clearly resolved. For a 10 °C accuracy (that is, no values exceeding 5 °C from the mean value) at temperatures up to at least 1700 °C, the required diffraction maxima location measurement accuracies for Cu $K\alpha_1$ radiation are 0·004° to 0·006°, 0·010° to 0·012°, 0·020° to 0·024°, and 0·040° to 0·044° 2θ for the 111, 311, 331, and 422 platinum maxima and 0·004° to 0·006°, 0·006° to 0·008°, 0·008 to 0·012°, 0·010° to 0·014°, and 0·036 to 0·040° 2θ for the 100, 101, 110, 112, and 105 BeO maxima in similar angular regions.

Because expansion data frequently are desired in other forms, the calculated BeO lattice-constant values at 100 °C intervals were used to compute the percentage expansions of the two axes: *i.e.*,

$$a\text{-axis} = \frac{(a_t - a_{28^\circ})}{a_{28^\circ}}\,100\%\,,$$

and the average linear (bulk) expansions, *i.e.*, $(2a+c)/3$, according to Hidnert & Souder (1950). These data are given in Table 5; the data at other temperature intervals may be calculated from the following equations:

$$a\text{-axis} = -0{\cdot}020_9 + 6{\cdot}91\times10^{-4}t + 3{\cdot}00\times10^{-7}t^2\%\,;$$

$$c\text{-axis} = -0{\cdot}018_6 + 5{\cdot}82\times10^{-4}t + 2{\cdot}90\times10^{-7}t^2\%\,;$$

and

$$\text{average linear (bulk)} = -0{\cdot}020_2 + 6{\cdot}54\times10^{-4}t + 2{\cdot}97\times10^{-7}t^2\%$$

where t is in °C and where the equations allow the user to calculate the corrections from the 28 °C room temperature of these experiments to any other room temperature condition .The unbiased standard errors of estimate of these equations are $6{\cdot}8\times10^{-4}$, $1{\cdot}1\times10^{-3}$, and $8{\cdot}0\times10^{-4}$, respectively; the coefficients of determination and the multiple regression coefficient values are 0·9999 in all instances.

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AB Compounds with Sc, Y and Rare Earth Metals. I. Scandium and Yttrium Compounds with CrB and CsCl Structure*

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The crystal structures of seven new compounds have been determined. ScSi, ScGe, ScGa, YGe and YGa crystallize with the TlI ($B33$) type (also known as CrB or B_f type) and ScMg, ScAl with the CsCl ($B2$) structure type. A survey of all known equiatomic compounds and their structures, having Sc, Y or rare earth metals as one component, is given and an effort is being made to find some general rules which govern the formation of these compounds and their structures.

Introduction

Only a few years ago, the alloy chemistry of Sc, Y and rare earth metals was a nearly unexplored area. Except for some isolated efforts, for example by Iandelli, no extensive research was conducted on these lines. However, the development of ion-exchangers for the separation of rare earth elements, a by-product of reactor fuel research, and the ready availability of the Sc, Y and rare earth metals on the market brought about an extremely rapid change. A rather intensive interest in the crystal chemistry of rare earth alloys developed about five years ago which resulted in an increased number of publications on Sc, Y and rare earth metals and their compounds. With many compounds and structures known today, it is already possible to make general conclusions concerning the compound formation in these alloys.

The compounds of interest in this study were the equiatomic compounds having Sc, Y or rare earth metals as one component, the other being another metal or nonmetal from other groups. It was found that

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* Part II, D. Hohnke & E. Parthé, submitted to *Acta Cryst.*

very little or no information was available on silicides, gallides, germanides, and plumbides. Therefore, it was of interest to synthesize a few of these *AB* compounds, mostly those having Sc and Y as one component, to determine their structure and then to compare their data with the structure data of other *AB* compounds containing Sc, Y or rare earth metals.

Experimental

Samples of ScSi, ScGe, ScGa, YGe, YGa, ScMg and ScAl were made by induction melting of compacted pellets of the mixed metals. Boron nitride was found a useful crucible material since no reaction of the sample with the crucible was observed. ScSi was melted in vacuum ($<10^{-3}$ mmHg) after repeated flushing with Purgon (purified argon), while all other samples were melted under a Purgon atmosphere. The alloys were homogenized in sealed, evacuated ($<10^{-4}$ mmHg) quartz tubes – after preheating at 1000 °C – at a final temperature of 1200 °C (ScMg and ScAl at 800 °C) for not longer than four hours. Samples, particularly those containing scandium, which were exposed to this temperature for a longer time, reacted with the quartz forming oxide phases. In the case of ScGe, the reaction with the quartz (1200 °C for 20 hours) can be described by the following equation: $ScGe+SiO_2 \rightarrow Sc_2O_3+$ (Ge – Si) mixed crystal $+ScGe_2$. This conclusion was the result of an X-ray investigation of the reaction product, which showed clearly the presence of the above mentioned phases. The compound $ScGe_2$ has not yet been reported in the literature and it was subject of a special investigation which has been reported elsewhere (Schob & Parthé, 1964).

Results of structure investigations

Compounds with TlI (B33) structure

Five of the seven investigated compounds were found to have the TlI (*B*33) crystal structure. ScSi was the sample on which a complete intensity calculation was performed and it is therefore now discussed in more detail.

