Probability Distribution of the Sum, Difference, Product and the Quotient of Normalized Bijvoet Differences from a Pair of Non-Centrosymmetric Crystals*

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The statistical distributions of the sum, difference, product and the quotient of the normalized Bijvoet differences from a pair of crystals are worked out for two cases, namely when the pair of crystals is isomorphous and when they are non-isomorphous. The distribution of these variables depends on the number of anomalous scatterers in the unit cell and four cases are considered, namely when the number is small (1 or 2) or large and in the latter case with either a centrosymmetric or non-centrosymmetric configuration. The moments of these variables in the various cases are also obtained. The theoretical distributions of these variables are given in the form of curves. The use of the results for testing the isomorphism of a pair of non-centrosymmetric crystals with anomalous scatterers is also discussed. The theoretical distributions have also been verified using suitable two-dimensional models. The results show that the difference and the quotient variables are likely to be useful for testing isomorphism in practice.

1. Introduction

The anomalous dispersion effect has the possibility of wide applications in X-ray crystal structure analysis; for example, for the determination of (1) the space group (Ramachandran & Parthasarathy, 1963); (2) the absolute configuration (Bijvoet, Peerdeman & van Bommel, 1951); and (3) the crystal structure (Ramachandran & Raman, 1956; Peerdeman & Bijvoet, 1956; Okaya & Pepinsky, 1961). In this paper we shall consider one more possible use of the anomalous dispersion effect, namely, in testing for isomorphism of a pair of non-centrosymmetric crystals using the values of the Bijvoet differences $|\Delta I|$ measured from them.

The method adopted in this paper is based on a very simple principle, namely, that intensities of X-ray reflexions are structure sensitive quantities and hence the intensity data from a pair of crystals must contain information about the isomorphism of the pair of crystals. Though a few tests for isomorphism from a pair of crystals are available (Bernal, Carlisle & Rosemeyer, 1959; Carlisle & Palmer, 1962; Ramachandran & Parthasarathy, 1963; Srinivasan, Sarma & Ramachandran, 1963; Srinivasan, Subramanian & Ramachandran, 1964; Srinivasan & Ramachandran, 1965; Parthasarathy & Ramachandran, 1966) yet they involve the use of intensity data under normal dispersion. The test proposed in this paper particularly suits a pair of non-centrosymmetric crystals when there is anomalous scattering of X-rays. Such a test is interesting, particularly because of the fact that a unique determination of the phase in a non-centrosymmetric crystal is possible by combining the isomorphous and anomalous dispersion data (see Ramachandran & Raman, 1956; North, 1965).

In this paper we shall closely follow the notation used in earlier papers from this department (see Parthasarathy & Srinivasan, 1964; Parthasarathy & Ramachandran, 1966; and these two papers will be hereafter denoted PS and PR respectively). It may be noted here that the isomorphism dealt with in this paper is of the substitutional type, *i.e.* one group of anomalous scatterers is replaced by another group (see equations (1) and (2) of PR). It is assumed that the anomalous scatterers in each crystal are of the same type and that the normal scatterers in the two crystals are all of nearly the same scattering power. (The designations for the various cases determined by the number of P-atoms in the unit cell are the same as those given in PR.)

2. Derivation of the density functions and expectation values of x_s, x_d, x_p, and x_q

2.1 *Principle of the method*

Consider a pair of non-centrosymmetric crystals (designated by superscripts 1 and 2) each of which contains P anomalous scatterers and Q normal scatterers in the unit cell of each crystal ($N=P+Q$). Let $f_p^{(1)}$ and $f_p^{(2)}$ be the atomic scattering factors of the anomalous scatterers in the two crystals and f_Q be that for the normal scatterers in either crystal. Let $x^{(1)}$ and $x^{(2)}$ be the normalized Bijvoet difference (see PS for definition of x) of a reflexion **H** in the two crystals. We have from PS that

$$x^{(i)} = y_p^{(i)} y_Q^{(i)} |\sin \psi^{(i)}|, \quad i=1,2 \qquad (1)$$

where

$$y_P = |F_p''|/\sigma_p'', \quad y_Q = |F_Q|/\sigma_Q, \qquad (2)$$
$$\psi^{(i)} = \alpha_Q^{(i)} - \alpha_p'^{(i)}.$$

We shall define the sum, difference, product and the quotient of the normalized Bijvoet differences from the two crystals by

$$x_s = x^{(1)} + x^{(2)} \qquad (3a)$$

$$x_d = x^{(1)} - x^{(2)} \qquad (3b)$$

$$x_p = x^{(1)} \cdot x^{(2)} \qquad (3c)$$

$$x_q = x^{(1)}/x^{(2)} . \qquad (3d)$$

The probability density functions (abbreviated as PDF) of these variables will depend on whether the crystal pair is isomorphous (denoted by I) or non-isomorphous (NI) (see PR). Thus the probability distributions of these variables and their expectation values would be useful in testing for the isomorphism of the pair. We shall now work out the density functions of x_s, x_d, x_p and x_q.

