
Crystal 1: \[ P \left[ f_p^{(1)} \right] = \cdots \]

Crystal 2: \[ P \left[ f_p^{(2)} \right] = \cdots \]

\[ j = 1 \text{ to } p, \quad k = 1 \text{ to } Q \quad (1) \]

That is, the crystals are isomorphous if

\[ f_p^{(1)} = f_p^{(2)}, \quad f_Q^{(1)} = f_Q^{(2)} \]

\[ j = 1 \text{ to } p, \quad k = 1 \text{ to } Q \quad (2) \]

and the two crystals are non-isomorphous if

\[ f_p^{(1)} \neq f_p^{(2)}, \quad f_Q^{(1)} \neq f_Q^{(2)} \quad (3) \]

for any \( j \) or \( k \). We shall use the symbol \( I \) to denote an isomorphous pair of crystals and \( NI \) for a non-isomorphous pair of crystals. Whenever needed, we shall use \( I \) and \( NI \) as subscripts to denote clearly that the subscripted quantity belongs to the \( I \) or \( NI \) pair of crystals respectively.

The vector diagram showing the structure factors of a reflection \( hkl \) for a pair of isomorphous non-centrosymmetric crystals is shown in Figure 1 and
**FIGURE 1** - Argand diagram showing the relation between the structure factors of an isomorphous pair of non-centrosymmetric crystals.

**FIGURE 2** - Argand diagram showing the relation between the structure factors of a non-isomorphous pair of non-centrosymmetric crystals.
that for a pair of non-isomorphous non-centrosymmetric crystals in Figure 2. From these figures (or from equations (1) to (3)) we obtain the following results:

**I-Pair**

\[
\begin{align*}
|F_P^{(1)}| &\neq |F_P^{(2)}|, \\
F_Q^{(1)} &\neq F_Q^{(2)} \\
F_Q &= F_Q = F_Q
\end{align*}
\]  

(4)

**II-Pair**

\[
\begin{align*}
|F_Q^{(1)}| &\neq |F_Q^{(2)}|, \\
|F_Q^{(1)}| &\neq |F_Q^{(2)}|
\end{align*}
\]  

(5)

Let the contributions to the local mean intensity from the P-, Q- and N-groups of atoms in the two crystals be denoted by \(\sigma_P^{(1)}\), \(\sigma_Q^{(1)}\) and \(\sigma_N^{(1)}\), respectively. That is

\[
\begin{align*}
\sigma_P^{(1)} &= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} |F_P^{(i)}|^2 \\
\sigma_Q^{(1)} &= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} |F_Q^{(i)}|^2 \\
\sigma_N^{(1)} &= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} |F_N^{(i)}|^2
\end{align*}
\]  

(6)

The fractional contribution to the local mean intensity from the P- and Q-groups are given by
\[
\sigma_1(i)^2 = \sigma_0(i)^2 / \sigma_1(i) \cdot \sigma_2(i) \cdot \sigma_3(i)
\]

\[
\sigma_2(i)^2 = \sigma_3(i)^2 / \sigma_1(i) \cdot \sigma_2(i) \cdot \sigma_3(i)
\]

\[
\sigma_1(i)^2 + \sigma_2(i)^2 = 1, \quad i = 1, 2
\]

(7)

The normalised intensity of a reflection \( H \) for the two crystals are given by

\[
S_N(i) = \left| \frac{\sigma_1(i)}{\sigma_0(i)} \right|^2 \cdot \frac{\sigma_1(i)^2 \cdot \sigma_2(i)^2}{\sigma_3(i)^2} \cdot \left( 1 - \frac{\sigma_1(i)^2 \cdot \sigma_2(i)^2}{\sigma_3(i)^2} \right)
\]

\[
= \left( \frac{\sigma_1(i)}{\sigma_0(i)} \right)^2 \cdot \frac{\sigma_1(i)^2 \cdot \sigma_2(i)^2}{\sigma_3(i)^2} \cdot \left( 1 - \frac{\sigma_1(i)^2 \cdot \sigma_2(i)^2}{\sigma_3(i)^2} \right)
\]

(8)

From (4), (5) and (8) it is clear that \( \sigma_0(i) \) and \( \sigma_1(i) \) are dependent random variables if they correspond to the I-pair and independent random variables if they correspond to the NI-pair of crystals. Another implicit result is that \( \langle \frac{\sigma_1(i)^2 \cdot \sigma_2(i)^2}{\sigma_3(i)^2} \rangle \) (independent of the nature of the pair of crystals) which arises from the fact that the P- and Q-atoms occupy independent locations in the unit cell. Let us consider a function of the variables \( \sigma_0(i) \) and \( \sigma_1(i) \) and let it be denoted by \( \left( \sigma_0(i), \sigma_1(i) \right) \) (or simply by \( f \)). The distribution of \( f \) will then
depend on the nature of the variables $z_N^{(1)}$ and $z_N^{(2)}$ themselves, that is, will differ depending on whether $z_N^{(1)}$ and $z_N^{(2)}$ are dependent or independent random variables. However, it is very difficult to obtain the distribution function of $f$ when the $P$-group contains a few dominating atoms. On the other hand, it is in general possible to calculate the statistical parameters like the moments of $f$ and since these quantities are characteristic of distribution of $f$ these parameters can be used as statistical criteria for testing the isomorphism of the pair.

In this chapter we consider three simple functions of the variables $z_N^{(1)}$ and $z_N^{(2)}$, namely, the sum, the difference and the product of $z_N^{(1)}$ and $z_N^{(2)}$ and these are denoted by $z_+$, $z_-$ and $z_x$ respectively. That is

\begin{align}
  z_+ &= z_N^{(1)} + z_N^{(2)} \\
  z_- &= z_N^{(1)} - z_N^{(2)} \\
  z_x &= z_N^{(1)} z_N^{(2)}
\end{align}

(9)  (10)  (11)
We are interested in calculating the higher moments of $s_+$, $s_-$ and $s_x$. The use of the normalised intensities $s_N^{(1)}$ and $s_N^{(2)}$ rather than the actual intensities $|F_N^{(1)}|^2$ and $|F_N^{(2)}|^2$ avoids the necessity of knowing scale factors and this is especially important and advantageous as well in this case, since the isomorphous replacement technique involves intensity data from two or more crystals and these are usually measured in different scales.

3. A PAIR OF ISOMORPHOUS NON-CENTROSYMMETRIC CRYSTALS

(a) The Sum and Difference Variables

From (8), we obtain the expression for the normalised intensities of a reflection $h$ in the two crystals as

$$s_N^{(1)} = \left( \frac{1}{\gamma} \right) \left[ |F_N^{(1)}|^2 + 2 \sum_{p} y_p^{(1)} y_q^{(1)} \psi^{(i)} \psi^{(1)} \psi^{(i)} \right]$$

$$+ 2 \sum_{p} y_p^{(1)} y_q^{(1)} \psi^{(i)} \psi^{(1)} \psi^{(i)} \psi^{(1)} \right]$$

$$+ 2 \sum_{p} y_p^{(1)} y_q^{(1)} \psi^{(i)} \psi^{(1)} \psi^{(i)} \psi^{(1)} \right]$$

where $y_p^{(1)}$ and $y_q^{(1)}$ are the normalised intensities.
due to contributions from the P- and Q-atoms respectively. That is

\[ y_p^{(i)} = \frac{F_p}{\sqrt{v}} \text{, } i = 1, 2 \]  (13)

Making use of (7) we can rewrite (12) as

\[ z_n^{(1)} = a_1^{(1)} \sigma^{(1)} + \sigma^{(1)} \text{, } \sigma^{(1)} \text{, } i = 1, 2 \]  (14)

Since the atoms in the P-group of each crystal are of one type and since the Q-group in the two crystals are identical (we assume here perfect isomorphism), it is clear that

\[ y_p^{(1)} = y_p^{(2)} = y_p \text{, say} \]

\[ y_Q^{(1)} = y_Q^{(2)} = y_Q \text{, say} \]

\[ \psi^{(1)} = \psi^{(2)} = \psi \text{, say} \]  (15)

