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The Crystal Structures of $CsCu_2Cl_3$ and $CsAg_2I_3$

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$CsCu_2Cl_3$ is orthorhombic with cell dimensions: $a = 9{\cdot}49$, $b = 11{\cdot}88$, $c = 5{\cdot}61$ Å. There are four molecules in the cell and the space group is *Cmcm*. $CsAg_2I_3$ is orthorhombic with cell dimensions: $a = 11{\cdot}08$, $b = 13{\cdot}74$, $c = 6{\cdot}23$ Å. There are four molecules in the cell and the space group is *Pbnm*. Weissenberg diagrams have been taken along the c axis (needle axis) with copper and molybdenum radiation. The positions of the atoms have been fixed by trial and subsequent Fourier methods.

The structures are closely related. The Cs and the Cl ions (Cs and I ions) lie in the symmetry planes perpendicular to the c axis; the Cu (Ag) ions lie between these planes. There are double chains of composition $Cu_2Cl_3(Ag_2I_3)$ in the direction of the c axis, formed by $CuCl_4(AgI_4)$ tetrahedra sharing edges. The Cs ions are situated between the chains and are surrounded in $CsCu_2Cl_3$ by six Cl ions at the corners of a trigonal prism and four more Cl ions on the lateral faces. In $CsAg_2I_3$ the Cs ions are surrounded by six I ions at the corners of a trigonal prism and two more I ions on two lateral faces.

Introduction

The investigation described in this paper is a continuation of the X-ray study of complex structures consisting of monovalent ions only, carried out in this laboratory. The former papers dealt with compounds of the general composition A_2B (Hal.)$_3$, where A is an alkali ion and B a copper or silver ion (survey: Brink & van Arkel, 1952). This paper describes two compounds of the composition AB_2 (Hal.)$_3$. The first compound, $CsCu_2Cl_3$, was prepared by the method described by Wells (1894). The colourless needles turned brown and afterwards green when exposed to the air. The X-ray work was therefore carried out with crystals sealed in Lindemann capillaries. The second compound, $CsAg_2I_3$, was prepared in the way reported by Marsh & Rhymes (1913). The colourless needles did not decompose in air. No crystallographic data for these compounds are given by the earlier investigators.

The crystal structure of $CsCu_2Cl_3$

The unit cell, space group and atomic positions

$CsCu_2Cl_3$ is orthorhombic. The cell dimensions, determined from oscillation diagrams about the needle axis [001] with Cu $K\alpha$ radiation, are

$$a = 9{\cdot}49\pm0{\cdot}02,\ b = 11{\cdot}88\pm0{\cdot}02,\ c = 5{\cdot}61\pm0{\cdot}04\ \text{Å},$$

whence

$$a:b:c = 0{\cdot}798:1:0{\cdot}472\,.$$

The density could not be determined accurately because of the decomposition of the needles. The density calculated for $4CsCu_2Cl_3$ in the unit cell is $3{\cdot}85$ g.cm.$^{-3}$, which seems to be a reasonable value (density of CsCl = $3{\cdot}98$ g.cm.$^{-3}$, density of CuCl = $4{\cdot}14$ g.cm.$^{-3}$).

The observed systematic absences were: hkl when $h+k$ is odd, $h0l$ when l is odd. Hence the space group may be: D_{2h}^{17}–*Cmcm*, C_{2v}^{12}–$Cmc2_1$ or C_{2v}^{16}–$C2cm$. The structure was developed on the assumption that the first-mentioned space group was the right one. This space group has two symmetry planes perpendicular to the c axis at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, i.e. in this case $2{\cdot}80$ Å apart. The centres of the caesium and the chlorine ions must be placed in the symmetry planes, as the diameters of both these ions are larger than $2{\cdot}80$ Å. The same argument does not hold for the copper ion. On inspection of the intensities of corresponding reflexions in the layer lines along [001] it was found that the intensities of $hk1$ reflexions are similar to $hk3$, and that the intensities of $hk0$ reflexions are similar to $hk4$ but different from $hk2$. This indicates that the copper ion has to be placed at $z = 0$ and $z = \frac{1}{2}$, i.e. between the symmetry planes. In this way it was possible to find positions for the ions that accounted for the observed intensities. Therefore the space groups $Cmc2_1$ and $C2cm$ were not considered.