2.2 Density functions of x_s, x_d, x_p and x_q

(a) Isomorphous pair

From equations (4a) and (10) of PR it is clear that for an I pair

$$y_p^{(1)} = y_p^{(2)} = y_P, \text{ say} \qquad (4a)$$

$$y_Q^{(1)} = y_Q^{(2)} = y_Q, \text{ say} \qquad (4b)$$

$$\psi^{(1)} = \psi^{(2)} = \psi, \text{ say} \qquad (4c)$$

so that

$$x^{(1)} = x^{(2)} = y_P y_Q |\sin \psi| = X, \text{ say} . \qquad (5)$$

From (3) and (5) we obtain

$$x_s = 2X, \ x_d = 0, \ x_p = X^2, \ x_q = 1 . \qquad (6)$$

The PDF of X will be the same as that for the normalized Bijvoet difference x (see PS). Denoting this by $P_x(X)$ we have

$$P_x(X) =$$
$$\begin{cases}
(2/\sqrt{\pi}) \exp{(-X^2)} & \text{for } P = 1 \\
(\sqrt{2}/\pi^{3/2}) \exp{(-X^2/4)} K_0(X^2/4) & \text{for } P = 2 \quad (7) \\
(2^{3/2}/\pi) K_0(\sqrt{2}X) & \text{for } P = MC \\
2 \exp{(-2X)} & \text{for } P = MA .
\end{cases}$$

From (6) and (7), the PDF's of x_s, x_d, x_p and x_q can be easily obtained by the usual method. We therefore have

$$P(x_s) =$$
$$\begin{cases}
(1/\sqrt{\pi}) \exp{(-x_s^2/4)} & \text{for } P = 1 \\
(2\pi^3)^{-1/2} \exp{(-x_s^2/16)} K_0(x_s^2/16) & \text{for } P = 2 \quad (8) \\
(\sqrt{2}/\pi) K_0(x_s/\sqrt{2}) & \text{for } P = MC \\
\exp{(-x_s)} & \text{for } P = MA
\end{cases}$$

$$P(x_d) = \delta(x_d) \text{ for all } P , \qquad (9)$$

where $\delta(x)$ is the Dirac delta function.

$$P(x_p) =$$
$$\begin{cases}
(\pi x_p)^{-1/2} \exp{(-x_p)} & \text{for } P = 1 \\
(2\pi^3 x_p)^{-1/2} \exp{(-x_p/4)} K_0(x_p/4) & \text{for } P = 2 \quad (10) \\
(\sqrt{2}/\pi \sqrt{x_p}) K_0(\sqrt{2x_p}) & \text{for } P = MC \\
x_p^{-1/2} \exp{(-2\sqrt{x_p})} & \text{for } P = MA
\end{cases}$$

$$P(x_q) = \delta(x_q - 1) \text{ for all } P . \qquad (11)$$

(b) Non-isomorphous pair

In this case $x^{(1)}$ and $x^{(2)}$ will be independent random variables (see PR for the physical arguments) and we shall use the principle of variable transformation (Wadsworth & Bryan, 1960) to obtain the PDF's of x_s, x_d, x_p and x_q.

Since both $x^{(1)}$ and $x^{(2)}$ have the same distribution as the normalized Bijvoet difference x, the PDF's of $x^{(i)}$ will be given by (see PS):

$$P_i(x^{(i)}) =$$
$$\begin{cases}
(2/\sqrt{\pi}) \exp{[-x^{(i)2}]} & \text{for } P = 1 \quad (12a) \\
(2/\pi^3)^{1/2} \exp{[-x^{(i)2}/4]} K_0[x^{(i)2}/4] & \text{for } P = 2 \quad (12b) \\
(2^{3/2}/\pi) K_0[\sqrt{2}x^{(i)}] & \text{for } P = MC \quad (12c) \\
2 \exp{[-x^{(i)}]} & \text{for } P = MA \quad (12d)
\end{cases}$$
$$0 \leq x^{(i)} < \infty, \ i = 1, 2 .$$

(i) Sum and difference variables

From the principle of variable transformation (see Wadsworth & Bryan, 1960) we obtain the joint PDF of x_s and x_d as

$$P(x_s, x_d) = \begin{cases}
\frac{1}{2} P_1 \left[\frac{x_s + x_d}{2} \right] P_2 \left[\frac{x_s - x_d}{2} \right] & \text{in the area } A_1 \\
& \text{of the } (x_s, x_d) \text{ plane}, \\
0 & \text{elsewhere}, \quad (13)
\end{cases}$$

where A_1 is the shaded area in Fig. 2. Making use of the property that $x^{(1)}$ and $x^{(2)}$ have identical density functions and also denoting $|x_d|$ by x_d itself for simplicity of writing we obtain from (13) that

$$P(x_s, x_d) = \begin{cases}
P_1 \left(\frac{x_s + x_d}{2} \right) P_2 \left(\frac{x_s - x_d}{2} \right) & \text{in } A_1', \\
0 & \text{elsewhere}, \quad (14)
\end{cases}$$

where A' is the wedge-shaped area in the first quadrant of the (x_s, x_d) plane (cross-hatched area in Fig. 1). The region A_1' can be defined either by

$$0 \leq x_s \leq x_d, \ 0 \leq x_s < \infty \qquad (15a)$$

or by

$$x_d \leq x_s < \infty, \ 0 \leq x_d < \infty . \qquad (15b)$$

From (14)–(15b) we obtain

$$P(x_s) = \int_0^{x_s} P(x_s, x_d) dx_d \qquad (16)$$

$$P(x_d) = \int_{x_d}^{\infty} P(x_s, x_d) dx_s . \qquad (17)$$

From (12) and (14) we obtain

$$P(x_s, x_d) =$$
$$\begin{cases}
(4/\pi) \exp{[-(x_s^2 + x_d^2)/2]} & \text{for } P = 1 \quad (18a) \\
(2/\pi^3) \exp{[-(x_s^2 + x_d^2)/8]} K_0 \left[\frac{(x_s + x_d)^2}{16} \right] \\
\quad \times K_0 \left[\frac{(x_s - x_d)^2}{16} \right] & \text{for } P = 2 \quad (18b) \\
(8/\pi^2) K_0[(x_s + x_d)/\sqrt{2}] K_0[(x_s - x_d)/\sqrt{2}] & \text{for } P = MC \\
& \quad (18c) \\
4 \exp{(-2x_s)} & \text{for } P = MA . \quad (18d)
\end{cases}$$