A diffractogram of ScSi could be indexed with an orthorhombic unit cell with $a=3{\cdot}988\pm0{\cdot}002$, $b=9{\cdot}882\pm0{\cdot}005$, and $c=3{\cdot}659\pm0{\cdot}002$ Å. The extinctions for *hkl* with $h+k=2n+1$ and *h*0*l* with $l=2n+1$ lead to possible space groups $Cmc2_1$ (C_{2v}^{12}), $C2cm$ (C_{2v}^{16}) and $Cmcm$ (D_{2h}^{17}). The similarity of the unit-cell dimensions and the agreement in the extinction laws with those of YSi (Parthé, 1959), suggested a structural analogy with the latter. However, the powder patterns of ScSi and YSi showed differences in the intensities of the diffraction lines which could not be explained alone by the differences in the scattering factors between Sc and Y. Notwithstanding an intensity calculation was performed assuming the same space group and same atomic sites as in YSi; that is, $Cmcm$ (D_{2h}^{17}) and 4Sc in 4(*c*) with $y_{Sc}=0{\cdot}146$ and 4Si in 4(*c*) with $y_{Si}=0{\cdot}440$. Without making a temperature factor correction the residual factor was calculated to 23·8%, which indicated that the structure proposal was in principle correct but the adjustable parameters needed to be refined. Space groups $Cmc2_1$ (C_{2v}^{12}) and $C2cm$ (C_{2v}^{16}) were also tried but were rejected because the only satisfactory packing was obtained when the Sc and Si atoms had the same *x* and *z* parameters; therefore space group $Cmcm$ (D_{2h}^{17}) was retained.

A certain indication of a shift in the two *y* parameters of the ScSi structure was given by the observation that ScSi diffractometer charts at first showed no agreement in the intensities with patterns made by the Debye–Scherrer film method. It was found that the intensities of the 0*k*0 reflections on the diffractometer charts varied greatly with the method of diffractometer sample preparation. The biggest deviations from the film intensities occurred when pressure was applied to the samples. This clearly demonstrated that the pressed ScSi diffractometer samples were preferentially oriented and indicated that ScSi might have a layer-like structure.

For the refinement of the structure, an IBM 1620 computer program was designed which was used to calculate the *F* values, compare them with the observed *F* values and directly determined the residual factor $R=\Sigma||F_{obs}|-|F_{calc}||/\Sigma|F_{obs}|$ for different combinations of *y* parameters. Using the *F* values of 42 measured intensities the best *R* index of 7·5% was obtained by selecting for $y_{Sc}=0{\cdot}140$ and for $y_{Si}=0{\cdot}419$. A comparison of observed and calculated $\sin^2\theta$ and *F* values for ScSi is given in Table 1. Since no temperature factor correction was made the *R* value is satisfactory.

The interatomic distances of ScSi and YSi are compared in Table 2. The YSi structure is characterized by Si–Si chains in which the distance between two close silicon atoms is 2·29 Å. These chains do not exist in ScSi, where the corresponding distance has increased to 2·43 Å. While in YSi the seven metal–silicon distances are very close to each other, in ScSi one finds five short distances and two longer ones. Assuming the respective radii for Sc, Y and Si of 1·60, 1·81 and 1·14 Å the differences between these two structures become obvious. In ScSi five *Me*–Si distances can be obtained accurately by adding the given radii, while all other existing distances in the ScSi structure are considerably bigger than the sum of the radii. On the other hand, in YSi the *Me*–*Me* and the Si–Si distances equal the sum of the radii, while the metal–silicon distances are only slightly bigger. In ScSi the five short *Me*–Si distances are an indication for strong bonds between these atoms, while all other bonds seem to be of less importance for the structure. In distinction to YSi the atomic arrangement in ScSi with its five strong *Me*–Si bonds per metal atom leads to a formation of layers with a thickness of two atom diameters parallel to the (0*k*0) planes. These structural characteristics offer an explanation for the orientation phenomena observed with the diffractometer specimens.

Table 1. *Intensity calculation for ScSi with* TlI($B33$) *structure type*

Cu $K\alpha$ radiation

hkl	d_c	1000 $\sin^2\theta_c$	1000 $\sin^2\theta_o$	I_o†	F_o	F_c
020	4·940 Å	24·3	24·2	2·0	10·65	11·38
110	3·699	43·4	—	< 1	3·78*	6·00
021	2·940	68·6	68·5	8·5	27·49	−29·76
111	2·600	87·7	87·4	75·0	66·32	−69·61
130	2·538	92·0	91·9	24·0	54·64	−57·84
040	2·470	97·2	97·0	25·0	81·45	−75·04
131	2·086	136·3	136·1	39·5	61·86	−63·71
041	2·047	141·5	141·5	16·0	57·04	52·87
200	1·994	149·2	149·2	19·0	91·07	91·60
220	1·894	173·5	—	< 1	7·90*	7·66
002	1·829	177·3	177·3	15·0	89·69	−88·40
150	1·770	189·2	—	< 1	8·59*	11·35
022	1·715	201·6	—	< 1	8·93*	−7·54
221	1·650	217·8	217·9	2·0	18·55	−22·77
060	1·647	218·7			4·12	−5·02
112	1·640	220·7	—	< 1	6·52*	−4·34
151	1·594	233·5	233·6	5·5	31·96	29·94
240	1·552	246·4	246·2	8·0	57·04	−60·83
061	1·502	263·0	263·0	4·5	44·33	43·97
132	1·484	269·3	269·2	9·5	46·05	44·13
042	1·470	274·5	274·6	8·0	60·14	58·61
241	1·4286	290·7	290·7	8·0	44·33	44·90
202	1·3480	326·5	326·5	10·0	74·92	−75·60
170	1·3308	335·0	334·7	9·0	72·85	71·85
310	1·3176	341·8	—	< 1	12·37*	2·96
222	1·3004	350·8	—	< 1	8·93*	−7·15
152	1·2723	366·5	—	< 1	8·93*	−10·22
260	1·2698	367·9	—	< 1	12·71*	−5·11
171	1·2506	379·3	—	< 1	8·93*	17·23
311	1·2396	386·1	386·2	9·0	47·77	−47·12
080	1·2353	388·8	388·7		15·80	14·51
330	1·2328	390·4	390·4		39·17	−39·10
062	1·2240	396·0	—	< 1	13·40*	5·35
261	1·1997	412·2	412·2	4·0	33·33	38·25
023	1·1840	423·2	423·5	7·0	16·15	17·76
242	1·1833	423·7			50·51	51·42
081	1·1704	433·1	433·0	8·0	47·77	−50·60
331	1·1683	434·7	435·1		43·64	47·02
113	1·1582	442·3	442·0	4·0	39·52	44·99
350	1·1029	487·6	—	< 1	14·77*	9·47
133	1·0994	490·9	490·7	5·0	46·05	45·64
043	1·0931	496·1	496·0	2·0	41·24	−38·17

† Uncorrected intensities as measured with a planimeter on a diffractometer pattern.