From (14) and (15), we obtain

\[ z_n^{(1)} = a_1^{(1)} \sigma^{(1)} + \sigma^{(1)} \text{, } \sigma^{(1)} + 2 \sigma^{(1)} \sigma^{(2)} \text{, } i = 1, 2 \]  (16)
where \( y_P \) and \( y_Q \) are the normalised structure amplitudes of the reflection \( h \) from the \( P \)- and \( Q \)-atoms in either crystal. From (9), (10) and (16) we obtain

\[
 s_+ = s_N^{(1)} + s_N^{(2)} = a_+ y_P^2 + b_+ y_Q^2 + c_+ y_P y_Q \cos \psi \tag{17}
\]

where we have used the simplifying notation

\[
a_+ = \ldots, b_+ = \ldots, c_+ = \ldots \tag{18}
\]

For convenience of writing, we shall denote \( a_+ \), \( b_+ \) and \( c_+ \) by \( a \), \( b \) and \( c \) respectively. With this notation in mind, (17) can be rewritten as

\[
 s_+ = a y_P^2 + b y_Q^2 + 2c y_P y_Q \cos \psi \tag{19}
\]

The pth moments of \( s_+ \) is given by

\[
\langle s_+^p \rangle = \langle (a y_P^2 + b y_Q^2 + 2c y_P y_Q \cos \psi)^p \rangle \tag{20}
\]
The $p$th moment of $z$ can be obtained by expanding the expression in the right hand side of (20) and then by using the following theorems from the theory of probability:

If $x_j$ ($j = 1$ to $n$) are a set of random variables, $p_j$ ($j = 1$ to $n$) are positive integers and $k$ and $c_j$ ($j = 1$ to $n$) are constants, then

\[
\langle k + \sum_{j=1}^{n} (c_j x_j^p) \rangle = k^p + \sum_{j=1}^{n} c_j \langle x_j^p \rangle \quad \text{(21a)}
\]

\[
\langle k^p \prod_{j=1}^{n} (c_j x_j^p) \rangle = k^{p(p-1)} \prod_{j=1}^{n} c_j \langle x_j^p \rangle \quad \text{(21b)}
\]

Equation (21a) is true independent of the nature of the variables while (21b) is true only when the $x_j$'s are independent random variables.

The expansion of the $p$th power of the expression in (20) can be achieved by making use of the multinomial theorem for integral exponent, namely (Barnard and Child, 1959)

\[
\left( \sum_{j=1}^{n} x_j \right)^p = \sum_{x_1, x_2, \ldots, x_n} \frac{p!}{x_1! x_2! \cdots x_n!} \prod_{j=1}^{n} x_j^{p_j} \quad \text{(22)}
\]
where the summation symbol

$$\sum_{k_1, k_2, \ldots, k_{n-1}}$$

(23)

stands for the summations over \((n - 1)\) dummy indices \(i_1, i_2, \ldots, i_{n-1}\) such that

\[
0 \leq i_1 < p \\
0 \leq i_2 < p - i_1 \\
\vdots \\
0 \leq i_{n-2} < p - i_1 - i_2 - \cdots - i_{n-3}
\]

That is

$$\sum_{i_1, i_2, \ldots, i_{n-1}} = \sum_{i_1=0}^{p} \sum_{i_2=0}^{p-i_1} \cdots \sum_{i_{n-2}=0}^{p-i_1-i_2-\cdots-i_{n-3}} a(k_1, k_2, \ldots, k_{n-1})$$

(24)

where the simplifying notation \(\sum_{i_1, i_2, \ldots, i_{n-1}}\) means that there
are \((n - 1)\) summations over the \((n - 1)\) dummy indices.

From (20), (21a), (21b) and (24) we obtain the
pth moment of \(s_+\) as

$$\langle s_+^p \rangle = \langle (b_1^2 + b_2^2 + \cdots + b_n^2)^{p/2} \rangle$$
\[
\begin{align*}
\mathbb{E} \left( \sum_{k=2}^{n} \frac{p^k (\lambda / k^2)^{k-2} e^{-\lambda / (k+1)^2} \psi^{k-2} \frac{k!}{k!}}{k!} \right) \\
= \sum_{k=2}^{n} \frac{p^k (\lambda / k^2)^{k-2} e^{-\lambda / (k+1)^2} \psi^{k-2} \frac{k!}{k!}}{k!} \\
= \sum_{k=2}^{n} \frac{p^k (\lambda / k^2)^{k-2} e^{-\lambda / (k+1)^2} \psi^{k-2} \frac{k!}{k!}}{k!}
\end{align*}
\]

where we have used the simplifying notation

\[
\sum_{2}^{n} = \sum_{k=2}^{n} \sum_{j=0}^{k-1} 
\]

from (24) and similar notations will also be used throughout this chapter.

Since \( \psi \) is uniformly distributed, that is,

\[
P(\psi) \, d\psi = \frac{1}{2\pi} \cdot \frac{1}{\tau} \quad \text{for} \quad -\tau < \psi < \tau
\]

we have

\[
\mathbb{E} \left( \frac{1}{n} \sum_{i=0}^{n-1} \psi_i \right) = \frac{1}{2\pi} \int_{-\tau}^{\tau} \frac{e^{i \psi \xi}}{\sqrt{1 + \xi^2}} \, d\psi \\
= \frac{1}{2\pi} \int_{-\tau}^{\tau} \frac{e^{i \psi \xi}}{\sqrt{1 + \xi^2}} \, d\psi
\]
Expanding $\cos^k \psi$ in a series of cosines of multiples of $\psi$ (see p.55 of Loney, 1952) and carrying out the integrations over the various terms, it is clear from the property

$$\int_0^\pi \cos(n\psi) d\psi = \begin{cases} 0 & \text{if } n = 1, 2, 3, \ldots \\ n & \text{if } n = 0 \end{cases}$$

(29)

that only the term independent of $\psi$ will be non-zero in (28). Only when $k$ is an even integer does a term independent of $\psi$ occur and this term has the value $\frac{k!}{2^k} \left[ \left\{ \frac{k}{2} \right\}! \right]^{-1}$. Thus (28) yields

$$\langle (\cos \psi)^k \rangle = \begin{cases} 0 & \text{if } k = \text{odd integer} \\ \frac{k}{2^k} \left[ \left\{ \frac{k}{2} \right\}! \right]^{-1} & \text{if } k = \text{even integer} \end{cases}$$

The above equation may be written compactly as

$$\langle \cos^k \psi \rangle = \frac{k}{2^k} \left[ \left\{ \frac{k}{2} \right\}! \right]^{-1}$$

(30)

where $\delta^k_{k, \text{even}}$ is used in the sense of a Kronecker delta, namely that

$$\delta^k_{k, \text{even}} = \begin{cases} 0 & \text{if } k = \text{odd integer} \\ 1 & \text{if } k = \text{even integer} \end{cases}$$

(31)
From (1-37), we obtain

$$\langle \gamma^{2j+k} \rangle = \prod_{i=1}^{j+k}$$  \hspace{1cm} (32)$$

Substituting (30) and (32) in (25) we obtain

$$\langle s^p \rangle = \sum_{\text{sym}} \frac{p! \prod_{i=1}^{j+k} \gamma^{i}}{2! \prod_{i=1}^{j+k} (i+k) \prod_{i=1}^{j+k} (i+k)}$$  \hspace{1cm} (33)$$

Substituting for $$\langle \gamma^{2j+k} \rangle$$ from (1-38) to (1-41) in (33) we obtain the expression for $$\langle s^p \rangle$$ in the cases $$P = 1, 2, 3, 4$$ and 5 as

$$\langle s^p \rangle = \sum_{\text{sym}} \frac{p! \prod_{i=1}^{j+k} \gamma^{i}}{2! \prod_{i=1}^{j+k} (i+k) \prod_{i=1}^{j+k} (i+k)}$$  \hspace{1cm} (34)$$

$$\left( \sum_{\text{sym}} \frac{p! \prod_{i=1}^{j+k} \gamma^{i}}{2! \prod_{i=1}^{j+k} (i+k) \prod_{i=1}^{j+k} (i+k)} \right)$$  \hspace{1cm} (35)$$

$$\left( \sum_{\text{sym}} \frac{p! \prod_{i=1}^{j+k} \gamma^{i}}{2! \prod_{i=1}^{j+k} (i+k) \prod_{i=1}^{j+k} (i+k)} \right)$$  \hspace{1cm} (36)$$
\[ b! \sum_{j=2}^{p} \frac{\Gamma(j+k_2+1)}{j!(p-j-k)!} \left( \frac{k_2}{j} \right)^2 \left( \frac{\alpha}{p-j-k} \right)^{p-j-k} \]  

