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# Test for Isomorphism Using Higher Moments of Intensities*

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A test for isomorphism of a pair of crystals uses the higher moments of the sum and difference of their normalized intensities (denoted by $z_+$ and $z_-$). The expressions for the general $p$th moment of $z_+$ and $z_-$ are first worked out for isomorphous and non-isomorphous pairs of crystals and from these the expressions for the second, third and the fourth moments of these quantities are deduced. Both centrosymmetric and non-centrosymmetric crystals are considered and in each type of crystal the expressions for the first four moments of $z_+$ and $z_-$ are given for isomorphous and non-isomorphous pairs of crystals, depending on the number of atoms in the replaceable group. The results of the theory are also applicable to a pair of crystals, one containing a simple molecule and the other its heavy atom derivative, which is the type which occurs in protein structures. The results of the theory may also be used to test whether the positions of the heavy atoms determined in an early stage of structure analysis are correct. The theoretical results have also been tested by using suitable two-dimensional models.

## 1. Introduction

The use of intensity data from a pair of isomorphous crystals for obtaining the phases is a well-known method. Under favourable conditions, the phases of reflexions can be determined with the use of a single pair of isomorphous crystals if the crystals are centrosymmetric, while the multiple isomorphous-replacement technique (Harker, 1956) is required for a unique determination of the phases in the case of non-centrosymmetric crystals. For a successful application of this technique, it is essential that the given pair of crystals are really isomorphous, namely that the atomic positions in the two crystals are the same (within reasonable limits). A method for testing for isomorphism before applying this method will therefore be very useful.

A number of very useful tests, based on the statistical distributions of the difference and the product of the structure factors corresponding respectively to the replaceable part and the whole crystal, have been developed by Srinivasan and others in this laboratory (Ramachandran, Srinivasan & Sarma, 1963; Srinivasan, Sarma & Ramachandran, 1963*a*, *b*; Srinivasan, Subramanian & Ramachandran, 1964). Their results however apply to the case in which there is a large number of atoms in the replaceable group. In this paper, we shall consider another possible way in which the measured intensities from the given pair of crystals can be used to test whether the pair is isomorphous or not. We consider both centrosymmetric and non-centrosymmetric crystals and in each crystal we shall consider a number of cases depending on whether the number of atoms in the replaceable group (also called the $P$-group in this paper) is 1, 2 or many. In the case of a non-centrosymmetric crystal with a large number of atoms in the $P$-group, the $P$-group may have either a centrosymmetric or a non-centrosymmetric configuration of atoms and these two cases are respectively denoted by $MC$ (many-centric) aand $MA$ (many-acentric).

The principle of the method is discussed in §2. §3 and §4 respectively deal with the theory for the cases of non-centrosymmetric and centrosymmetric crystals. §5 deals with a discussion of these theoretical results and §6 with the verification of the expressions derived in §3 and §4 in hypothetical cases.

## 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 ($P$-group, $P$ in number) and a non-replaceable group of atoms ($Q$-group, $Q$ in number). The $P$-group usually contains heavy atoms like Cl or Br and the $Q$-group usually contains light atoms like C, N, and O, in the case of organic crystals; however, the theory does not make use of the 'heaviness' of the $P$-atoms. Let $N\,(=P+Q)$ be the total number of atoms in the unit cell of each crystal. Let $f_P^{(1)}$ and $f_P^{(2)}$ be the atomic scattering factors of the atoms in the $P$-group of the two crystals. (The number 1 or 2 in parenthesis attached to any variable indicates that the variable corresponds to crystal 1 or 2 of the given pair.) Let $f_{Qk}$ ($k=1$ to $Q$) be the atomic scattering

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factors of the atoms in the $Q$-group in either crystal. We further assume that the atoms in the $P$-group of each crystal are identical* and that the two crystals have a geometrical similarity. The given pair of crystals is said to be perfectly isomorphous if the coordinates of 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 non-isomorphous if the coordinates of 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:

$$\begin{aligned} &\text{Crystal 1} \quad P[f_P^{(1)}, \mathbf{r}_{Pj}^{(1)}]+Q[f_{Qk}, \mathbf{r}_{Qk}^{(1)}] \\ &\text{Crystal 2} \quad P[f_P^{(2)}, \mathbf{r}_{Pj}^{(2)}]+Q[f_{Qk}, \mathbf{r}_{Qk}^{(2)}] \\ &\qquad j=1 \text{ to } P,\ k=1 \text{ to } Q\,. \end{aligned} \tag{1}$$

The two crystals are isomorphous if

$$\begin{aligned} \mathbf{r}_{Pj}^{(1)} &= \mathbf{r}_{Pj}^{(2)} \text{ for each } j\ (j=1 \text{ to } P) \\ \mathbf{r}_{Qk}^{(1)} &= \mathbf{r}_{Qk}^{(2)} \text{ for each } k\ (k=1 \text{ to } Q) \end{aligned} \tag{2}$$

and non-isomorphous if

$$\begin{aligned} \mathbf{r}_{Pj}^{(1)} &\neq \mathbf{r}_{Pj}^{(2)} \text{ for each } j\ (j=1 \text{ to } P) \\ \mathbf{r}_{Qk}^{(1)} &\neq \mathbf{r}_{Qk}^{(2)} \text{ for each } k\ (k=1 \text{ to } Q)\,. \end{aligned} \tag{3}$$

We shall use the symbol $I$ as subscript to any quantity that belongs to the isomorphous pair of crystals and the symbol $NI$ in the same way, if the crystal pair is non-isomorphous.