* One half of the F value obtained from the smallest observable intensity value.

Table 2. *Interatomic distances in* ScSi *and* YSi

	ScSi	YSi
Me–Me	3·32 Å (2)	3·60 Å (4)
	3·47 Å (4)	3·62 Å (2)
Me–Si	2·76 Å (1)	3·00 Å (4)
	2·77 Å (4)	3·04 Å (2)
	2·96 Å (2)	3·09 Å (1)
Si–Si	2·43 Å (2)	2·29 Å (2)

Other compounds found isotypic to ScSi were ScGe, ScGa, YGe and YGa. The powder patterns of these compounds are all very similar except naturally for a line shift due to the different size of the atoms. Their respective unit cell dimensions and their adjustable parameters are listed in the first section of Table 3. For the evaluation of the adjustable parameters it seemed sufficient in these cases to consider only the intensities of the reflections 021, 111, 130, 040, 131, 041, 200 and 002 which had been measured very carefully with a planimeter on a diffractometer chart.

The occurrence of the TlI (B 33) *structure type*

The structure of ScSi and the other isotypic phases: ScGe, ScGa, YSi, YGe and YGa belongs to a well-known structure type which is reported for some seventy compounds. However, the identity of the structures of these different compounds was not immediately realized with the result that the same structure type received different names each time it was rediscovered. The first compound found was TlI and its structure type was given in the *Strukturberichte* of 1936 as $B33$ type.

The structure type was rediscovered in 1949 and depending on the literature one reads, it was called CaSi or CrB type and later in Pearson's compilation B_f type. Many new isotypic compounds were found which were not recognized as identical with any of those types. The confusion was compounded by the unfortunate situation that the literature on the structure data of TlI ($B33$) type phases is full of errors which

Table 3. *AB compounds with* TlI (*B*33) *structure type**

	Lattice parameters for setting: *Cmcm*			Adjustable parameters ($r_A > r_B$)		
Compound	*a*(Å)	*b*Å	*c*(Å)	y_A	y_B	Reference
Group I compounds						
CaSi (a)	4·50±0·05	10·705±0·008	3·91 ±0·04	0·14	0·43	(1)
CaGe	4·575±0·002	10·845±0·001	4·001±0·001	0·136	0·424	(2)
	4·556	10·815	3·997	0·138	0·424	(3)
CaSn	4·821±0·004	11·52±0·02	4·349±0·004	0·133	0·416	(2)
SrSi	4·83±0·01	11·33±0·01	4·04±0·01	0·140	0·434	(28)
SrGe						(3)
SrSn						(3)
BaPb	5·29 ±0·01	12·60 ±0·02	4·78 ±0·01	0·127	0·420	(4)
ScGa	4·022±0·004	10·205±0·008	3·895±0·004	0·138±0·002	0·417±0·002	(5)
ScSi	3·988±0·002	9·882±0·005	3·659±0·002	0·140±0·001	0·419±0·001	(5)
ScGe	4·007±0·004	10·06 ±0·01	3·762±0·004	0·138±0·002	0·417±0·002	(5)
YAl (b)	3·884±0·002	11·522±0·004	4·385±0·002	0·15	0·43	(6)
YGa	4·302±0·004	10·86 ±0·01	4·073±0·004	0·138±0·002	0·417±0·002	(5)
YSi	4·25$_1$	10·52$_6$	3·82$_6$	0·146	0·440	(7)
YGe	4·262±0·002	10·694±0·005	3·941±0·002	0·138±0·002	0·417±0·002	(5)
LaGa	4·50±0·01	11·39 ±0·03	4·23 ±0·01			(8)
CeGa	4·47±0·01	11·34 ±0·03	4·21 ±0·01			(8)
PrGa (b)	4·452	11·331	4·195	0·144	0·425	(9)
PrGe (c)	4·474	11·098	4·064	0·141	0·426	(3), (9)
GdGa (d)	4·341±0·008	11·02±0·02	4·066±0·003			(10)
GdGe (d)	4·175±0·002	10·61±0·01	3·960±0·003			(10)
TbGa	4·33	10·90	4·06	0·141	0·426	(11)
DyGa (d), (e)	4·300±0·004	10·89±0·02	4·067±0·001	0·140	0·426	(10)
DyGe (d)	4·112±0·002	10·81 ±0·02	3·924±0·006			(10)
ZrAl	3·353	10·866	4·266	0·166	0·424	(12)
	3·359±0·001	10·887±0·003	4·274±0·001	0·16	0·43	(13)
ZrSi$_{0·7}$Al$_{0·3}$ (f)	3·787	10·07	3·787			(14)
ZrSi (g)	3·762	9·91$_2$	3·754			(14)
HfAl	3·24$_6$	10·82$_2$	4·27$_8$			(15)
	3·25$_3$	10·83$_1$	4·28$_2$	0·167	0·425	(16)
HfSi$_{0·5}$Al$_{0·5}$ (f)	3·714	9·88$_9$	3·754			(14)
ThAl (h)	4·42	11·45	4·19	0·147	0·443	(17)
VB	3·10	8·17	2·98	0·146	0·440	(18)
NbB	3·298	8·724	3·166	0·146	0·444	SR **13**
TaB	3·276	8·669	3·157	0·146	0·440	SR **12**
CrB	2·969	7·858	2.932	0·146	0·440	SR **12**
β–MoB (i)	3·16	8·61	3·08			SR **16**
β–WB (i)	3·19	8·40	3·07			SR **16**
NiB	2·925	7·396	2·966	0·146	0·440	SR **16**
Group II compounds						
CaAg (j)	4·08	11·48	4·65	0·165	0·425	(19)
LaRh	3·986±0·001	11·144±0·001	4·245±0·001			(20)
LaNi	3·907±0·001	10·810±0·001	4·396±0·001			(20)
LaPt	3·974±0·001	11·037±0·001	4·558±0·001			(20)
CeRh	3·852±0·001	10·986±0·001	4·152±0·001			(20)
CeNi	3·77 ±0·01	10·46 ±0·02	4·37 ±0·01	0·139±0·002	0·428±0·004	(21)
	3·788±0·001	10·556±0·001	4·366±0·001			(20)
CePt	3·921±0·001	10·920±0·001	4·524±0·001			(20)
PrRh	3·905±0·001	10·910±0·001	4·210±0·001			(20)
PrNi	3·816±0·001	10·503±0·001	4·354±0·001			(20)
NdRh	3·890±0·002	10·839±0·007	4·247±0·004			(20)
NdNi	3·803±0·001	10·461±0·001	4·339±0·001			(20)
SmNi	3·776±0·001	10·358±0·001	4·291±0·001			(20)
GdNi (k)	3·766±0·001	10·316±0·001	4·244±0·001	0·135	0·435	(20)
ZrNi	3·268±0·008	9·937±0·004	4·101±0·005	0·139±0·008	0·418±0·002	(22)
ZrPt	3·409±0·001	10·315±0·001	4·277±0·001			(20)
HfNi	3·220±0·005	9·820±0·006	4·12 ±0·01			(22)
HfPt	3·345±0·001	10·269±0·001	4·288±0·001			(20)
ThRu	3·878±0·002	11·29 ±0·01	4·071±0·002	0·14	0·41	(23)
ThCo (l)	3·74	10·88	4·16	0·136	0·416	(24)
ThRh	3·866±0·003	11·24 ±0·01	4·220±0·003	0·140±0·004	0·410±0·004	(25)

