the Straumanis manner rather than in that of van Arkel. The use of film techniques for the isolation of reflexions makes the θ-method both lengthy and tedious and considerable improvement could be effected by the introduction of an ionization method.

The authors wish to express their thanks to Dr W. H. Taylor for his helpful criticism of the text of this paper. One of us (W. F. C.) wishes to express his thanks to the University of Western Australia for the award of a Hackett Research Studentship during the tenure of which the present work was carried out. The other authors are indebted to the Department of Scientific and Industrial Research for financial aid.

References

BRADLEY, A. J. & JAY, A. H. (1932). *Proc. Phys. Soc., Lond.*, **44**, 563.

BUERGER, M. J. (1937). *Z. Krystallogr.* **97**, 433.

BUERGER, M. J. (1942). *X-ray Crystallography.* New York: Wiley.

CHAO, S. H., SMARE, D. L. & TAYLOR, W. H. (1939). *Miner. Mag.* **25**, 338.

COHEN, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.

FARQUHAR, M. C. M. & LIPSON, H. (1945). *Proc. Phys. Soc., Lond.*, **58**, 200.

LONSDALE, K. (1944). *Nature, Lond.*, **153**, 22.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc., Lond.*, **57**, 160.

WILSON, A. J. C. & LIPSON, H. (1941). *Proc. Phys. Soc., Lond.*, **53**, 245.

Acta Cryst. (1948). **1**, 88

The Crystal Structures of Zinc and Magnesium Benzene Sulphonates

BY JUNE M. BROOMHEAD AND A. D. I. NICOL

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 18 *December* 1947)

The crystal structures of the isomorphous zinc and magnesium benzene sulphonates have been determined. The crystals are monoclinic, with space group $P2_1/n$ and two molecules in a unit cell with edges $a = 22{\cdot}6$ A., $b = 6{\cdot}32$ A., $c = 6{\cdot}94$ A., $\beta = 93°\ 36'$ (magnesium compound).

The signs of the structure amplitudes were fixed by comparison of corresponding reflexions from the isomorphous structures, and Fourier projections along the b and c axes were used to determine the structure.

In the structure, metal atoms are surrounded by regular octahedra of water molecules, which are linked by hydrogen bonds to oxygen atoms of the sulphonate group. These oxygen atoms and a carbon atom of the benzene ring are joined to a sulphur atom by bonds which make angles of approximately 109° with each other. The benzene ring is plane and the minimum distance between neighbouring rings is about 3·5 A. The position and orientation of the molecules in the structure suggest an explanation of the observed twin growth.

Introduction

An investigation on a series of isomorphous benzene and toluene sulphonates was started in Manchester by Hargreaves and one of us (A. D. I. N.) with a view to obtaining a complete structural analysis by X-ray methods. It was hoped that this would provide useful information about the configuration of the sulphonate group. Hargreaves (1946) has described the b axis projection of the isomorphous zinc and magnesium toluene sulphonate structures.

It was found that zinc and magnesium benzene sulphonates were isomorphous, with space group $P2_1/n$, and two molecules in unit cells with the dimensions given in Table 1. In order to conform with the usual convention, the angle β given corresponds to the supplement of that quoted by Hargreaves (1946).

Table 1. *Cell dimensions of* $Mg(C_6H_5SO_3)_2 . 6H_2O$ *and* $Zn(C_6H_5SO_3)_2 . 6H_2O$

Compound	a in A.	b in A.	c in A.	β
Zinc benzene sulphonate	22·5	6·32	6·98	93° 36′
Magnesium benzene sulphonate	22·6	6·32	6·94	93° 36′

As the space group is centrosymmetrical a positive or negative sign is associated with each structure amplitude, and since the metal atoms must be situated at symmetry centres it was decided to fix the signs of the structure amplitudes by comparison of corresponding reflexions from the two isomorphous structures, and then to obtain Fourier projections of the unit cell along the b and c crystallographic axes. From these two projections it was hoped that it would be possible to fix the positions of all the atoms in the unit cell and so to calculate interatomic bond distances.

Experimental

Two crystals with square cross-sections small by comparison with the dimension along the b and c axes respectively were used to take a series of zero layer-line Weissenberg photographs with Cu $K\alpha$ radiation; exposure times varied between 6 min. and 20 hr. Intensities of X-ray reflexions were estimated visually, using an intensity scale constructed by exposing different parts of a film to an X-ray reflexion from the crystal for regularly increasing intervals of time. Polarization and Lorentz corrections were applied in the usual way and a set of numbers, proportional to F^2, was obtained.