From (16)–(18) we obtain the PDF of x_s (see Appendix A) and that of x_d (see Appendix B) as

$P(x_s) =$

$$\begin{cases} (2^{3/2}/\sqrt{\pi}) \exp(-x_s^2/2) \operatorname{erf}(x_s/\sqrt{2}) \text{ for } P=1 & (19a) \\[2mm] (2/\pi^3)x_s \exp(-x_s^2/8)\int_0^1 \exp\left[-\frac{x_s^2 y^2}{8}\right] \\[2mm] \qquad \times K_0\left[\frac{x_s^2(1+y)^2}{16}\right] K_0\left[\frac{x_s^2(1-y)^2}{16}\right] dy \text{ for } P=2 \\[2mm] \hfill (19b) \\[2mm] (8/\pi^2)x_s\int_0^1 K_0[x_s(1+y)/\sqrt{2}]K_0[x_s(1-y)/\sqrt{2}]dy \\[1mm] \hfill \text{for } P=MC \quad (19c) \\[2mm] 4x_s \exp(-2x_s) \text{ for } P=MA & (19d) \end{cases}$$

$P(x_d) =$

$$\begin{cases} (2^{3/2}/\sqrt{\pi}) \exp(-x_d^2/2) \operatorname{erfc}(x_d/\sqrt{2}) \text{ for } P=1 & (20a) \\[2mm] (4/\pi^3) \exp(-x_d^2/8)\int_0^\infty \exp\left[-\frac{(2y+x_d)^2}{8}\right] K_0(y^2/4) \\[2mm] \qquad \times K_0\left[\frac{(y+x_d)^2}{4}\right] dy \text{ for } P=2 \quad (20b) \\[2mm] \frac{16}{\pi^2}\int_0^\infty K_0(\sqrt{2}y)K_0[\sqrt{2}(y+x_d)]dy \text{ for } P=MC \\[1mm] \hfill (20c) \\[2mm] 2\exp(-2x_d) \text{ for } P=MA , & (20d) \end{cases}$$

where the values of the integrals in (19b, c) and (20b, c) are to be obtained by numerical or graphical methods.

(ii) Product and quotient variables

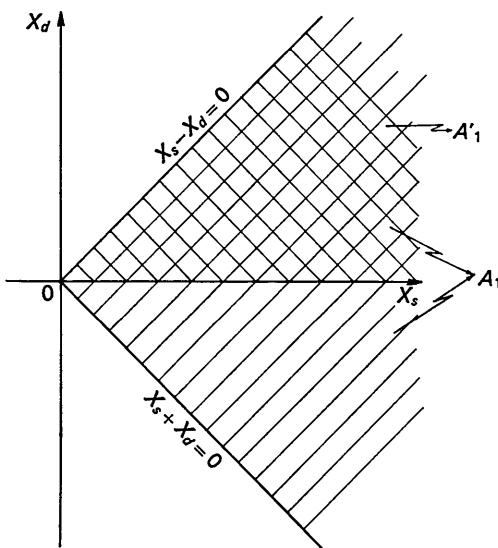From the principle of variable transformation we obtain the joint PDF of x_p and x_q as

Fig. 1. Diagram showing the domain in which the joint density function $P(x_s, x_d)$ is non-zero.

$$P(x_p, x_q) = \begin{cases} (2x_q)^{-1}P_1(\sqrt{x_p x_q})P_2(\sqrt{x_p/x_q}) \text{ in the area} \\ \hfill A_2 \text{ of the } (x_p, x_q) \text{ plane} \\ 0 \text{ elsewhere}, \hfill (21) \end{cases}$$

where A_2 is the shaded area in Fig. 2 between the lines $x_p=0$ and $x_q=0$, namely, $0 \le x_p, x_q < \infty$. The PDF's of x_p and x_q will therefore be given by

$$P(x_p) = \int_0^\infty P(x_p, x_q)dx_q \qquad (22)$$

$$P(x_q) = \int_0^\infty P(x_p, x_q)dx_p . \qquad (23)$$

From (12) and (21) we obtain

$P(x_p, x_q) =$

$$\begin{cases} (2/\pi x_q) \exp[-x_p x_q - (x_p/x_q)] \text{ for } P=1 & (24a) \\[2mm] \frac{1}{\pi^3 x_q} \exp\left[-\frac{1}{4}\left(\frac{x_p}{x_q} + x_p x_q\right)\right] \\[2mm] \qquad \times K_0(x_p x_q/4)K_0\left(\frac{x_p}{4x_q}\right) \text{ for } P=2 \quad (24b) \\[2mm] (4/\pi^2 x_q)K_0(\sqrt{2x_p x_q})K_0(\sqrt{2x_p/x_q}) \text{ for } P=MC \\[1mm] \hfill (24c) \\[2mm] (2/x_q) \exp[-\sqrt{x_p x_q} - \sqrt{x_p/x_q}] \text{ for } P=MA . \\[1mm] \hfill (24d) \end{cases}$$

From (22)–(24) we obtain the PDF of x_p (see Appendix C) and that of x_q (see Appendix D) as

$P(x_p) =$

$$\begin{cases} (4/\pi)K_0(2x_p) \text{ for } P=1 & (25a) \\[2mm] \frac{1}{\pi^3}\int_0^\infty \exp[-(y+x_p^2/16y)]K_0(y)K_0(x_p^2/16y)dy/y \\[1mm] \hfill \text{for } P=2 \quad (25b) \\[2mm] \frac{8}{\pi^2}\int_0^\infty K_0(y)K_0(2x_p/y)dy/y \text{ for } P=MC & (25c) \\[2mm] 8K_0(4\sqrt{x_p}) \text{ for } P=MA . & (25d) \end{cases}$$
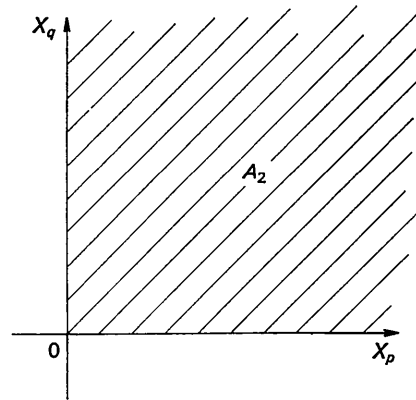

Fig. 2. Diagram showing the domain in which the joint density function $P(x_p, x_q)$ is non-zero.