* *Note added in proof*: Recently many more rare earth compounds with TlI (*B*33) structure type have been found. See *e.g.* Parthé, Hohnke, Jeitschko & Schob (1965).

Table 3 (*cont.*)

	Lattice parameters for setting: *Cmcm*			Adjustable parameters ($r_A > r_B$)		
Compound	a(Å)	b(Å)	c(Å)	y_A	y_B	Reference
ThIr	3·894 ± 0·003	11·13 ± 0·01	4·266 ± 0·003	0·14	0·41	(23)
ThPt	3·900 ± 0·003	11·09 ± 0·01	4·454 ± 0·003	0·140 ± 0·002	0·410 ± 0·004	(25)
PuNi	3·59 ± 0·01	10·21 ± 0·02	4·22 ± 0·01	0·1421 ± 0·0009	0·422 ± 0·003	(26)
Group III compounds						
InBr	4·460 ± 0·005	12·39 ± 0·02	4·73 ± 0·01	0·114	0·34	SR **13**
InI	4·75	12·76	4·91	0·102 ± 0·001	0·355 ± 0·001	(27)
TlI (m)	4·582	12·92	5·251	0·108 ± 0·002	0·367 ± 0·002	SB* **4**, **17**
Group IV compounds						
α–NaOH	3·39 ± 0·03	11·32 ± 0·05	3·39 ± 0·03	0·16	0·37	SR† **11**
α–KOH	4·03	11·4	3·95	0·14	0·39	SR **11**
α–RbOH	4·30	12·2	4·15			SR **11**

* *Strukturbericht.*

† *Structure Reports.*

(a) Orientation error (*Cmmc* instead of *Amma*) in original paper, different orientation error in *Structure Reports* **13** (*Bbmm* instead of *Amma*).

(b) The adjustable parameters in the original paper are interchanged erroneously.

(c) In the 1955 paper, correct data are given for PrGe; in the 1960 paper, the adjustable parameters have been interchanged erroneously. With the wrong y_{Pr} value of 0·075, one calculates a Pr radius of 1·35 Å while the true Pr radius is about 1·85 Å.

(d) In the original paper, the lattice parameters b and c have been interchanged erroneously, while the space group is given correctly.

(e) Dr Dwight has informed us that the different c value of 4·047 ± 0·001 is given in the thesis of Mr Moriarty. Without experiments it is not possible to determine if the copying error is in the thesis or the publication. From the lanthanide contraction, the smaller value is more probable.

(f) Isolated ternary phase.

(g) Second modification with FeB type.

(h) Wrong space group chosen by Braun & van Vucht (1955). Identity with *B*33 type was pointed out by Kripyakevich (1962). The Al parameter was questioned by Thomson (1962*b*).

(i) High temperature modification.

(j) Calvert *et al.* (1957) listed wrong space group. Identity with *B*33 type was pointed out by Kripyakevich (1962).

(k) Baenziger & Moriarty (1961*b*) reported FeB type for GdNi.

(l) Identy of ThCo with *B*33 type was recognized by Kripyakevich (1962).

(m) Yellow modification.

Table 3 – Literature references

(1) Hellner (1950)
(2) Eckerlin, Meyer & Woelfel (1955)
(3) Iandelli (1955)
(4) Sands, Wood & Ramsey (1964)
(5) This work
(6) Dagerhamn (1963)
(7) Parthé (1959)
(8) Hohnke & Parthé (1965)
(9) Iandelli (1960)
(10) Baenziger & Moriarty (1961*a*)
(11) Cable & Wollan (1964)
(12) Pötschke & Schubert (1962)
(13) Spooner & Wilson (1962)
(14) Schob, Nowotny & Benesovsky (1961)
(15) Boller, Nowotny & Wittmann (1961)
(16) Edshammar (1961)
(17) Braun & van Vucht (1955)
(18) Blumenthal (1952)
(19) Calvert, Dunsmore, Kuhi & Tse (1957)
(20) Dwight, Conner & Downey (1965)
(21) Finney & Rosenzweig (1961)
(22) Kirkpatrick, Bailey & Smith (1962)
(23) Thomson (1962*a*)
(24) Florio, Baenziger & Rundle (1956)
(25) Thomson (1962*b*)
(26) Cromer & Roof (1959)
(27) Jones & Templeton (1955)
(28) Rocktaeschel & Weiss (1962)

certainly made the recognition of identical structure types very difficult. The errors consist of a wrong space group (CaAg and ThAl), incorrect setting of axes for given space group (CaSi), interchange of unit-cell parameters (GdGa, GdGe, DyGa and DyGe), finally a mix-up of the adjustable parameters (PrGa, PrGe, YAl). Some of the errors and structural identities had been recognized by Kripyakevich (1962). A complete list of all compounds with TlI (*B*33) structure is given in Table 3 with their unit-cell dimensions, adjustable parameter values, literature references and any necessary corrections.