The estimation of intensities in the b axis photographs was complicated by the fact that the crystals were twinned across the face (100). Reciprocal nets of the two components of the twin showed that $(\bar{h}00)$ and $(\bar{h}05)$ reflexions from one component would overlap completely $(h00)$ and $(h-2,0,5)$ reflexions from the other. Partial overlap of $(\bar{h}04)$ and $(\bar{h}06)$ reflexions from one component with $(h-2,0,4)$ and $(h-2,0,6)$ from the other must also be expected. A correction for complete overlap was applied by finding the ratio between the intensities of reflexions from the two components. This was done by direct comparison of corresponding reflexions from the two components where no overlap occurs and substituting in a correcting formula. No really satisfactory method of correcting for partial overlap was discovered and this limitation reduced the accuracy of the final projection along this axis for both magnesium and zinc compounds.

Determination of the structure

(*a*) *c axis projection.* The structure factor for reflexions of the type $(hk0)$ in the space group $P2_1/n$ is

$$S(hk) = 4\cos 2\pi hx \cos 2\pi ky, \qquad \text{when } (h+k)=2n;$$

$$S(hk) = -4\sin 2\pi hx \sin 2\pi ky, \qquad \text{when } (h+k)=2n+1.$$

Assuming that all corresponding atoms have the same co-ordinates in the crystal structures of the two isomorphous compounds,

$$F_{\mathrm{Zn}}(hk) = 2f_{\mathrm{Zn}} + \sum_i S_i(hk) f_i, \qquad \text{when } (h+k)=2n;$$

$$F_{\mathrm{Mg}}(hk) = 2f_{\mathrm{Mg}} + \sum_i S_i(hk) f_i, \qquad \text{when } (h+k)=2n;$$

$$F_{\mathrm{Zn}}(hk) = F_{\mathrm{Mg}}(hk) = \sum_i S_i(hk) f_i, \qquad \text{when } (h+k)=2n+1.$$

where f_{Zn}, f_{Mg} and f_i are the atomic scattering factors for the zinc, the magnesium and the rest of the atoms respectively. As the metal atoms do not contribute to the odd reflexions, only the signs of the even terms can be determined by the isomorphous replacement method. These signs were obtained as follows.

By experiment a set of coefficients, G's, proportional to F's is obtained:

$$G_{\mathrm{Zn}}(hk) = g_{\mathrm{Zn}} F_{\mathrm{Zn}}(hk), \qquad G_{\mathrm{Mg}}(hk) = g_{\mathrm{Mg}} F_{\mathrm{Mg}}(hk),$$

and, since $F_{\mathrm{Zn}}(hk) = F_{\mathrm{Mg}}(hk)$ when $(h+k)=2n+1$,

$$\frac{G_{\mathrm{Zn}}(hk)}{G_{\mathrm{Mg}}(hk)} = \frac{g_{\mathrm{Zn}}}{g_{\mathrm{Mg}}}.$$

Thus the ratio $g_{\mathrm{Zn}}/g_{\mathrm{Mg}}$ and its variation with $\sin\theta$ can be determined from the odd reflexions and used to put the experimentally determined coefficients from the two compounds on the same scale. The signs of the even terms can then be determined by direct comparison.

A Fourier synthesis was computed using the even terms only, and the resulting projection contained a centre of symmetry additional to that required by the true crystal symmetry. The projection, therefore, contains peaks corresponding to the atomic positions and also images of these atoms produced by the operation of a spurious centre of symmetry. The false peaks were identified as follows. A Patterson projection on the (001) plane was computed and the x and y co-ordinates of the sulphur atom were obtained by inspection. The quantity Sf_{S} was then determined for all terms having $(h+k)$ odd and a Fourier synthesis computed using the odd terms with signs fixed by the sulphur atom alone. This was superimposed on the Fourier synthesis using terms having $(h+k)$ even and it was found that the numbers coinciding with a peak and its image, produced by the spurious centre of symmetry, were in one case positive and in the other negative. The peak whose height was enhanced was taken to be the true one.

