Let $\mathbf{p}_0$ be some point in P_0 such that $^-\mathbf{p}_0$ is not in P_0. Then (41) implies

$$\tau_0\mathbf{p}_0+\sum_{j=1}^{h}\alpha_j\tau_j\mathbf{p}_j=-(\tau_0\mathbf{q}_0+\sum_{j=1}^{k}\beta_j\tau_j\mathbf{q}_j)$$

for some $\mathbf{q}_0$ in P_0 and some $\mathbf{p}_j$ and $\mathbf{q}_j$ in P_j $(j=1,\ldots,n)$. Then

$$\tau_0(\mathbf{p}_0+\mathbf{q}_0)+\sum_{j=1}^{k}\tau_j(\alpha_j\mathbf{p}_j+\beta_j\mathbf{q}_j)=0\,. \tag{42}$$

But $\mathbf{q}_0\neq-\mathbf{p}_0$, and all the points

$$\mathbf{p}_0+\mathbf{q}_0,\ \alpha_j\mathbf{p}_j+\beta_j\mathbf{q}_j\ (j=1,\ldots,k)$$

have *rational* coordinates. The linear independence of $\tau_0,\ldots,\tau_k$ over the rationals now implies that (42) is impossible. Therefore (41) is impossible.

Suppose instead:

$$\mathsf{R}(\alpha_1,\ldots,\alpha_k)=\mathsf{R}(\beta_1,\ldots,\beta_k)\,. \tag{43}$$

Define the set of indices

$$\mathsf{J}=\{j \text{ such that } \alpha_j\neq\beta_j\}\,. \tag{44}$$

Assume J is not empty. Then (43) and Theorem 3 imply

$$\sum_{j\in\mathsf{J}}\alpha_j\tau_j\mathsf{P}_j=\sum_{j\in\mathsf{J}}\beta_j\tau_j\mathsf{P}_j\,. \tag{45}$$

Now we proceed as before: let h be a particular member of J, and let $\mathbf{p}_h$, but not $-\mathbf{p}_h$, lie in P . Now (44) implies

$$\sum_{\mathsf{J}}\alpha_j\tau_j\mathbf{p}_j=\sum_{\mathsf{J}}\beta_j\tau_j\mathbf{q}_j \tag{46}$$

where $\mathbf{p}_j$ and $\mathbf{q}_j$ are in J. Since $\alpha_j=-\beta_j$ for $j\in$J, we find

$$\sum_{\mathsf{J}}\alpha_j\tau_j(\mathbf{p}_j+\mathbf{q}_j)=\mathbf{0} \tag{47}$$

where $\mathbf{p}_j+\mathbf{q}_j\neq\mathbf{0}$ for $j=h$. But then (47) is impossible because the τ_j are independent over the rationals. Therefore, J must be empty; in other words, (43) implies $\alpha_j=\beta_j(j=1,\ldots,n)$.

I want to thank Dr Edward W. Hughes for telling me about the problem of homometric sets, and for generously giving me much time.

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Probability Distribution of Bijvoet Differences. II*

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The earlier theoretical treatment of the probability distribution of Bijvoet differences [Parthasarathy & Srinivasan (1964). *Acta Cryst.* **17**, 1400–1407], has been extended to four new situations, namely, when the non-anomalous scatterers (Q) take up centrosymmetric configuration with the anomalous scatterers (P) corresponding to $P=$ one, $P=$ two, $P=$ many atoms with centrosymmetric (MC) and $P=$ many atoms with non-centrosymmetric (MNC) configuration. The theoretical distributions have been verified with hypothetical models.

Introduction

The probability distribution of the Bijvoet differences in the presence of anomalous scatterers in a non-centrosymmetric crystal was considered by Parthasarathy & Srinivasan (1964, hereafter referred to as part I). This had led to useful information on the optimum condition for measuring Bijvoet differences. The Bijvoet ratio has been considered by Parthasarathy & Parthasarathi (1973). In all these studies four situations have generally been considered for which probability distributions were derived in part I. These correspond to the Q atoms (light atoms) being non-centrosymmetric with the P atoms (anomalous scatterers) being one of the four types, namely (i) $P=$ one, (ii) $P=$ two, (iii) $P=$ many atoms with centrosymmetric

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configuration (*MC* for brevity) and (iv) *P*=many atoms with non-centrosymmetric configuration (*MNC*). A few other possible situations were not considered in part I.