Structure determination

The c period of $CsCu_2Cl_3$ ($5{\cdot}61$ Å) is very similar to the cell edge of CuCl ($5{\cdot}40$ Å). This suggests some analogy in the arrangement of the copper and chlorine ions. In CuCl (zincblende structure) chlorine tetrahedra share edges in the direction of a principal axis in the way indicated in Fig. 1(a); there is a copper ion in the centre of every second tetrahedron. The pronounced fibre cleavage makes it probable that chains occur in the direction of the c axis. A chain of the type shown in Fig. 1(a) accounts for the observed c period. Now,

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however, the centres of *all* tetrahedra must be occupied by copper ions, as the chlorine ions are situated in the symmetry planes. A chain of composition Cu_2Cl_3 is obtained by building up a double chain, consisting of tetrahedra which also share edges in a direction perpendicular to the *c* axis (Fig. 1(*b*)). The arrangement of the positive and negative ions in this double chain is analogous to that found in compounds crystallizing with the antifluorite type of structure (Na_2O, K_2O). In the latter compounds the structure is of course extended into three dimensions in such a way that no chains occur. Two tetrahedra sharing an edge with both centres occupied by a positive ion occur in the double molecules of the aluminium halides. The double chain was fitted into the cell in agreement with the symmetry elements, leaving holes large enough to contain the caesium ions.

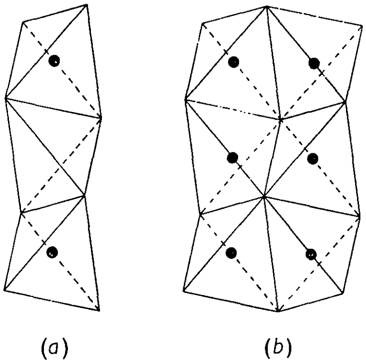

Fig. 1. (*a*) Succession of tetrahedra in CuCl in the direction of a principal axis. (*b*) Double chain in $CsCu_2Cl_3$ and $CsAg_2I_3$.

Support for this model was given by the Patterson projection along [001] and the vector-convergence diagram derived from it (Beevers & Robertson, 1950). The intensities of the *hk*0 reflexions were estimated visually on the zero-layer Weissenberg diagram along [001] taken with Mo *K* radiation, and corrected with the Lorentz and polarization factors.

On the basis of this model the structure factors were calculated and the signs were used in evaluating a Fourier projection along [001]. The result of the third synthesis is shown in Fig. 2. There are marked diffraction rings round the heavy atoms. This effect is remarkable for a synthesis based on intensities derived from a film taken with molybdenum radiation. It must be due to the small value of the Lorentz polarization factor in the θ region where the highest reflexions were observed. A Fourier projection using the calculated structure factors, as suggested by Booth (1946), showed analogous diffraction rings. The heavy ions were not displaced in this synthesis; the displacements for the chlorine ions were 0·03–0·08 Å. After applying the finite-series correction, the coordinates given in Table 1 were obtained. Fig. 3 gives a comparison of the observed and calculated structure factors. In Table 2 the intensities of the reflexions

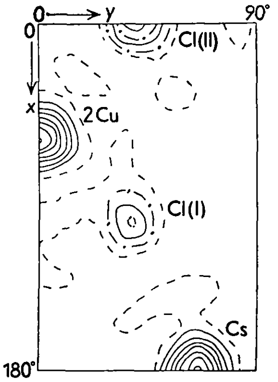

Fig. 2. Electron-density projection of $CsCu_2Cl_3$ along [001]. Contours at intervals of 9 e.Å^{-2} for chlorine and 18 e.Å^{-2} for the other atoms. The lowest contour line, at 6 e.Å^{-2}, is broken.