In this way it was possible to find approximate x and y co-ordinates for all the atoms in the unit cell and then to apply the usual method of successive approximations. When the final set of structure amplitudes had been computed, the observed coefficients were put on the same scale as the calculated F's and the accuracy of the projection estimated from the value of

$$\frac{\Sigma\,\big|\,|F_{\mathrm{obs.}}| - |F_{\mathrm{calc.}}|\,\big|}{\Sigma\,|F_{\mathrm{obs.}}|},$$

which was found to be 0·27 for the magnesium compound and 0·30 for the zinc compound. The greater inaccuracy in the case of the zinc compound is due to the fact that the crystal used in taking the Weissenberg photographs was very small. This would necessitate long exposures in order to register weak reflexions, but it was found that the increased background intensity on long exposure photographs made it impossible to estimate these reflexions and resulted in a high proportion of absences.

(*b*) *b axis projection.* The structure factor for reflexions of the type $(h0l)$ in the space group $P2_1/n$ is

$$S(hl) = 4\cos 2\pi(hx+lz), \qquad \text{when } (h+l)=2n;$$

$$S(hl) = 0, \qquad \text{when } (h+l)=2n+1.$$

Therefore

$$F_{\mathrm{Zn}}(hl) = 2f_{\mathrm{Zn}} + \sum_i S_i f_i, \qquad \text{when } (h+l)=2n;$$

$$F_{\mathrm{Zn}}(hl) = F_{\mathrm{Mg}}(hl) = 0, \qquad \text{when } (h+l)=2n+1.$$

It was possible, therefore, to determine the signs of all the structure amplitudes by the method of isomorphous replacement. A projection of the unit cell along the *b* axis was calculated, and the usual method of successive approximations applied. The accuracy of the final projection may again be estimated from the value of $\frac{\Sigma||F_{\text{obs.}}|-|F_{\text{calc.}}||}{\Sigma|F_{\text{obs.}}|}$ which was found to be 0·31 for the magnesium compound and 0·21 for the zinc compound.

Comparison of these values illustrates the limitations inherent in the use of the expression above as an estimate of the accuracy of the projection. The supposed higher accuracy of the zinc compound (*b* projection) is due to the larger $\Sigma|F_{\text{obs.}}|$ in the denominator of the expression. Again, comparison of the estimate for the zinc *c* and *b* projections suggests that the *b* projection is more accurate than the *c* projection, whereas owing to difficulties caused by twinning it is undoubtedly less accurate. It must be remembered, however, that the zinc atoms contribute only to the even terms in the *c* projection, whereas they contribute to all the terms in the *b* projection, making $\Sigma|F_{\text{obs.}}|$ greater in the latter case. If a comparison of the accuracy of the four projections is required, it is better to compare the quantities $\Sigma||F_{\text{obs.}}|-|F_{\text{calc.}}||$. This can be done as all four projections include approximately the same number of terms, and it is then apparent that the *c* projections are more accurate than the *b* projections.

Description of the structure

From the *b* and *c* axis projections *x*, *y* and *z* co-ordinates were obtained for all the atoms in the unit cell: they are listed in Table 2.

Table 2. *Co-ordinates of atoms in the unit cell*

	Magnesium compound			Zinc compound		
Atom	*x* in A.	*y* in A.	*z* in A.	*x* in A.	*y* in A.	*z* in A.
Mg or Zn	0	0	0	0	0	0
S	2·37	2·44	3·60	2·36	2·44	3·64
O_1	2·30	0·98	3·60	2·29	1·02	3·64
O_2	2·11	3·03	4·85	1·91	3·03	4·79
O_3	1·73	3·03	2·46	1·73	3·03	2·48
$(H_2O)_1$	0·98	1·75	0·13	0·98	1·72	0·08
$(H_2O)_2$	1·24	5·60	1·68	1·35	5·60	1·62
$(H_2O)_3$	1·28	5·60	5·55	1·28	5·60	5·45
C_1	6·85	3·25	3·53	6·84	3·28	3·45
C_2	6·44	1·97	3·93	6·45	1·79	3·95
C_3	5·12	1·80	3·93	5·06	2·72	3·93
C_4	4·22	2·80	3·48	4·13	3·99	3·44
C_5	4·48	4·01	3·03	4·58	4·29	3·06
C_6	5·99	4·29	3·04	5·98	4·29	3·11

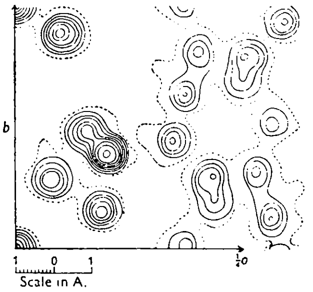

Fig. 1*a*. Fourier projection of magnesium benzene sulphonate along the *c* axis. The contour lines enclosing the resolved carbon and oxygen atoms and water molecules are drawn at intervals of two electrons per A.² and those enclosing the rest at intervals of four electrons per A.² The two-electron line is dotted.