$P(x_q) =$

$$\frac{2}{[\pi(x_q^2+1)]} \text{ for } P=1 \qquad (26a)$$

$$\frac{1}{\pi^3 x_q} \int_0^\infty \exp\left[-\frac{x_p}{4}(x_q+x_q^{-1})\right]$$

$$\times K_0\left(\frac{x_p x_q}{4}\right) K_0\left(\frac{x_p}{4x_q}\right) dx_p \text{ for } P=2 \quad (26b)$$

$$\frac{4}{\pi^2 x_q} \int_0^\infty K_0(\sqrt{2x_p x_q}) K_0(\sqrt{2x_p/x_q}) dx_p$$
$$\text{for } P=MC \quad (26c)$$

$$(x_q+1)^{-2} \text{ for } P=MA, \qquad (26d)$$

where the integrals in (25b,c) and (26b,c) are to be evaluated by a numerical or graphical method.
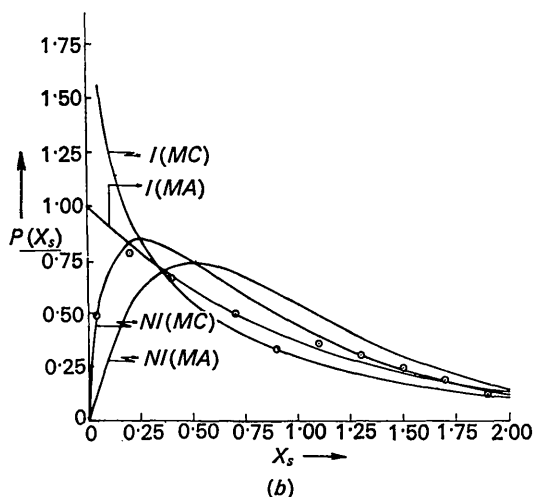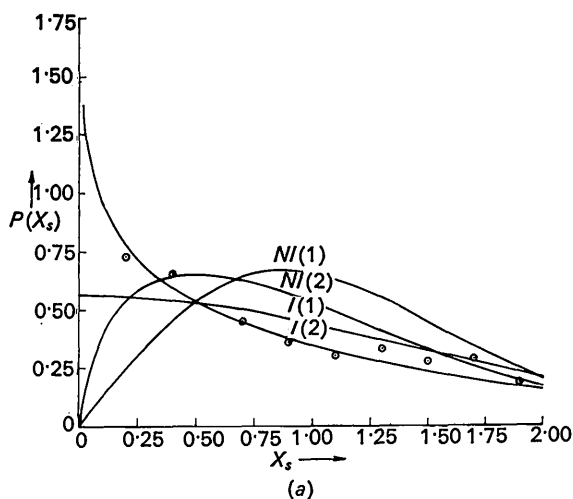

(a)

(b)

Fig. 3. Density function of x_s [$=x^{(1)}+x^{(2)}$] for a pair of crystals: (a) for the cases $P=1$ and 2; and (b) for the cases $P=MA$ and MC. The symbols I and NI refer to the isomorphous and non-isomorphous pairs respectively. The number in parentheses near each curve refers to the number of atoms in the P-group.

2.3 Expectation values of x_s, x_d, x_p and x_q

(a) Isomorphous pair

Let us denote the expectation value of the normalized Bijvoet difference x by $\langle x \rangle$ (see PS for the values of $\langle x \rangle$ in the various cases). Since

$$\langle x_s \rangle = \langle x^{(1)} + x^{(2)} \rangle$$
$$= \langle x^{(1)} \rangle + \langle x^{(2)} \rangle = 2\langle x \rangle \qquad (27)$$

it is clear from PS that $\langle x_s \rangle = 2/\sqrt{\pi}$, $2(2/\pi)^{3/2}$, $2\sqrt{2/\pi}$ and 1 for $P=1,2$, MC and MA respectively. From (9) we obtain $\langle x_d \rangle = 0$. From (5) and (6) we obtain

$$\langle x_p \rangle = \langle X^2 \rangle = \langle y_P^2 \, y_Q^2 \sin^2\psi \rangle$$
$$= \langle y_P^2 \rangle \langle y_Q^2 \rangle \langle \sin^2\psi \rangle$$
$$= \tfrac{1}{2} \text{ for all } P,$$

where we have used the known results that $\langle y_P^2 \rangle = \langle y_Q^2 \rangle = 1$ and that ψ is uniformly distributed in $-\pi < \psi \leq \pi$. From (11) we obtain $\langle x_q \rangle = 1$.