The vector diagram showing the structure factors of the pair of crystals is shown in Fig. 1 for an isomorphous pair (also called $I$-pair) and in Fig. 2 for a non-isomorphous pair (also called $NI$-pair) of crystals. Using the notation shown in these figures, it is clear that: for an $I$-pair

$$\begin{aligned} &|F_P^{(1)}| \neq |F_P^{(2)}|,\ \alpha_P^{(1)}=\alpha_P^{(2)}=\alpha_p, \text{ say} \\ &F_Q^{(1)}=F_Q^{(2)}=F_Q, \text{ say and } \psi^{(1)}=\psi^{(2)}=\psi, \text{ say,} \end{aligned} \tag{4a}$$

and for an $NI$-pair

$$\begin{aligned} &|F_P^{(1)}| \neq |F_P^{(2)}|,\ \alpha_P^{(1)} \neq \alpha_P^{(2)} \\ &|F_Q^{(1)}| \neq |F_Q^{(2)}|,\ \alpha_Q^{(1)} \neq \alpha_Q^{(2)} \text{ and } \psi^{(1)} \neq \psi^{(2)}\,. \end{aligned} \tag{4b}$$

We shall indicate the mean contributions to the intensity from the $P$- and the $Q$-groups by $\sigma_P^2$ and $\sigma_Q^2$, defined by the equations

$$\sigma_P^{(i)2}=\sum_{j=1}^{P} f_{Pj}^{(i)2},\ \sigma_Q^{(i)2}=\sum_{k=1}^{Q} f_{Qk}^{(i)2} \text{ and } \sigma_N^{(i)2}=\sigma_P^{(i)2}+\sigma_Q^{(i)2},\ i=1, 2\,. \tag{5}$$

The fractional contributions to the mean intensity from the $P$- and $Q$-groups are given by

$$\sigma_1^{(i)2}=\sigma_P^{(i)2}/\sigma_N^{(i)2},\ \sigma_2^{(i)2}=\sigma_Q^{(i)2}/\sigma_N^{(i)2} \text{ and } \sigma_1^{(i)2}+\sigma_2^{(i)2}=1,\ i=1, 2\,. \tag{6}$$

The normalized intensity $z^{(i)}$ for the two crystals may be defined by

$$\begin{aligned} z^{(i)} &= |F_N^{(i)}|^2/\sigma_N^{(i)2}=|F_P^{(i)}+F_Q^{(i)}|^2/\sigma_N^{(i)2} \\ &= [|F_P^{(i)}|^2+|F_Q^{(i)}|^2+2|F_P^{(i)}||F_Q^{(i)}| \cos \psi^{(i)}]/\sigma_N^{(i)2},\ i=1, 2\,. \end{aligned} \tag{7}$$

From (4$a$), (4$b$) and (7) it is clear that $z^{(1)}$ and $z^{(2)}$ are dependent random variables if they correspond to the $I$-pair and independent random variables if they correspond to the $NI$-pair of crystals. The distribution of a variable which is defined as a function $f[z^{(1)}, z^{(2)}]$ of the variables $z^{(1)}$ and $z^{(2)}$ will depend on the nature of the variables $z^{(1)}$ and $z^{(2)}$ themselves, *i.e.* will differ depending on whether $z^{(1)}$ and $z^{(2)}$ are dependent or independent random variables. However, it is difficult to obtain the distribution function of $f$, especially when $z^{(1)}$ and $z^{(2)}$ are dependent variables. On the other hand it is possible in most cases to calculate the statistical parameters like moments, variances *etc.* of

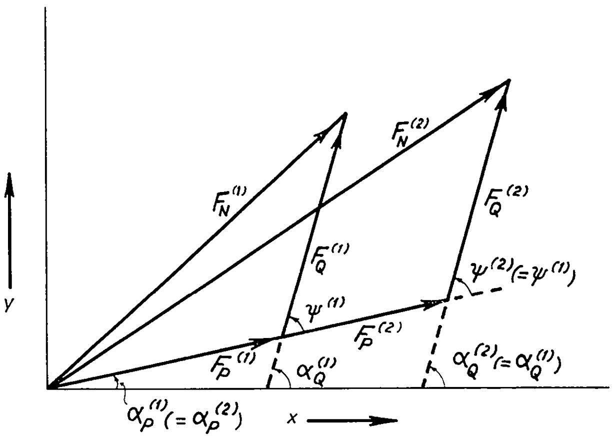

Fig. 1. Vector diagram showing the relation between the structure factors of an isomorphous pair of non-centrosymmetric crystals.

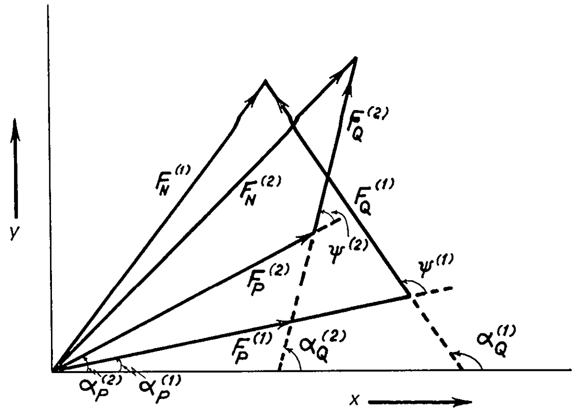

Fig. 2. Vector diagram showing the structure factors of a non-isomorphous pair of non-centrosymmetric crystals.

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* This condition is not essential for a general theory, but the formulae for $P=2$ are valid only under this condition. For $P=MC$ and $MA$ (see below), the atoms in the $P$-group need not be identical.

† One could also think of a case in which the coordinates of the $Q$-atoms in the two crystals are identical, while those of the $P$-group are different. Such a pair of crystals may be called 'semi-isomorphous' but the mathematics of this case is still under study.

$f$ and since these quantities are characterized by the distribution of $f$, these parameters can be used as statistical tests for isomorphism.

In this paper we shall consider two simple functions of the variables $z^{(1)}$ and $z^{(2)}$, defined by

$$z_+ = z^{(1)} + z^{(2)} \quad (8a)$$

$$z_- = z^{(1)} - z^{(2)} \quad (8b)$$

and calculate the higher moments of these variables* $z_+$ and $z_-$. The use of the normalized intensities $z^{(1)}$ and $z^{(2)}$ 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 absolute scales.

It may be mentioned that the distribution function of $|F^{(1)}|^2 - |F^{(2)}|^2$ has been obtained in this laboratory by Srinivasan & Venkatachalam (unpublished). This function would provide an alternative method of testing for isomorphism, and a test of this will be published elsewhere.