Table 1. *Final coordinates for* $CsCu_2Cl_3$

	x/a	y/b	z/c
Cs	0·5	0·183	0·25
Cu	0·336	0·5	0
Cl(I)	0·218	0·398	0·25
Cl(II)	0·5	0·620	0·25

Table 2. *Observed intensities for hk*1 *and hk*2 *reflexions of* $CsCu_2Cl_3$ *and corresponding calculated structure factors, assuming scattering factors as for hk*0 *reflexions*

hk	$\lvert F^{\text{calc.}}_{(hk1)}\rvert$	$I_{(hk1)}$	$\lvert F^{\text{calc.}}_{(hk2)}\rvert$	$I_{(hk2)}$
11	32	*ss*	—	—
02	64	*s*	76	*ss*
20	0	—	62	*s*
22	75	*ss*	13	*vw*
13	33	*ss*	14	*w*
31	43	*s*	49	*s*
04	55	*s*	86	*ss*
24	29	*m*	20	*m*
33	10	*vw*	71	*ss*
40	0	—	92	*ss*
15	16	*vw*	63	*ss*
42	27	*w*	3	—
06	64	*m*	26	*vw*
35	34	*w*	15	*w*
51	17	*w*	40	*s*
44	43	*m*	2	—
26	0	—	58	*s*
53	33	*m*	19	*m*
17	48	*m*	10	—
60	0	—	4	*w*
62	40	*m*	57	*s*
46	20	*w*	36	*m*
37	31	*m*	44	*m*
08	19	*vw*	50	*m*
55	15	*vw*	35	*m*
28	11	—	11	*w*
64	28	*w*	41	*m*
71	34	*m*	14	—
19	21	*w*	7	—
73	2	—	1	—
57	51	*m*	4	—
48	12	—	1	—
66	13	—	6	—
39	29	*vw*	57	*m*
0,10	24	*vw*	4	—

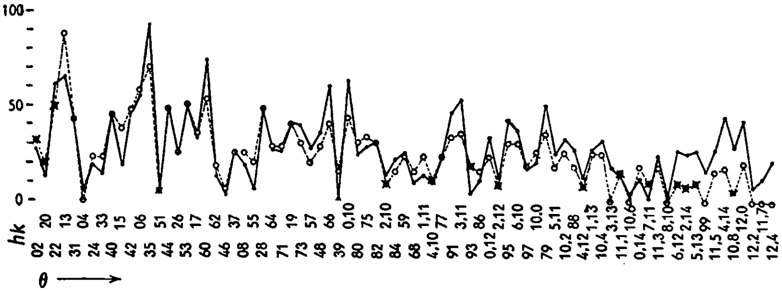

Fig. 3. Structure factors $F(hk0)$ for CsCu$_2$Cl$_3$. Full line: calculated values; broken line: observed values. No temperature factor applied. Circles: Mo K radiation; crosses: Cu $K\alpha$ radiation.

Table 2 (*cont.*)

hk	$\lvert F^{\text{calc.}}_{(hk1)}\rvert$	$I_{(hk1)}$	$\lvert F^{\text{calc.}}_{(hk2)}\rvert$	$I_{(hk2)}$
8,0	0	—	47	*m*
75	14	*vw*	67	*s*
82	20	*w*	6	—
2,10	16	—	20	*vw*
84	25	*vw*	2	—
59	19	*vw*	1	—
68	2	—	53	*m*
1,11	9	—	46	*w*
4,10	21	*vw*	42	*w*
77	19	*vw*	12	—
91	12	—	13	—
3,11	2	—	7	—
93	26	*vw*	56	*m*
86	9	—	31	*w*
0,12	15	*vw*	14	*vw*
2,12	42	*vw*	17	—
95	8	—	13	—
6,10	16	—	16	—
97	45	*m*	37	—
10,0	0	—	58	*m*
79	26	*vw*	18	*w*
5,11	15	—	45	*w*
10,2	22	*vw*	3	—
88	0	—	8	—
4,12	20	*vw*	17	—
1,13	14	—	1	—
10,4	19	*w*	2	—
3,13	9	—	31	—
11,1	23	*vw*	6	—
10,6	13	*vw*	29	—
0,14	17	*vw*		
7,11	2	—		
11,3	4	—		
8,10	10	*vw*		
6,12	31	*vw*		
2,14	10	*vw*		
5,13	7	—		
99	28	*vw*		
11,5	10	*vw*		

with indices *hk*1 and *hk*2 are compared with the calculated structure factors.

The crystal structure of CsAg$_2$I$_3$

For CsAg$_2$I$_3$ the following data were obtained:

$$a = 11{\cdot}08 \pm 0{\cdot}02,\quad b = 13{\cdot}74 \pm 0{\cdot}02,\quad c = 6{\cdot}23 \pm 0{\cdot}04\ \text{Å}\,,$$
$$a:b:c = 0{\cdot}807:1:0{\cdot}453\,.$$

Observed density: 4·76 g.cm.$^{-3}$, calculated number of CsAg$_2$I$_3$ per unit cell: 3·8.

