of observation, the values of I, I_l and J found for non-equatorial diffuse spots must be multiplied by $\sec^2 \chi$, $\sec \chi$ and 1 respectively.

Table 1 summarizes the values found for the partial inclination factors by which the observed quantities I', I_l' and J' are to be multiplied. The total inclination factor is obtained by multiplying the three factors along the appropriate horizontal line.

The total factor for J is similar to the 'film-absorption factor' found by Cox & Shaw (1930) in their study of integrated reflexion. It is plotted in Fig. 4 (curve (b)) as a function of $\zeta = \sin \chi$, using Cox & Shaw's experimental values for C and (μt). In the same figure, the corresponding inclination factor for I has also been plotted (curve (a)).

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The Crystal and Molecular Structure of B_4Cl_4

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The molecule B_4Cl_4 consists of a nearly regular tetrahedron of boron atoms surrounded by a larger, nearly regular tetrahedron of chlorine atoms with B–Cl single bonds (1·70 Å) directed away from the center of the tetrahedra. The molecular symmetry is D_{2d}–$\bar{4}2m$, but differs only slightly from T_d–$\bar{4}3m$, and the average B–B distance is 1·70 Å. Molecular centers are at 0, 0, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0 in the space group D_{4h}^{15}–$P4_2/nmc$, with $a = b = 8{\cdot}09$ Å and $c = 5{\cdot}45$ Å.

The unusual compound, B_4Cl_4, has recently been discovered by Urry, Wartik & Schlesinger (1952), who have kindly supplied us with a sample for molecular structure determination by the X-ray diffraction method. This study is part of a general program of structure determinations of electron deficient compounds of boron.

The sample was distilled carefully into thin-walled pyrex capillaries in a vacuum line previously flushed with BF_3 in order to remove reactive compounds adsorbed on the glass surfaces. The samples in these capillaries were stored about two weeks at about 35° C. with a small temperature gradient in the capillary in order to grow a single crystal about 0·3 by 0·5 by 1·2 mm. The symmetry of the tetragonal reciprocal lattice is D_{4h}–$4/mmm$. The unit-cell dimensions of

$$a = b = 8{\cdot}09 \pm 0{\cdot}02 \quad \text{and} \quad c = 5{\cdot}45 \pm 0{\cdot}01 \text{ Å}$$

lead to a unit cell volume of 356 Å^3. Assuming the usual values for van der Waals radii this unit cell must contain two molecules of B_4Cl_4, and the crystal therefore has the reasonable calculated density of 1·724 g.cm.$^{-3}$. Because of the reactivity of the compound no independently measured value is known.

Buerger precession photographs of the $\{0kl\}$, $\{hhl\}$, $\{h,2h,l\}$ and $\{h,3h,l\}$ zones, and Weissenberg photographs of the $\{hk0\}$ zone were taken with Mo $K\alpha$ radiation. Intensities were estimated visually with the aid of standard scales prepared by timed exposures of a reflection from the crystal, and timed exposures of the various zones or multiple-film techniques were employed as additional aids. The revised Lorentz factor (Waser, 1951) was used in the reduction of the intensities of the precession photographs. Systematic extinctions of hhl when l is odd and of $hk0$ when $h+k$ is odd lead uniquely to the space group D_{4h}^{15}–$P4_2/nmc$. The presence of only two molecules in this space group requires the molecular symmetry to be D_{2d}–$\bar{4}2m$.

Both packing considerations and the presence of fairly strong reflections which would be approximately extinguished by choice of positions 8(e) or 8(f) lead to the positions 8(g) (*Internationale Tabellen*, 1935, p. 222) for the chlorine atoms. The x and z parameters in these positions,

$$0, x, z;\; x, 0, \bar{z};\; \tfrac{1}{2}, \tfrac{1}{2}+x, \tfrac{1}{2}-z;\; \tfrac{1}{2}+x, \tfrac{1}{2}, \tfrac{1}{2}+z;$$
$$0, x, \bar{z};\; \bar{x}, 0, \bar{z};\; \tfrac{1}{2}, \tfrac{1}{2}-x, \tfrac{1}{2}-z;\; \tfrac{1}{2}-x, \tfrac{1}{2}, \tfrac{1}{2}+z,$$

were estimated by trial-and-error methods with the aid of charts described by Bragg & Lipson (1936). The electron-density projections along [001] and [100] were then synthesized with the use of signs evaluated from the chlorine contributions only. Although no assumption had been made of the boron positions, these atoms appeared on the electron-density maps in