## 3. Non-centrosymmetric crystal

### (*a*) *Isomorphous pair*

The normalized intensities of a reflexion in the two crystals are given by [see equation (7)]

$$z^{(i)} = [\sigma_P^{(i)2} y_P^{(i)2} + \sigma_Q^{(i)2} y_Q^{(i)2} + 2\sigma_P^{(i)}\sigma_Q^{(i)} y_P^{(i)} y_Q^{(i)} \cos \psi^{(i)}]/\sigma_N^{(i)2},\; i = 1, 2\,. \quad (9a)$$

where

$$y_P^{(i)} = |F_P^{(i)}|/\sigma_P^{(i)} \quad \text{and} \quad y_Q^{(i)} = |F_Q^{(i)}|/\sigma_Q^{(i)},\; i = 1, 2. \quad (9b)$$

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

$$y_P^{(1)} = y_P^{(2)} = y_P, \text{ say}$$

$$y_Q^{(1)} = y_Q^{(2)} = y_Q, \text{ say.} \quad (10)$$

From (4), (6), (9) and (10) we thus obtain

$$\begin{aligned} z^{(i)} &= \sigma_1^{(i)2} y_P^2 + \sigma_2^{(i)2} y_Q^2 + 2\sigma_1^{(i)}\sigma_2^{(i)} y_P y_Q \cos \psi \\ &= \sigma_1^{(i)2} z_P + \sigma_2^{(i)2} z_Q + 2\sigma_1^{(i)}\sigma_2^{(i)} z_P^{1/2} z_Q^{1/2} \cos \psi,\; i = 1, 2\,, \end{aligned} \quad (11)$$

where $z_P$ $(= y_P^2)$ and $z_Q$ $(= y_Q^2)$ are the normalized intensities of the reflexion from the $P$- and $Q$-groups in either crystal. As defined in (8), we have

$$\begin{aligned} z_{\pm,I} &= z^{(1)} \pm z^{(2)} \\ &= [\sigma_1^{(1)2} \pm \sigma_1^{(2)2}] z_P + [\sigma_2^{(1)2} \pm \sigma_2^{(2)}] z_Q \\ &\quad + 2[\sigma_1^{(1)}\sigma_2^{(1)} \pm \sigma_1^{(2)}\sigma_2^{(2)}] z_P^{1/2} z_Q^{1/2} \cos \psi\,. \end{aligned} \quad (12)$$

If we make the simplifying notation

$$\begin{aligned} a_\pm &= \sigma_1^{(1)2} \pm \sigma_1^{(2)2} \\ b_\pm &= \sigma_2^{(1)2} \pm \sigma_2^{(2)2} \quad \text{and} \\ c_\pm &= \sigma_1^{(1)}\sigma_2^{(1)} \pm \sigma_1^{(2)}\sigma_2^{(2)} \end{aligned} \quad (13)$$

(12) becomes

$$z_{\pm,I} = a_\pm z_P + b_\pm z_Q + 2c_\pm z_P^{1/2} z_Q^{1/2} \cos \psi\,. \quad (14)$$

For simplicity, we shall use only $a$, $b$, $c$ and $z$ for $a_\pm$, $b_\pm$, $c_\pm$ and $z_\pm$ respectively, since the definition of $z$ in any particular case will clearly define which of the quantities are actually meant. With this, (14) can be rewritten as

$$z_I = a z_P + b z_Q + 2c z_P^{1/2} z_Q^{1/2} \cos \psi\,. \quad (15)$$

The $p$th moment of $z_I$ is given by

$$\langle z_I^p \rangle = \langle (a z_P + b z_Q + 2c z_P^{1/2} z_Q^{1/2} \cos \psi)^p \rangle\,, \quad (16)$$

where the symbol $\langle\rangle$ enclosing any quantity represents the expectation value of the quantity. In obtaining the value of $\langle z_I^p \rangle$ as a function of the higher moments of $z_P$ and $z_Q$ we may make use of two well-known results from the theory of mathematical probability (see Cramer, 1945, p. 170–174) which are as follows:

If $x_j$ $(j = 1$ to $r)$ are a set of random variables, $p_j$ are positive integers and $k$ and $c_j$ $(j = 0$ to $r)$ are constants then

$$\langle c_0 + \sum_{j=1}^{r} c_j x_j^{p_j} \rangle = c_0 + \sum_{j=1}^{r} c_j \langle x_j^{p_j} \rangle \quad (17)$$

$$\langle k \prod_{j=1}^{r} c_j x_j^{p_j} \rangle = (k \prod_{j=1}^{r} c_j) \prod_{j=1}^{r} \langle x_j^{p_j} \rangle\,. \quad (18)$$

Equation (17) is true independently of the nature of the variables, while (18) is true only when the $x_j$'s are independent random variables. Since $|F_P|$, $|F_Q|$ and $\psi$ are independent variables, so are $y_P$, $y_Q$ and $\psi$. The general $p$th moment of $z_I$ can therefore be obtained by expanding the expressions in the right hand side of (16) and then applying the results in (17) and (18)*. To obtain this expression, we use the multinomial theorem for integral exponent, *viz.*,

$$(\alpha + \beta + \gamma)^p = \sum_{j=0}^{p} \sum_{k=0}^{p-j} \frac{p!\,\alpha^j \beta^k \gamma^{p-j-k}}{j!\,k!\,(p-j-k)!}\,. \quad (19)$$

From (16) and (19) we obtain

$$\begin{aligned} \langle z_I^p \rangle &= \langle (b z_Q + 2c z_P^{1/2} z_Q^{1/2} \cos \psi + a z_P)^p \rangle \\ &= \left\langle \sum_{j=0}^{p} \sum_{k=0}^{p-j} \frac{p!}{j!\,k!\,(p-j-k)!} \times (b z_Q)^j (2c z_Q^{1/2} z_P^{1/2} \cos \psi)^k (a z_P)^{p-j-k} \right\rangle \\ &= \sum_{j=0}^{p} \sum_{k=0}^{p-j} \frac{p!\,2^k a^{p-j-k} b^j c^k}{j!\,k!\,(p-j-k)!} \times \langle z_Q^{j+k/2} \rangle \langle z_P^{p-j-k/2} \rangle \langle \cos^k \psi \rangle\,. \end{aligned} \quad (20)$$

Since $\psi$ is uniformly distributed, *i.e.*

$$P(\psi) d\psi = (\tfrac{1}{2}\pi) d\psi\,, \quad -\pi < \psi \le \pi$$

we have

$$\langle \cos^k \psi \rangle = \frac{1}{2\pi} \int_{-\pi}^{\pi} \cos^k \psi\, d\psi = \frac{1}{\pi} \int_0^{\pi} \cos^k \psi\, d\psi$$

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* The higher moments of the product variable $z_\times = z^{(1)}.z^{(2)}$ have also recently been worked out and the results will be published shortly.