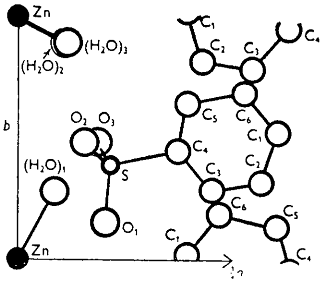

Fig. 1*b*. The projection of the structure of magnesium benzene sulphonate along the *c* axis.

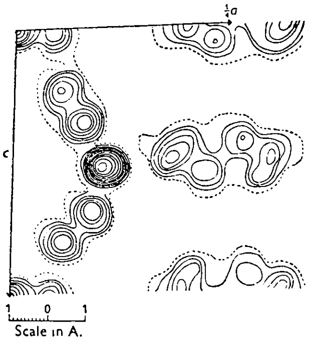

Fig. 2. Fourier projection of magnesium benzene sulphonate along the *b* axis. The contour lines enclosing the magnesium atom and (sulphur + oxygen$_1$) group are drawn at intervals of four electrons per A.² and those enclosing the rest at intervals of two electrons per A.² The two-electron line is dotted. This diagram may be compared with the right-hand side of Fig. 3*a*.

The general nature of the structure is shown in Figs. 1 and 2 which are *c* and *b* axis projections for the magnesium compounds. It is very similar to that suggested by the *b* axis projections of the isomorphous zinc and magnesium toluene sulphonates as published by Hargreaves (1946). The metal atoms are surrounded by regular octahedra of water molecules, the average metal to water distance in the magnesium compound being 2·04 A. and in the zinc compound 2·08 A. The sulphur atom is surrounded by a group consisting of three oxygen atoms of the sulphonate radical and one carbon atom of the benzene ring. The average S–O distance is 1·42 A. in the magnesium compound and 1·39 A. in the zinc compound, the individual values ranging from 1·35 to 1·46 A. There is no reason to suppose that these bond lengths should be different, and averaging over the six separate values from the two compounds the value obtained is 1·41 A. It is interesting to compare this with the value 1·44 A. ± 0·03 obtained by Cox & Brown (1940) for the S–O distance in potassium sulphonate and with 1·44 A. ± 0·02 obtained by Cox & Jeffrey (1942) for the S–O distance in β isoprene sulphone. The S–C distance is 1·90 A. in the magnesium compound and 1·82 A. in the zinc compound. The difference again probably represents experimental error which is large on account of the difficulty in making a good estimate of the z co-ordinate of the carbon atom C_4 (see Fig. 2). The values obtained by Toussaint (1945) for S–C distances, where the sulphur atom is joined to a benzene ring, range from 1·75 to 1·84 A. The disposition of bonds from the sulphur atom appears to be regular tetrahedral, the angles between the bonds being about 109°. The benzene ring is plane and the average distance between adjacent carbon atoms is 1·40 A., individual values ranging from 1·32 to 1·47 A.

Hydrogen bonding occurs between the water molecules surrounding the metal atoms and the oxygen atoms of the sulphonate groups. Each water molecule is linked to one metal atom and to two oxygen atoms of different sulphonate groups, and the bonds lie nearly in a plane. The individual H_2O–O distances range between 2·72 and 2·86 A., the average value being 2·77 A. This may be compared, for example, with the value 2·75 A. ± 0·02 found in the copper sulphate structure (Beevers & Lipson, 1934).

The minimum distances between neighbouring molecules occur between C_3 and C_2 of one ring and C_6 and C_5 of an adjacent ring; these distances are 3·5 and 3·6 A. respectively. Other intermolecular distances exceed 3·9 A.

Discussion on accuracy

High accuracy for the bond lengths stated is not claimed. Inaccuracies arise from two sources.

(a) *Experimental.* The accuracy of the b projections is reduced by the difficulty in estimating intensities of certain ($h0l$) reflexions which partially over-lap reflexions from the twin component. Both c and b projections are affected by the relatively high proportion of missing reflexions due to the small crystals used.

