doubtlessly creates difficulty in solving the intensity distribution in diffraction topographs for various types of imperfection. This complexity merely reflects the fact that, in an imperfect crystal, the beams tend to spread out as they scatter from different places in the crystal, and conversely, the beams at one point are under the influence of many beams created at different locations before they reach that point.

If one can assert that the beams inside the crystal proceed along a path, then the integral equation (7.9) can be reduced to a differential equation and the Ψ matrix becomes the matricant of the system. In this case, the determination of the path itself becomes a separate problem. For instance, in the calculation of the propagator g in § 6, one could have employed the approximation of the stationary phase, as demonstrated previously by Kuriyama (1968). Then, by retaining only the anomalous transmission mode, a path could have been established. Along this path, the final equation could have assumed a differential equation form, making the Ψ matrix a matricant. The diffraction conditions in high-energy electron diffraction make this approximation practical, since the Bragg angles are extremely small.

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The Use of X-ray Anomalous Scattering for the Detection of Small Deviations from Centrosymmetry*

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(*Received* 20 *November* 1972; *accepted* 22 *January* 1974)

A quantitative relation is obtained between Bijvoet differences and the deviations from centrosymmetry of a structure. An expression is derived for the root-mean-square value of Δ, where

$$\Delta=[I(\mathbf{H})-I(\bar{\mathbf{H}})]/\sigma_N^2,\ \sigma_N^2=\sum_{j=1}^{N} f_j^2,$$

in terms of $\langle|\Delta\mathbf{r}_j|\rangle$ and k'' where $\Delta\mathbf{r}_j$ are the deviations in atomic coordinates from ideal centrosymmetry, and $k''=\Delta f''/f'$. Curves are given connecting r.m.s. Δ with $\langle|\Delta\mathbf{r}_j|\rangle$ for a two-dimensional hypothetical model. When $\langle|\Delta\mathbf{r}_j|\rangle$ is small the r.m.s. Δ is quite sensitive to $\langle|\Delta\mathbf{r}_j|\rangle$ with a moderate anomalous scatterer present in the structure. The behaviour of the Bijvoet ratio is also studied empirically.

1. Introduction

In a recent paper from this laboratory (Srinivasan & Vijayalakshmi, 1972) the use of X-ray anomalous scattering as a sensitive tool for resolving the space-group ambiguity of dibenzyl disulphide was discussed. The use of X-ray anomalous scattering effects for space group determination is well known (Okaya & Pepinsky, 1961; Ramachandran & Parthasarathy, 1963; Parthasarathy & Ramachandran, 1963). However, it has not been apparent that it could be used successfully in cases where the distinction between alternate space groups is a subtle one involving small deviations from centrosymmetry. This was in fact the case with dibenzyl disulphide where it was shown that if the

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structure proposed in the space group Cc were correct, which involved mean deviations of ~0·05 Å in atomic coordinates from ideal centrosymmetry, significant Bijvoet differences were to be expected theoretically for a reasonable number of reflexions. The failure to observe any such Bijvoet differences supported strongly the space group $C2/c$. This led us to a study of the quantitative relation between the Bijvoet differences and the amount of deviation from centrosymmetry. In this paper we work out such a relation between a convenient statistical parameter involving the Bijvoet differences and the deviations from ideal centrosymmetry. The results are verified using a hypothetical two-dimensional model structure.

2. Derivation of formulae

The statistical distribution of Bijvoet differences has been treated earlier (Parthasarathy & Srinivasan, 1964; Parthasarathy, 1967). While, in principle, one can work out any of the statistical parameters such as the mean value of the Bijvoet difference $\Delta I=[I(\mathbf{H})-I(\bar{\mathbf{H}})]$, the Bijvoet ratio $X=\Delta I/\frac{1}{2}[I(\mathbf{H})+I(\bar{\mathbf{H}})]$ or other similar quantities, we will use in this paper mainly the root-mean-square value of the quantity Δ defined by

$$\Delta=(\Delta I)/(\sigma_N^2) \qquad (1)$$

where $\sigma_N^2=\sum_{j=1}^{N} f_j'^2$. The Bijvoet ratio X, although it has some practical advantages, is more difficult to handle theoretically. Its use in this paper is confined to an empirical comparison with the r.m.s. Δ.