The known TlI (*B*33) type compounds are conveniently separated into four divisions depending on the position of the components in the periodic system. The following divisions are used in Table 3.

Group I *A*: Alkaline earth metals or transition metals
B: B, Al, Ga, Si, Ge, Sn, Pb

Group II *A*: Alkaline earth metals or transition metals of 3rd or 4th group
B: Transition metal of 8th group or metal of Cu group

Group III *A*: In or Tl
B: Halogen elements

Group IV *A*: Alkali elements
B: Hydroxyl group

For the compounds listed under group I and II, the *A* component is always bigger than the *B* partner. Only compounds of groups I and II have metallic character while group III and group IV compounds are ionic.

The distinction between group I and group II phases is not based only on the position of the compound partners in the Periodic System. Fig. 1 shows the plots of all *B*33 type phases from groups I, II and III in a *b*/*a versus a*/*c* diagram. They are all positioned in a rather narrow band; however, compounds of group I have axial ratios different from those of group II compounds. With the exception of aluminides (YAl, ZrAl, HfAl) the plots of all group I compounds are located in the lower right half of the band in Fig. 1, but compounds of group II in the upper left half of the band. The unusual axial ratios of the aluminides remain unexplained. These exceptions, however, do not occur if Al is partly replaced by Si. The two silico-aluminides Zr(Si, Al) and Hf(Si, Al) have their plots together with those of other compounds of group I.

It seems impossible to make any incontestable statements on the electron transfer in these compounds. However, a correlation exists between the number of valence electrons of the atoms and the *a*/*c* or *b*/*a* axial ratio of the compounds. Such considerations certainly have to be restricted to those compounds which contain no transition elements from a group higher than four. Thus, not too many compounds remain for which the valence electrons of the participating atoms are known: Ca(Si, Sn, Ge); (Sc, Y) (Ga, Si, Ge); CaAg and perhaps also (Pr, Gd, Dy) (Ga, Ge); (Zr, Hf) Al and ZrSi. If one calculates the difference: number of valence electrons of the *B* element minus the valence electron number of the bigger *A* element, one obtains values between +2 (for example for CaSi) and −1 (for example for CaAg). These values – where available – are listed with each appropriate plot in Fig. 1. Large *a*/*c* values occur with large positive difference values. For *a*/*c* about unity the *A* and *B* atoms have equal number of valence electrons, and with negative electron number differences the *a*/*c* ratio is smaller than one. Summarizing, it appears in group I (except ZrAl and HfAl) that the *B* atoms have more electrons than the *A* atom and that the *a*/*c* is bigger than unity, while in group II compounds (including ZrAl and HfAl) everything is reversed. Group I and group II compounds are thus related like type and antitype compounds similar to other type–antitype pairs, for example CaF_2–Mg_2Si, $PbCl_2$–Ca_2Si, La_2O_3–Mg_3P_2, Li_3Bi–BiF_3 or $PuNi_3$ and $NbBe_3$. The three known aluminides fit best with group II compounds. Additional agreement is obtained if one assumes for each aluminum atom the unusual number of two valence electrons.

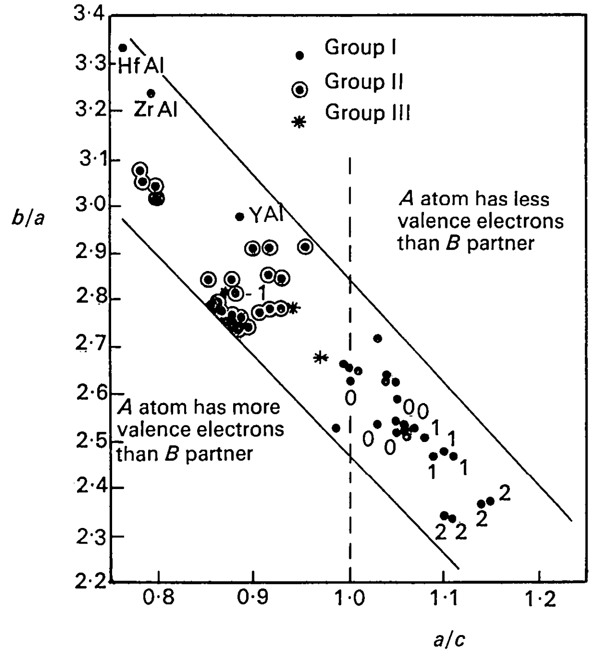


Fig. 1. The axial ratios of the TlI (*B*33) type phases.

Compounds with CsCl (*B*2) *structure*

An X-ray diffraction pattern of a sample of ScMg could be indexed with a cubic unit cell of $a = 3{\cdot}597 \pm 5$ Å. The relative intensities of the diffraction lines indicated a partly disordered *B*2 (CsCl) structure. For all diffraction lines with $h+k+l = \text{odd}$ smaller intensities were observed in comparison with those expected for perfect order. The sample was stored at room temperature for 10 days and then again X-rayed. The new diffraction pattern showed that the order in the sample had increased. The intensities of the diffraction lines corresponded now to a perfectly ordered *B*2 (CsCl) structure. The observed lattice parameter of ScMg agrees well with the calculated value assuming a Sc radius of 1·57 Å and a Mg radius of 1·57 Å, which are the metallic radii corrected for 8-coordination. All ScMg specimens gave somewhat diffuse powder patterns; however, they were all single phased.