(b) Non-isomorphous pair

It is evident that the value of $\langle x_s \rangle$ (for a given P) will be the same for the I and NI pairs. It can be easily shown that $\langle x_d \rangle = 0.4674$, 0.511, 0.5065 and 0.5 for $P=1,2$, MC and MA respectively (see Appendix B). It is clear that

$$\langle x_p \rangle = \langle x^{(1)} \cdot x^{(2)} \rangle = \langle x^{(1)} \rangle \cdot \langle x^{(2)} \rangle = \langle x \rangle^2,$$

so that $\langle x_p \rangle = 1/\pi$, $(2/\pi)^3$, $2/\pi^2$ and $\frac{1}{4}$ for $P=1,2$, MC and MA respectively. For the quotient variable it can be shown that $\langle x_q \rangle = \infty$ (for any P) and this follows from the fact that the distribution of x_q corresponds to the distribution of the quotient of two quantities chosen independently from a given population obeying a specific distribution in the range 0 to ∞. For example (26a) is the well-known Cauchy distribution for which the expectation value is known to be undefined (Munroe, 1951, p.99).

3. Discussion of the results

The PDF's of x_i obtained in § 2 are in the normalized form, since the PDF's of $x^{(1)}$ and $x^{(2)}$ used to obtain them were themselves in the normalized form. The PDF's of x_s, x_d, x_p and x_q for the various cases, depending on the number of anomalous scatterers in the unit cell, are represented in Figs. 3 to 6.

The density functions of x_i, $i=s,d,p,q$ can be used for testing for isomorphism of a pair of non-centrosymmetric crystals containing a group of replaceable atoms which can be excited to scatter X-rays of some suitable wavelengths. The best test function would be the one for which the distinction between $P_I(x_i)$ and $P_{NI}(x_i)$ is marked for a fixed value of the number (P) of anomalous scatterers in the unit cell. A study of Figs. 3 to 6 yields the following conclusions.

(i) The function $P(x_s)$

The function $P_I(x_s)$ has a singularity at the origin for the cases $P=2$ and MC while for the cases $P=1$ and MA, it has a finite maximum at the origin. The value of $P_I(x_s)$ in all these cases decreases monotonically with increasing value of x_s. On the other hand the values for $P_{NI}(x_s)$ in all the cases start at the origin, increase to a maximum (which lies at $x=0.88$, 0.52, $0.5, 0.25$ for the cases $P=1,2$, MA and MC respectively) and then decrease thereafter.

(ii) The function $P(x_d)$

The function $P_I(x_d)$ is a delta function at the origin for all cases. However, the functions $P_{NI}(x_d)$ all start from a maximum value of x_d. The distinction between the $P_I(x_d)$ and $P_{NI}(x_d)$ curves for a given number of atoms in the P-group is very marked and much better than that displayed by the $P(x_s)$ functions.

(iii) The function $P(x_p)$

Both the functions $P_I(x_p)$ and $P_{NI}(x_p)$ in all cases have a singularity at the origin and decrease monotonically with increasing value of x_p. The distinction between the curves representing $P_I(x_p)$ and $P_{NI}(x_p)$, for a given number of atoms in the P-group, is much poorer than the distinction obtained with either of the functions $P(x_s)$ or $P(x_d)$.

(iv) The function $P(x_q)$

The function $P_I(x_q)$ for all the cases is a delta function at $x_q=1$ while the values for the functions $P_{NI}(x_q)$ start with a maximum at the origin and decrease mono-

tonically with increasing value of x_q. Thus the distinction between the curves $P_I(x_q)$ and $P_{NI}(x_q)$ for a given number of atoms in the P-groups is quite marked.

The above study regarding the nature of the curves of the density functions shows that the functions $P(x_d)$ and $P(x_q)$ are distinctly better than the functions $P(x_s)$ and $P(x_p)$ for the purpose of testing the isomorphism of a pair of non-centrosymmetric crystals. A study of the expectation values (see § 2.3) also shows that x_q and x_d are more useful than the variables x_p and x_s for this purpose.

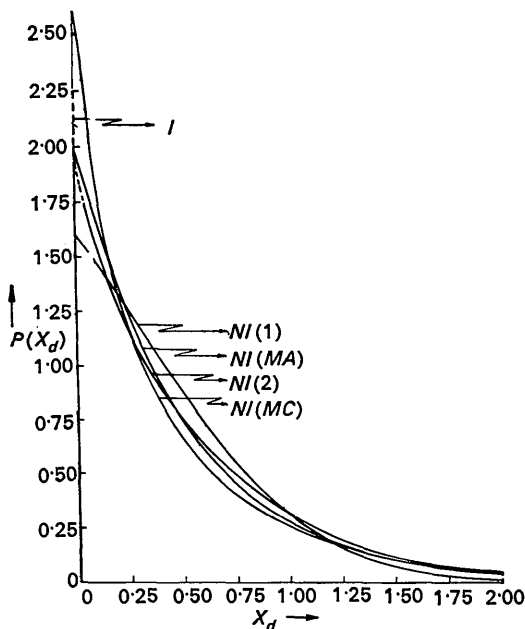There are two advantages in using the normalized Bijvoet difference x. First, when dealing with a series

(a)

