positions is less satisfactory because of the contribution made to the residual by all the deviations in the difference map and not merely the contribution from the atomic centres, and in all cases the error given by these tables is overestimated.

Table 1. *Values of* $\sigma(r)$ *as a function of* $(1)R$ *and* B *in two dimensions*

B	0·0	2·0	4·0	6·0	8·0	10·0
R						
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·05	0·017	0·019	0·022	0·024	0·027	0·029
0·10	0·034	0·038	0·043	0·048	0·054	0·058
0·15	0·051	0·058	0·065	0·073	0·081	0·089
0·20	0·069	0·079	0·090	0·101	0·112	0·122
0·25	0·090	0·102	0·117	0·132	0·146	0·159
0·30	0·113	0·129	0·148	0·167	0·186	0·204
0·40	0·175	0·204	0·237	0·269	0·300	0·328
0·50	0·315	0·380	0·440	0·500	0·561	0·623

Table 2. *Values of* $\sigma(r)$ *as a function of* $(\bar{1})R$ *and* B *in two dimensions*

B	0·0	2·0	4·0	6·0	8·0	10·0
R						
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·05	0·011	0·012	0·014	0·015	0·017	0·018
0·10	0·021	0·024	0·027	0·031	0·034	0·037
0·15	0·033	0·037	0·042	0·047	0·052	0·057
0·20	0·045	0·051	0·057	0·064	0·071	0·078
0·25	0·057	0·065	0·074	0·083	0·092	0·100
0·30	0·071	0·080	0·091	0·103	0·114	0·125
0·40	0·100	0·116	0·132	0·149	0·165	0·181
0·50	0·138	0·160	0·184	0·209	0·232	0·254
0·60	0·192	0·225	0·262	0·298	0·331	0·361

Table 3. *Values of* $\sigma(r)$ *as a function of* $(\bar{1})R$ *and* B *in three dimensions*

B	0·0	2·0	4·0	6·0	8·0	10·0
R						
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·05	0·009	0·010	0·011	0·012	0·013	0·014
0·10	0·018	0·019	0·021	0·023	0·025	0·028
0·15	0·027	0·029	0·031	0·035	0·038	0·042
0·20	0·036	0·040	0·043	0·048	0·053	0·057
0·25	0·047	0·051	0·056	0·061	0·067	0·073
0·30	0·057	0·062	0·069	0·077	0·083	0·091
0·40	0·081	0·089	0·098	0·108	0·119	0·130
0·50	0·109	0·120	0·133	0·148	0·163	0·178
0·60	0·146	0·162	0·180	0·202	0·224	0·247

Table 4. *Values of* $\sigma(r)$ *as a function of* $(1)R$ *and* B *in three dimensions*

B	0·0	2·0	4·0	6·0	8·0	10·0
R						
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·05	0·014	0·015	0·016	0·018	0·020	0·021
0·10	0·028	0·030	0·033	0·036	0·040	0·043
0·15	0·042	0·046	0·050	0·055	0·060	0·066
0·20	0·057	0·062	0·067	0·075	0·082	0·090
0·25	0·073	0·079	0·088	0·096	0·106	0·116
0·30	0·091	0·099	0·109	0·121	0·134	0·146
0·40	0·135	0·150	0·167	0·186	0·206	0·226
0·50	0·214	0·242	0·276	0·312	0·349	0·383

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The structure of metallic dodecaborides.

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The most common polyhedral grouping of boron atoms is that in which 12 boron atoms occupy the vertices of an icosahedron. The existence of such a group has been convincingly proven in a number of higher borides and boron structures such as boron carbide, B_4C (Zhdanov & Sevastianov, 1941; Clark & Hoard, 1943), boron phosphide, $B_{12}P_2$ (La Placa & Post, 1961), an aluminum borocarbide, AlC_4B_{24} (Matkovich, Economy & Giese, 1964), α-boron (Decker & Kasper, 1959), β-boron (Hughes, Kennard, Sullinger, Weakliem, Sands & Hoard, 1963) and tetragonal boron (Hoard, Hughes & Sands, 1958).

A different grouping of 12 boron atoms, *i.e.* a cubo-octahedral arrangement, was proposed by Bertaut & Blum (1949) for UB_{12} on the basis of steric considerations. Subsequently, Post & Glaser (1952) showed that the X-ray powder lines of ZrB_{12} are consistent with the cubo-octahedral boron grouping, and demonstrated the existence of an isotypic series of metal dodecaborides. In their calculations they assumed the structure proposed by Bertaut & Blum (1949) and did not consider other possibilities. (It should be noted that the icosahedral grouping is consistent with the observed space group extinctions.) Since the degree of refinement of the ZrB_{12} structure was relatively low, it was felt desirable to establish more accurately the form of the boron grouping in the cubic dodecaboride series.