In the powder diffraction pattern of a ScAl sample two phases were found, one of which was identified as a CsCl type phase with a unit-cell parameter of 3·450 ± 0·005 Å. This value is in good agreement with 3·44 Å obtained by summing Sc and Al radii. It was not possible to obtain the *B*2 pattern free of any other diffraction lines. Similar difficulties were encountered by Baenziger & Moriarty (1961*b*) in their synthesis of the isotypic compounds GdAl and DyAl. As discussed later, many aluminides with CsCl (*B*2) structure are probably only metastable phases.

Survey of equiatomic compounds with Sc, Y and rare earth metals

Table 4 shows a survey of *AB* compounds and their structures, where *A* denotes Sc, Y or a rare earth metal and *B* stands for a transition metal of the Co, Ni group or an element of the Cu, Zn, Ga group together with Mg and Al, and further, all elements of the carbon, nitrogen and oxygen group. The table consists of different panels, one each for every *B* component. In each panel in the first row are listed the known Sc and Y compounds and below in the next rows, the compounds of the rare earth metals in the sequence they appear in the Periodic System. All listed compounds are enclosed in a small frame. From the special shape of the frame, one can deduce the structure of the compound by using the little table in the inscription. Only four structure types are known to occur with the *AB* compounds of Table 4. They are *B*1 (NaCl), *B*2 (CsCl), B27 (FeB) and *B*33 (TlI).

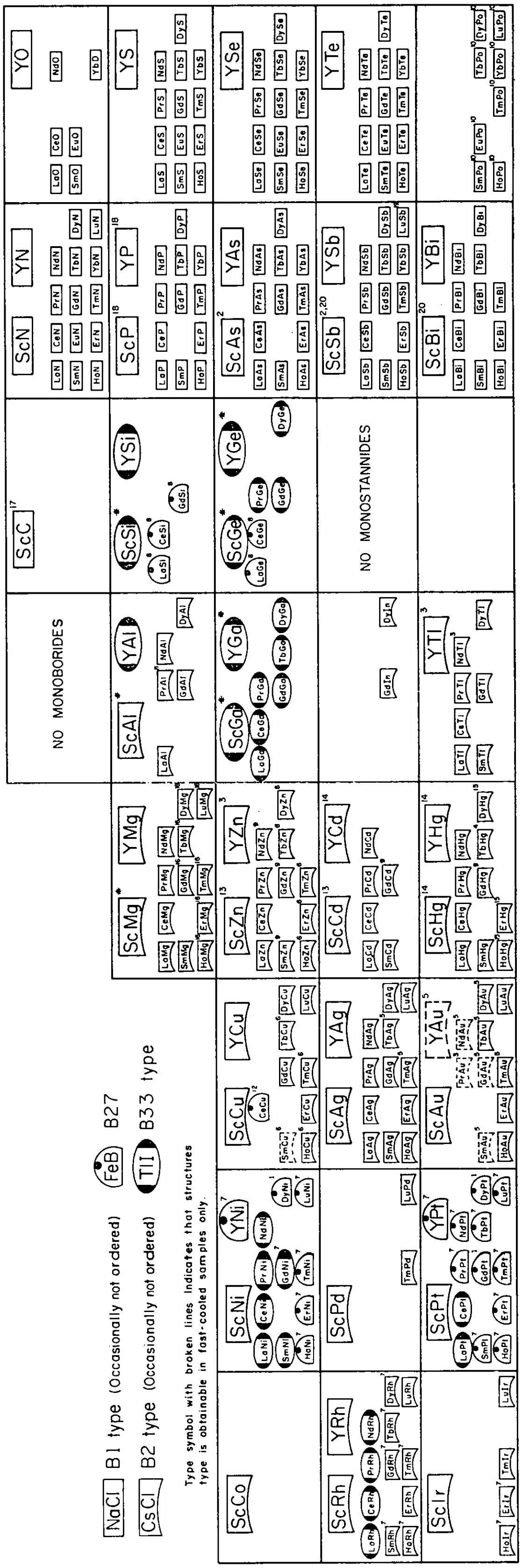
Except for ScC the *B*1 (NaCl) structure type is found only with elements of the nitrogen and oxygen groups.

The occurrence of nitrides and homologues with *B*1 (NaCl) structure might appear as not surprising. As Sc, Y and the rare earth elements usually have three electrons in their outer shell, it might be expected that elements with five electrons like N, P, As, Sb and Bi react to form ionic *AB* structures, for example, the NaCl structure. However, these compounds have metallic and not ionic properties and sometimes the atoms on the NaCl structure sites are not completely ordered (attenuation of the intensity of all lines with $h+k+l=2n+1$) which certainly is not to be expected with ionic compounds. The assumption that the rare earth elements are trivalent in these compounds has now been proven experimentally by Iandelli (1961) who measured the magnetic moment of some of these compounds. The measured moments agree fairly well with those calculated for atoms in the 3+ valence state. One can safely assume that this is true for all Sc, Y and rare earth monophosphides and homologues. Support for this is given by the regularity with which the lattice parameters change within the series of *B*1 type compounds as shown in Fig. 2.

From Sc to the La compounds one observes an increase in the lattice parameters to be expected with a change of period and from La to the Lu compounds the parameters decrease steadily owing to the lanthanide contraction. The curves for the nitrides, phosphides, arsenides, antimonides and bismuthides are similar except for a vertical displacement due to size difference of the *B* partners and a small deviation with CeN.

The occurrence of the NaCl (*B*1) structure type in the sulfides, selenides and tellurides can only be partially explained. One would expect that only two-valent elements would form an ionic *AB* structure with S and homologues. Surprisingly three-valent rare-earth elements also participate in the formation of these compounds. From measurements of magnetic moments (Iandelli, 1961) and the slope of the lattice parameter curves in Fig. 3, which show bumps for Sm, Eu and Yb compounds, one can conclude that except for Sm, Eu and Yb, which behave like two-valent elements, all others including Y are trivalent in their equiatomic compounds with S, Se or Te.