* For clarity, we may state that $F_N{}^{(1)}$ and $F_N{}^{(2)}$ are independent variables for the non-isomorphous case and $\langle F_N{}^{(1)}\, F_N{}^{(2)} \rangle = 0$. Another implicit result is that $\langle F_P F_Q \rangle = 0$ for the isomorphous case also, arising from the fact that the $P$-atoms and the $Q$-atoms occupy different locations in the unit cell.

$$=\begin{cases}0 \text{ if } k \text{ is an odd integer}\\ \dfrac{k!2^{-k}}{[(k/2)!]^2} \text{ if } k \text{ is an even integer.}\end{cases} \tag{21}$$

Equation (21) is a simple result that follows from the expansion of $\cos^k \psi$ in a series of cosines of multiples of $\psi$ and then integrating the resulting series term by term (Loney, 1957, p. 55). It is known that (Srinivasan & Subramanian, 1964) for a non-centrosymmetric crystal

$$\langle z_Q^{j+k/2}\rangle=\Gamma(j+\tfrac{1}{2}k+1)\,. \tag{22}$$

Substituting (21) and (22) in (20) we obtain

$$\langle z_I^p\rangle=\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{p!\Gamma(j+\frac{1}{2}k+1)}{j!(p-j-k)![(k/2)!]^2} \times a^{p-j-k}b^jc^k\langle z_P^{p-j-k/2}\rangle \tag{23}$$

where the prime over the second summation indicates that only terms with $k$ = an even integer are to be included in the summation, since the terms for which $k$ is an odd integer vanish identically. Since only the terms for which $k$ is an even integer exist, $\Gamma(j+\frac{1}{2}k+1)$ can be conveniently replaced by $(j+\frac{1}{2}k)!$. Thus (23) becomes

$$\langle z_I^p\rangle=p!\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{(j+\frac{1}{2}k)!a^{p-j-k}b^jc^k}{j!(p-j-k)![(k/2)!]^2}\langle z_P^{p-j-k/2}\rangle\,. \tag{24}$$

This is a general expression, valid for any type of $P$-group, in which the values of $\langle z_P^{p-j-k/2}\rangle$ depending on the number of atoms in the $P$-group have to be put in. We shall consider four cases, *viz.* when $P=1$, 2, $MC$ and $MA$. It is well-known that

$$\langle z_P^{p-j-1/2k}\rangle=\begin{cases}1 \text{ when } P=1 & (25a)\\[4pt] \dfrac{2^{p-j-1/2k}}{\sqrt{\pi}}\,\dfrac{\Gamma(p-j-\frac{1}{2}k+\frac{1}{2})}{\Gamma(p-j-\frac{1}{2}k+1)} \text{ when } P=2 & (25b)\\[4pt] \dfrac{2^{p-j-1/2k}}{\sqrt{\pi}}\,\Gamma(p-j-\frac{1}{2}k+\frac{1}{2}) \text{ when } P=MC & (25c)\\[4pt] \Gamma(p-j-\frac{1}{2}k+1) \text{ when } P=MA\,. & (25d)\end{cases}$$

From (24) and (25) we obtain (note the prime over the second summation in (26) to (29), indicating that only terms with $k$ even are to be included in them):

$$\langle z_I^p\rangle=p!\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{(j+\frac{1}{2}k)!a^{p-j-k}b^jc^k}{j!(p-j-k)![(k/2)!]^2} \text{ when } P=1 \tag{26}$$

$$\langle z_I^p\rangle=\frac{p!}{\sqrt{\pi}}\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{(j+\frac{1}{2}k)!\Gamma(p-j-\frac{1}{2}k+\frac{1}{2})2^{p-j-k/2}}{j!(p-j-k)![(k/2)!]^2\Gamma(p-j-\frac{1}{2}k+1)} \times a^{p-j-k}b^jc^k \text{ when } P=2 \tag{27}$$

$$\langle z_I^p\rangle=\frac{p!}{\sqrt{\pi}}\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{(j+\frac{1}{2}k)!\Gamma(p-j-\frac{1}{2}k+\frac{1}{2})2^{p-j-k/2}}{j!(p-j-k)![(k/2)!]^2} \times a^{p-j-k}b^jc^k \text{ when } P=MC \tag{28}$$

$$\langle z_I^p\rangle=p!\sum_{j=0}^{p}\ {\sum_{k=0}^{p-j}}' \frac{(j+\frac{1}{2}k)!\Gamma(p-j-\frac{1}{2}k+1)}{j!(p-j-k))![(k/2)!]^2} \times a^{p-j-k}b^jc^k \text{ when } P=MA\,. \tag{29}$$

For any given integral value of $p$ the right hand side of each of the equations (26) to (29) can be expanded into a homogeneous polynomial of degree $p$ in the variables $a$, $b$ and $c$. For convenience of application of these results in practical cases, where the first few moments of $z_I$ would be sufficient, we give below the simplified expressions of $\langle z_I^p\rangle$ for $p=2$, 3 and 4. It may be noted that the case $p=1$ does not afford any test value, since the relation

$$\langle z^{(1)}\pm z^{(2)}\rangle=\langle z^{(1)}\rangle\pm\langle z^{(2)}\rangle \tag{30}$$

holds whether $z^{(1)}$ and $z^{(2)}$ are independent or not.