Single crystals of ScB_{12} and YB_{12} were prepared by heating the metal oxides and boron with B:Me ratio of 7:1 in an induction coupled plasma torch apparatus similar to that described by Reed (1961). The samples were heated to a temperature of 2000–2500°C and then quenched by dropping directly into a beaker of water. After washing with concentrated hydrochloric acid, crystals of ScB_{12} and YB_{12} could be easily handpicked under the microscope.

Rotation and Weissenberg photographs of ScB_{12} crystals indicated a tetragonal unit cell with $a=5{\cdot}22$, $c=7{\cdot}35$ Å. The systematic extinctions are consistent with the space group $I4/mmm$ and its subgroups. This cell is pseudo-cubic and dimensionally related to the cubic dodecaboride series. The examined crystals were twinned on the (111) plane. The tetragonal cell is in disagreement with the findings of

Table 1. *Observed and calculated structure factors*

	h	*l*	KF_{obs}	F_{calc}
k=0	0	2	120·6	132·3
	0	4	111·6	113·0
	0	6	143·6	148·2
	0	8	64·8	60·0
	2	2	87·5	90·0
	2	4	79·0	80·8
	2	6	84·9	78·6
	2	8	57·0	50·1
	4	4	80·4	72·5
	4	6	74·4	75·1
	4	8	31·8	46·7
	6	6	104·5	104·9
k=1	1	1	100·7	100·2
	1	3	142·3	144·0
	1	5	77·4	72·8
	1	7	60·9	62·5
	1	9	53·8	65·8
	3	3	111·1	101·7
	3	5	100·7	101·9
	3	7	86·5	78·9
	5	5	57·7	55·5
	5	7	45·1	50·3
k=2	2	2	142·3	146·5
	2	4	119·7	115·5
	2	6	65·3	62·1
	2	8	76·8	76·1
	4	4	91·2	97·0
	4	6	55·0	57·2
	4	8	54·4	67·3
	6	6	44·2	58·0
k=3	3	3	20·6	20·5
	3	5	89·1	82·3
	3	7	61·5	58·7
	5	5	85·7	82·0
	5	7	73·0	66·2
k=4	4	4	85·4	84·2
	4	6	49·0	53·2

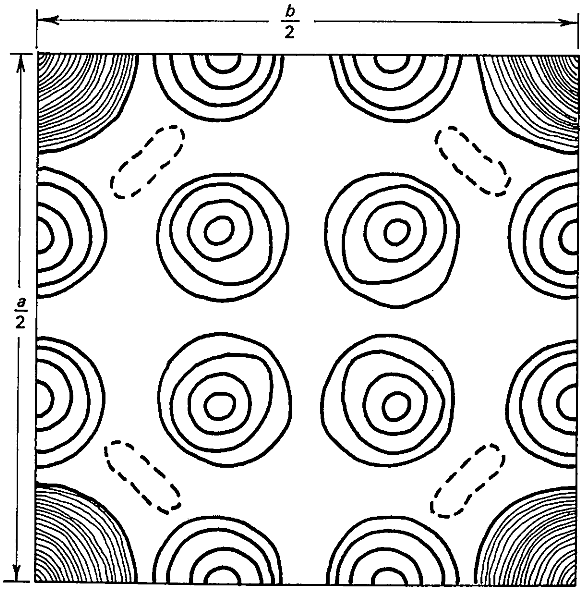

Fig. 1. Electron density projection on the (001) plane of YB_{12}. Yttrium atoms are in the corners. The contour lines are drawn at arbitrary intervals.

Table 2. *Structure parameters as fractions of the unit-cell edge*

	YB_{12}			R=0·061		
Atom	*x*	*y*	*z*	σy	*B*	σB
Y	0	0	0		0·56	0·07
B	½	0·1706	0·1706	0·0016	1·41	0·28
	ZrB_{12}			R=0·047		
	x	*y*	*z*	σy	*B*	σB
Zr	0	0	0		−0·04	0·10
B	½	0·1699	0·1699	0·0018	0·53	0·62
	UB_{12}			R=0·02		
	x	*y*	*z*	σy	*B*	σB
U	0	0	0		−0·03	0·04
B	½	0·1707	0·1707	0·0018	0·09	0·38

Przybylska, Reddoch & Ritter (1963) who reported a cubic symmetry on basis of examination of an ScB_{12} powder sample.

The body centered tetragonal cell of the above size may accommodate two B_{12} groups. However, if such groups are present they could not have the icosahedral form as this form does not have the required fourfold symmetry. Further X-ray studies of these crystals were not undertaken.

Crystals of YB_{12} were found to be cubic (a=7·50 Å), in agreement with earlier observations (Seybolt, 1960; La Placa, Binder & Post, 1961). The systematic extinctions are consistent with the space group *Fm*3*m* and its subgroups. The diffraction symmetry was $4/m\,\bar{3}\,2/m$, which rules out the space groups *Fm*3 and *F*32 and, in conjunction with the size of the unit cell, eliminates the possible presence of an icosahedral unit.

