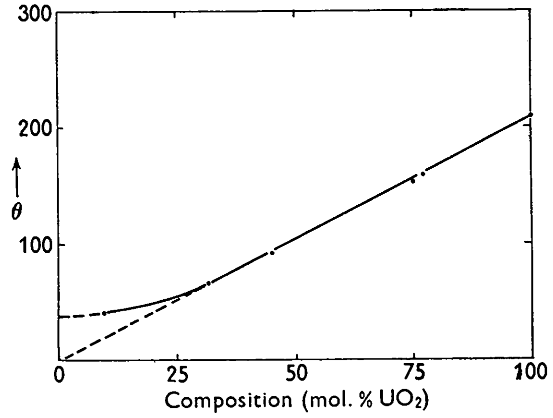

Fig. 3. Paramagnetic Curie temperature as a function of composition.

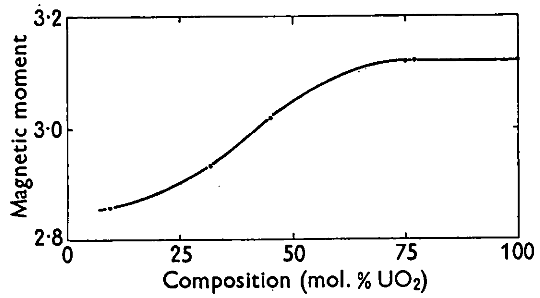

Fig. 4. Magnetic moment as a function of composition.

(Corliss, Delabarre & Elliott, 1950). This interpretation is not the only one, however, and further work with other systems is needed to give better understanding of the importance of the several modes of exchange (Zener, 1951; Anderson, 1950). Below 31 mol. % UO_2 deviation from linearity was observed. The effect seems to be real, for it was found in three solid solutions containing 5, 9 and 15 mol. % UO_2. Data for the 5 and 15 mol. % solutions have not been included because the X-ray photographs indicated somewhat less satisfactory solid-solution formation than in the other cases.

The suggestion we have here of a residual θ at high dilution indicates a crystalline field of considerable magnitude. This in turn casts some doubt on the calculation of magnetic moments from the Curie constants, for it is well known that the Weiss–Curie law is only approximate in this case (Van Vleck, 1932, Chap. 11).

We wish to thank Dr Raymond Stoenner for making the chemical analyses of the materials, and Drs Jacob Bigeleisen, Lester Corliss, Julius Hastings and Max Wolfsberg for their interest in the problem.

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A Refinement of the Crystal Structure of Potassium Benzylpenicillin

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Better crystals of potassium benzylpenicillin have been obtained which give many more reflexions than were used in the previous analysis. The terms derived from these have been included in one further stage of refinement of the atomic coordinates by Fourier synthesis.

Introduction

The X-ray analyses of sodium and potassium benzylpenicillin were first undertaken to assist in determining the chemical structure of penicillin at a time when this was largely unknown (Crowfoot, Bunn & Rogers-Low, 1949, p. 310). The details of the crystal structures of these two salts, as eventually derived from the second three-dimensional Fourier synthesis in each case, proved amply sufficient to show the bonding arrangements within the molecule, but abnormal interatomic distances and rather large fluctuations in the background level of electron density showed that there were still imperfections in the series. That this should be so is obvious first for the reason that the experimental observations were limited by the poor quality of the original crystals, and secondly because the space-groups of both crystals lack centres of symmetry so that the atomic coordinates require more prolonged refinement, being dependent on phase angles rather than on signs of the Fourier coefficients. These imperfections were immaterial to the purpose of the investigation, which had been served when it was demonstrated that the molecule had the thiazolidine β-lactam configuration.