We consider now the *Q* group to be centrosymmetric while the *P* group could be one of the following,* (v) *P*=one, (vi) *P*=two, (vii) *P*=*MC* and (viii) *P*=*MNC*, the structure as a whole being non-centrosymmetric. It is obvious that these situations can arise in practice since a light-atom group having a centrosymmetric configuration with one or two heavy atoms determining a non-centrosymmetric space group is not uncommon. Case (viii) may be seen to be identical with case (iv) since the situations are identical except for a change in nomenclature of the *P* and *Q* groups. Case (vii) corresponds to both *P* and *Q* groups being centrosymmetric. It is of course implied for the cases (v) to (vii) that the *P* group should be such as not to have a centre of symmetry with respect to the centre of symmetry of the *Q* group.

Derivation of the probability distribution

The derivation here follows the steps of part I and accordingly this section may be treated as a continuation of § 2 thereof. Equations and sections of part I are referred to hereafter with a prefix I. The distribution of the normalized difference x can be derived from (I–4) where we now have to assume the distribution of y_Q to be centrosymmetric given by

$$P_2(y_Q)=\sqrt{2/\pi}\,\exp(-y_Q^2/2)\,. \qquad (1)$$

The distribution of $P_1(|\sin\psi|)$ can be taken to be the same as (I–5). This follows from the fact that *P* and *Q* do not have a common centre of symmetry and the angle ψ can be assumed to be uniformly distributed in the range 0 to 2π.

We now follow the steps outlined in (I–7) to (I–9) to arrive at the distribution of $t=y_Q|\sin\varphi|$

$$P_3(t)=\frac{\sqrt{2}}{\pi^{3/2}}\int_0^{\pi}\operatorname{cosec}\psi\,\exp\left(-\frac{t^2}{2}\operatorname{cosec}^2\psi\right)d\psi\,. \qquad (2)$$

This on integration gives

$$P_3(t)=\frac{\sqrt{2}}{\pi^{3/2}}\exp(-t^2/4)K_0(t^2/4) \qquad (3)$$

where K_0 is the modified Bessel function of order zero with imaginary argument (Watson, 1944, p. 181).

We can now substitute $P_4(y_P'')$ for the various cases, using the steps outlined in § I–2 (*a*), (*b*) and (*c*).

One-atom case: (*case* v)

Since $P_4(y_P'')$ is a delta function $\delta(y_P''-1)$ the distribution of x is

$$P(x)=\frac{\sqrt{2}}{\pi^{3/2}}\exp\left(-\frac{x^2}{4}\right)K_0\left(\frac{x^2}{4}\right)\,. \qquad (4)$$

The function is in the normalized form and it can be verified by checking that the integral reduces to unity.

The expectation value for the present case is given by

$$\langle x\rangle=\frac{\sqrt{2}}{\pi^{3/2}}\int_0^{\infty}x\exp\left(-\frac{x^2}{4}\right)K_0\left(\frac{x^2}{4}\right)dx\,. \qquad (5)$$

The integral can be shown to reduce to $\langle x\rangle=(2/\pi)^{3/2}=0{\cdot}5029$ (Appendix I of part I).

Two-atom case: (*case* vi)

The distribution of y_P'' with the origin chosen midway between the two anomalous scatterers is (Srinivasan, 1960)

$$P_5(y_P'')=\frac{2}{\pi\sqrt{2-y_P''^2}}\,,\quad 0\le y_P''\le\sqrt{2}\,. \qquad (6)$$

Making use of (4), (6) and (I–13) with the substitution $y_P''=\sqrt{2}\,\operatorname{sech}u$ we get

$$P(x)=\frac{2}{\pi^{5/2}}\int_0^{\infty}\exp\left(-\frac{x^2}{8}\cosh^2u\right)K_0\left(\frac{x^2}{8}\cosh^2u\right)du. \qquad (7)$$

The above integration was carried out by numerical methods. The distribution is given in the form of a curve in Fig. 1.

The expectation value of the present case is given by

$$\langle x\rangle=\frac{2}{\pi^{5/2}}\int_0^{\infty}x\exp\left(-\frac{x^2}{8}\cosh^2u\right)\times K_0\left(\frac{x^2}{8}\cosh^2u\right)du\,. \qquad (8)$$

The value was found by numerical integration to be $\langle x\rangle=0{\cdot}452$.

* For convenience the earlier four cases are referred to as (i) to (iv) and the new ones as (v) to (viii).

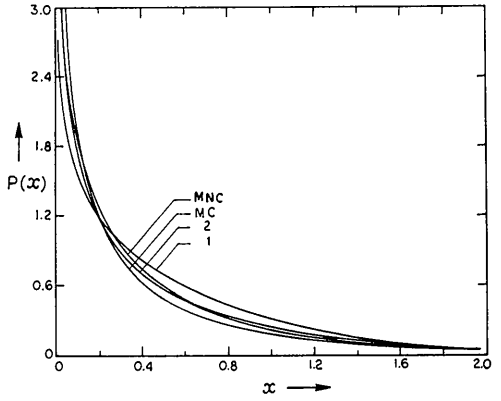

Fig. 1. Theoretical probability density function for the normalized Bijvoet difference x corresponding to the anomalous scattering group (*P*) containing one (1), two (2), many centrosymmetric (*MC*) and many non-centrosymmetric (*MNC*) atoms.