(37)

(b) The Product Variable \( z_x \)

The product of the normalised intensities of a reflection \( H \) for an I-pair of crystals can be written from (11) and (16) as

\[ z_x = z_N^{(1)} z_N^{(2)} \]

\[ = \prod_{\lambda=1}^{2} \left( \frac{\sigma_1^{(\lambda)} \sigma_2^{(\lambda)}}{\gamma} \right)^{1/2} \left( \frac{1}{\eta} \right)^{1/2} \]

which after simplification reduces to

\[ z_x = \frac{\rho_{12}^{1/2}}{\rho_{11}^{1/2} \rho_{22}^{1/2}} \left( \frac{\omega_{11} \omega_{22}}{\omega_{12} \omega_{21}} \right)^{1/2} \left( \frac{\sigma_1^{(1)} \sigma_1^{(2)}}{\gamma} \right)^{1/2} \left( \frac{1}{\eta} \right)^{1/2} \]

(38)

where we have used the following simplifying notation
\[
\begin{align*}
\alpha_1 &= 2\sigma_1^{(1)}\sigma_2^{(2)}(3\sigma_1^{(3)}\sigma_2^{(4)})\cdots \sigma_1^{(n)}\sigma_2^{(n)} \\
\alpha_2 &= 2\sigma_1^{(1)}\sigma_1^{(2)}(\sigma_1^{(3)}\sigma_2^{(4)})\cdots \sigma_1^{(n)}\sigma_1^{(n)} \\
\alpha_3 &= 4\sigma_1^{(1)}\sigma_1^{(2)}(\sigma_1^{(3)}\sigma_2^{(4)}-\sigma_1^{(4)}\sigma_2^{(3)}) \\
\alpha_4 &= \sigma_1^{(1)}\sigma_2^{(2)}(2\sigma_1^{(3)}\sigma_2^{(4)})\cdots \sigma_1^{(n)}\sigma_2^{(n)} \\
\alpha_5 &= \sigma_2^{(1)}\sigma_2^{(2)}(2\sigma_1^{(3)}\sigma_2^{(4)})\cdots \sigma_2^{(n)}\sigma_2^{(n)} \\
\alpha_6 &= \sigma_1^{(1)}\sigma_1^{(2)}(3\sigma_1^{(3)}\sigma_2^{(4)})\cdots \sigma_1^{(n)}\sigma_1^{(n)}
\end{align*}
\]

Making use of the multinomial theorem, we obtain from (39) that

\[
\langle 3^p \rangle = \sum_{\pi} \beta_{\pi} \langle (a_{\pi_{i}}\cdots a_{\pi_{i}+k+\cdots +m}) \rangle,
\]

(40)

where we have used the simplifying notation

\[
\beta_{\pi} = \frac{\prod a_{\pi_{i}}\sigma_{\pi_{i}}\cdots \sigma_{\pi_{i}+k+\cdots +m}}{\pi! (i+1)\cdots (k+i+m)}
\]

(41)

and the notation in (24) for \( \sum_{\pi} \). Substituting for the
higher moments of $\cos \omega$, $y_q$ and $y_p$ respectively from (30), (1-37) and the equations (1-36) to (1-41) in (40) we obtain the expression for the $p$th moment of $e^x$ in the cases $P = 1, 2, \infty$ and $\infty$ as follows:

\[
\langle e^{x^p} \rangle = \sum_{5} \frac{B_{A_X}(x+j+x+k)}{\sqrt{n}} \left[ \left( \frac{x+j+x+k}{2} \right) \right]^{2p-1} \left( \frac{x+j+x+k}{2} \right) \cdots \left( \frac{x+j+x+k}{2} \right) 
\]

(42)

\[
\sum \frac{B_{A_X}(x+j+x+k)}{\sqrt{n}} \left[ \left( \frac{x+j+x+k}{2} \right) \right]^{2p-1} \left( \frac{x+j+x+k}{2} \right) \cdots \left( \frac{x+j+x+k}{2} \right) 
\]

(43)

\[
\sum \frac{B_{A_X}(x+j+x+k)}{\sqrt{n}} \left[ \left( \frac{x+j+x+k}{2} \right) \right]^{2p-1} \left( \frac{x+j+x+k}{2} \right) \cdots \left( \frac{x+j+x+k}{2} \right) 
\]

(44)

\[
\sum \frac{B_{A_X}(x+j+x+k)}{\sqrt{n}} \left[ \left( \frac{x+j+x+k}{2} \right) \right]^{2p-1} \left( \frac{x+j+x+k}{2} \right) \cdots \left( \frac{x+j+x+k}{2} \right) 
\]

(45)
where we have used the notation \( \bar{c}_{\pm 1, \pm 2, \ldots} = \tilde{c}_{\pm 1, \pm 2, \ldots} \) (which follows because \( 2k \) is always an even integer).

4. A PAIR OF ISOMORPHOUS CENTROSYMMETRIC CRYSTALS

(a) The Sum and Difference Variables

In the case of a centrosymmetric crystal the structure factors are all real quantities and the equation for the normalised intensities of a reflection \( H \) in the two crystals can be written as

\[
E_N(1) = |F_P(1) + \bar{F}_Q(1)|^2 = \left( \frac{1}{2} F_P^2 + \frac{1}{2} \bar{F}_Q^2 + \bar{s}(1) \right) \nonumber
\]

\[
= \left( \frac{1}{2} F_P^2 + \frac{1}{2} \bar{F}_Q^2 + \bar{s}(1) \right) + \frac{1}{2} s(1) \left( F_P^2 + \bar{F}_Q^2 \right) \quad \ldots \quad (46)
\]

where \( s(1) \) is the product of the signs of \( F_P(1) \) and \( F_Q(1) \) as given by

\[
s(1) = s_P(1) s_Q(1), \quad 1 = 1, 2 \quad (47)
\]

For the \( \lambda \)-pair it is clear that

\[
s(1) = s(2) = s, \quad \text{say} \quad (48)
\]
As in the case for the non-centrosymmetric crystal, (46) can be written as

\[ z_N^{(1)} = \frac{\alpha^2}{2} y_a^2 + \alpha y_a y_a' + y_a y_a'' + 2y_b y_c y_a y_a' + \ldots \]  

(49)

From (49) we obtain

\[ z_\pm = z_N^{(1)} \pm z_N^{(2)} = ay_p^2 + by_q^2 + 2cy_p y_q \]  

(50)

where \( a, b \) and \( c \) (standing respectively for \( a_+, b_+ \) and \( c_+ \)) are defined in (19). From (50) we obtain

\[ \langle z_\pm \rangle = \langle (ay_p^2 + by_q^2 + 2cy_p y_q) \rangle = \sum \frac{1}{2} \frac{1}{|k|} \frac{1}{|k'|} \frac{1}{|k''|} \frac{1}{|k'''|} \frac{1}{|k''''|} \frac{1}{|k'''''|} \frac{1}{|k''''''|} \ ]  

(51)

where we have made use of the statistical theorems given in (24) and (21b) and the multinomial theorem. Since \( F_p \) and \( F_Q \) are independent, \( s_p \) and \( s_Q \) are also independent so that

\[ \langle s \rangle = \langle s_p s_Q \rangle = \langle s_p \rangle \langle s_Q \rangle \]  

(52)
Since \( s_Q \) can take the values +1 and -1 with equal probability, the probability function of \( s_Q \) will be \( P(s_Q) = 1/2 \) so that

\[
\langle s_Q \rangle = (+1)P(+1) + (-1)P(-1) = \frac{1}{2} - \frac{1}{2} = 0 \quad (52)
\]

Equation (52) means that \( s \cdot s = 0 \). Since \( s^{2n} = 1 \) and \( s^{2n+1} = s \cdot s^n = x \) we have

\[
\langle s^k \rangle = \begin{cases} 
1 & \text{if } k \text{ is even integer} \\
0 & \text{if } k \text{ is odd integer}
\end{cases}
= \delta_{k, \text{even}} \quad (53)
\]