*One-atom case*

$$\langle z_I^2\rangle=2[\tfrac{1}{2}a^2+ab+b^2+c^2] \tag{31a}$$

$$\langle z_I^3\rangle=6[\tfrac{1}{6}a^3+\tfrac{1}{2}a^2b+ac^2+2bc^2+ab^2+b^3] \tag{31b}$$

$$\langle z_I^4\rangle=24[\tfrac{1}{24}a^4+\tfrac{1}{6}a^3b+\tfrac{1}{2}a^2c^2+\tfrac{1}{2}c^4+\tfrac{1}{2}a^2b^2+2abc^2+3b^2c^2+ab^3+b^4] \tag{31c}$$

*Two-atom case*

$$\langle z_I^2\rangle=2[\tfrac{3}{4}a^2+ab+b^2+c^2] \tag{32a}$$

$$\langle z_I^3\rangle=6[\tfrac{5}{12}a^3+\tfrac{3}{4}a^2b+\tfrac{3}{2}ac^2+2bc^2+ab^2+b^3] \tag{32b}$$

$$\langle z_I^4\rangle=24[\tfrac{35}{192}a^4+\tfrac{5}{12}a^3b+\tfrac{5}{4}a^2c^2+\tfrac{3}{4}c^4+\tfrac{3}{4}a^2b^2+3abc^2+3b^2c^2+ab^3+b^4] \tag{32c}$$

*Many-atom case*: $(P=MC)$

$$\langle z_I^2\rangle=2[\tfrac{3}{2}a^2+ab+b^2+c^2] \tag{33a}$$

$$\langle z_I^3\rangle=6[\tfrac{5}{2}a^3+\tfrac{3}{2}a^2b+3ac^2+2bc^2+ab^2+b^3] \tag{33b}$$

$$\langle z_I^4\rangle=24[\tfrac{35}{8}a^4+\tfrac{5}{2}a^3b+\tfrac{15}{2}a^2c^2+\tfrac{3}{2}c^4+\tfrac{3}{2}a^2b^2+6abc^2+3b^2c^2+ab^3+b^4] \tag{33c}$$

*Many-atom case*: $(P=MA)$

$$\langle z_I^2\rangle=2[a^2+ab+b^2+c^2] \tag{34a}$$

$$\langle z_I^3\rangle=6[a^3+a^2b+2ac^2+2bc^2+ab^2+b^3] \tag{34b}$$

$$\langle z_I^4\rangle=24[a^4+a^3b+3a^2c^2+c^4+a^2b^2+4abc^2+3b^2c^2+ab^3+b^4] \tag{34c}$$

### (*b*) *Non-isomorphous pair*

In this case $z^{(1)}$ and $z^{(2)}$ are independent variables. The $p$th moment of $z_{\pm,NI}=z^{(1)}\pm z^{(2)}$ is therefore given by

$$\langle z^p_{\pm,NI}\rangle=\langle(z^{(1)}\pm z^{(2)})^p\rangle\,. \tag{35}$$

Expanding $[z^{(1)}\pm z^{(2)}]^p$ as a polynomial using the binomial theorem we obtain

$$\langle z^p_{\pm,NI}\rangle=\sum_{j=0}^{p}\frac{(\pm)^{p-j}p!}{j!(p-j)!}\langle z^{(1)j}\rangle\langle z^{(2)p-j}\rangle \tag{36}$$

where we have used the criterion of independence of $z^{(1)}$ and $z^{(2)}$ and equations (17) and (18). The values of the higher moments of $z^{(1)}$ and $z^{(2)}$ depend on the number of atoms in the $P$-group and their contribution to the mean intensity (*i.e.* on the values of $\sigma_1^{(1)2}$ and $\sigma_1^{(2)2}$). For a specific value of $p$, the expression in the right hand side of (36) can be simplified. The expressions for $p=2$, 3 and 4 are given below:

$$\langle z^2_{\pm,NI}\rangle=\langle z^{(1)^2}\rangle+\langle z^{(2)^2}\rangle\pm 2 \tag{37a}$$

$$\langle z^3_{\pm,NI}\rangle=\langle z^{(1)^3}\rangle\pm 3\langle z^{(1)^2}\rangle+3\langle z^{(2)^2}\rangle\pm\langle z^{(2)^3}\rangle \tag{37b}$$

$$\begin{aligned}\langle z^4_{\pm,NI}\rangle=\langle z^{(1)^4}\rangle\pm 4\langle z^{(1)^3}\rangle+6\langle z^{(1)^2}\rangle\langle z^{(2)^2}\rangle\\ \pm 4\langle z^{(2)^3}\rangle+\langle z^{(2)^4}\rangle\,,\end{aligned} \tag{37c}$$

where we have used the result $\langle z^{(i)}\rangle=1$, $i=1, 2$.

## 4. Centrosymmetric crystal

### (*a*) *Isomorphous pair*

In this case, the structure factors are all real and the equation for the normalized intensities in the two crystals can be written

$$\begin{aligned}z^{(i)}&=|F_P^{(i)}+F_Q^{(i)}|^2/\sigma_N^{(i)2}\\ &=[|F_P^{(i)}|^2+|F_Q^{(i)}|^2+2|F_P^{(i)}||F_Q^{(i)}|s^{(i)}]/\sigma_N^{(i)2}, \quad i=1,2\,.\end{aligned} \tag{38}$$

where $s^{(i)}=s_P^{(i)}s_Q^{(i)}$, the product of the signs of $F_P^{(i)}$ and $F_Q^{(i)}$, $i=1, 2$. It is clear that

$$s^{(1)}=s^{(2)}=s, \quad \text{say}\,. \tag{39}$$

As in the case of the non-centrosymmetric crystal, (38) can be rewritten

$$z^{(i)}=\sigma_1^{(i)2}z_P+\sigma_2^{(i)2}z_Q+2\sigma_1^{(i)}\sigma_2^{(i)}z_P^{1/2}z_Q^{1/2}s, \quad i=1,2\,. \tag{40}$$

The test variables are, by definition,

$$\begin{aligned}z_{\pm,I}&=z^{(1)}\pm z^{(2)}\\ &=az_p+bz_Q+2cz_P^{1/2}z_Q^{1/2}s=z_I, \quad \text{say}\,.\end{aligned} \tag{41}$$

The $p$th moment of $z_I$ is given by

$$\langle z_I^p\rangle=\langle(bz_Q+2cz_Q^{1/2}z_P^{1/2}s+az_P)^p\rangle\,. \tag{42}$$