The preparation of better crystals of the potassium salt at a later date made it apparent that the former source of inaccuracy could now be greatly reduced, and it was felt to be worth while to collect the additional data and carry out one further refinement of the series. The structure is not of a type suitable for very accurate study, which would occupy an inordinate length of time and provide little fundamental information which could not be more easily derived from simpler systems. The further work to be described here was undertaken to round off the investigation by applying a first correction to the approximate atomic coordinates previously published. It will be shown that a distinct improvement in the appearance of the electron-density map and in the 'normality' of the bond lengths results from this correction, but the refinement of the series is still incomplete.

Experimental

The crystal used for X-ray photography was grown from solution in *n*-butyl alcohol and water by B. W. Low, and measured about $1{\cdot}5\times0{\cdot}25\times0{\cdot}25$ mm., the greatest length being parallel to the *b* axis, and the cross-section perpendicular to this axis being roughly hexagonal. Equi-inclination Weissenberg photographs were taken of the layers $k = 0, 1, \ldots, 4$ of the reciprocal lattice. The crystal was then broken and a fragment of length about 0·3 mm. was remounted and photographs were taken for the layers $h=0, 1, \ldots, 6$. A few reflexions with $h > 6$ and $k > 4$ were recorded on oscillation photographs about the *c* axis. Intensities of all reflexions were estimated visually and reduced to structure amplitudes in the usual manner; simple corrections for variation of size of reflexion and for absorption were applied. The structure amplitudes were brought to a roughly absolute scale by comparison with the calculated values, and in the cases of a few reflexions with very small θ values, which were not recorded on the new series of photographs, the original absolute values were then adopted. In all cases where both old and new values were available these were checked one against the other; for very strong reflexions the new values were in general somewhat lower than the old (presumably owing to greater extinction) and again the old values were adopted. The number of reflexions estimated in the new series was 1680, compared with 650 in the old series. While some of the extra reflexions were relatively near-in weak ones, which had previously been considered absent, the majority were in the range $d < 1{\cdot}2$ Å, where the old series of photographs had shown practically no reflexions at all owing to the imperfect nature of the crystals. In the new series the reflexions extended to the edge of photographs with copper radiation (becoming rather diffuse towards the end of the sequence, however). A test photograph with molybdenum radiation indicated that a few more reflexions could have been recorded in this way, but owing to difficulty in indexing when the radiation was markedly impure and the reflexions very close together ($\lambda/c = 0{\cdot}024$) this was not attempted.

Fourier synthesis

Using the atomic coordinates given in Table 15(*c*) of the work cited above,* the A_c and B_c parts of the structure amplitudes F_c were calculated for all reflexions within the range of copper radiation. The trigonometric parts were calculated on desk multipliers, and a system of checking applied as described in the appendix. The *f* functions used were as before, namely for potassium and sulphur the Hartree values modified by a temperature factor $B = 3{\cdot}5$ Å^2, and for carbon, nitrogen and oxygen the empirical curve given by Robertson with suitable weights. The phase angles $\alpha = \tan^{-1} B_c/A_c$ were not calculated explicitly, but the observed structure amplitudes F_o were resolved into A_o and B_o, where

$$A_o/A_c = B_o/B_c = |F_o|/|F_c| \ .$$

From this it follows that $A_o = |F_o| \cos \alpha$ and $B_o = |F_o| \sin \alpha$, which quantities are required in the Fourier synthesis. This resolution can be performed very rapidly at the same time as A_c and B_c are compounded to give F_c with the help of graph paper and Pythagoras's theorem.

The Fourier synthesis was evaluated over the repeating volume at intervals of $a/60$, $b/30$, $c/120$ by the use of punched-card methods, and contour maps were constructed for each section perpendicular to the *b* axis. Fig. 1 is a view of a molecule made up from these maps by the selection of the contours in the section nearest to each atomic centre. A projection of the electron density on a plane perpendicular to the *a* axis was also calculated in order to discover how much extra detail could be resolved because of the inclusion

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* Throughout this work the screw axes of the space group $P2_12_12_1$ were chosen to lie along the lines $0, \frac{1}{4}, z$; $x, 0, \frac{1}{4}$; $\frac{1}{4}, y, 0$ rather than the more conventional arrangement along the lines $\frac{1}{4}, 0, z$; $x, \frac{1}{4}, 0$; $0, y, \frac{1}{4}$, and in the present refinement this has been continued. The equivalent general positions are x, y, z; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}+x, \bar{y}, \frac{1}{2}-z$; $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$.