(b) *The nature of the projections.* The b and c projections give two independent values of the x co-ordinate, and, as an atom which is not resolved in one projection appears clearly resolved in the other, it is possible to determine this co-ordinate to within 0·03 A. Only one estimate of the y and z co-ordinates can be made and from Figs. 1 and 2 it can be seen that the y co-ordinates of O_2, O_3, $(H_2O)_2$, $(H_2O)_3$ and the z co-ordinates of S, O_1, C_1, C_4, C_5, C_2 cannot be determined with great accuracy; it is estimated that the error may be as much as 0·2 A., although in most cases it is probably less.

Explanation of twinning

When work on these compounds was started a thorough but unsuccessful search was made for an untwinned crystal. The persistence of the twinning, which takes place on a submicroscopic scale, can be explained in terms of the structure by considering the position of the oxygen atoms and water molecules on opposite sides of the twin boundary. If twinning does not occur, the atomic groups on opposite sides of the (100) plane passing through the origin are related by a centre of symmetry and are situated as shown in Fig. 3a. A twin is produced by rotating a unit cell through 180° about the z axis and the relation between a unit cell and its twin is shown in Fig. 3b. The heights of the atoms are recorded on the diagram.

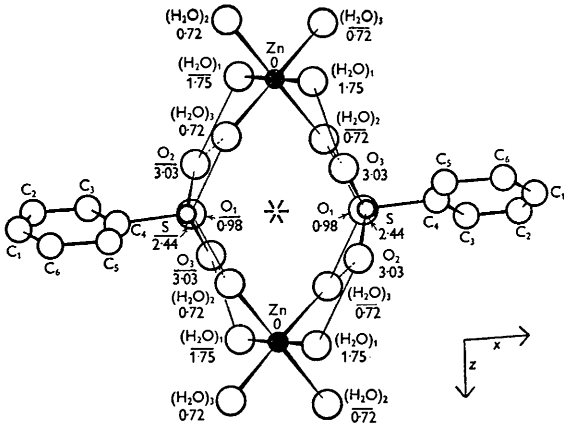

Fig. 3a. Projection of the untwinned structure of magnesium benzene sulphonate along the b axis, in the neighbourhood of a possible twin axis, the c axis of a unit cell. Hydrogen bonds between water molecules and oxygen atoms are drawn with narrow black lines unless the y co-ordinate of the oxygen atom is that shown $\pm b$ when the line is broken. Other bonds are drawn with thicker black lines.

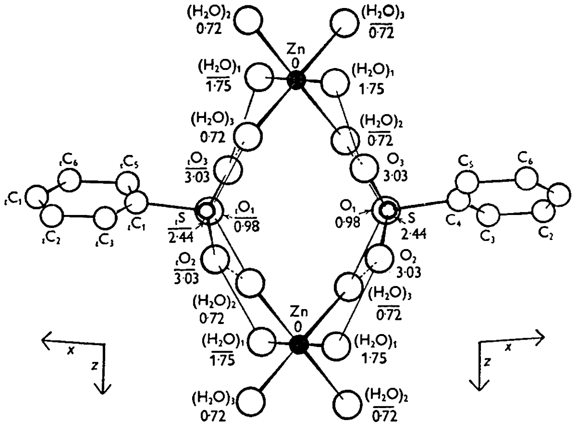

Fig. 3b. Projection of the structure of magnesium benzene sulphonate along the b axis, in the neighbourhood of a twin axis. The component on the left is produced by a rotation of 180° about the c axis of the component on the right. Bonds are shown as in Fig. 3a.

If twinning is to occur with ease, the positions of the atoms in the cells of the twinned structures and untwinned structures must be nearly identical. Comparison of Figs. 3*a* and 3*b* shows that this is so, and that whereas in the untwinned structure $(H_2O)_2$ formed hydrogen bonds with O_1 and O_3, in the twinned structure it can form hydrogen bonds of approximately the same length with $_tO_1$ and $_tO_2$. Similarly $(H_2O)_1$ can form bonds with $_tO_2$ and $_tO_3$ and $(H_2O)_3$ with $_tO_1$ and $_tO_3$.

The explanation can be summarized by saying that the operation of a diad axis with a mirror plane perpendicular to it is equivalent to a centre of symmetry, and since in this structure β is nearly 90° and the plane (001) is almost a plane of symmetry the twinning operation, or rotation of the structure through 180° about the *z* axis, is nearly equivalent to the operation of a centre of symmetry in the actual structure.