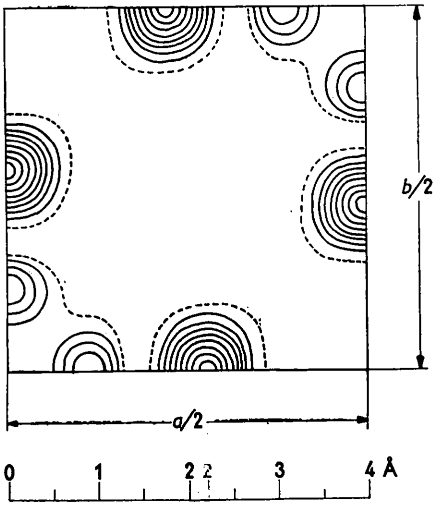

Fig. 1. Electron-density projection along the *c* axis. Contours are at 2 (broken), 6, 10, 14... e.Å^{-2} except around the resolved boron atoms, for which contours are at 2 (broken), 4, 6, 8 e.Å^{-2}.

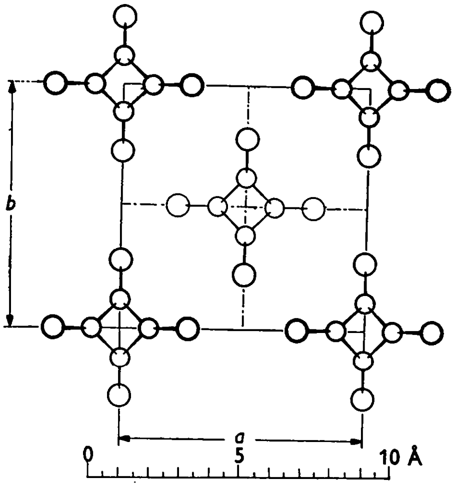

Fig. 2. Projection of the structure of B_4Cl_4 on (001). The complete unit cell is shown.

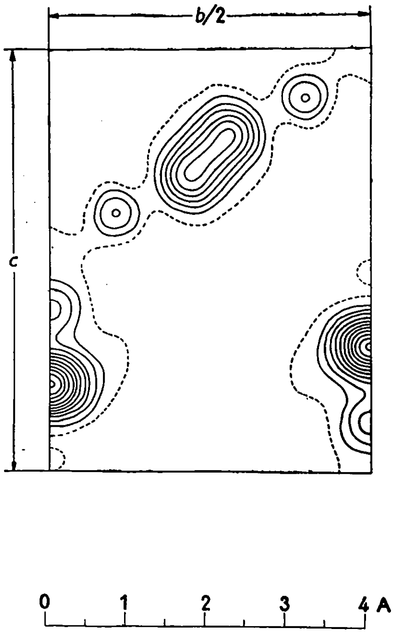

Fig. 3. Electron-density projection along the *a* axis. Contours are at levels as described for Fig. 1.

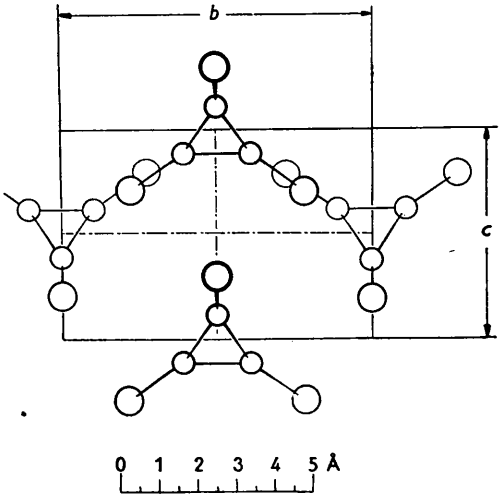

Fig. 4. Projection of the structure of B_4Cl_4 on (100). The complete unit cell is shown.

positions 8(*g*), and subsequent refinement was then carried out until no further sign changes occurred. These final Fourier projections are shown in Fig. 1 and 3, their interpretation is given in Figs. 2 and 4, and a plan of the molecule is shown in Fig. 5. Similar Fourier projections, carried out with the use of calculated structure factors as coefficients, gave back-shift corrections for termination of the series, but resulted in no further sign changes. In addition, the parameters and their probable errors were determined by least squares with the use of the method and weighting factors described by Hughes (1941). The

Table 1. *The atomic parameters of* B_4Cl_4

	{*hk*0} Fourier	{0*kl*} Fourier	{0*kl*} least squares	Weighted average	Probable errors
x_{Cl}	0·2750	0·2750	0·2761	0·2756	0·0010
z_{Cl}	—	0·2041	0·2058	0·2050	0·0009
x_B	0·107	0·104	0·1036	0·1043	0·0037
z_B	—	0·385	0·3896	0·3873	0·0041