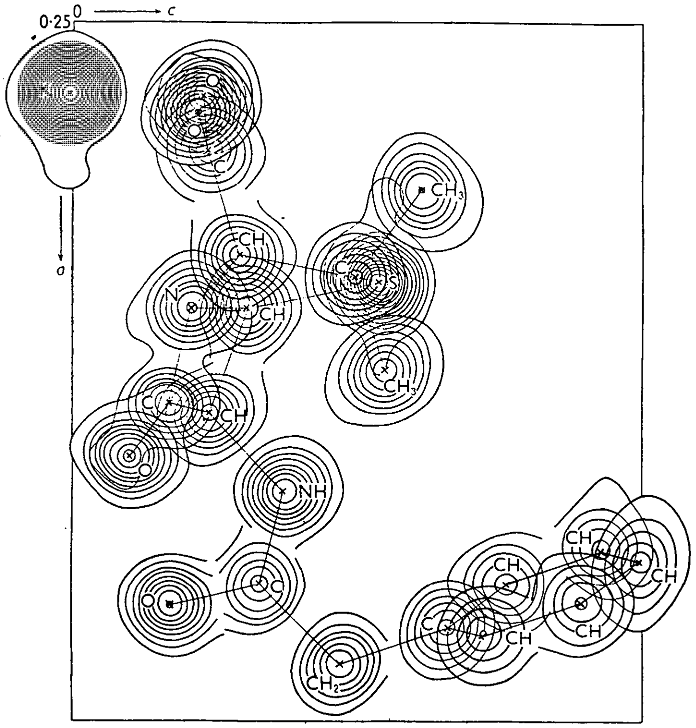

Fig. 1. Composite diagram of molecule composed of the contours in sections passing nearest to the atomic centres. Contours at intervals of 1 e.Å^{-3}, except for potassium ion and sulphur atom, where the interval is doubled.

of more terms. The projection on a plane perpendicular to the *b* axis was not recalculated because the original series was practically complete in this zone. In considering the results thus obtained the following points should be borne in mind:

(i) The coordinates used in the calculations of the phases were in most cases those derived from the previous three-dimensional synthesis, but about twenty of the parameters were adjusted in order to give more plausible bond lengths (in particular in the benzene ring).

(ii) The phases not only of the 650 terms previously used but also of the 1030 additional terms have to be based on these parameters, in the deduction of which only the first group had been used.

The results do not therefore constitute an example of pure Fourier refinement, and it is not possible to use them as a test of the validity of the *n*-shift rule (Shoemaker, Donohue, Schomaker & Corey, 1950).

Results

Comparison of the new electron-density maps with the previous ones shows that there is significant improvement in a number of respects. In the projection on a plane perpendicular to the *a* axis three atoms previously unresolved can now be clearly seen (O_{13}, C_6, C_{18}) (Fig. 2), and it is likely that refinement could have been carried further in the centrosymmetrical projections before recourse to three-dimensional syntheses. As shown in Table 1, the peak heights have increased on an average by over 30%, and are now more nearly in accord with the atomic numbers of the atoms concerned. There is still a marked tendency for the peaks in the benzene ring to be low and broad, which may be attributed to the greater