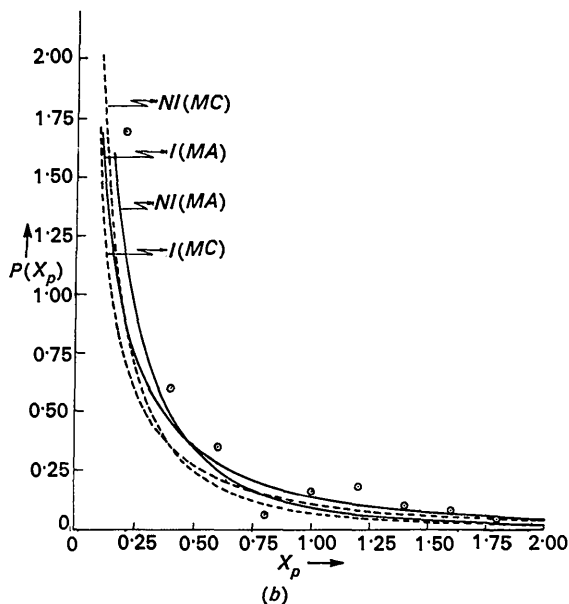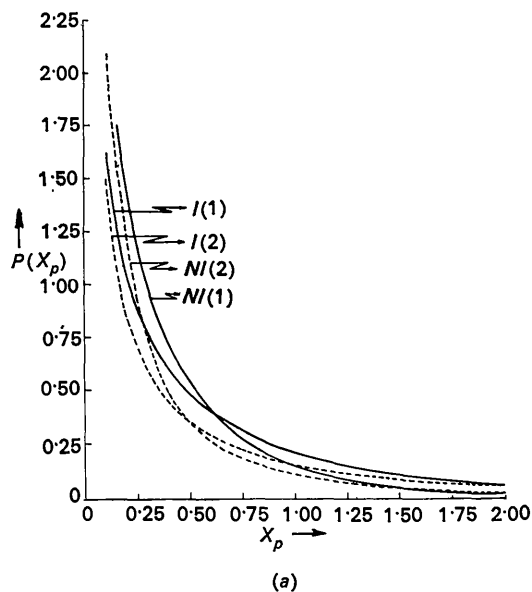Fig. 4. Density function of x_d ($=|x^{(1)}-x^{(2)}|$) for a pair of crystals.

(b)

Fig. 5. Density function of x_p [$=x^{(1)}.x^{(2)}$] for a pair of crystals (a) and (b).

of n isomorphous crystals we can generalize equation (5), thus

$$x^{(1)}(\mathbf{H}) = x^{(2)}(\mathbf{H}) = \ldots = x^{(i)}(\mathbf{H}) = \ldots = x^{(n)}(\mathbf{H}) \,, (27)$$

where $\mathbf{H}$ relates to the same reflexion (hkl) from each crystal. The independence of the values of x_d and x_q with regard to the reflexion index $\mathbf{H}$ the number (P) and contribution (σ_1^2) from the atoms in the P-group for a pair of isomorphous crystals is a direct consequence of the normalization. Secondly, it may be noted that (27) holds even when X-rays of different wavelengths are used for measuring the Bijvoet differences in the different crystals. So, instead of trying to find a single wavelength capable of exciting all the anomalous scatterers in the series, we are at liberty to use a different wavelength for each member, chosen suitable for its efficiency in exciting the relevant P-atoms.

4. Test of the theoretical results

The theoretical results were tested by means of data from a pair of non-centrosymmetric isomorphous
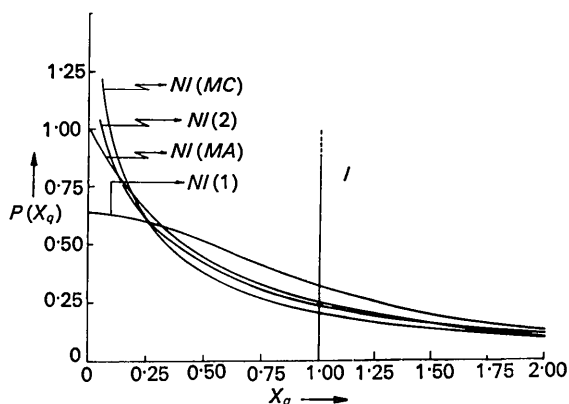

Fig. 6. Density function of x_q [$= x^{(1)}/x^{(2)}$] for a pair of crystals.

crystals. The details regarding the crystals are given in Table 1.

A parameter p which is a measure of the degree of isomorphism is the mean value of the deviations in the atomic coordinates and is defined by

$$p = \frac{1}{n} \sum_{i=1}^{n} \sqrt{(\Delta x)_i^2 + (\Delta y)_i^2},$$

where n is the number of atoms in the asymmetric unit and $(\Delta x)_i$ and $(\Delta y)_i$ are the deviations in the x and y coordinates of atom i in the crystal pair. The values of p for the various crystal pairs were calculated with the use of the known atomic coordinates and the mean values of the cell dimensions of the two crystals constituting the crystal pair. These values of p for the various crystal pairs are also given in Table 1. For the perfectly isomorphous pairs, namely cases 1 and 2 in Table 1, p has zero value. However, for the pairs 3, 4 and 5 in Table 1 the values of p are practically the same showing thereby that they are isomorphous to the same degree. The value of p for pair 6 is slightly higher than that for the pairs 3, 4 and 5 so that the degree of isomorphism is slightly poor.

In order to test the theoretical results under ideal conditions, the calculated Bijvoet differences for the hypothetical models where there is perfect isomorphism, namely cases 1 and 2 in Table 1, were first used to obtain the 'experimental' density functions of all the four variables (the dots in Figs. 3–6). A comparison of the theoretical and experimental distribution curves (see Figs. 3 to 6) of the variables x_i and also a study of their moments given in Table 1 clearly confirms that the distribution of x_d is a delta function at $x_d = 0$ and of x_q is a delta function at $x_q = 1$; and that the variables x_d and x_q could be used for testing the isomorphism (substitution type) of a pair of non-centrosymmetric crystals containing suitable anomalous scatterers.