Applying the multinomial theorem (19) in (42), we obtain

$$\langle z_I^p\rangle=\sum_{j=0}^{p}\sum_{k=0}^{p-j}\frac{p!2^ka^{p-j-k}b^jc^k}{j!k!(p-j-k)!}\langle s^k\rangle\langle z_Q^{j+k/2}\rangle\langle z_P^{p-j-k/2}\rangle\,. \tag{43}$$

It is well known (Srinivasan & Subramanian, 1964) that for a centrosymmetric crystal

$$\langle z_Q^{j+k/2}\rangle=2^{j+k/2}\pi^{-\frac{1}{2}}\Gamma(j+\tfrac{1}{2}k+\tfrac{1}{2})\,. \tag{44}$$

Since $F_P$ and $F_Q$ are independent, $s_P$ and $s_Q$ are also independent so that by (18)

$$\langle s\rangle=\langle s_Ps_Q\rangle=\langle s_P\rangle\langle s_Q\rangle\,. \tag{45}$$

It is clear that the probability function of $s_Q$ is

$$\begin{aligned}P(s_Q)=\tfrac{1}{2} \quad &\text{so that } \langle s_Q\rangle\\ &=(+1)P(+1)+(-1)P(-1)=\tfrac{1}{2}-\tfrac{1}{2}=0\,.\end{aligned} \tag{46}$$

That is, $\langle s\rangle=0$.

Since $s^{2n}=1$ and $s^{2n+1}=s^{2n}s=s$, we have

$$\langle s^{2n}\rangle=1 \quad \text{and} \quad \langle s^{2n+1}\rangle=\langle s\rangle=0\,. \tag{47}$$

Using (44) and (47) in (43), we obtain

$$\langle z_I^p\rangle=\frac{p!}{\sqrt{\pi}}\sum_{j=0}^{p}\sideset{}{'}\sum_{k=0}^{p-j}\frac{2^{j+3/2k}\Gamma(j+\frac{1}{2}k+\frac{1}{2})}{j!k!(p-j-k)!}\,a^{p-j-k}b^jc^k\langle z_P^{p-j-k/2}\rangle \tag{48}$$

where the prime over the second summation shows that terms for which $k$ is an odd integer vanish identically. The value of $\langle z_P^{p-j-k/2}\rangle$ will depend on the number of atoms in the $P$-group and we shall consider three cases, *viz.* when $P=1$, 2 and many. The values of $\langle z_P^{p-j-k/2}\rangle$ for these three cases are given by (25 *a*, *b*, *c*). Substituting (25 *a*, *b*, *c*) in (48) we obtain [note the prime over the second summation in (49), (50), (51)]

$$\langle z_I^p\rangle=\frac{p!}{\sqrt{\pi}}\sum_{j=0}^{p}\sideset{}{'}\sum_{k=0}^{p-j}\frac{2^{j+3k/2}\Gamma(j+\frac{1}{2}k+\frac{1}{2})}{j!k!(p-j-k)!}\,a^{p-j-k}b^jc^k \quad \text{when } P=1 \tag{49}$$

$$\langle z_I^p\rangle=\frac{p!}{\pi}\sum_{j=0}^{p}\sideset{}{'}\sum_{k=0}^{p-j}\frac{2^{p+k}\Gamma(j+\frac{1}{2}k+\frac{1}{2})\Gamma(p-j-\frac{1}{2}k+\frac{1}{2})}{j!k!(p-j-k)!\Gamma(p-j-\frac{1}{2}k+1)}\times a^{p-j-k}b^jc^k \quad \text{when } P=2 \tag{50}$$

$$\langle z_I^p\rangle=\frac{p!}{\pi}\sum_{j=0}^{p}\sideset{}{'}\sum_{k=0}^{p-j}\frac{2^{p+k}\Gamma(j+\frac{1}{2}k+\frac{1}{2})\Gamma(p-j-\frac{1}{2}k+\frac{1}{2})}{j!k!(p-j-k)!}\times a^{p-j-k}b^jc^k \quad \text{when } P=MC. \tag{51}$$

As in the case of the non-centrosymmetric crystal, these expressions can be evaluated for any given positive integral value of $p$. For the purpose of practical application, we shall give the expressions for $\langle z_I^p\rangle$ for specific values of $p$, *viz.* $p=2$, 3 and 4. The expressions are given below.

*One-atom case*

$$\langle z_I^2\rangle=3[\tfrac{1}{3}a^2+\tfrac{4}{3}c^2+\tfrac{2}{3}ab+b^2] \tag{52a}$$

$$\langle z_I^3\rangle=15[\tfrac{1}{15}a^3+\tfrac{1}{5}a^2b+\tfrac{4}{5}ac^2+\tfrac{12}{5}bc^2+\tfrac{3}{5}ab^2+b^3] \tag{52b}$$

$$\begin{aligned}\langle z_I^4\rangle=105[\tfrac{1}{105}a^4+\tfrac{4}{105}a^3b+\tfrac{8}{35}a^2c^2+\tfrac{16}{35}c^4+\tfrac{48}{35}abc^2\\ +\tfrac{6}{35}a^2b^2+\tfrac{24}{7}b^2c^2+\tfrac{4}{7}ab^3+b^4]\,.\end{aligned} \tag{52c}$$

*Two-atom case*

$$\langle z_I^2\rangle=3[\tfrac{1}{2}a^2+\tfrac{4}{3}c^2+\tfrac{2}{3}ab+b^2] \tag{53a}$$

$$\langle z_I^3\rangle=15[\tfrac{1}{6}a^3+\tfrac{3}{10}a^2b+\tfrac{6}{5}ac^2+\tfrac{12}{5}bc^2+\tfrac{3}{5}ab^2+b^3] \tag{53b}$$

$$\begin{aligned}\langle z_I^4\rangle=105[\tfrac{1}{24}a^4+\tfrac{2}{21}a^3b+\tfrac{4}{7}a^2c^2+\tfrac{24}{35}c^4+\tfrac{72}{35}abc^2\\ +\tfrac{9}{35}a^2b^2+\tfrac{24}{7}b^2c^2+\tfrac{4}{7}ab^3+b^4]\end{aligned} \tag{53c}$$