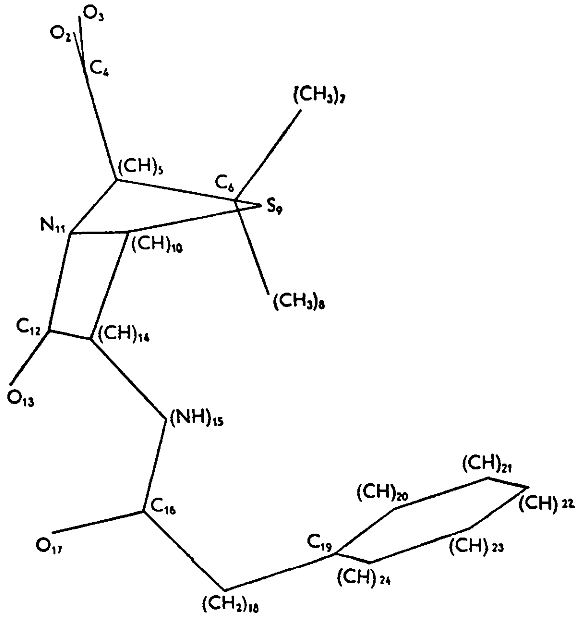

Fig. 2.

Table 1. *Heights of maxima of electron density*

		2nd synthesis	3rd synthesis
1	K	24·0 e.$Å^{-3}$	32·4 e.$Å^{-3}$
3	O	8·1	10·1
3	O	8·2	10·8
4	C	5·1	6·8
5	CH	6·1	7·4
6	C	5·5	7·3
7	CH_3	5·1	7·1
8	CH_3	5·6	7·0
9	S	19·4	26·3
10	CH	5·6	7·7
11	N	6·6	8·2
12	C	5·0	6·9
13	O	6·5	9·4
14	CH	5·0	7·3
15	NH	6·9	8·8
16	C	5·0	6·2
17	O	6·6	9·3
18	CH_2	5·5	6·9
19	C	5·0	6·5
20	CH	4·4	5·7
21	CH	4·1	5·2
22	CH	3·6	5·4
23	CH	4·1	5·1
24	CH	4·3	5·1

Table 2. *Final atomic coordinates*

		x/a	y/b	z/c
1	K	0·350	0·528	−0·001
2	O	0·381	−0·127	0·055
3	O	0·358	0·205	0·058
4	C	0·433	0·044	0·060
5	CH	0·585	0·061	0·073
6	C	0·616	0·094	0·124
7	CH_3	0·491	0·015	0·154
8	CH_3	0·752	−0·019	0·137
9	S	0·624	0·372	0·134
10	CH	0·660	0·442	0·077
11	N	0·657	0·243	0·052
12	C	0·796	0·247	0·041
13	O	0·871	0·121	0·025
14	CH	0·810	0·467	0·060
15	NH	0·923	0·506	0·092
16	C	1·054	0·577	0·082
17	O	1·083	0·617	0·042
18	CH_2	1·167	0·569	0·118
19	C	1·117	0·521	0·164
20	CH	1·053	0·686	0·191
21	CH	1·000	0·635	0·231
22	CH	1·020	0·425	0·249
23	CH	1·077	0·267	0·224
24	CH	1·123	0·318	0·180

amplitude of vibration where the intermolecular forces are weak. Imperfections in the previous series caused fluctuations in the background electron density of the order of 1·5 e.$Å^{-3}$, and in the neighbourhood of the potassium ion these rose to 2·5 e.$Å^{-3}$; the corresponding figures for the new synthesis are 0·8 and 1·5 e.$Å^{-3}$, respectively.

The maxima of all peaks were located by parabolic interpolation using $3 \times 3 \times 3$ entries, with the largest recorded entry as the central one of the 27. To a close

Table 3. *Bond lengths in the molecule and distances within the coordination sphere of the potassium ion*