Intensity measurements were made with a Weissenberg camera equipped with a Geiger counter. Convergent Cu $K\alpha$ radiation was used and monochromatization was obtained using Ni–Co balanced filters. Non-equivalent reflections were measured in layers along the *a* axis, and the usual Lorentz and polarization corrections were made. A three-dimensional electron density map was computed with the IBM 7090 computer. The program ERFR-2 was used (Sly, Shoemaker & Van den Hende, 1962). The phase angles were obtained from the yttrium atoms and the map showed a cubo-octahedral arrangement of boron atoms. In the least-squares refinement all 37 observed reflections were given a weight of unity. The refinement program minimizes the function $\underset{hkl}{\Sigma}\, w(K^2F_o^2-F_c^2)^2$. An R value $(\Sigma||KF_o|-|F_c||/\Sigma|KF_o|)$ of 0·061 was obtained. The form factors were taken from the *International Tables for X-ray Crystallography* (1962) and dispersion corrections (from the same source) were applied to the yttrium form factors. Observed and calculated structure factors are listed in Table 1. An electron density projection on the (001) plane is shown in Fig. 1. Thus, the cubo-octahedral boron grouping proposed by earlier workers is confirmed.

Examination of the boron–boron distances showed that the internal cubo-octahedral B–B distances are longer than the external B–B distances. To verify the existence of two types of B–B distance in other cubic dodecaborides, the available date on ZrB_{12} (Post & Glaser, 1952) and UB_{12} (Bertaut & Blum, 1949) were used to refine the parameters in these compounds. The parameters and bond lengths of YB_{12}, ZrB_{12} and UB_{12} are compared in Tables 2 and 3. As can be seen in Table 3 the metal–boron distance increases with the unit-cell size; however, this is not related to the

Table 3. *Comparison of bond lengths* (Å) *in* Yb_{12}, ZrB_{12} *and* UB_{12}

	YB_{12}	ZrB_{12}	UB_{12}
Unit-cell edge	7·500	7·408	7·473
B–B (intercubo-octahedral)	1·809 ± 0·024	1·780 ± 0·026	1·803 ± 0·026
B–B (intracubo-octahedral)	1·684 ± 0·024	1·678 ± 0·026	1·675 ± 0·026
Metal–B	2·783 ± 0·012	2·750 ± 0·013	2·771 ± 0·013
Metallic radius (Pauling) (coordination number 12)	1·797	1·597	1·516

atomic size of the metal atoms. Thus, in the cubic dodecaboride series, variations in the unit-cell dimensions are controlled by the internal B–B distances in the cubo-octahedron. These, in turn, are probably affected by the electron transfer between the boron and the metal atoms.

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On the preparation and crystallography of tetramethylammonium chloride hydrogen chloride*.

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A number of studies of compounds which appear to contain the bichloride ($Cl\text{-}H\text{-}Cl^-$) ion have been reported recently (Herbrandson, Dickerson & Weinstein, 1952; Waddington, 1958; Sharp, 1958; Vallee & McDaniel, 1962; Chang & Westrum, 1962). No X-ray studies have appeared, however, with the exception of the brief report of Waddington (1958) which included results of X-ray powder measurements on tetramethylammonium chloride hydrogen chloride (hereafter: TMACl-HCl). An orthorhombic unit cell containing 8 molecules with $a = 14{\cdot}81$, $b = 11{\cdot}46$, $c = 10{\cdot}38$ Å, was reported for TMACl-HCl by the above author.

We have prepared TMACl-HCl by adding anhydrous hydrogen chloride to tetramethylammonium chloride in anhydrous methanol. Needle crystals of TMACl-HCl, stable in sealed capillaries, were obtained from the latter solvent. Analysis of single-crystal material gave C,32·3; H,9·13; Cl,47·98 %. $(CH_3)_4N^+HCl_2^-$ requires C,32·9; H,8·9; Cl,48·5 %.

Crystals sealed in glass capillaries were examined with Cu $K\alpha$ radiation, employing Weissenberg and precession techniques. The needle crystals were observed to be orthorhombic with the needle axis the b axis of the cell, $a = 9{\cdot}27 \pm 0{\cdot}01$, $b = 7{\cdot}73 \pm 0{\cdot}01$, $c = 11{\cdot}59 \pm 0{\cdot}01$ Å. The diffraction symbol is $mmmPn\,.\,a$ indicating possible space groups $Pnma$ and $Pn2_1a$. The calculated crystal density for 4 molecules per unit cell is 1·168; $\varrho_{obs} = 1{\cdot}15$.

This cell, slightly less than half the size of the unit cell chosen by Waddington, is considerably more amenable to X-ray structure study. We do not, at present, plan further X-ray structural work on this material.

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