Substituting for the higher moments of \( s, y_Q \) and \( y_P \) respectively from (53), (1-36) and (1-38) to (1-40) in (51) we obtain the expressions for \( z_P^j \), for the cases \( P = 1, 2 \) and \( M \) as follows:

\[
\frac{\eta}{2} \sum_{2}^{2^P} \left\{ \frac{j + \frac{3}{2}K}{j + \frac{1}{2} + k + \frac{1}{2}} \right\} \frac{K}{j + k + \frac{1}{2}}^{P - 1} = \quad (54)
\]
\begin{align*}
\frac{p!}{\pi^2} \sum_{2}^{p+k} \frac{1}{j! k! (p-j-k)!} r^{p-j-k} \ldots j^{j-k} \ldots k^{k-j} \quad \text{for } P = 2 \quad (55) \\
\frac{p!}{\pi^2} \sum_{2}^{p+k} \frac{1}{j! k! (p-j-k)!} r^{p-j-k} \ldots j^{j-k} \ldots k^{k-j} \quad \text{for } P = N \quad (56)
\end{align*}

(b) The Product Variable

From (49) we obtain

\[ z_x = z_N^{(1)} \cdot z_N^{(2)} \]

which on simplification becomes

\[ z_x = b_1 y_p y_Q^3 s + b_2 y_p^3 y_Q s + b_3 y_p^2 y_Q^2 + b_4 y_Q^4 + b_5 y_p^4 \quad (57) \]

In (57) we have used the simplifying notation
\[ b_1 = a_1, \quad b_2 = a_2, \quad b_3 = a_3 + a_4 \]
\[ b_4 = a_5, \quad b_5 = a_6 \]

(58)

where the \( a_i \)'s are defined in (39). From (57) we obtain

\[
\langle z^p_x \rangle = \langle (b_1 y_p y_Q^3 \lambda + b_2 y_p y_Q^3 \nu \lambda + b_3 y_p^2 y_Q^2 \lambda + b_4 y_Q^4 + b_5 y_p^4) \rangle.
\]

(59)

Making use of the multinomial theorem and the statistical theorems given in (21a) and (21b), we can obtain from (59) that

\[
\langle z^p_x \rangle = \sum_{\lambda} B_{Gx} \langle \cdots \rangle.
\]

(60)

where we have used the simplifying notation

\[
B_{Gx} = \frac{\lambda_1^{i_1} \lambda_2^{i_2} \cdots \lambda_5^{i_5}}{i_1! i_2! \cdots i_5!}
\]

(61)

and the notation in (24) for \( \lambda \). Substituting for the higher moments of \( \lambda, y_Q \) and \( y_p \) respectively from
(53), (1-36) and (1-38) to (1-40) in (60) we obtain the expressions for \( \langle z^P \rangle \) for the cases \( P = 1, 2 \) and \( M \) as follows:

\[
\langle z^P \rangle = \sum_{\nu} \frac{B_{c,\nu} 2^{2i+\frac{1}{2}+k+\frac{1}{2}}}{\sqrt{\pi}} \left( \frac{3}{2} i + \frac{1}{2} + k + \frac{1}{2} \right) \left( \frac{1}{2} + \frac{1}{2} \right) \left( \frac{1}{2} + \frac{1}{2} \right) \cdots \text{for } P = 1 \quad (62)
\]

\[
\sum_{\nu} \frac{B_{c,\nu} 2^p \Gamma \left( \frac{3}{2} i + \frac{1}{2} + k + \frac{1}{2} \right)}{\pi \prod \left( \frac{1}{2} + \frac{1}{2} \right) \left( \frac{1}{2} + \frac{1}{2} \right) \cdots} \text{ for } P = 2 \quad (63)
\]

\[
\sum_{\nu} \frac{B_{c,\nu} 2^p \Gamma \left( \frac{3}{2} i + \frac{1}{2} + k + \frac{1}{2} \right)}{\pi \prod \left( \frac{1}{2} + \frac{1}{2} \right) \left( \frac{1}{2} + \frac{1}{2} \right) \cdots} \text{ for } P = M \quad (64)
\]

5. A PAIR OF NON-ISOMORPHOUS (CENTROSYMMETRIC OR NON-CENTROSYMMETRIC) CRYSTALS

(a) The Sum and Difference Variables

For an HI-pair of crystals (both centrosymmetric or both non-centrosymmetric) the normalised intensities
\( z_N^{(1)} \) and \( z_N^{(2)} \) will be independent random variables. We therefore obtain the pth moment of \( z_+ \) as

\[
\langle z_+^p \rangle = \langle (z_N^{(1)} + z_N^{(2)})^p \rangle
\]

\[
= \sum_{j=0}^{p} \frac{(p)!}{j!(p-j)!} \langle z_N^{(1)} \rangle^j \langle z_N^{(2)} \rangle^{p-j}
\]

(65)

where we have used the binomial theorem for integral exponent and the statistical theorems given in (21a) and (21b). For further simplification of (65) the values of the higher moments of \( z_N^{(1)} \) are to be substituted and these have been worked out in Chapter 7 as a function of the heavy atom contribution.

(b) The product Variable

Since \( z_N^{(1)} \) and \( z_N^{(2)} \) are independent random variables, the pth moment of \( z_X \) will be given by

\[
\langle z_X^p \rangle = \langle (z_N^{(1)} z_N^{(2)})^p \rangle = \langle z_N^{(1)} \rangle^p \langle z_N^{(2)} \rangle^p
\]

\[
= \langle z_N^{(1)} \rangle^p \langle z_N^{(2)} \rangle^p
\]

(66)
where the values of the higher moments of \( \langle z \rangle \) can be obtained from Chapter 7 depending on the number and contributions of the atoms in the \( R \)-group.

6. EXPLICIT EXPRESSIONS FOR THE FIRST FEW MOMENTS OF \( z_+ \) AND \( z_x \) FOR AN I-PAIR OF NON-CENTROSYMMETRIC CRYSTALS

We have obtained the expressions for the general \( p \)th moment of \( z_+ \) and \( z_x \) for an I-pair of non-centrosymmetric crystals in Section (3). These expressions involve multiple summations over a number of dummy indices and to obtain the explicit expression for any given higher moment of \( z_+ \) and \( z_x \) we have to expand these summations into homogeneous polynomials, remembering that the terms for which \( n \) is an odd integer vanish if the term contains \( s_n \) even as a factor. For convenience of application of these results in practical cases, where the first few moments would suffice, we give below the explicit expressions for \( \langle z_+^p \rangle \) for \( p = 2, 3 \) and 4 and of \( \langle z_x^p \rangle \) for \( p = 1, 2 \) and 3. However, the case \( p = 1 \) for the variables \( z_+ \) does not afford any
test value, since the relation

\[ \langle z_+ \rangle = \langle z_N^{(1)} \pm z_N^{(2)} \rangle = \langle z_N^{(1)} \rangle \pm \langle z_N^{(2)} \rangle \]

holds whether \( z_N^{(1)} \) and \( z_N^{(2)} \) are independent or not. We shall presently list the expressions for the first few moments of \( z_+ \) and \( z_X \) in the various cases.

(a) The Sum and Difference Variables

One-atom Case

\[ \langle z_+^2 \rangle = 2 \left( \frac{1}{2} a^2 + ab + b^2 + c^2 \right) \]
\[ \langle z_-^3 \rangle = 6 \left( \frac{1}{6} a^3 + \frac{1}{2} a^2 b + a c^2 + 2 b c^2 + a b^2 + b^3 \right) \]
\[ \langle z_+^4 \rangle = 24 \left( \frac{1}{24} a^4 + \frac{1}{6} a^3 b + \frac{1}{2} a^2 c^2 + b c^4 + a b^2 + 2 a b c^2 + 3 b^2 c^2 + a b^3 + b^4 \right) \]

Two-atom Case

\[ \langle z_+^2 \rangle = 2 \left( \frac{1}{2} a^2 + ab + b^2 + c^2 \right) \]
\[
\begin{align*}
\langle s_+^3 \rangle &= 6 \left( \frac{5}{12} a^3 + b^2 + \frac{3}{2} ab^2 + \frac{3}{4} b^3 \right) \\
\langle s_+^4 \rangle &= 24 \left( \frac{35}{192} a^4 + \frac{5}{12} ab^3 + \frac{5}{4} a^2 b^2 + \frac{5}{2} c^4 + \frac{1}{2} a^2 b^2 \right) \\
&\quad + 3 abc^2 + 3 b^2 c^2 + ab^3 + b^4 \quad (68a,b,c)
\end{align*}
\]