		2nd synthesis	3rd synthesis
2– 4	Carboxyl O–C	1·24 Å	1·21 Å
3– 4	Carboxyl O–C	1·21	1·25
4– 5	Carboxyl C–CH	1·50	1·48
5– 6	CH –C	1·67	1·59
6– 7	C –CH_3	1·47	1·55
6– 8	C –CH_3	1·48	1·52
6– 9	C –S	1·78	1·80
9–10	S –CH	1·81	1·84
10–11	CH –N	1·51	1·47
11– 5	N –CH	1·48	1·47
11–12	N –C of β-lactam CO	1·34	1·34
12–13	C –O of β-lactam CO	1·18	1·17
12–14	C –CH	1·47	1·52
14–10	CH –CH	1·49	1·51
14–15	CH –NH	1·47	1·46
15–16	NH –C of amide CO	1·39	1·33
16–17	C –O of amide CO	1·23	1·25
16–18	C –CH_2	1·55	1·52
18-19	CH_2–C in benzene ring	1·50	1·52
19–20	Benzene C–CH	1·44	1·45
20–21	Benzene CH–CH	1·47	1·36
21–22	Benzene CH–CH	1·39	1·45
22–23	Benzene CH–CH	1·32	1·37
23–24	Benzene CH–CH	1·42	1·42
24–19	Benzene C –CH	1·47	1·38
K–O(2)	of carboxyl group at $x, (1+y), z$	2·83	2·81
K–O(3)	of carboxyl group at x, y, z	2·75	2·74
K–O(2)	of carboxyl group at $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$	2·89	2·88
K–O(3)	of carboxyl group at $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$	2·82	2·83
K–O(13)	of β-lactam group at $\frac{3}{2}-x, \frac{1}{2}+y, \bar{z}$	2·75	2·76
K–O(17)	of amide group at $\frac{3}{2}-x, -\frac{1}{2}+y, \bar{z}$	2·98	2·96
K–O(17)	of amide group at $-1+x, y, z$	2·89	2·91
	Mean K–O	2·84	2·84

approximation all peaks were found to have spherical symmetry over the volume surveyed, except those of the benzene ring which were somewhat ellipsoidal. The atomic coordinates thus deduced are listed in Table 2; compared with the corresponding coordinates derived from the previous synthesis there is a mean shift of $0{\cdot}05_6$ Å (maximum $0{\cdot}15_8$ Å for C_{21}), while compared with the coordinates used in the calculation of the phases for this synthesis (see (i) above) the mean shift is $0{\cdot}04_1$ Å (maximum $0{\cdot}08_5$ Å for C_7). The resulting bond lengths are shown in Table 3, and the bond angles in Table 4. Taking those bonds which might be expected on *a priori* grounds to approximate to pure single character, the previous coordinates gave a mean departure of $0{\cdot}04_4$ Å (maximum 0·13 Å for C_5–C_6), whereas the revised figures are $0{\cdot}01_8$ Å maximum 0·05 Å for C_5–C_6).* Similarly the mean departure from 1·39 Å of the sides of the benzene ring has fallen from $0{\cdot}05_2$ Å to $0{\cdot}03_5$ Å. There are small, but probably real, deviations from planarity in the carboxyl group, the amido group, and the β-lactam ring owing to the exigencies of packing. Compared with these deviations, those in the benzyl group are now quite small. As in the case of other five-membered rings recently investigated, in the thiazolidine ring four of the atoms lie close to a plane from which the fifth is displaced about 0·5 Å.

Table 4. *Bond angles*

2– 4– 3	O –C –O	120·5°
2– 4– 5	O –C –CH	119·5
3– 4– 5	O –C –CH	120
4– 5–11	C –CH –N	116
4– 5– 6	C –CH –C	119
11– 5– 6	N –CH –C	103·5
5– 6– 9	CH –C –S	108
7– 6– 8	CH_3 –C –CH_3	109
5– 6– 7	CH –C –CH_3	113
5– 6– 8	CH –C –CH_3	109·5
7– 6– 9	CH_3 –C –S	104·5
8– 6– 9	CH_3 –C –S	113
6– 9–10	C –S –CH	94·5
9–10–11	S –CH –N	105·5
10–11– 5	CH –N –CH	118
9–10–14	S –CH –CH	121
5–11–12	CH –N –C	124
10–11–12	CH –N –C	95
11–12–14	N –C –CH	90·5
12–14–10	C –CH –CH	87
14–10–11	CH –CH –N	86·5
11–12–13	N –C –O	132
13–12–14	O –C –CH	137
10–14–15	CH –CH –N	118
12–14–15	C –CH –NH	118·5
14–15–16	CH –NH –C	124·5
15–16–17	NH –C –O	120·5
17–16–18	O –C –CH_2	123
15–16–18	NH –C –CH_2	117
16–18–19	C –CH_2 –C	117·5
18–19–20	CH_2 –C –CH	119·5
18–19–24	CH_2 –C –CH	120·5
20–19–24	CH –C –CH	120
19–20–21	C –CH –CH	118·5
20–21–22	CH –CH –CH	120·5
21–22–23	CH –CH –CH	121
22–23–24	CH –CH –CH	117·5
23–24–19	CH –CH –C	122