2.1 *Small deviations from centrosymmetry*

It is useful to deduce first the r.m.s. value of Δ for a non-centrosymmetric structure containing N atoms in random positions, some of which (P) scatter anomalously and the rest (Q) scatter normally. We will also assume that there is only one kind of anomalous scatterer present. The Bijvoet difference ΔI in such a case is given by the general expression (Parthasarathy & Srinivasan, 1964),

$$\Delta I=4[A_Q'B_P''-A_P''B_Q'] . \qquad (2)$$

The average $\langle(\Delta I)^2\rangle$ can be obtained from (2) by squaring the right-hand side and expanding. Since the contributions from the P and Q atoms are independent, only the square terms survive on averaging, leading to

$$\langle(\Delta I)^2\rangle=16k''^2[\langle A_Q'^2\rangle\langle B_P'^2\rangle+\langle A_P'^2\rangle\langle B_Q'^2\rangle] \qquad (3)$$

where $k''=\Delta f''/f'$.

From (3) it is readily deduced using the standard results,

$$\langle A_P'^2\rangle=\langle B_P'^2\rangle=\sigma_P^2/2 , \quad \langle A_Q'^2\rangle=\langle B_Q'^2\rangle=\sigma_Q^2/2 ,$$

that

$$\langle(\Delta I)^2\rangle=8\,k''^2\sigma_P^2\sigma_Q^2 ,$$

where $\sigma_P^2=\sum_j^P f_j^2$, $\sigma_Q^2=\sum_j^Q f_j^2$. Thus the r.m.s. value of Δ becomes

$$\langle\Delta^2\rangle^{1/2}=2\sqrt{2}k''\sigma_1\sigma_2 , \qquad (4)$$

where

$$\sigma_1=\sigma_P/\sigma_N \quad \text{and} \quad \sigma_2=\sigma_Q/\sigma_N .$$

Consider now a non-centrosymmetric crystal containing N atoms, P of which are anomalous scatterers, all alike. Let us assume that these N atoms have an approximate centre of symmetry; that is to say, they are obtained by introducing small random deviations in the atomic coordinates of an initial structure having an exact centre of symmetry. If the coordinates of one half of the atoms are denoted by $\mathbf{r}_{Nj}$, $j=1,2,\ldots N/2$ those of the other half related by an approximate

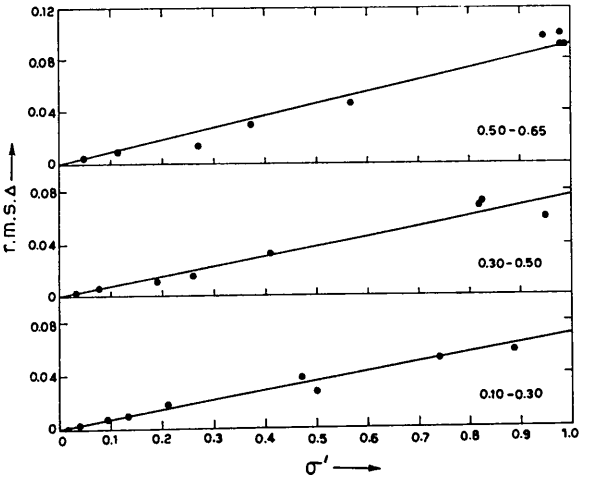

Fig. 1. R.m.s. Δ *versus* σ' for a hypothetical model with the P group centrosymmetric. Ranges marked near each graph pertain to $(\sin\theta)/\lambda$ values.

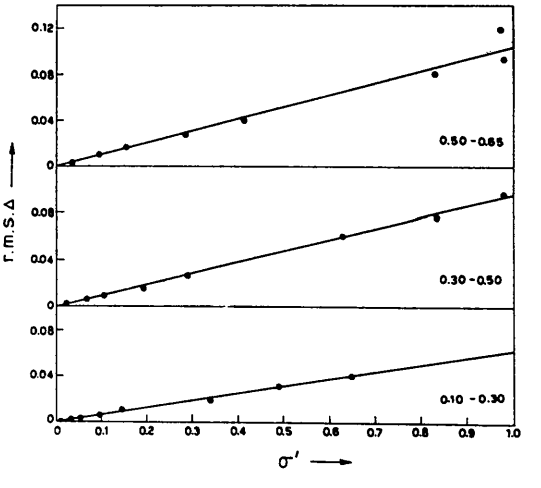

Fig. 2. R.m.s. Δ *versus* σ' for a hypothetical model with errors in both P and Q atoms. Ranges marked near each graph pertain to $(\sin\theta)/\lambda$ values.

centre of symmetry may be written as $\mathbf{r}'_{Nj}=-\mathbf{r}_{Nj}+\Delta\mathbf{r}_{Nj}$.