*Many-atom case*

$$\langle z_I^2\rangle=3[a^2+\tfrac{4}{3}c^2+\tfrac{2}{3}ab+b^2] \tag{54a}$$

$$\langle z_I^3\rangle=15[a^3+\tfrac{3}{5}a^2b+\tfrac{12}{5}ac^2+\tfrac{12}{5}bc^2+\tfrac{3}{5}ab^2+b^3] \tag{54b}$$

$$\begin{aligned}\langle z_I^4\rangle=105[a^4+\tfrac{4}{7}a^3b+\tfrac{24}{7}a^2c^2+\tfrac{48}{35}c^4+\tfrac{144}{35}abc^2\\ +\tfrac{18}{35}a^2b^2+\tfrac{24}{7}b^2c^2+\tfrac{4}{7}ab^3+b^4]\end{aligned} \tag{54c}$$

(*b*) *Non-isomorphous pair*

In this case $z^{(1)}$ and $z^{(2)}$ are independent variables and the expressions for the higher moments of $z_{\pm,NI}=z^{(1)}\pm z^{(2)}$ are again given by expressions (35), (36) and (37).

## 5. Discussion of the theoretical results

It may be noted that the expressions for $\langle z^p_{NI}\rangle$ are identical for centrosymmetric and non-centrosymmetric crystals. However, the actual values of $\langle z^{(1)p}\rangle$ and $\langle z^{(2)p}\rangle$ which are to be substituted in these expressions are determined by the nature of the crystal (*i.e.* by whether it is centrosymmetric or non-centrosymmetric). The values of $\langle z^{(i)p}\rangle (i=1, 2)$ depend on the number ($P$) and the contribution $\sigma_1^{(i)2}$ from the atoms in the $P$-group and the values of $\langle z^{(i)p}\rangle$ for different values of $p$ are available as numerical tables (Parthasarathy & Ramachandran, 1965). The values of $\langle z^{(i)p}\rangle$ obtained from these tables corresponding to the contributions $\sigma_1^{(1)2}$ and $\sigma_1^{(2)2}$ of the atoms in the $P$-groups of the two crystals may be used to obtain the theoretical value of $\langle z^p_{NI}\rangle$.

We have given explicit expressions (see equations (31) to (34) and (52) to (54)] for $\langle z^p_{\pm}\rangle$ ($p=2$, 3 and 4) only for a few cases as a function of the number of atoms in the $P$-group; *viz.* for the cases for which $P=1$, 2 and many. Equations (20) and (43) are, however, quite general and apply to any pair of crystals of any space group symmetry. (Both the crystals of the given pair should, however, belong to the same space group.) In using these expressions for calculating the theoretical values of $\langle z^p_{\pm}\rangle$ for any given pair of experimental crystals belonging to a space group of symmetry other than 1 or $\bar{1}$, 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 by using the tabulated results of Foster & Hargreaves (1963).

Though we have considered only the case of a replacement of one $P$-group of atoms by another of a different scattering power [*i.e.* replacement isomorphism as defined in (1) and (2)], the results of the theory in the earlier sections apply also to a pair of crystals of the type:

Crystal 1 $Q[f_{Qk}, \mathbf{r}^{(1)}_{Qk}]+P[f^{(1)}_P, \mathbf{r}^{(1)}_{Pj}]$
Crystal 2 $Q[f_{Qk}, \mathbf{r}^{(2)}_{Qk}], j=1 \text{ to } P, k=1 \text{ to } Q\,.$ (55)

The situation described in (55) is only a particular case of the general theory and often arises in the structure analysis of proteins. In such cases we have to put $\sigma_1^{(2)2}=0$ and $\sigma_2^{(2)2}=1{\cdot}0$ to obtain the theoretical values for $\langle z^p_{\pm,I}\rangle$ and $\langle z^p_{\pm,NI}\rangle$.

In the early stage of structure analysis using a crystal with heavy atoms, the positions of heavy atoms are first determined. We often require simple tests for knowing whether the assumed positions of the heavy atoms (say determined from the Patterson function) are correct. Such a test is provided by applying the results of the theory. This case corresponds to isomorphism defined by

Crystal 1 $P[f^{(1)}_P, \mathbf{r}^{(1)}_{Pj}]+Q[f_{Qk}, \mathbf{r}^{(1)}_{Nk}]$
Crystal 2 $P[f^{(1)}_P, \mathbf{r}^{(2)}_{Pj}], j=1 \text{ to } P, k=1 \text{ to } Q.$ (56)

The situation described in (56) is only a particular case of the general theory and in this case we have to put $\sigma_1^{(2)2}=1{\cdot}0$ and $\sigma_2^{(2)2}=0$ to obtain the theoretical values of $\langle z^p_{\pm,I}\rangle$ and $\langle z^p_{\pm,NI}\rangle$. A comparison of the experimental values of $\langle z^p_{\pm}\rangle$ with the values of $\langle z^p_{\pm,I}\rangle$ and $\langle z^p_{\pm,NI}\rangle$ would indicate whether the assumed locations of the heavy atoms are correct or not. (In this particular case, the actual distribution function of $y=y^{(1)}-y^{(2)}$ has been worked out by Srinivasan & Ramachandran, 1965.)

Expressions (31) to (34) and (52) to (54) must satisfy the following physical conditions. When there is only one crystal, the expressions for $\langle z^p_{\pm,I}\rangle$ should reduce to the corresponding simple $p$th moment of $z(=|F_N|^2/\sigma_N^2$, the normalized intensity) for that crystal (*i.e.* the Foster & Hargreaves (1963) test values]. That is, the following limit must hold good, *viz.*

$$\text{limit } \sigma_1^{(2)2}\rightarrow 0 \text{ and } \sigma_2^{(2)2}\rightarrow 0\ \langle z^p_I\rangle=\langle z^p\rangle\,. \tag{57}$$

To prove (57) we note that when $\sigma_i^{(2)2}=0$ ($i=1$, 2)

$$\begin{aligned} a_{\pm} &\rightarrow \sigma_1^{(1)2}=\sigma_1^2, \text{ say} \\ b_{\pm} &\rightarrow \sigma_2^{(1)2}=\sigma_2^2, \text{ say} \\ c_{\pm} &\rightarrow \sigma_1^{(1)}\sigma_2^{(1)}=\sigma_1\sigma_2, \text{ say}\,. \end{aligned} \tag{58}$$

Using (58) in the expressions for $\langle z^p_{\pm,I}\rangle$ it has been tested and found that (57) is satisfied.