Table 1. *Details of the crystal structures chosen for the verification of the theory*

No.	Name of the crystal pair	P	Q	Plane group	p		$\langle x_d \rangle$	$\langle x_p \rangle$	$\langle x_q \rangle$
1.	Hypothetical model	20	20	pg	0·0000 Å	E^*	0·000	0·526	1·0
						I	0·000	0·500	1·0
						NI	0·500	0·250	∞
2.	Hypothetical model	2	46	pg	0·0000	E	0·000	0·616	1·0
						I	0·000	0·500	1·0
						NI	0·511	0·258	∞
3.	L-Tyrosine hydrohalides, (001) projection	2	26	pg	0·0784	E	0·201	0·619	0·970
						I	0·000	0·500	1·000
						NI	0·511	0·258	∞
4.	L-Arginine hydrohalides, (001) projection	4	52	pg	0·755	E	0·220	0·331	2·427
						I	0·000	0·500	1·000
						NI	0·511	0·258	∞
5.	L-Arginine hydrohalides, (100) projection	4	52	pg	0·0781	E	0·194	0·294	2·253
						I	0·000	0·500	1·000
						NI	0·511	0·258	∞
6.	Glucosamine hydrohalides, (100) projection	2	24	pg	0·0882	E	0·264	0·775	1·640
						I	0·000	0·500	1·000
						NI	0·511	0·258	∞

* E = experimental value, I = theoretical value for a pair of isomorphous crystals and NI = theoretical value for a pair of non-isomorphous crystals.

To test the usefulness of the probability distributions of x_d and x_q in practical cases, they were tried on actual crystal pairs (see Table 1 for details of these structures) such as the hydrohalides of L-tyrosine (Srinivasan, 1959a,b), L-arginine* (Mazumdar, 1964) and glucosamine (Chandrasekharan, 1966). The calculated Bijvoet differences for these crystal pairs were used to obtain the cumulative function $N(x_d)$ of x_d (Fig. 7) and the PDF of x_q (Fig. 8). The cumulative function of x_q was not used for these cases, since it may not yield useful results in such practical cases (where the pair of crystals slightly differ in their cell dimensions). This is because the theoretical curves for the I and NI cases start at $x_q=0$ and cross over each other at $x_q=1$. It is seen from Fig. 7 that the degree of isomorphism for the pairs 3, 4 and 5 is practically the same as required by the value of p and that for pair 6 it is slightly poorer. The PDF of x_q (Fig. 8) also shows a prominent peak at $x_q=1$, showing that all the pairs are isomorphous. However, owing to the inherent fluctuations in the PDF, the PDF of x_q seems to be less useful than the cumulative function of x_d.

It is seen from Table 1 that, of the three quantities $\langle x_d \rangle$, $\langle x_p \rangle$ and $\langle x_q \rangle$, the mean value of x_q offers the best result in practice. This is to be expected since, in the presence of discrepancies such as the small differences in the cell dimensions, the delta function for x_q spreads on both sides of $x_q=1$ whereas the delta function for x_d at $x_d=0$ spreads asymmetrically.

The tests carried out with the hypothetical and actual crystal pairs thus show that the cumulative function of x_d and the mean value of x_q could be profitably used for testing the isomorphism of a pair of non-centrosymmetric crystals containing anomalous scatterers.

APPENDIX A
Calculations of $P_{NI}(x_s)$

From (16) and (18a) we obtain for the case $P=1$ that

$$P(x_s) = \frac{4}{\pi}\exp\left(-x_s^2/2\right)\int_0^{x_s}\exp\left(-x_d^2/2\right)dx_d$$

$$= \frac{2\sqrt{2}}{\sqrt{\pi}}\exp\left(-x_s^2/2\right)\operatorname{erf}\left(x_s/\sqrt{2}\right). \quad (A\text{-}1)$$

From (16) and (18b) we obtain for the case $P=2$ that

$$P(x_s) = \frac{2}{\pi^3}\int_0^{x_s}\exp\left[-(x_s^2+x_d^2)/8\right]K_0[(x_s+x_d)^2/16]$$
$$\times K_0[(x_s-x_d)^2/16]dx_d. \quad (A\text{-}2)$$

It seems difficult to integrate $(A\text{-}2)$ by an analytical method. To make it suitable for numerical integration, we make the substitution $x_d=x_s y$ to obtain

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* Though $P=4$ for L-arginine hydrohalides, we shall use the theoretical distributions corresponding to the case $P=2$. This will not affect our results since the PDF's for the cases $P=2$ and MA are not very different (see Figs. 4 and 6 and Table 1 for the moments of the variables x_i).

$$P(x_s) = \frac{2x_s}{\pi^3}\exp\left(-x_s^2/8\right)\int_0^1\exp\left(-x_s^2 y^2/8\right)$$
$$\times K_0[x_s^2(1+y)^2/16]K_0[x_s^2(1-y)^2/16]dy, \quad (A\text{-}3)$$

which can be evaluated by a numerical method.

From (16) and (18c) we obtain for the case $P=MC$, that

$$P(x_s) = \frac{8x_s}{\pi^2}\int_0^1 K_0[x_s(1+y)/\sqrt{2}]K_0[x_s(1-y)/\sqrt{2}]dy, \quad (A\text{-}4)$$

where we have made the substitution $x_d=x_s y$. The integral in $(A\text{-}4)$ is to be evaluated by a numerical method. From (16) and (18d) we obtain for the case $P=MA$ that

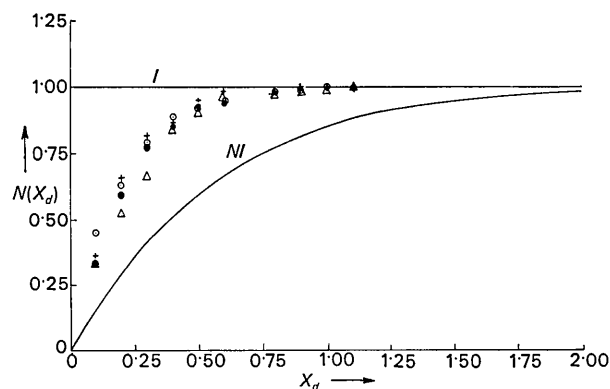$$P(x_s)=4x_s\exp\left(-2x_s\right). \quad (A\text{-}5)$$