The conclusion may be drawn that the new atomic coordinates are definitely more accurate than the old, but that the atoms of the benzene ring remain less accurately placed than the rest of the molecule. It is not felt that any useful purpose would be served in attempting to place more definite limits on the errors in the atomic coordinates. The conclusions previously reached with regard to the stereochemistry of the molecule have been confirmed and the evidence for them further strengthened by the demonstration that the structure proposed is refineable, i.e. that the displacements of the peaks in the synthesis tend to be in directions which regularize the anomalies. Structure amplitudes have not been recalculated from the new atomic coordinates and therefore it is not possible to quote a value of the disagreement factor for the final structure. The R factor before the final Fourier synthesis had increased to 0·24 from the value of 0·19 calculated on 650 terms at the previous stage, owing to the inclusion of the additional terms, most of which are of small magnitude.

One unexplained feature of the Fourier sections is the appearance of 'ghost' peaks at positions related to the potassium and sulphur peaks by a translation of $\frac{1}{2}b$, their heights being about $\frac{1}{17}$ and $\frac{1}{10}$ of the respective main peaks (i.e. about 2–3 e.Å^{-3}). These are higher than the general background fluctuations and form no part of the postulated molecule. Similar peaks occurred on the previous synthesis which was based on essentially different experimental observations, so it is unlikely that the effect is caused by the application of incorrect scaling factors to sets of $F(hkl)$ with constant k. It may be a consequence of the still incomplete refinement of the series, but in this case the heights of the ghost peaks might be expected to have diminished in the course of the last refinement, and this is not so.

I am grateful to Mrs D. M. Hodgkin for the invitation to carry out this work, and to the Department of Scientific and Industrial Research for a generous grant covering the undertaking. The National Physical Laboratory, Teddington, kindly performed the major part of the calculation of structure amplitudes (Mr E. T. Goodwin, to whom I am also indebted for the system of checking described in the appendix) and the computation of the Fourier synthesis (Mr T. B. Boss). Miss E. G. Crowfoot again gave invaluable help in the preparation of the contour maps and the diagram in this paper.

Editorial note.—Tables of A_c, A_o, B_c, B_o, F_c and F_o for all hkl values have been deposited with the Institute of Physics, 47 Belgrave Square, London S.W. 1, England. Application to inspect these tables should be made to the Secretary of the Institute.

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* Lengths of single bonds taken to be: C–C 1·54, C–N 1·47, S–C 1·79 Å.

APPENDIX

The summations involved in the evaluation of the structure amplitudes are of the type

$$\sum_{\substack{i\\1}}^{N} Z_i \substack{\cos\\ \sin} 2\pi hx_i \substack{\cos\\ \sin} 2\pi ky_i \substack{\cos\\ \sin} 2\pi lz_i$$

over the whole molecule (excepting the potassium ion and sulphur atom which are treated separately). The variation of scattering amplitude with θ was introduced after these preliminary summations.