Systematic absences: $0kl$ with k odd, $h0l$ with $h+l$ odd.

Possible space groups: D_{2h}^{16}–*Pbnm* or C_{2v}^{9}–*Pbn*2$_1$.

$I(hk0)$ similar to $I(hk4)$, but different from $I(hk2)$; $I(hk1)$ similar to $I(hk3)$.

Assumed space group: *Pbnm*.

The intensities were derived from a zero-layer Weissenberg diagram taken with Cu $K\alpha$ radiation and corrected with Lorentz, polarization and absorption factors. The crystal was a needle along the c axis with maximum diameter perpendicular to the c axis of 0·13 mm. and minimum diameter 0·09 mm. In calculating the absorption correction it was assumed that the crystal was cylindrical.

The axial ratios found for CsAg$_2$I$_3$ are very similar to those for CsCu$_2$Cl$_3$ and the intensities of the corresponding reflexions are very much alike. The reflexions with indices $h+k = 2n+1$, which do not appear on the CsCu$_2$Cl$_3$ films, are very weak on the CsAg$_2$I$_3$ films. It was therefore tried to fit a double chain, as found for CsCu$_2$Cl$_3$, into the cell of CsAg$_2$I$_3$. A good fit with holes large enough for the caesium ions was obtained by rotating the chains about the c axis through an angle of a few degrees. The intensities

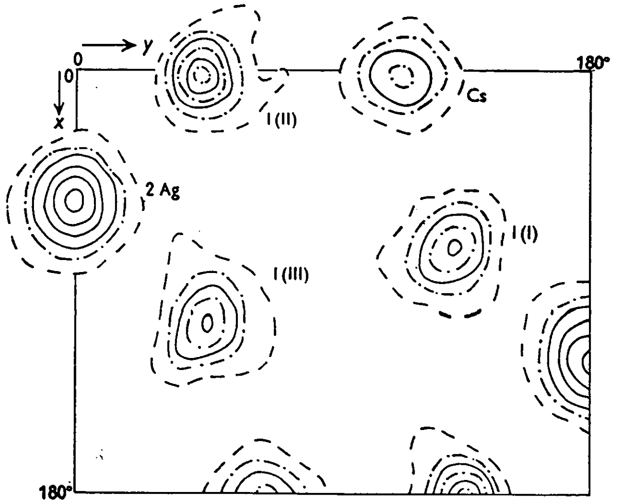

Fig. 4. Electron-density projection of CsAg$_2$I$_3$ along [001]. Contours at intervals of 20 e.Å^{-2} for iodine and caesium and of 40 e.Å^{-2} for silver. The lowest contour line, at 8 e.Å^{-2}, is broken. Scale: 1 cm. = 1 Å.

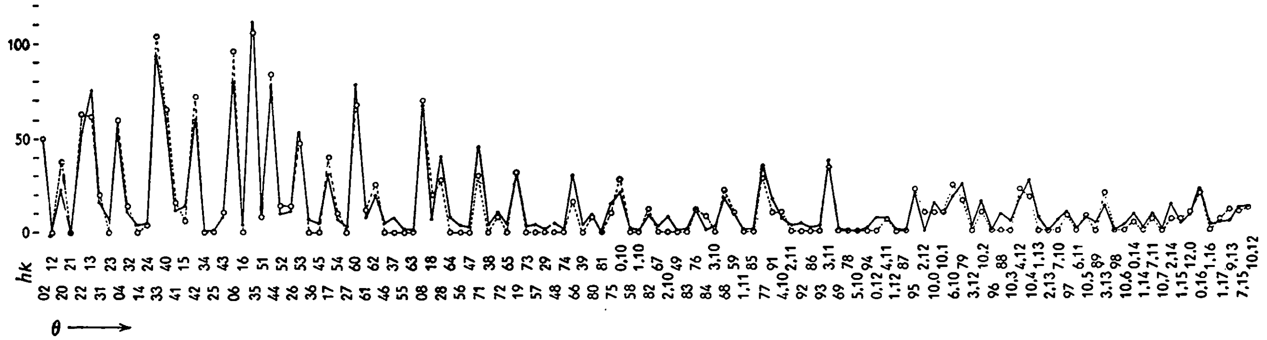

Fig. 5. Structure factors $F(hk0)$ for $CsAg_2I_3$. Full line: calculated values; broken line: observed values. Cu $K\alpha$ radiation. Calculated values corrected with experimental curve.