We wish to thank Sir Lawrence Bragg and Dr W. H. Taylor for facilities and constant encouragement, and Dr Rodd of Imperial Chemical Industries Ltd., Dyestuffs Division, for suggesting this problem and providing material. One of us (J. M. B.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

References

Beevers, C. A. & Lipson, H. (1934). *Proc. Roy. Soc.* A, **146**, 570.
Cox, E. G. & Brown, C. J. (1940). *J. Chem. Soc.* p. 1.
Cox, E. G. & Jeffrey, G. A. (1942). *Trans. Faraday Soc.* **38**, 241.
Hargreaves, A. (1946). *Nature, Lond.*, **158**, 620.
Toussaint, J. (1945). *Bull. Soc. chim. Belg.* nos. 9–12.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1948). **1**, 92

The accuracy of electron-density maps in X-ray structure analysis.

By E. G. Cox and D. W. J. Cruickshank. *Chemistry Department, The University, Leeds* 2, *England*

(*Received* 5 *March* 1948)

With the increasing application of X-ray crystallography to the study of details of molecular structure, considerable attention is now being given to the accuracy of the electron-density maps obtained in X-ray crystallography. To obtain the maximum value from the results of structure analysis, as of any scientific investigation, it is necessary to eliminate systematic errors, and, having estimated the random errors, to subject any metrical interpretation of the results to standard statistical tests of significance. The systematic errors of electron-density maps are due to the use of finite Fourier series; Booth (1945, 1946*a*, 1947) has shown how these may be corrected by evaluating syntheses in which the coefficients are structure factors calculated from the 'final' atomic co-ordinates. These syntheses have their peaks slightly displaced due to the finite series; corrected co-ordinates are then obtained by applying these displacements with reversed signs to the 'final' co-ordinates.

The random errors are due to the method of correction for finite series, experimental errors, and rounding-off errors in computation. In the case of three-dimensional syntheses it can be shown that the experimental and finite-series-correction errors lead to a standard deviation (s.d.) of the error in the slope of the electron density in the *x*-direction (at any point in the unit cell) given by

$$\sigma\,(A_x)=\frac{2\pi}{aV}\left[\sum_3 mh^2\overline{\Delta F}^2\right]^{\frac{1}{2}}, \qquad (1)$$

and to similar expressions for $\sigma\,(A_y)$ and $\sigma\,(A_z)$. In this and following expressions ΔF is the difference between observed and calculated structure factors; $\sigma\,(U)$ or σ_u is a s.d.; A_p and A_{pq} are first and second differentials respectively of the electron-density ρ; h, k and l are Miller indices (for brevity the subscripts in ΔF_{hkl} are omitted); a, b and c are cell dimensions; and V is the volume of the unit cell ($=abc\sin\beta$ in the monoclinic case). In (1) each independent ΔF appears once only and m is the multiplicity of the F concerned; alternatively, the contents of the bracket may be written $\sum_3 h^2\overline{\Delta F}^2$, the summation then being over every plane in the synthesis. The s.d.'s of the errors in the density and second differentials are

$$\sigma\,(\rho)=\frac{1}{V}\left[\sum_3 m\overline{\Delta F}^2\right]^{\frac{1}{2}},\quad \sigma\,(A_{xy})=\frac{4\pi^2}{abV}\left[\sum_3 mh^2k^2\overline{\Delta F}^2\right]^{\frac{1}{2}}.$$

The corresponding formulae for plane projections are exactly analogous. The above results are for centrosymmetric structures; for non-centrosymmetric structures they must be multiplied by $\sqrt{2}$.

The s.d.'s of a peak position are obtained, after substituting $\sigma\,(A_x)$, $\sigma\,(A_y)$ and $\sigma\,(A_z)$, by statistical solutions of Booth's (1946*b*) differential equations for peak positions. For spherically symmetrical peaks in a monoclinic cell this gives

$$\sigma_y=\sigma\,(A_y)/A_{yy}$$

and

$$\sigma_x=[\overline{\sigma\,(A_x)}^2-\cos^2\beta\,\overline{\sigma\,(A_z)}^2\,]^{\frac{1}{2}}/A_{xx}\sin^2\beta,$$

with a similar expression for σ_z, where A_{pq}, the second differential at the peak, is obtained either from the