For each atom the trigonometrical factors required are listed, and the sums

$$\sum_{\substack{h\\0}}^{H} \substack{\cos\\ \sin} 2\pi hx_i$$

etc. are derived. These sums provide the checks according to the formulae

$$T_1 \equiv \sum_{\substack{h\\0}}^{H} \cos 2\pi hx_i = \tfrac{1}{2} \cos 2\pi Hx_i + \tfrac{1}{2} \cot \pi x_i \sin 2\pi Hx_i + \tfrac{1}{2}\ ,$$

$$T_2 \equiv \sum_{\substack{h\\0}}^{H} \sin 2\pi hx_i = \tfrac{1}{2} \cot \pi x_i (1 - \cos 2\pi Hx_i) + \tfrac{1}{2} \sin 2\pi Hx_i .$$

If however $x_i \leq 0{\cdot}1$ or $x_i \geq 0{\cdot}9$ the magnitude of $\cot \pi x_i$ is large and the rounding-off errors disguise any real error in the tabulated values. In such cases the following formulae are to be preferred:

$$\sum_{\substack{h\\0}}^{H} (-1)^h \cos 2\pi hx_i = \tfrac{1}{2} + \tfrac{1}{2}(-1)^H \cos 2\pi Hx_i - \tfrac{1}{2}(-1)^H \sin 2\pi Hx_i \tan \pi x_i\ ,$$

$$\sum_{\substack{h\\0}}^{H} (-1)^h \sin 2\pi hx_i = -\tfrac{1}{2} \tan \pi x_i + \tfrac{1}{2}(-1)^H \tan \pi x_i \cos 2\pi Hx_i + \tfrac{1}{2}(-1)^H \sin 2\pi Hx_i .$$

The various factors having been checked in this way, the products

$$\substack{\cos\\ \sin} 2\pi hx_i \substack{\cos\\ \sin} 2\pi ky_i$$

are formed and checked in a similar way, e.g.

$$T_3 \equiv \sum_{\substack{h\\0}}^{H} \cos 2\pi hx_i \cos 2\pi ky_i \quad (k \text{ constant})$$

$$= \cos 2\pi ky_i \sum_{\substack{h\\0}}^{H} \cos 2\pi hx_i = T_1 \cos 2\pi ky_i .$$

The third stage, in which the triple products are formed, is checked in the same manner again, i.e.

$$T_4 \equiv \sum_{\substack{h\\0}}^{H} Z_i \cos 2\pi hx_i \cos 2\pi ky_i \cos 2\pi lz_i = Z_i T_3 \cos 2\pi lz_i . \quad (k, l \text{ constant})$$

For the final summation of these products, the check applied was of the form

$$T \equiv \sum_{\substack{h\\0}}^{H} \left(\sum_{\substack{i\\1}}^{N} Z_i \cos 2\pi hx_i \cos 2\pi ky_i \cos 2\pi lz_i \right) = \sum_{\substack{i\\1}}^{N} T_4 . \quad (k, l \text{ constant})$$

The nature of the expressions for the structure factors makes it convenient to separate odd and even values of the indices at various stages, but this has been omitted here in order to avoid confusion.

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The Crystal Structure of Realgar

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The crystal structure of realgar, AsS, has been worked out by the Fourier-synthesis method, using Weissenberg photographs (Cu $K\alpha$ $\lambda = 1{\cdot}54$ Å). The signs for F's were initially derived by the phase-inequality relations of Harker & Kasper. The unit cell has $a = 9{\cdot}27$, $b = 13{\cdot}50$, $c = 6{\cdot}56$ Å, $\beta = 106°\ 37'$. The space group is $P2_1/n$. The unit cell contains sixteen AsS. The structure is built up of separate As_4S_4 molecules of the cradle type held together by van der Waals forces. The cleavage and the relationships to orpiment, As_2S_3, are explained in terms of the structure.

Introduction

The crystal structure of realgar, notwithstanding its simple chemical composition, defeated our repeated attempts to work it out by the usual methods. The absence of any peculiar regularity in the X-ray reflexions, other than the space-group criteria, is partly responsible for this situation. However, the