**Many-atom Case (i.e., P = ‘C)**

\[
\begin{align*}
\langle z_+^4 \rangle &= 2 \left( \frac{3}{2} a^2 + ab + b^2 + c^2 \right) \\
\langle z_+^3 \rangle &= 6 \left( \frac{5}{2} a^3 + \frac{3}{2} b^2 + 3 ac^2 + 2 ab^2 + ab^2 + b^3 \right) \\
\langle z_+^4 \rangle &= 24 \left( \frac{35}{8} a^4 + \frac{5}{2} ab^3 + \frac{15}{2} a^2 c^2 + \frac{3}{2} c^4 + \frac{3}{2} a^2 b^2 \right) \\
&\quad + 6 abc^2 + 3 b^2 c^2 + ab^3 + b^4 \quad (69a,b,c)
\end{align*}
\]

**Many-atom Case (i.e., P = ‘A)**

\[
\begin{align*}
\langle z_+^2 \rangle &= 2 \left( a^2 + ab + b^2 + c^2 \right) \\
\langle z_+^3 \rangle &= 6 \left( a^3 + a^2 b + 2 ab^2 + 2 ac^2 + ab^2 + b^3 \right) \\
\langle z_+^4 \rangle &= 24 \left( a^4 + a^3 b + 3 a^2 c^2 + c^4 + a^2 b^2 + 4 abc^2 \right) \\
&\quad + 3 b^2 c^2 + ab^3 + b^4 \quad (70a,b,c)
\end{align*}
\]
(b) The Product Variable

One-atom Case

\[ \langle z_X \rangle = \frac{1}{2} a_3 + a_4 + 2a_5 + a_6 \]

\[ \langle z_X^2 \rangle = 3a_1^2 + 3a_2^2 + 3a_3^2 + 2a_4^2 + 24a_5^2 + a_6^2 + 2a_1a_2 + a_3(2a_4 + 6a_5 + a_6) + 2a_4(6a_5 + a_6) + 4a_5a_6 \]

\[ \langle z_X^3 \rangle = \frac{15}{8} a_3^3 + 6a_4^3 + 720a_5^3 + a_6^3 + 9a_1^2 (3a_3 + 4a_4 + 20a_5 + a_6) + 3a_2^2 (4a_3 + a_4 + 3a_5 + 1a_6) + 9a_3^2 (3a_4 + 3a_5 + 1a_6) + 6a_4^2 (12a_5 + a_6) + 72a_5^2a_1 + 3a_3(3a_4^2 + 60a_5^2 + 1a_6^2) + 3a_4^2 \times (120a_5 + a_6^2) + 6a_5a_6 + 6a_1a_2 (9a_3 + 3a_4 + 12a_5 + a_6) + 6a_3a_4 (12a_5 + a_6) + 18a_5a_6 + 36a_4a_5a_6 \]

(71a, b, c)
\[ \langle s_X \rangle = a_3 + a_4 + 2a_5 + \frac{3}{2} a_6 \]

\[ \langle s_X^2 \rangle = 3a_1^2 + \frac{5}{4} a_2^2 + \frac{9}{8} a_3^2 + 3a_4^2 + 24a_5^2 + \frac{35}{8} a_6^2 + 3a_1a_2 + a_3(3a_4 + 6a_5 + \frac{5}{2} a_6) + a_4(12a_5 + 5a_6) + 6a_5a_6 \]

\[ \langle s_X^3 \rangle = \frac{75}{16} a_3^3 + 15a_4^3 + 720a_5^3 + \frac{231}{8} a_6^3 + 9a_1^2 (\frac{9}{2} a_3 + 6a_4 + 20a_5 + \frac{5}{2} a_6) + 3a_2^2 (\frac{105}{16} a_3 + \frac{35}{4} a_4 + 15a_5 + \frac{63}{8} a_6) + 9a_3^2 (\frac{15}{4} a_4 + 9a_5 + \frac{35}{16} a_6) + a_4^2 (108a_5 + 105a_6) + 108a_5 a_6 + 9a_3 (\frac{5}{2} a_4^2 + 20a_5^2 + \frac{21}{16} a_6^2) + 9a_4 (40a_5^2 + 21a_6^2) + 105a_5 a_6 + 3a_1 a_2 (\frac{45}{4} a_3 + 15a_4 + 36a_5 + 35a_6) + 3a_2 a_4 (36a_5 + 35a_6) + 45a_3 a_5 a_6 + 90a_4 a_5 a_6 \]

\[ \langle s_X \rangle = a_3 + a_4 + 2a_5 + 3a_6 \]
\[ \langle s_x^2 \rangle = 3a_1^2 + \frac{15}{2}a_2^2 + 9a_3^2 + 6a_4^2 + 24a_5^2 + 105a_6^2 + 6a_1a_2 + 3a_3(2a_4 + 2a_5 + 5a_6) + 6a_4(2a_5 + 5a_6) + 12a_5a_6 \]

\[ \langle s_x^3 \rangle = \frac{225}{8}a_3^3 + 90a_4^3 + 720a_5^3 + 10395a_6^3 + 9a_1^2 \]

\[ \times (9a_3^2 + 13a_4^2 + 20a_5 + 15a_6^2) + 15a_2^2(\frac{63}{4}a_3^2 + 21a_4 + 9a_5 + \frac{182}{2}a_6) + 9a_3^2(\frac{45}{4}a_4 + 9a_5 + \frac{105}{4}a_6) \]

\[ + 16a_4^2(12a_5 + 35a_6) + 16a_5^2a_6 + 45a_3(3a_4^2 + 4a_5^2 + \frac{63}{2}a_6) + 45a_4(8a_5^2 + 63a_6^2) + 630a_5a_6^2 \]

\[ + 9a_1a_2(\frac{45}{2}a_3^2 + 30a_4 + 24a_5 + 7a_6) + 15a_3a_4(12a_5 + 35a_6) + 270a_3a_5a_6 + 540a_4a_5a_6 \]

\[ (73a_1, b, c) \]

**Many-atom Case** *(i.e., \( \ell = 1 \))*

\[ \langle z_x \rangle = \frac{1}{2}a_3 + a_4 + 2a_5 + 2a_6 \]
\[ \langle s_1^2 \rangle = 3a_1^2 + 3a_2^2 + \frac{3}{2}a_3^2 + 4a_4^2 + 24a_5^2 + 24a_6^2 + 4a_1a_2 + 2a_3(2a_4 + 2a_5 + 3a_6) + 12a_4(a_5 + a_6) + 8a_5a_6 \]

\[ \langle s_1^3 \rangle = \frac{45}{4}a_3^3 + 36a_4^3 + 720a_5^3 + 720a_6^3 + 18a_1^2 \cdot (3a_3 + 4a_4 + 10a_5 + 3a_6) + 18a_2^2(3a_3 + 4a_4 + 3a_5 + 10a_6) + 9a_3^2(2a_4 + 6a_5 + 6a_6) + 144a_4^2 \cdot \cdot \cdot \]

\[ \cdot (a_5 + a_6) + 144a_5^2 \cdot + 18a_2^2(3a_4^2 + 10a_5^2 + 10a_6^2) + 360a_4(a_5^2 + a_6^2) + 144a_5a_6^2 + 9a_1a_2 \cdot \cdot \cdot \]

\[ \cdot (9a_3 + 12a_4 + 16a_5 + 16a_6) + 144a_3a_4(a_5 + a_6) + 108a_3a_5a_6 + 216a_4a_5a_6 \quad (74a_1, 1, 0) \]
7. **EXPLICIT EXPRESSIONS OF THE FIRST FEW MOMENTS OF**

\( z_+ \) **AND** \( z_- \) **FOR AN I-PAIR OF CENNSYMMETRIC CRYSTALS**

(a) **Sum and Difference Variables**

**One-atom Case**

\[
\begin{align*}
\langle z_+^2 \rangle &= 3 \left( \frac{1}{3} a^2 + \frac{4}{3} c^2 + \frac{2}{3} ab + b^2 \right) \\
\langle z_+^3 \rangle &= 15 \left( \frac{1}{15} a^3 + \frac{1}{5} a^2 b + \frac{4}{5} a c^2 + \frac{12}{5} b c^2 + \frac{3}{5} a b^2 + b^3 \right) \\
\langle z_+^4 \rangle &= 105 \left( \frac{4}{105} a^4 + \frac{4}{105} a^3 b + \frac{3}{35} a^2 c^2 + \frac{16}{7} c^4 + \right. \\
&\left. \frac{48}{35} a b c^2 + \frac{6}{35} a^2 b^2 + \frac{24}{7} b^2 c^2 + \frac{4}{7} a b^3 + b^4 \right)
\end{align*}
\]