Table 2. *Observed and calculated structure factors**

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	9·6	−8·9	024	2·4	2·2	0,10,1	2·2	3·0
400	28·2	30·1	025	< 2·1	1·1	0,10,2	2·0	−2·2
600	2·4	−4·9	026	< 2·1	−0·1	121	11·8	−10·8
800	7·4	9·0	027	2·2	−1·9	122	5·6	−5·6
10,0,0	3·4	−4·6	031	5·1	6·1	123	11·1	−12·5
110	4·4	−2·6	032	< 1·7	−0·3	124	6·9	−7·2
130	9·0	7·6	033	12·0	12·5	125	4·6	−4·0
150	11·6	11·6	034	5·0	−5·0	126	4·2	−3·9
170	7·6	6·9	035	9·4	9·5	241	22·5	−21·2
190	< 4·8	3·5	036	3·2	−3·3	242	< 1·6	1·2
220	41·0	−38·7	041	5·2	−6·7	243	11·8	−12·8
240	3·6	3·9	042	19·0	19·7	244	< 1·8	−0·5
260	15·4	−15·6	043	3·2	1·9	245	< 1·8	−1·7
280	< 4·4	2·7	044	5·6	5·4	246	< 1·6	0·1
330	13·4	−12·9	045	2·2	0·9	361	< 1·7	−1·1
350	5·8	−5·7	046	2·0	−1·0	362	3·8	3·7
370	8·2	−8·4	051	< 1·8	−1·0	363	< 1·8	−0·2
390	< 4·8	−1·6	052	4·4	5·8	364	4·6	4·4
440	13·8	14·0	053	< 2·0	−1·9	365	< 1·6	1·1
460	< 2·8	0·9	054	10·4	10·7	481	< 1·8	−1·3
480	4·2	4·9	055	< 2·1	−1·3	482	3·3	3·8
550	15·6	15·3	056	7·1	6·3	483	2·4	−1·9
570	< 3·2	−0·3	061	16·1	17·4	112	6·9	5·9
660	7·8	−7·9	062	< 2·0	−2·9	114	4·7	4·4
680	< 3·6	1·0	063	3·6	5·2	116	< 1·8	−0·8
770	6·2	−6·0	064	< 2·0	−0·5	222	24·2	−26·1
002	35·6	33·7	065	< 2·0	0·2	224	8·3	−9·6
004	5·2	4·1	071	3·0	3·0	226	< 1·8	1·8
006	< 2·1	−0·8	072	2·0	1·2	332	10·8	−9·8
011	4·8	2·2	073	6·1	7·5	334	5·3	−3·9
012	12·4	11·7	074	< 2·1	−0·7	336	< 1·6	0·7
013	6·6	−6·4	075	6·4	6·3	442	14·0	13·2
014	11·4	11·0	081	2·9	−4·2	444	5·8	5·8
015	8·9	−8·3	082	3·4	5·5	552	8·2	7·6
016	5·6	5·4	083	< 2·0	−1·6	554	< 1·5	0·7
017	2·4	−2·5	084	< 2·0	0·7	662	3·7	−4·3
021	48·6	46·2	901	2·4	1·3	664	< 1·8	−0·5
022	< 1·6	−0·2	902	4·0	4·2	772	4·9	−4·4
023	16·2	15·1	903	3·1	0·7			

* The origin is at ¼, ¼, ¼ with respect to the origin in the *Internationale Tabellen*. The values from which these structure factors were calculated are $x_{\mathrm{Cl}} = 0{\cdot}275$, $z_{\mathrm{Cl}} = 0{\cdot}204$, $x_{\mathrm{B}} = 0{\cdot}105$ and $z_{\mathrm{B}} = 0{\cdot}385$. The differences between structure factors calculated from these and from our final parameters (Table 1) are well within our uncertainties in the F_o's.

probable errors in the parameters were calculated from the residuals $\sqrt{w}.|F_c-F_o|$ on the assumption that these differences are random errors. The final parameters and their corresponding probable errors are summarized in Table 1. The Fourier results have been corrected for back-shift, which is $-0{\cdot}04$ Å for x_{B} and within $\pm 0{\cdot}01$ Å for all other parameters. The temperature factor constant $B = 3{\cdot}5$ Å^2 was found from the least-squares treatment, and the factor $\exp(-B \sin^2\theta/\lambda^2)$ has been multiplied into the F_c of Table 2 which shows a comparison of observed and calculated structure factors. The usual index of reliability, $\Sigma||F_c|-|F_o||\div\Sigma|F_o|$ is 0·09 when non-observed reflections are omitted, and 0·14 if they are included.