calculated for the low-order reflexions were rather good and a Fourier projection was made. The electron-density projection obtained after three refinements is given in Fig. 4. The comparison of observed and calculated structure factors is shown in Fig. 5. The experimental values fall off rather rapidly with increasing θ. This may be partly due to an overestimation of the absorption correction. The calculated structure factors were made to fall off in the same way. Table 3 lists the final coordinates obtained for $CsAg_2I_3$.

Table 3. *Final coordinates for* $CsAg_2I_3$

	x/a	y/b	z/c
Cs	0·505	0·185	0·25
Ag	0·342	0·499	0
I(I)	0·214	0·366	0·25
I(II)	0·495	0·622	0·25
I(III)	0·802	0·372	0·25

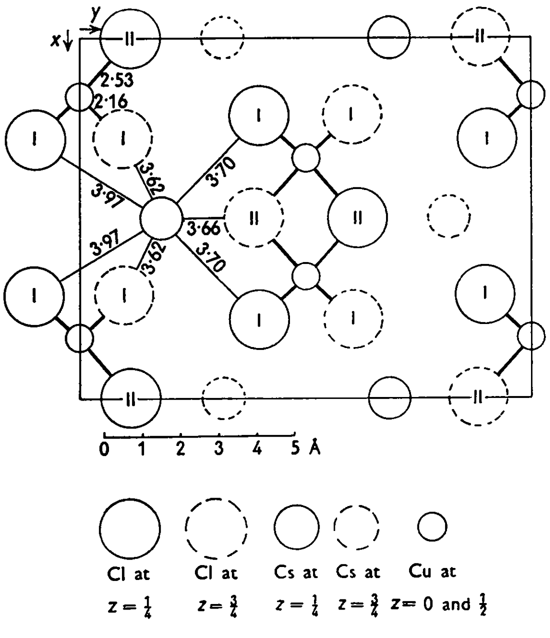

Fig. 6. Projection of the unit cell of $CsCu_2Cl_3$ along [001]. Cu is tetrahedrally surrounded by 4 Cl. Cs at $z = \frac{1}{4}$ is surrounded by 3 Cl at $z = \frac{3}{4}$, 3 Cl at $z = -\frac{1}{4}$ (forming a trigonal prism round Cs) and 4 Cl at $z = \frac{1}{4}$.

Discussion of the structures

A projection of the structures of $CsCu_2Cl_3$ and $CsAg_2I_3$ is given in Figs. 6 and 7, with the calculated distances between the ions drawn in. The maximum error in the distances is estimated at about 0·10 Å. The tetrahedra formed by the copper (silver) and the halogen ions form double chains in the direction of the *c* axis, as successive tetrahedra share edges both in the direction of the *c* axis and in the direction of the *a* axis. The single chain, without the doubling along the *a* axis, is the type of chain found in SiS_2 (Zintl & Loosen, 1935) and $KFeS_2$ (Boon & MacGillavry, 1942). One Cu–Cl distance of 2·16 Å seems to be rather short (distance in CuCl: 2·34 Å). The Ag–I distances are the same as, or larger than, the distances found in AgI (2·80 Å).