The contributions to the real part of the structure factor from a pair of atoms at $\mathbf{r}_j$ and $-\mathbf{r}_j+\Delta\mathbf{r}_j$ takes the form

$$A'_j=f'_j[\cos\varphi_j+\cos(-\varphi_j+\psi_j)]$$
$$=f'_j[\cos\varphi_j(1+\cos\psi_j)+\sin\varphi_j\sin\psi_j] \quad (5)$$

where

$$\varphi_j=2\pi\mathbf{H}\,.\,\mathbf{r}_j \quad \text{and} \quad \psi_j=2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_j\,.$$

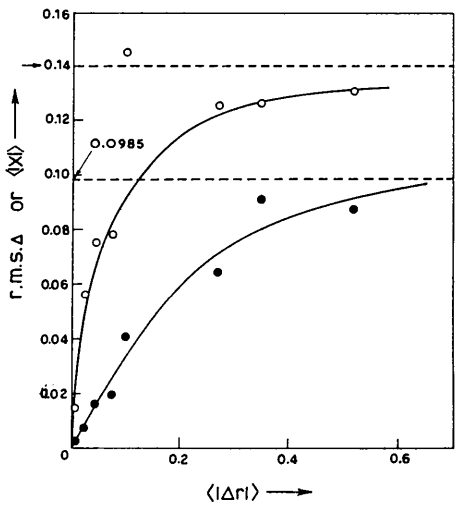

Fig. 3. Comparison of r.m.s. Δ (dots) and mean Bijvoet ratios (circles) as a function of $\langle|\Delta\mathbf{r}_j|\rangle$ for the case of no errors in P atoms ($P=2$, $Q=14$). Theoretical curve of r.m.s. Δ *versus* $\langle|\Delta\mathbf{r}_j|\rangle$ shown by thick line. Theoretical limiting values of $\langle|X|\rangle$ and r.m.s. Δ for large errors are the dotted lines marked 0·0985 and 0·14 respectively.

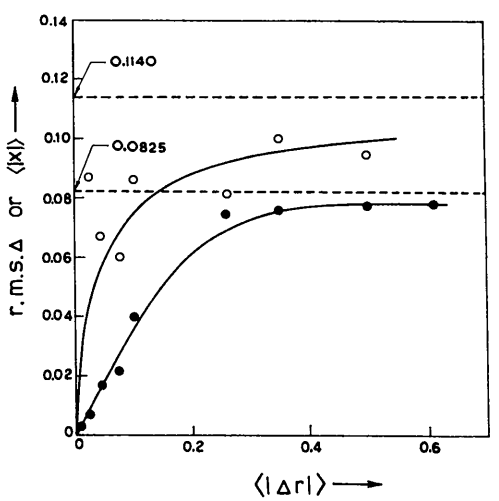

Fig. 4. Comparison of r.m.s. Δ (dots) and the mean Bijvoet ratio (circles) as a function of $\langle|\Delta\mathbf{r}_j|\rangle$ for the case of errors in both P and Q atoms ($P=4$, $Q=12$). Theoretical limiting values of $\langle|X|\rangle$ and r.m.s. Δ for large errors are the dotted lines marked 0·0825 and 0·114 respectively.