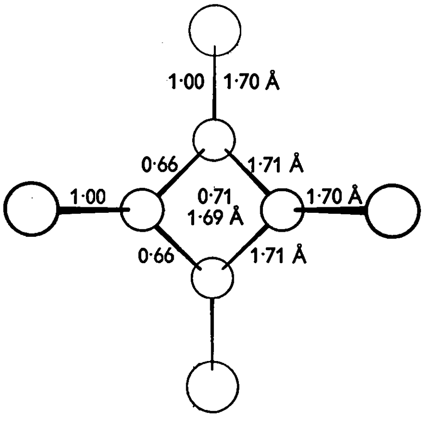

Fig. 5. Topological diagram of the B_4Cl_4 molecule with bond lengths shown on the right and bond numbers on the left.

The molecular dimensions, calculated from the averaged parameters of Table 1, are $B_1B_2 = B_2B_3 = B_3B_4 = B_4B_1 = 1{\cdot}71 \pm 0{\cdot}04$ Å, $B_1B_3 = B_2B_4 = 1{\cdot}69 \pm 0{\cdot}04$ Å, all B–Cl = 1·70±0·03 Å, four Cl · · · Cl = 4·50±0·01 Å, and two Cl · · · Cl = 4·46±0·01 Å. The molecule, of symmetry D_{2d}, is shown in Fig. 5. The two types of Cl · · · Cl distances are different within the probable errors, and while we feel that the deviation from T_d symmetry is real this deviation is so slight that it may be associated with the molecular packing in the solid, and the true symmetry of isolated molecules in the gas phase may well be T_d.

Bond orders in B_4Cl_4 have been discussed in a preliminary note (Atoji & Lipscomb, 1953) in which only the final Fourier parameters were reported. Bond orders for the final averaged parameters are 1·00 for BCl, 0·66 for the longer B–B bonds, and 0·71 for the shorter B–B bonds, thus yielding a total bond order of 8·04 for the molecule. These values, based on normal B–Cl and B–B single bond distances* of 1·70 and 1·60 Å, respectively, are insignificantly different from those previously reported by us. While the mean B–B–B valency angle is 60°, as it is in the tetrahedral P_4 and As_4 molecules, the hybridization must be quite different, inasmuch as *d* orbitals are not available for boron. That the 60° angle represents some sort of strained bond seems probable, and seems to be supported by the average B–B–Cl angle of 144·6°, which seems larger than normal, even for boron.

The molecular packing is quite reasonable as is indicated by the intermolecular Cl · · · Cl distances of 3·63, 3·74 and 3·87 Å. These values are consistent with the van der Waals radius of 1·8 Å usually assigned to Cl.

It is a pleasure to acknowledge support of this investigation by the Office of Naval Research.

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* These distances are obtained from the covalent radius of 0·80 Å for B (Hedberg, 1952) and 0·99 Å for Cl, plus a shortening of 0·09 Å for B–Cl due to the electronegativity difference between B and Cl (Schomaker & Stevenson, 1941).

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Traitement Statistique des Erreurs dans le Cas d'une Structure Pseudo-Centrosymétrique

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A statistical calculation has been used to determine a relation between the empirical function $\langle (F_o^2-F_c^2)^2\rangle/\langle F_c^4\rangle$ and the mean error in atomic positions in the following cases: (*a*) F_o and F_c non-centrosymmetrical; (*b*) F_o and F_c centrosymmetrical; (*c*) F_c centrosymmetrical, F_o noncentrosymmetrical; (*d*) the analogue of (*c*) but in which the atoms are approximately situated on a symmetry element.

On peut être amené, dans la détermination des structures cristallines, à admettre que les atomes adoptent, en première approximation, une configuration centrosymétrique, alors qu'en réalité la structure n'a pas de centre de symétrie. Les séries de Fourier calculées avec les phases correspondant à cette hypothèse sont centrosymétriques: si l'écart entre la structure centrosymétrique et la structure réelle est faible, il peut être difficile de déterminer les positions correctes des atomes, ou même d'estimer l'erreur commise.

C'est le cas qui s'est présenté au cours de l'étude de la structure cristalline de $NaOH.4H_2O$ (Hemily, 1952). Cette substance cristallise dans le système monoclinique, groupe de symétrie $C2$; on a résolu sa structure en supposant que tous les atomes étaient contenus dans le plan $y = 0$, qui devient ainsi un plan miroir (le groupe de symétrie devient $C2/m$). Une fois la structure déterminée, dans l'hypothèse centrosymétrique, nous avons cherché à connaître l'écart moyen des atomes des positions centrosymétriques.

Nous nous proposons ici de déterminer les lois de distribution des parties réelle et imaginaire de la différence $\mathbf{\Delta F}$ entre les facteurs de structure corre-

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