## 6. Verification of the results of the theory in practical cases

The results of the theory have been tested by using appropriate two-dimensional models. The details of the test are given in Table 1. The crystal pair $A$ consisted of a pair of two-dimensional hypothetical isomorphous structures each having two atoms in the $P$-group, chosen to be such that $\sigma_1^{(1)2}=0{\cdot}6$ and $\sigma_1^{(2)2}=0{\cdot}3$. The crystal pair $B$ was similar to pair $A$ except that $\sigma_1^{(1)2}=0$ and $\sigma_1^{(2)2}=0{\cdot}3$ and the isomorphism of this pair correspond to that described in (55). Crystal pair $C$ consisted of two-dimensional hypothetical isomorphous structures each having 20 atoms in the $P$-group and 20 atoms in the $Q$-group such that $\sigma_1^{(1)2}=0{\cdot}6$ and $\sigma_1^{(2)2}=0{\cdot}3$. Crystal pair $D$ was similar to pair $C$ except that $\sigma_1^{(1)2}=0$ and $\sigma_1^{(2)2}=0{\cdot}3$ and that the isomorphism of this pair correspond to that described in (55). In each case, the values of the normalized intensities of reflexions in each of the crystals of the pair were first determined. The second, third and fourth moments of $z_{\pm}=z^{(1)}\pm z^{(2)}$ were then determined and these represent the 'experimental' value denoted by $E$. The theoretical values of $\langle z^p_{\pm,I}\rangle$ and $\langle z^p_{\pm,NI}\rangle$ ($p=2$, 3 and 4) were calculated by making use of the known values of $\sigma_1^{(i)2}$ ($i=1$, 2) and are listed in the rows marked $I$ and $NI$. A comparison between the 'experimental' and theoretical data for the higher moments shows that the most suitable quantities for the test are the second and fourth moments of $z_-$.

From the general expressions for the $p$th moment of $z_\pm$ it is possible to obtain the expressions for $\langle z^p_\pm\rangle$ for any specific value of $p$. We have however given expressions of $\langle z^p_\pm\rangle$ only for $p=2$, 3 and 4. It is generally not necessary to compute higher moments of $z_\pm$ than the fourth, since experimental errors will unduly affect the test values when $p$ is very large. When $p$ is small, say 2, the theoretical values of $\langle z^2_{\pm,I}\rangle$ and $\langle z^2_{\pm,NI}\rangle$ are not very different so that the second moment test is not very effective. Further the values of the third moment of the difference in the intensities, *i.e.* of $\langle z^3_{-,I}\rangle$ and $\langle z^3_{-,NI}\rangle$ are not widely different, since both positive and negative terms occur in these expressions. It seems therefore that the 4th moment of $z_-$ would provide the most useful test for isomorphism in practical cases.

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Table 1. *Experimental verification of the results of the theory in some non-centrosymmetric isomorphous pairs of hypothetical two-dimensional models*

(*a*) Description of the cases

| Type | Nature of the *P*-atoms | Plane group | Crystal number ($i$) | $P$ | $Q$ | $\sigma_1^{(i)2}$ |
|---|---|---|---|---|---|---|
| *A* | Two-atom case | *pg* | 1 | 2 | 46 | 0·6 |
| | | | 2 | 2 | 46 | 0·3 |
| *B* | Two-atom case | *pg* | 1 | 0 | 46 | 0·0 |
| | | | 2 | 2 | 46 | 0·3 |
| *C* | *MA* case | *pg* | 1 | 20 | 20 | 0·6 |
| | | | 2 | 20 | 20 | 0·3 |
| *D* | *MA* case | *pg* | 1 | 0 | 20 | 0·0 |
| | | | 2 | 20 | 20 | 0·3 |

(*b*) Values of higher moments

| Type | Nature* | $\langle z_+^2\rangle$ | $\langle z_+^3\rangle$ | $\langle z_+^4\rangle$ | $\langle z_-^2\rangle$ | $\langle z_-^3\rangle$ | $\langle z_-^4\rangle$ | Remarks |
|---|---|---|---|---|---|---|---|---|
| *A* | *E* | 7·744 | 41·50 | 278·7 | 0·1141 | −0·0261 | 0·0527 | All moments give isomorphism |
| | *I* | 7·413 | 39·50 | 271·2 | 0·1370 | −0·0548 | 0·1030 | |
| | *NI* | 5·775 | 21·54 | 97·9 | 1·7750 | −0·6210 | 16·1800 | |
| *B* | *E* | 7·229 | 40·58 | 303·2 | 0·5067 | 0·1615 | 1·1422 | |
| | *I* | 7·355 | 40·29 | 293·8 | 0·5550 | 0·2430 | 1·4610 | |
| | *NI* | 5·955 | 23·49 | 117·5 | 1·9550 | 0·3430 | 19·8200 | |
| *C* | *E* | 8·360 | 51·90 | 407·2 | 0·1406 | 0·0205 | 0·0842 | |
| | *I* | 9·438 | 45·82 | 358·0 | 0·3620 | 0·0000 | 0·0107 | |
| | *NI* | 6·000 | 24·00 | 120·0 | 2·0000 | 0·0000 | 24·0000 | |
| *D* | *E* | 7·116 | 35·05 | 212·4 | 0·7942 | −0·1646 | 3·3920 | $\langle z_+^p\rangle$ ambiguous but $\langle z_-^2\rangle$ and $\langle z_-^4\rangle$ confirm isomorphism |
| | *I* | 7·580 | 40·80 | 299·8 | 0·7800 | 0·0000 | 2·1600 | |
| | *NI* | 6·000 | 24·00 | 120·0 | 2·0000 | 0·0000 | 24·0000 | |

* *E* ‘Experimental’ values computed from the distribution of the structure factors actually calculated.
*I* Theoretical values for an isomorphous pair.
*NI* Theoretical values for a non-isomorphous pair.

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