(75a, b, c)

**Two-atom Case**

\[
\begin{align*}
\langle z_+^2 \rangle &= 3 \left( \frac{1}{3} a^2 + \frac{4}{3} c^2 + \frac{2}{3} ab + b^2 \right) \\
\langle z_+^3 \rangle &= 15 \left( \frac{1}{6} a^3 + \frac{3}{10} a^2 b + \frac{6}{5} a c^2 + \frac{12}{5} b c^2 + \right. \\
&\left. \frac{3}{5} a b^2 + b^3 \right)
\end{align*}
\]
\[ \langle s_\pm^4 \rangle = 105 \left( \frac{1}{24} a^4 + \frac{2}{21} a^3 b + \frac{4}{7} a^2 b^2 + \frac{24}{35} a^4 + \frac{72}{35} a b c^2 \right. \\
+ \frac{9}{35} a^2 b^2 + \frac{24}{7} b^2 c^2 + \frac{4}{7} a b^3 + b^4 \left. \right) \quad (76a, b, c) \]

**Many-atom Case**

\[ \langle s_\pm^2 \rangle = 3 \left( a^2 + \frac{4}{3} c^2 + \frac{2}{3} a b + b^2 \right) \]

\[ \langle s_\pm^3 \rangle = 15 \left( a^3 + \frac{3}{5} a^2 b + \frac{12}{5} a c^2 + \frac{12}{5} b c^2 + \frac{3}{5} a b^2 + b^3 \right) \]

\[ \langle s_\pm^4 \rangle = 105 \left( a^4 + \frac{4}{7} a^3 b + \frac{24}{35} a^2 b^2 + \frac{48}{35} a b^3 + \frac{144}{35} a b c^2 \right. \\
+ \frac{18}{35} a^2 b^2 + \frac{24}{7} b^2 c^2 + \frac{4}{7} a b^3 + b^4 \left. \right) \quad (77a, b, c) \]

**(b) The Product Variable**

**One-atom Case**

\[ \langle b_x \rangle = b_3 + 3b_4 + b_5 \]

\[ \langle b_x^2 \rangle = 15b_1^2 + b_2^2 + 3b_3^2 + 105b_4^2 + b_5^2 + 6b_4 b_2 + 2b_3 (15b_4 + b_5) + 6b_4 b_5 \]
\[\langle 3^3_x \rangle = 15b_3^3 + 10395b_4^3 + b_5^3 + 45b_1^2(7b_3 + 63b_4 + b_5) + 3b_2^2(3b_3 + 15b_4 + b_5) + 9b_3^2(35b_4 + b_5) + 315b_4^2b_5 + 3b_3(945b_4^2 + b_5^2) + 9b_4b_5^2 + 18b_1b_2^2 \\
\times (5b_3 + 35b_4 + b_5) + 90b_3b_4b_5 \quad (7a_b, b, c)\]

Two atom Case

\[\langle 3_x \rangle = b_3 + 3b_4 + \frac{1}{3}b_5\]

\[\langle 3^2_x \rangle = 15b_1^2 + \frac{5}{2}b_2^2 + \frac{9}{2}b_3^2 + 105b_4^2 + \frac{35}{3}b_5^2 + 9b_1b_2 + 5b_3(6b_4 + b_5) + 9b_4b_5\]

\[\langle 3^3_x \rangle = \frac{75}{2}b_3^3 + 10395b_4^3 + \frac{231}{16}b_5^3 + 45b_1^2(\frac{21}{2}b_3 + 63b_4 + \frac{5}{2}b_5) + 9b_2^2(\frac{35}{4}b_3 + 25b_4 + \frac{21}{4}b_5) + \frac{315}{2}b_3^2b_4 + 945b_5^2b_4^2b_5 + 27b_3(105b_4^2 + 7b_5^2) + \frac{315}{8}b_4^2b_5^2 + 45b_1b_2(5b_3 + 21b_4 + \frac{7}{4}b_5) \\
\times (3b_4 + 1b_5) + \frac{945}{2}b_4^2b_5 + 27b_3(105b_4^2 + 7b_5^2) + \frac{315}{8}b_4^2b_5^2 + 45b_1b_2(5b_3 + 21b_4 + \frac{7}{4}b_5) \quad (79a_b, b, c)\]
Many-atom Case

\[ \langle z_{x} \rangle = b_3 + 3b_4 + 3b_5 \]

\[ \langle z_{x}^2 \rangle = 15(b_1^2 + b_2^2) + 9b_3^2 + 105(b_4^2 + b_5^2) + 18b_1b_2 + 30b_3(b_4 + b_5) + 18b_4b_5 \]

\[ \langle z_{x}^3 \rangle = 225b_3^3 + 10395(b_4^3 + b_5^3) + 135b_1^2(7b_3 + 21b_4 + 5b_5) + 135b_2^2(7b_3 + 5b_4 + 21b_5) + 945b_3^2(b_4 + b_5) + 945b_4b_5^2 + 2035b_3(b_4^2 + b_5^2) + 945b_4b_5^2 + 270b_1b_2(5b_3 + 7b_4 + 7b_5) + 1350b_3b_4b_5 \]

(80a, b, c)

8. Explicit Expressions of the First Few Moments of \( z_{x} \) and \( z_{y} \) for an Ni-Iair CP (Centrosymmetric) or Non-Centrosymmetric Crystals

Putting \( p = 2, 3 \) and 4 in (65) we obtain

\[ \langle z_{\pm}^2 \rangle = \langle z_{\pm}^2 \rangle_{N} + \langle z_{\pm}^2 \rangle_{N} + 2 \]  

(81a)
\[ \langle z^3 \rangle = \langle z_N^3 \rangle + 2 \langle z_N^2 z_N' \rangle + \langle z_N' \rangle \]
\[ \quad \pm \langle z_N' \rangle \]  
(81b)

\[ \langle z^4 \rangle = \langle z_N^4 \rangle + 4 \langle z_N^3 z_N' \rangle + \quad \pm 4 \langle z_N^2 z_N' \rangle + \pm \langle z_N' \rangle \]
(81c)

where we have used the well-known result that the value of the normalised intensity is always unity, namely the result 
\[ z_N^{(1)} \cdot z_N^{(1)} = 1 \cdot 1 = 1, 2. \]

From (63) we obtain, for \( p = 1, 2 \) and 3, that

\[ \langle z_X \rangle = 1 \]  
(82a)

\[ \langle z_X^2 \rangle = z_N^{(1)} \cdot z_N^{(2)} \]  
(82b)

\[ \langle z_X^3 \rangle = z_N^{(1)} \cdot z_N^{(2)} \]  
(82c)
(a) Some General Remarks

(1) In the previous sections we have given the expressions for the first few moments of $\xi_a$ and $\xi_b$ for an I- and an Ni-pair of centrosymmetric and non-centrosymmetric crystals. The expressions for $\langle \xi_i \rangle$ (in this section we shall use the subscript $m$ to denote one of $+, -,$ or $\times$). We shall also use the subscript $m$ to $+-,$ $-$ to denote I or Ni. Thus $\xi_m$ means $\xi_+,$ $\xi_-,$ and $\langle \xi \rangle_{\text{Ni}}$ means $\langle \xi_+ \rangle,$ $\langle \xi_- \rangle,$ $\langle \xi_{\times} \rangle,$ $\langle \xi \rangle_{\text{I}}$ which in turn are functions of the two fundamental quantities $a_+,$ $a_-$ and $b_+,$ $b_-$ which are the fractional contributions to the local mean intensity from the group of replaceable atoms in the two crystals. Since $a_+,$ $a_-,$ $b_+,$ $b_-,$ can be calculated directly from a knowledge of the number and scattering powers of the atoms in the unit cell, their values will be known even before computing the Patterson synthesis for locating the I-atoms themselves. Making use of these values of $a_+,$ $a_-,$ $b_+,$ $b_-,$ the theoretical values of $\langle \xi_m \rangle_{ij}$ and $\langle \xi \rangle_{\text{Ni}}$ (see next paragraph) for any given value of $p$ can be calculated. A comparison of the experimental
values of the higher moments (denoted by $\langle \xi_i^m \rangle_{\text{NI}}$, $m = \frac{1}{2}, 1, 2$) with the corresponding theoretical moments for the I and NI-pair of crystals will reveal whether the pair of crystals under study are I or NI.