The total contribution from $P/2$ such pairs will give for

$$A'_P=\sum_j^{P/2}A'_{Pj}=\sum f'_{Pj}[\cos\varphi_{Pj}(1+\cos\psi_{Pj})$$
$$+\sin\varphi_{Pj}\sin\psi_{Pj}]\,. \quad (6)$$

We require in (3) typically a quantity $\langle A'^2_P\rangle$. It is readily seen that if the coordinates x_{Pj}, y_{Pj}, z_{Pj}, are random, $\langle\cos\varphi_{Pj}\rangle=\langle\sin\varphi_{Pj}\rangle=0$, $\langle\sin^2\varphi_{Pj}\rangle=\langle\cos^2\varphi_{Pj}\rangle=\frac{1}{2}$. Also, if the errors $\Delta\mathbf{r}_j$ are Gaussian, it is readily shown that $\langle\sin\psi_j\rangle=0$ since $+\Delta\mathbf{r}_j$ and $-\Delta\mathbf{r}_j$ are equally probable. We note that $\langle\cos\psi_{Pj}\rangle$ exists and let

$$D_P=\langle\cos\psi_{Pj}\rangle\,.$$

With these assumptions $\langle A'^2_P\rangle$ from (6) can be shown to reduce to

$$\langle A'^2_P\rangle=\left[\frac{1+D_P}{2}\right]\sigma_P^2\,, \quad (7)$$

wherein the average D_P for all the P atoms has been assumed to be the same and also $\Delta\mathbf{r}_{Pj}$ are assumed to be independent of $\mathbf{r}_{Pj}$.

An exactly similar procedure leads us to the relation

$$\langle B'^2_P\rangle=\left[\frac{1-D_P}{2}\right]\sigma_P^2\,. \quad (8)$$

The forms of expressions (7) and (8) can be used for the components A'_Q and B'_Q also with the only change that D_P in (7) and (8) will be replaced by D_Q, where $D_Q=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_{Qj}\rangle$. With these substitutions equation (3) can now be shown to reduce to

$$\langle(\Delta I)^2\rangle=8\,k''^2\sigma_P^2\sigma_Q^2(1-D_PD_Q) \quad (9)$$

so that

$$\langle\Delta^2\rangle^{1/2}=2\sqrt{2}\,k''\sigma_1\sigma_2\sigma' \quad (10)$$

where

$$\sigma'=\sqrt{1-D_PD_Q}\,.$$

When the errors in the P atoms are zero, expression (8) reduces to

$$\langle\Delta^2\rangle^{1/2}=2\sqrt{2}\,k''\sigma_1\sigma_2(1-D)_Q^{1/2}. \quad (11)$$

This will be of some practical interest since structures with just two heavy atoms in the unit cell are not uncommon and the above equation will be applicable for such cases. We may notice that r.m.s. value of Δ will be zero when all the $\Delta\mathbf{r}_j$'s are zero and that it will be $2\sqrt{2}\sigma_1\sigma_2\,k''$ when the $\Delta\mathbf{r}_j$'s are very large as obviously it should be since this corresponds to equation (4) already deduced for the ideally non-centrosymmetric structure.

It has been shown (Luzzati, 1952) that for a two-dimensional case, when $\Delta\mathbf{r}_j$'s have a Gaussian distribution D can be given by the expression

$$D=\exp-(4\pi|\mathbf{H}|^2\langle|\Delta\mathbf{r}|\rangle^2)\,. \quad (12)$$

Substitution of this expression in (10) enables us to obtain the theoretical curve of r.m.s. Δ against $\langle|\Delta\mathbf{r}_j|\rangle$.

3. Verification of the theoretical results

3.1 *Calculations on a hypothetical model*

The results derived above have been verified using a hypothetical two-dimensional model. An orthogonal unit cell of dimensions $a=5{\cdot}0$ and $b=10{\cdot}0$ Å was taken in the plane group $p2$. Two cases were considered; in Case I, two of the 16 atoms were assumed to be anomalous scatterers (*viz.*, sulphur) and the rest non-anomalous scatterers (nitrogen). Since there are only two atoms in the P group, they are automatically centrosymmetric and hence $\Delta\mathbf{r}_{Pj}=0$. This case provided data to check equation (11).