Many-atom case: *P group centric* (*case* vii)

The distribution of y''_P in this case is given by (Wilson, 1949; Ramachandran & Srinivasan, 1959)

$$P_6(y''_P)=\sqrt{2/\pi}\exp(-y''^2_P/2)\,. \tag{9}$$

After equations (4) and (9) are used in (I–13), the distribution of x takes the form

$$P(x)=\frac{2}{\pi^2}\int_0^\infty \exp\left(-\frac{y''^2_P}{2}-\frac{x^2}{4y''^2_P}\right)K_0\left(\frac{x^2}{4y''^2_P}\right)\frac{dy''_P}{y''_P}\,. \tag{10}$$

With the substitution $z=y''^2_P$ (10) reduces to

$$P(x)=\frac{1}{\pi^2}\int_0^\infty \exp\left[-\frac{z}{2}-\frac{1}{2z}\left(\frac{x^2}{4}+\frac{x^2}{4}\right)\right]\times K_0\left(\frac{x^2}{4z}\right)\frac{dz}{z}\,. \tag{11}$$

With the use of the table of integrals (Gradshteyn & Ryzhik, 1965, pp. 725, 6.653) the integral (11) reduces to the form

$$P(x)=\frac{2}{\pi^2}[K_0(x/2)]^2. \tag{12}$$

The probability density function is in the normalized form and the expectation value of x in this case is equal to 0·409.

Many-atom case: *P group non-centrosymmetric* (*case* viii)

This case may be seen to be identical with case (iii) of part I, except for a change in the nomenclature of P and Q. Thus the distribution of $P(x)$ is the same as (I–20), namely

$$P(x)=\frac{2\sqrt{2}}{\pi}K_0(x\sqrt{2}), \tag{14}$$

and the expectation value of x is given by $\langle x\rangle=\sqrt{2}/\pi=$ 0·450.

Nature of the probability distribution

The probability density functions for cases (v) to (viii) are shown in Fig. 1. All the density functions have a singularity at the origin, as they contain the Bessel function $K_0(x)$. For convenience, we deal with the cumulative function $N(x)$,

$$N(x)=\int_0^\infty P(x)dx,$$

which has been calculated for all the cases by numerical integration. The $N(x)$ curves are shown in Fig. 2. The complementary cumulative functions $\bar{N}(x)=1-N(x)$ are given in Table 1. Our main interest in these curves is to compare their behaviour for fairly large values of x. It is clear from Fig. 2 that the curve for the one-atom case passes well above the others for moderate and large values of x, indicating that it is the most favourable. Moreover, the probability density function for case (v) is exactly the same as that for case (ii).

The progressive change in the behaviour of the curves is also reflected in the mean values of x. For instance $\langle x\rangle$ is a maximum for case (v) (0·502) and a minimum for case (vii) (0·409). The values for cases (vi) and (viii) are nearly the same (0·452). If we make the overall comparison of all the eight cases in terms of the mean value of x, it may be noted that the Q group's being non-centrosymmetric is in general more favourable than when it is centrosymmetric for the different cases of $P=1$, 2, *MN* and *MNC*.

The theoretical $N(x)$ curves shown in Fig. 2 have

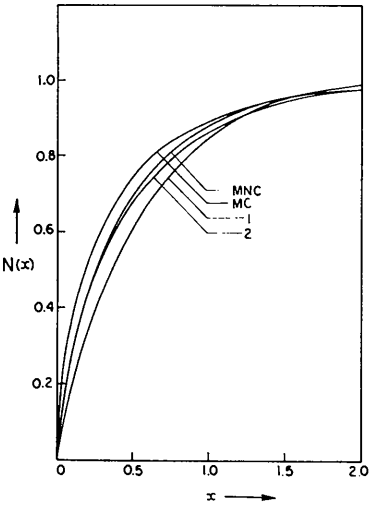

Fig. 2. Theoretical cumulative function $N(x)$ for the normalized Bijvoet difference x for 1, 2, *MC* and *MNC* cases of Fig. 1.