(ii) It may be noted that the expressions for $\langle \xi_i^m \rangle_{\text{NI}}$ have identical functional form for the centrosymmetric and non-centrosymmetric cases. However, the actual values of $\langle \xi_i^m \rangle_{\text{NI}}$ for $i = 1, 2$ which are to be substituted in these expressions are determined by the nature of the crystal (i.e., centrosymmetric or non-centrosymmetric). The values of $\langle \xi_i^m \rangle_{\text{NI}}$ for $i = 1, 2$ also depend on the number and contribution of the first few higher moments of the normalised intensity $z_N$ (that is for a single crystal) available in Tables (7-1) and (7-2) as a function of $i$ and $m$. The values of $\langle \xi_i^m \rangle_{\text{NI}}$ for $i = 1, 2$ obtained from these tables corresponding to the contributions $\xi_i^m$ and $\xi_i^m$ of the P-atoms in the two crystals when used in equations (81a) to (82c) directly give the theoretical values of the higher moments of $z_N$ ($m = \frac{1}{2}, 1$) for the NI-pair.
(iii) We have given explicit expressions (see equations (67a) to (82c)) for $\langle x^p \rangle$ (p = 2, 3 and 4) and $\langle x^p \rangle$ (p = 1, 2, 3) only for a few cases as a function of the number of atoms in the $\Pi$-group, namely for the cases for which $\Pi = 1, 2$ and $\Pi$ for an I-pair of centrosymmetric crystals and for the cases for which $\Pi = 1, 2, 3, 4$ and $\Pi$ for an I-pair of non-centrosymmetric crystals. The equations (25), (40), (51) and (60) are however quite general and apply to any I-pair of crystals of any space group (both the crystals of the given pair should however belong to the same space group symmetry). In using these expressions for calculating the theoretical values of $\langle x^p \rangle$, for any given pair of experimental crystals we must use the appropriate values of the corresponding moments, as determined by the crystal symmetry and atomic positions (special or general). These quantities can be obtained using the tabulated results of Foster and Longreaves (1963b).

(b) Application of the Theoretical Results in the Study of Different Types of Isomorphous Crystals

The theoretical results in the previous sections were obtained for the general case in which one $\Pi$-group
of atoms is replaced by another of a different scattering power (i.e., replacement isomorphism). That is, we have considered a pair of isomorphous crystals of the type

Crystal 1: \[ P \left[ f_p^{(1)}, E_p \right] + S \left[ f_Q^{(1)}, E_Q \right] \]

Crystal 2: \[ P \left[ f_p^{(2)}, E_p \right] + S \left[ f_Q^{(2)}, E_Q \right] \]

\[ j = 1 \text{ to } p \text{ and } k = 1 \text{ to } S \quad (83) \]

This is the usual type of isomorphism met with in structure analysis of ordinary organic molecules like the chlorine and bromine derivatives. We shall presently describe a few interesting particular cases of (83). Thus, we shall consider a pair of crystals of the type

Crystal 1: \[ Q \left[ f_Q^{(1)}, E_Q \right] \]

Crystal 2: \[ P \left[ f_p^{(2)}, E_p \right] + Q \left[ f_Q^{(2)}, E_Q \right] \]

\[ j = 1 \text{ to } p \text{ and } k = 1 \text{ to } Q \quad (84) \]

This is a particular case of (83) and follows from (83) for \( f_p^{(1)} = 0 \). The present case thus describes an I-pair of crystals such that a group of
'atoms' of 'zero' scattering power in crystal 1 is replaced by a group of atoms of scattering power $f_p^{(2)}$ to obtain crystal 2 (i.e. substitution isomorphism). Thus, we have to put $\beta_1 = 0$ and $\beta_2 = 1$ to calculate the theoretical values of $F$. This type of isomorphism arises in protein crystallography** wherein the first crystal represents the parent protein, while the second represents the heavy atom derivative of the parent protein. Thus, the theoretical results in this chapter can be used to test whether the addition of heavy atoms to the parent protein has caused any appreciable change in the parent protein part of the derivative. However, since the present theory is based on Wilson's statistics which is known to be a poor approximation for proteins (Harker, 1956; Luzzati, 1955) it is not possible to say much about the utility of the theoretical results in this chapter to protein crystallography.

** It is important to note that the nomenclature used in our present study is different from that used in protein crystallography. We use $P$ in (64) to denote the group of heavy (or substituted) atoms while in protein crystallography $P$ is often used to denote the parent structure. In (84) the parent structure is denoted by $Q$. 
Another particular case of (64) will be given by

Crystal 1: \[ P \left[ f_p(1), r_p \right] \]

Crystal 2: \[ P \left[ f_p(1), r_p \right] + \sum f_{qk}, t_{qk} \]

\[ j = 1 \text{ to } l \] and \[ k = 1 \text{ to } Q \] \hspace{1cm} (65)

The present case thus represents an 1-pair of crystals such that the first crystal is nothing but a part of the second crystal. That is, the \( l \) and \( k \) atoms do not correspond to two different crystals, but the \( k \)-atoms is a part of the whole \( l \) of the single crystal. For this case, we have to put \( \sum f'_{p1} = l \) and \( \sum f'_{p2} = 0 \) in order to obtain the theoretical values of \( c_{pq} \).

This type of isomorphism referred to as 'relatedness' by Ramachandran and coworkers - see for example Srinivasan et al., 1965b) arises in the structure analysis of single crystals with heavy atoms wherein the 'first' crystal represents the group of heavy atoms which are to be located from the Patterson synthesis and the 'second' crystal represents the experimental crystal (which contains the heavy atoms as a sub-unit). Thus, the results
of the present theory can be used to test whether the assumed positions of the heavy atoms (say determined from the Patterson) are correct. It may be noted that the application of the theoretical results of this chapter to this case has a greater validity than to the case of a pair of crystals (i.e. the cases described in (83) and (84)) since the latter very rarely possess identical cell dimensions which is implicitly required by the theory.

It may incidentally be noted here that the isomorphism described by (87) can also be tested by using the anomalous dispersion method. This possibility is discussed in detail in Chapter 12.

We could also think of the case of a pair of crystals in which the coordinates of the \(Q\)-atoms in the two crystals are identical, while those of the \(r\)-atoms are different. Such a pair of crystals may be called 'semi-isomorphous' and this type of isomorphism arises in the multiple isomorphous replacement method. The present theory cannot be applied to test such semi-isomorphism of a pair of crystals. However, the isomorphism of the \(Q\)-group in each of the semi-isomorphous
pair can be studied by comparing the isomorphism of the
Q-group in each of the two crystals with the parent
crystal (which is the crystal with only the 2-atoms)
and for such a study, the present theory holds as such.
The theory of the 'semi-isomorphous' pair is under
investigation.

10. VERIFICATION OF THE PRACTICAL APPLICATIONS
IN PRACTICAL CHEMISTRY, THEORETICAL, AND INDUSTRIAL.

The results of the theory have been tested
using appropriate two-dimensional models, the details of
which are given in Table 1. The crystal pair A con-
sisted of a pair of 2-dimensional hypothetical isomor-
phous structures each having two atoms in the Q-group,
chosen to be such that $\sigma_{1}^{(1)} = 0.6$ and $\sigma_{2}^{(2)} = 0.3$.
The crystal pair B was similar to pair A except that
$\sigma_{1}^{(1)} = 0$ and $\sigma_{2}^{(2)} = 0.3$ and the isomorphism of
this pair correspond to that described in (44). Crys-
tal pair C consisted of 2-dimensional hypothetical
isomorphous structures each having 20 atoms in the
P-group and 20 atoms in the Q-group such that
$\sigma_{1}^{(1)} = 0.6$ and $\sigma_{2}^{(2)} = 0.3$. Crystal pair D
was similar to pair C except that $\tau = 0$ and $\sigma_1(2)^2 = 0.3$ and that the isomorphism of this pair correspond to that described in (34). In each case, the values of the normalised intensities of reflections in each of the crystals of the pair were first determined. The second, third and fourth moments of $z_+$ and the first, second and third moments of $x_+$ were then determined and these represent the 'experimental' value free from the errors of observation denoted by E.