Table 4. *Survey of AB compounds with* Sc,Y *and rare earth elements*



Literature references: *This work, 1: Baenziger & Moriarty (1961*a*), 2: Brixner (1960), 3: Bruzzone & Ruggiero (1962), 4: Cable, Koehler & Wollan (1964), 5: Chao, Luo & Duwez (1963), 6: Chao, Luo & Duwez (1964), 7: Dwight, Conner & Downey (1965), 8: Hohnke & Parthé (1965), 9: Iandelli (1960*b*), 10: Kershner, Heidelberg & Steinmeyer (1964). 11: Kripyakevich, Gladyshevskii, Zarechnyuk, Evdokimenko, Zalutskii & Frankevich (1964), 12: Larson & Cromer (1961), 13: Laube & Nowotny (1963*a*), 14: Laube & Nowotny (1963*b*), 15: Kirchmayr, (1964), 16: Miller & Daane (1964), 17: Nowotny & Auer-Welsbach (1961), 18: Parthé & Parthé (1963), 19: Przybylska, Reddoch & Ritter (1963), 20: Zhuravlev & Smirnova (1962). Unmarked compounds with *B*33 structure are found in Table 3, all others in the compilations by Gschneidner (1961), Iandelli (1961), Nevitt (1963), and Spedding & Daane (1961).

The CsCl ($B2$) structure is the second most frequent structure in Table 4. It occurs in all panels from the Co group to the Al group (except for Ga compounds for which no CsCl ($B2$) structure is known), and is the exclusive structure type found in the Mg–Zn group. Just as previously mentioned in the $B1$ type structures some of these compounds are also not ordered.

The number of the valence electrons of the B partner is apparently of little influence on the formation of the CsCl ($B2$) structure. Fig. 4 contains lattice parameter curves for Sc, Y and rare-earth alloys with metals having two valence electrons such as Mg, Zn, Cd and Hg. In addition, one curve is drawn for Ag alloys (one valence electron per Ag atom) and one for thallium

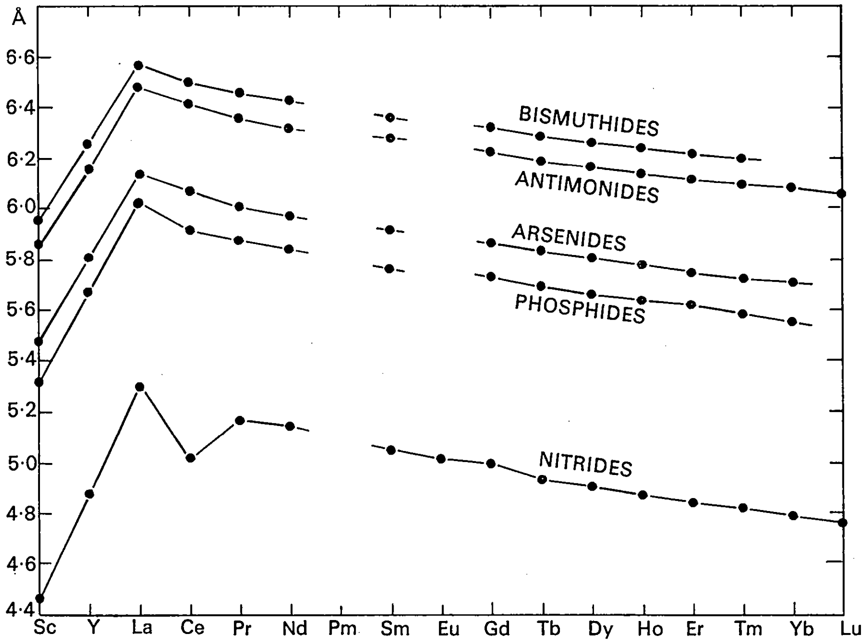


Fig. 2. Lattice parameters of the $B1$ (NaCl) structures observed with nitrides, phosphides, arsenides, antimonides and bismuthides of Sc, Y and rare earth elements.

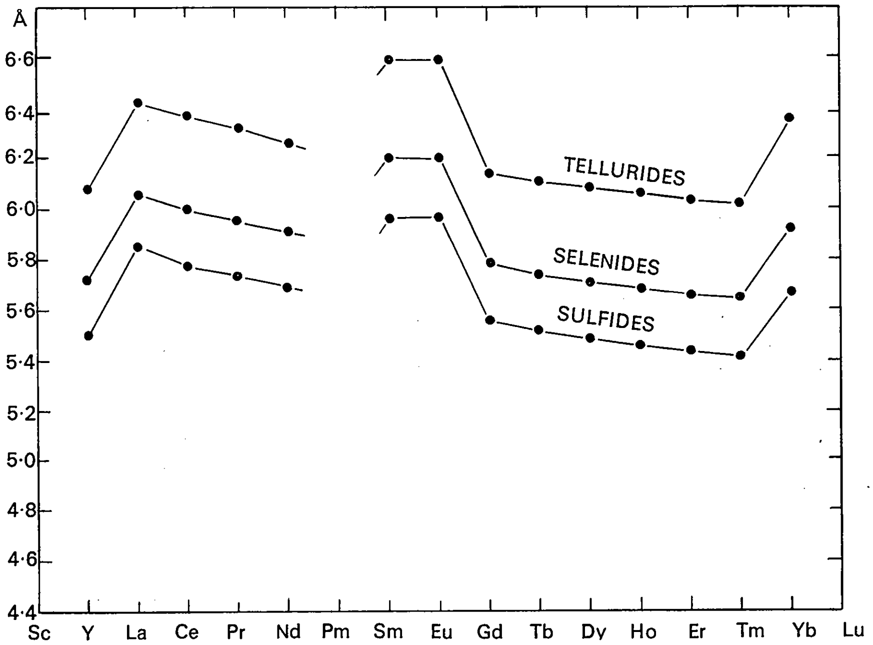


Fig. 3. Lattice parameters of $B1$ (NaCl) structures observed with sulfides, selenides and tellurides of Y and rare earth elements.

alloys (three valence electrons per Tl atom). All six curves rise sharply from Sc to La and then decrease rather uniformly. There are slight changes in slope; however, the curves show no bumps as observed in Fig. 3. Unfortunately, data for Eu and Yb alloys are missing and, therefore, final conclusions can not be made at this time. However, the data available now (listed in Fig. 4) indicate that there are no significant differences in the lattice parameter curves for alloys having *B* partners with one, two, or three valence electrons.