Fig. 7. Experimental verification of the cumulative function of x_d. The solid line represents the theoretical curve for the case with $P=2$. The experimental points are shown as follows:
△ Glucosamine hydrohalides, (100) projection;
● L-Arginine hydrohalides, (001) projection;
+ L-Arginine hydrohalides, (100) projection;
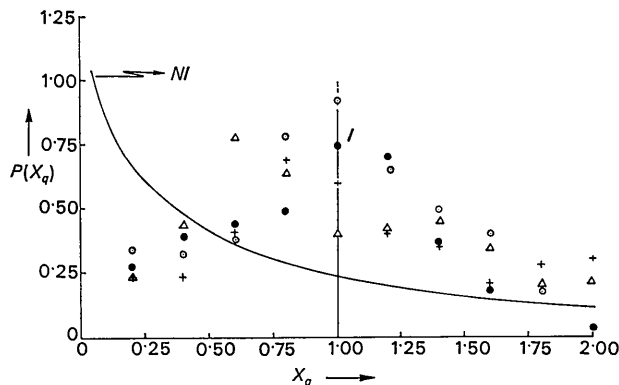○ L-tyrosine hydrohalides, (001) projection.

Fig. 8. Experimental verification of the density function of x_q. The solid line represents the theoretical curve for the case with $P=2$. The experimental points are shown as in Fig. 7.

APPENDIX B
Calculation of $P_{NI}(x_d)$ and $\langle x_d \rangle_{NI}$

From (17) and (18a) we obtain for the case $P=1$ that

$$P(x_d) = \frac{2\sqrt{2}}{\sqrt{\pi}} \exp\left(-x_d^2/2\right) \mathrm{erfc}\left(x_d/\sqrt{2}\right), \quad (B\text{-}1)$$

where

$$\mathrm{erfc}\,(x) = 1 - \mathrm{erf}\,(x).$$

From (B-1) we obtain

$$\langle x_d \rangle = \frac{2\sqrt{2}}{\sqrt{\pi}} \int_0^\infty x_d \exp\left(-x_d^2/2\right) \mathrm{erfc}\left(x_d/\sqrt{2}\right) dx_d. \quad (B\text{-}2)$$

Making use of the known result that $\mathrm{erfc}\,(x) = \pi^{-1/2}\Gamma(\frac{1}{2}, x^2)$ and the substitution $y = x_d^2/2$ in (B-2) we obtain

$$\langle x_d \rangle = \frac{2\sqrt{2}}{\pi} \int_0^\infty \Gamma(\tfrac{1}{2}, y) \exp\left(-y\right) dy$$

$$= \frac{\sqrt{\pi}}{2} \,_2F_1(1, \tfrac{3}{2}; 2; \tfrac{1}{2})$$

$$= \frac{2}{\sqrt{\pi}} (\sqrt{2} - 1) \simeq 0\cdot4674 \quad (B\text{-}3)$$

where we have used equation (16) in p.309, Vol. II of Erdelyi (1954) and equation (10) in p.70 of Rainville (1960). From (17) and (18b) we obtain for case $P=2$ that

$$P(x_d) = \frac{4}{\pi^3} \exp\left(-x_d^2/8\right) \int_0^\infty \exp\left[-(2y + x_d)^2/8\right]$$

$$\times K_0(y^2/4) K_0[(y + x_d)^2/4] dy, \quad (B\text{-}4)$$

where we have used the substitution $x_s - x_d = 2y$. Equation (B-4) is to be evaluated by a numerical method. From (17) and (18c) we obtain for the case $P = MC$ that

$$P(x_d) = \frac{16}{\pi^2} \int_0^\infty K_0(\sqrt{2}y) K_0[\sqrt{2}(y + x_d)] dy, \quad (B\text{-}5)$$

where we have used the substitution $x_s - x_d = 2y$. Equation (B-5) is to be evaluated by a numerical method. From (17) and (18d) we obtain for the case $P = MA$ that

$$P(x_d) = 2 \exp\left(-2x_d\right), \quad (B\text{-}6)$$

which gives

$$\langle x_d \rangle = \int_0^\infty 2x_d \exp\left(-2x_d\right) dx_d = 0\cdot5. \quad (B\text{-}7)$$

It is found graphically that $\langle x_d \rangle \simeq 0\cdot511$ for the case $P=2$ and $\langle x_d \rangle \simeq 0\cdot506$ for the case $P = MC$.

APPENDIX C
Calculation of $P_{NI}(x_p)$ and $P_{NI}(x_q)$

Equation (25a) can be easily obtained from (22) and (24a) by making use of equation (17) in p.313, Vol. I of Erdelyi (1954). Equation (25b) can be obtained from (22) and (24b) by using the substitution $x_q = 4y/x_p$ in the integral. Equation (25c) can be obtained from (22)

and (24c) by using the substitution $x_q = y^2/2x_p$ in the integral. Equation (25d) can be obtained from (22) and (24d) by making use of equation (17) in p.313, Vol. I of Erdelyi (1954).

From (23) and (24a) equation (26a) follows directly. From (23) and (24b) equation (26b) follows, provided we make use of the substitution $x_p = 4x_q y$ in the integral. From (23) and (24c) equation (26c) follows, provided we make use of the substitution $x_p = y^2/2x_q$ in the integral. From (23) and (24d) we can obtain equation (26d) by making use of equation (15) on p.313, Vol. I of Erdelyi (1954).

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