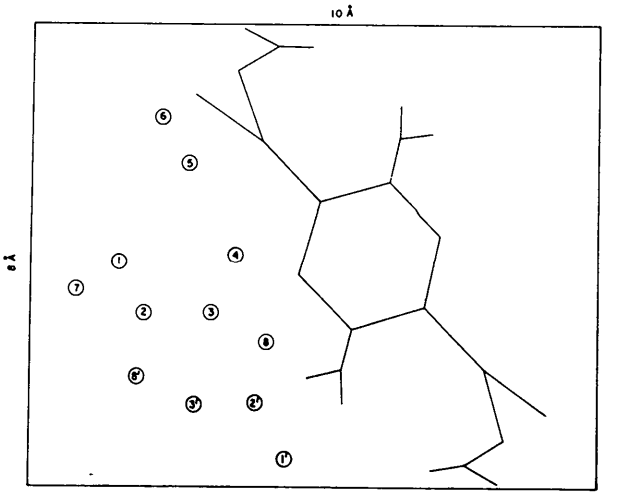

Fig. 3. Hypothetical structure in the plane-group symmetry $P1$, used for testing the theoretical curves.

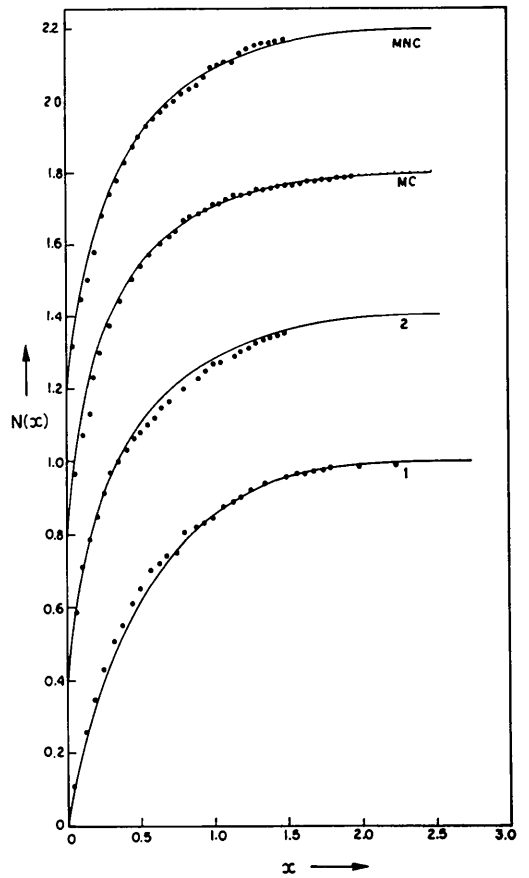

Fig. 4. Comparison of the experimental data with theoretical cumulative function $N(x)$ for the cases of Fig. 1. The theoretical curves are shown by solid lines and the experimental points are marked as dots. For convenience the origin for $N(x)$ is shifted along y by 0·4, 0·8 and 1·2 respectively for the cases 2, *MC* and *MNC*.

been tested with a hypothetical model shown in Fig. 3. The heavy atoms are marked as open circles. For the one and two-atom cases the heavy atoms 1 and 1, 2, respectively, were used. For the case *MC*, the atoms 1,1′, 2,2′, 3,3′ and 8,8′ were used and for the case *MNC* only the unprimed atoms were used. In all the cases the agreement with the theoretical distributions is reasonable (Fig. 4).

Table 1. *Values of the complementary cumulative function*

	1	2	*MC*	*MNC*
0·00	100·0%	100·0%	100·0%	100·0%
0·05	87·9	81·0	75·4	83·0
0·10	79·4	70·6	63·5	72·3
0·15	72·2	62·7	55·0	63·8
0·20	65·9	56·3	48·3	56·8
0·25	60·3	50·8	42·9	50·9
0·30	55·2	46·1	38·3	45·8
0·35	50·5	42·0	34·5	41·3
0·40	46·3	38·3	31·1	37·3
0·45	42·4	35·0	28·2	33·8
0·50	38·8	32·0	25·7	30·7
0·55	35·5	29·4	23·4	27·9
0·60	32·4	26·9	21·4	25·4
0·65	29·6	24·7	19·6	23·2
0·70	27·0	22·7	17·9	21·2
0·75	24·6	20·9	16·5	19·3
0·80	22·3	19·2	15·1	17·7
0·85	20·3	17·6	13·9	16·2
0·90	18·4	16·2	12·9	14·8
0·95	16·7	14·9	11·9	13·6
1·00	15·1	13·7	11·0	12·5
1·10	12·3	11·6	9·4	10·5
1·20	10·0	9·7	8·0	8·8
1·30	8·0	8·2	6·9	7·5
1·40	6·4	6·9	6·0	6·3
1·50	5·1	5·8	5·1	5·4
1·75	2·7	3·7	3·6	3·6
2·00	1·4	2·3	2·5	2·4

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