In the second case, four out of the 16 atoms were assumed to be anomalous scatterers (sulphur) and the remainder, non-anomalous (nitrogen). This provided data to check equation (10). In each of these cases, different sets of calculations were performed, each set corresponding to the introduction of small errors* in the coordinates of the atoms, destroying the centrosymmetry. These sets correspond to $\langle|\Delta\mathbf{r}_j|\rangle=0{\cdot}01, 0{\cdot}025, 0{\cdot}05, 0{\cdot}075, 0{\cdot}1, 0{\cdot}25, 0{\cdot}35$ and $0{\cdot}5$ Å. The shifts were given arbitrarily in random directions and it was also checked that $\langle\Delta\mathbf{r}_j\rangle=0$. The r.m.s. Δ was calculated for each set using the calculated structure factors. An isotropic temperature factor of $B=2{\cdot}5$ Å^2 was used for all the atoms. Anomalous dispersion values used for sulphur were $\Delta f'=0{\cdot}319$ and $\Delta f''=0{\cdot}557$ (for Cu $K\alpha$). In addition to r.m.s. Δ the Bijvoet ratios X were also calculated, to study their behaviour empirically.

The results for both the cases are plotted graphically in Figs. 1 and 2 and listed in Table 1.

Table 1. *Observed and theoretical values of k'' for model structure with two anomalous scatterers (case* I*) and four anomalous scatterers (case* II*)*

	$(k'')_{obs}$		
$(\sin\theta)/\lambda$	Case I	Case II	$(k'')_{Th}$
0·200	0·045	0·052	0·050
0·400	0·070	0·066	0·071
0·575	0·079	0·086	0·082

From equation (10), the plot of r.m.s. Δ against σ' should be linear with a slope equal to $2\sqrt{2}\,k''\sigma_1\sigma_2$. This result can be expected to be true only in regions of $(\sin\theta)/\lambda$ within which k'' (and also σ_1 and σ_2) can be assumed to be a constant. Accordingly in Figs. 1 and 2 results for three groups of reflexions for regions of $(\sin\theta)/\lambda$ 0·1–0·3, 0·3–0·5 and 0·5–0·65 are shown. From the slopes of these graphs and knowing $\sigma_1\sigma_2$ for each range, k'' has been deduced and is entered as $(k'')_{obs}$ in Table 1. As is to be expected from theory, the graphs are linear in Figs. 1 and 2 and also the k'' deduced agrees fairly well with the mean value of k'' calculated for the different ranges from a krowledge of $\Delta f''$ and f' (entered as $(k'')_{Th}$ in Table 1).

3.2 *Empirical behaviour of r.m.s. Δ*

The calculations on the hypothetical model were used to study the variations of r.m.s. Δ with different values of $\langle|\Delta\mathbf{r}_j|\rangle$. This is compared with the theoretical curves obtainable using expression (12). Incidentally, the values of $\langle|X|\rangle$ were also calculated and its variation as function of $\langle|\Delta\mathbf{r}_j|\rangle$ could thus be studied empirically.

These two results are shown graphically in Figs. 3 and 4 for both cases I and II. The observed r.m.s. Δ may be seen to follow closely the theoretical curve. For the Bijvoet ratio, although the theoretical curve is not available the limiting value for large errors can be estimated from the results of Parthasarathy (1967) and is indicated in Figs. 3 and 4. It may be noticed from Figs. 3 and 4 that both r.m.s. Δ and $\langle|X|\rangle$ uniformly increase as $\langle|\Delta\mathbf{r}_j|\rangle$ increases, reaching the value for the random case asymptotically. The behaviour of the curves for small values of $\langle|\Delta\mathbf{r}_j|\rangle$ is interesting in that it rises rather steeply in this region. This signifies the rather high sensitivity of the Bijvoet differences for small deviations from ideal centrosymmetry. In fact, the curve for the Bijvoet ratio appears to rise much more steeply compared to r.m.s. Δ and appears to be, therefore, more sensitive. The observed points for the Bijvoet ratio for Case II alone seem to have rather large scatter and this may be because the number of P atoms is perhaps not sufficiently large for a good randomization. Nevertheless, the broad feature that is apparent is that $\langle|X|\rangle$ values are systematically larger than the r.m.s. Δ. A theoretical treatment of $\langle|X|\rangle$ is perhaps worth while although it is likely to be difficult to handle compared to r.m.s. Δ which we have studied here.

One of us (B.K.V.) would like to thank the University Grants Commission, India, for financial assistance.

* The mean errors in P and Q atoms were made equal for for convenience. Thus

$$\langle|\Delta\mathbf{r}_{Pj}|\rangle = \langle|\Delta\mathbf{r}_{Qj}|\rangle = \langle|\Delta\mathbf{r}_j|\rangle\,.$$

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