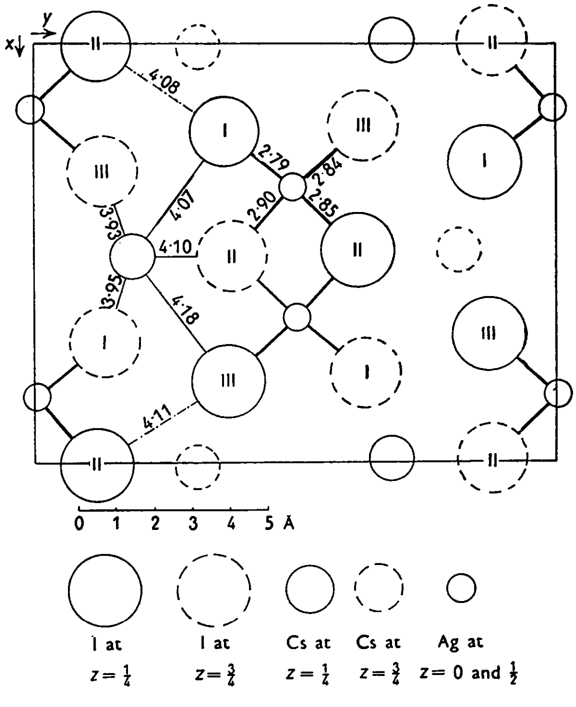

Fig. 7. Projection of the unit cell of $CsAg_2I_3$ along [001]. Ag is tetrahedrally surrounded by 4 I. Cs at $z = \frac{1}{4}$ is surrounded by 3 I at $z = \frac{3}{4}$, 3 I at $z = -\frac{1}{4}$ (forming a trigonal prism round Cs) and 2 I at $z = \frac{1}{4}$.

The shared edges in $CsCu_2Cl_3$ are 3·76 and 4·00 Å, the unshared ones 3·71 and 3·94 Å. In $CsAg_2I_3$ the shared edges are: 4·58, 4·70, 4·84 Å, the unshared ones: 4·49, 4·54, 4·76 Å. Thus in both compounds there is no marked shortening of shared edges as is observed in ionic crystals (e.g. in TiO_2 and Al_2O_3) and also in SiS_2.

In $CsCu_2Cl_3$ the caesium ion is surrounded by six chlorine ions at the corners of a trigonal prism and two more chlorine ions on two lateral faces. On the third lateral face there are two chlorine ions at a distance only ±0·3 Å larger. In $CsAg_2I_3$ eight iodine ions surround the caesium ion, six at the corners of a trigonal prism and two on two lateral faces.

The Cl–Cl distances are all larger than twice the ionic radius of the chlorine ion. The I–I distances are also normal, except two distances of 4·08 and 4·11 Å (crystal radius of iodine ion = 2·16 Å).

Pauling's electrostatic valence rule (1939) is not strictly satisfied by these structures. The sum of the strength of the electrostatic bonds to Cl(I) is 0·9 and to Cl(II) is 1·20 (taking ten chlorine neighbours for the caesium ion). In $CsAg_2I_3$ these figures are 0·88 for I(I) and 1·25 for I(II) (taking eight iodine neighbours for the caesium ion). But of course these complexes do not strictly belong to the group of stable ionic compounds.

The optical behaviour of $CsCu_2Cl_3$ is as one would expect for a chain structure: the largest refractive index is in the chain direction. It is remarkable that in $CsAg_2I_3$ the smallest refractive index is in the chain direction. This may be a result of the rather small distances in the planes perpendicular to the z axis at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ between the iodine ions of different chains. Thus the highly polarizable iodine and caesium ions form rows in planes perpendicular to the chain direction.

We wish to thank Prof. Dr A. E. van Arkel and Prof. Dr C. H. MacGillavry for their interest in this study and the 'Organisatie voor Zuiver Wetenschappelijk onderzoek' for installing in this laboratory an X-ray diffraction apparatus which was used in this investigation.

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X-ray Scattering by Aggregates of Bonded Atoms. IV. Applications to the Carbon Atom

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The methods of previous papers are applied in the calculation of effective scattering factors for the carbon atom in diamond and in graphite, taking full account of the bonds. The factors are no longer isotropic, but the various extreme f-curves do not depart very greatly from that for the isolated atom; the differences may be significant for carbon, and for the other strongly bonded, light atoms common in organic molecules, but probably not elsewhere.

Further progress, and the full utilization of bonded-atom factors, would seem to demand a thorough investigation of thermal vibration and of 'temperature corrections'.

1. Introduction

In previous papers (McWeeny, 1951, 1952, 1953, hereafter referred to as I, II, III) the atomic scattering factors (f) for light atoms, as given by James & Brindley (1931), have been recalculated (I) using the best available analytical wave functions; the definition of such a factor has been extended to include the effect of bonding with neighbouring atoms (II); and a general approximate method of calculating certain 'bond scattering factors', which are then required, has been developed (III). It is now possible to calculate

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