The theoretical values of $z_m^2$ ($m = 1, p = 2, 3$ and $4; m = x, p = 1, 2, 3$ and $4, m = 1, X$) for these pairs of crystals were calculated by using the known values of $\sigma_i(2)^2$ ($i = 1, 2$) and are listed in the rows marked I and X (see Tables 2, 3 and 4 for the tests based on the variables $z_+, z$ and $x_+$). From a comparison between the 'experimental' and theoretical data for the higher moments in Tables 2, 3 and 4 we obtain the following results:

(i) The variables $z_+$ and $x_+$ give isomorphism for all the pairs except that the tests based on $\langle z_+^4 \rangle, \langle x_+^2 \rangle$ and $z_+^3$ are indeterminate for the pair D.
(ii) The test based on $\langle z_2^2 \rangle$ and $\langle z_4^4 \rangle$ give isomorphism for all the pairs while the test based on $\langle z_3^3 \rangle$ for the pairs $\alpha$ and $\beta$ are indeterminate. (It may be mentioned that this happens so for $z_3^3$ because of the occurrence of both positive and negative terms in the expression for $z_3^3$. This difficulty can however be removed by calculating the expression for $\langle (z_3^3)^3 \rangle$ which is not considered here).

(iii) The theoretical values of the moments for the I- and MI-pairs differ to the largest extent for the $\langle z_4^4 \rangle$-test thus for any higher moment of any variable considered in this chapter.

Thus of all the tests, the test based on the fourth moment of $z_3$ seems to be the best.

It would be useful to note the following two points while applying the results to actual crystals:

(a) Since the errors in the observed intensity adversely affect the experimental values of the higher moments of $z_m$ (see Chapter 5) it would be necessary to carry out such tests by making use of intensity data which is as accurate as possible (note that such an
accuracy would also be helpful in phase determination by the isomorphous replacement method and by confining to the first few moments.

(b) Though the test based on the difference variable \( z_- \) is the most promising, it would be profitable to perform the tests using all three variables, namely \( z_+ \), \( z_- \) and \( z_\lambda \). This is because the deduction based on a number of test variables would be more reliable than that based on a single one.
### Table 11: 1

**Details of the Two-Dimensional Hypothetical Isomorphous Pair of Non-Centrosymmetric Crystals Used for Testing the Theoretical Results**

<table>
<thead>
<tr>
<th>Name of the Crystal pair</th>
<th>Nature of the P-group</th>
<th>Plane Group</th>
<th>Description of C-group (asymmetric unit)</th>
<th>Crystal Number (i)</th>
<th>P</th>
<th>G</th>
<th>$\sigma _{i}^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Two-atom Case</td>
<td>PG</td>
<td>C23*</td>
<td>1</td>
<td>2</td>
<td>46</td>
<td>0.6</td>
</tr>
<tr>
<td>B</td>
<td>Two-atom Case</td>
<td>PG</td>
<td>C23</td>
<td>2</td>
<td>2</td>
<td>46</td>
<td>0.3</td>
</tr>
<tr>
<td>C</td>
<td>MA Case</td>
<td>PG</td>
<td>Cl10**</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>0.6</td>
</tr>
<tr>
<td>D</td>
<td>MA Case</td>
<td>PG</td>
<td>Cl10</td>
<td>2</td>
<td>20</td>
<td>20</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Notes to Table 11: 1**

* C = Carbon Atom; ** Cl = 'normal' Chlorine atom

The scattering power of the P-atoms in each case is of the type $g f_p$, where the value of $g$ for each crystal is so adjusted as to give the required value for $\sigma _{i}^{(2)}$. 
<table>
<thead>
<tr>
<th>Name of the Crystal pair</th>
<th>$&lt;s^2&gt;$</th>
<th>$&lt;s^3&gt;$</th>
<th>$&lt;s^4&gt;$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.444</td>
<td>41.50</td>
<td>276.7</td>
<td>All moments give</td>
</tr>
<tr>
<td></td>
<td>7.413</td>
<td>39.50</td>
<td>271.2</td>
<td>isomorphism</td>
</tr>
<tr>
<td></td>
<td>5.775</td>
<td>21.54</td>
<td>97.9</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>7.229</td>
<td>40.58</td>
<td>303.2</td>
<td>-do-</td>
</tr>
<tr>
<td></td>
<td>7.355</td>
<td>40.29</td>
<td>293.8</td>
<td>-do-</td>
</tr>
<tr>
<td></td>
<td>5.955</td>
<td>23.49</td>
<td>117.5</td>
<td>-do-</td>
</tr>
<tr>
<td>C</td>
<td>8.360</td>
<td>51.90</td>
<td>407.2</td>
<td>-do-</td>
</tr>
<tr>
<td></td>
<td>7.818</td>
<td>45.82</td>
<td>358.0</td>
<td>-do-</td>
</tr>
<tr>
<td></td>
<td>6.000</td>
<td>24.00</td>
<td>120.0</td>
<td>-do-</td>
</tr>
<tr>
<td>D</td>
<td>7.116</td>
<td>35.05</td>
<td>212.4</td>
<td>$&lt;s^4&gt;$ test is</td>
</tr>
<tr>
<td></td>
<td>7.400</td>
<td>40.80</td>
<td>299.8</td>
<td>indeterminate</td>
</tr>
<tr>
<td></td>
<td>6.000</td>
<td>24.00</td>
<td>120.0</td>
<td>-do-</td>
</tr>
</tbody>
</table>

*E = Experimental values without any errors of observation.

I = Theoretical Value for an isomorphous pair.

NI = Theoretical Value for a non-isomorphous pair.

This notation will also be followed in Tables 3 & 4.
**TABLE 11.3**

**TEST FOR ISOMORPHISM USING THE RIGOUR OF KELTCH OF E**

FOR THE PAIRS OF CRYSTALS DESCRIBED IN TABLE 1

<table>
<thead>
<tr>
<th>Name of the Crystal pair</th>
<th>$a^2$</th>
<th>$a^3$</th>
<th>$a^4$</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.1141</td>
<td>-0.0261</td>
<td>0.0517</td>
<td>All moments give isomorphism</td>
</tr>
<tr>
<td>I</td>
<td>0.1370</td>
<td>-0.0548</td>
<td>0.1030</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.7750</td>
<td>-0.6210</td>
<td>16.1800</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.5067</td>
<td>0.1615</td>
<td>1.1442</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.5550</td>
<td>0.2430</td>
<td>1.4610</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.9550</td>
<td>0.3430</td>
<td>19.8200</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.1406</td>
<td>0.0205</td>
<td>0.0842</td>
<td>$a^3$ test is indeterminate</td>
</tr>
<tr>
<td>I</td>
<td>0.1818</td>
<td>0.0000</td>
<td>0.0676</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>2.0000</td>
<td>0.0000</td>
<td>24.0000</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.7942</td>
<td>-0.1646</td>
<td>3.3920</td>
<td>-do-</td>
</tr>
<tr>
<td>I</td>
<td>0.6000</td>
<td>0.0000</td>
<td>2.1600</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>2.0000</td>
<td>0.0000</td>
<td>24.0000</td>
<td></td>
</tr>
<tr>
<td>Name of the Crystal pair</td>
<td>$\langle s_x \rangle$</td>
<td>$s_x^2$</td>
<td>$s_x^3$</td>
<td>remarks</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------------</td>
<td>--------</td>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.906</td>
<td>17.08</td>
<td>281.5</td>
<td>All moments give isomorphism</td>
</tr>
<tr>
<td>I</td>
<td>1.819</td>
<td>16.65</td>
<td>332.3</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.000</td>
<td>3.56</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td><strong>B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.679</td>
<td>18.26</td>
<td>399.8</td>
<td>-do-</td>
</tr>
<tr>
<td>I</td>
<td>1.700</td>
<td>17.07</td>
<td>427.5</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.000</td>
<td>3.91</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td><strong>C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2.055</td>
<td>25.06</td>
<td>545.9</td>
<td>-do-</td>
</tr>
<tr>
<td>I</td>
<td>1.909</td>
<td>21.85</td>
<td>601.3</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.000</td>
<td>4.00</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td><strong>D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.581</td>
<td>11.27</td>
<td>137.2</td>
<td>$s_x^2$ and $s_x^3$ tests are indeterminate</td>
</tr>
<tr>
<td>I</td>
<td>1.700</td>
<td>17.16</td>
<td>436.2</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>1.000</td>
<td>4.00</td>
<td>36.0</td>
<td></td>
</tr>
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