The TlI (*B*33) structure type occurs with silicides, germanides, gallides and in alloys with metals of the Co and Ni group. The characteristic sevenfold coordinated figure of the TlI type is also found in the FeB (*B*27) structure type, but differently arranged. One may consider the TlI and the related FeB structure type as a transition type between the NaCl type having 6 coordinated atoms and the CsCl type with 8 coordinated atoms. This is also indicated by the relative position and shape of the space filling curves of the CsCl, FeB, CrB and NaCl type, which have already been compared elsewhere (Parthé, 1961). It was suggested at that time that the CsCl structure type should occur with radius ratios from 1·0 to 1·3 and the CrB and FeB type with larger ratios. If geometrical factors alone were responsible for the formation of these compounds, such radius ratio dependence certainly would hold rigorously; however, this is not the case here. Nevertheless, the sequence of structures observed within each panel – from the alloys with large rare earth metals like La and Ce to the alloys with the small Sc – follows a pattern which agrees in principle with the results of the space-filling curve study. If the *B*2 (CsCl) and the *B*33 or *B*27 structure types all occur in one panel the *B*2 (CsCl) structure type will occur with the smaller rare earth metals and the *B*33 or *B*27 type with the larger ones. To demonstrate this, it is necessary at first to list the rare earth metals (plus Sc and Y) according to their size. Since absolute values of the size of the rare earth elements are not needed in this context, one can use as an indication of their relative size the lattice parameters of the monophosphides and homologues shown in Fig. 2. Sc is the smallest element, followed by Lu, Yb, Tm... Dy, Y, Tb, Gd..., the biggest elements being Ce and La. If all compounds within one panel are arranged according to size of the rare earth element (including Sc and Y) one will find the *B*2 (CsCl) structure with the smaller elements – there are 14 Sc compounds in Table 4 which crystallize with the CsCl structure – and the *B*33 or *B*27 structure type in compounds with larger rare earth metals.

The structure change may happen between Sc and Lu as in Ni and Pt systems (see Table 4), somewhere in the middle of the series as in Rh and Cu systems, or never at all, as in Ag, Mg, Zn, Cd and Hg systems where even the La compounds all crystallize with the *B*2 (CsCl) structure type. At first sight this rule seems to be broken in the case of the monoaluminides, where YAl has the TlI structure type and the other compounds with bigger rare earth elements crystallize with CsCl structure type. However, the *B*2 phases with big rare earth elements are probably only metastable phases similar to the gold compounds where certain *B*2 phases can be obtained only in rapid-cooled samples. Unfortunately the exact conditions for the preparation of the monoaluminides are not always given in the original literature. To avoid reaction of the rare earth elements with the crucible material the homogenizing time was usually kept to a minimum. Many authors report that the *B*2-type aluminides could not be obtained as a single phase. The structures of the stable monoaluminides crystallize probably with the *B*33 type as, for example, YAl, perhaps with the *B*27 type or an unknown orthorhombic structure type reported for CeAl.

Yttrium has the same size as dysprosium and the structure of yttrium compounds is therefore the same as that for dysprosium compounds. Examples to prove this point are DyCu and YCu or DyRh and YRh with *B*2 structure. Accordingly, one can predict that YNi

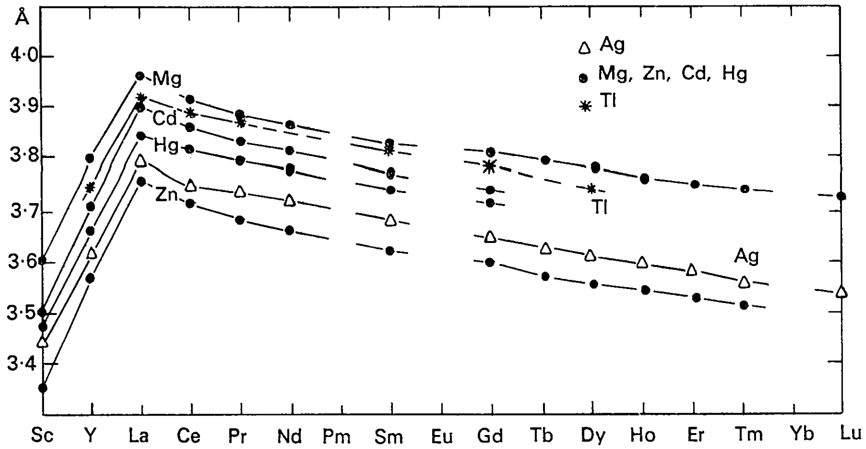


Fig. 4. Lattice parameters of *B*2 (CsCl) structures observed with alloys of Ag, Mg, Zn, Cd, Hg and Tl with Sc, Y and rare earth elements.

and YPt do not crystallize with the *B*2 (CsCl) structure type as the corresponding scandium compounds do. In agreement with these predictions YNi and YPt were found to have the same structure type as DyNi and DyPt, namely the FeB (*B*27) structure type.

This relationship between Y and Dy compounds obviously holds also for gallides and germanides (see Table 4) and perhaps for silicides. It is reasonable to guess that monogermanides and silicides with small rare earth metals from Lu to Dy all crystallize with the *B*27 or *B*33 type. It is clear from the above considerations that *B*2 (CsCl) structures are not to be expected here. Whether the *B*27 or the *B*33 type occurs can not be predicted. In Ni systems the FeB structure type occurs with the small rare earth elements and the TlI structure type with the big rare earth elements, but with monosilicides and germanides it is the reverse.

It is known from phase diagram studies that monostannides do not form. Plumbides do exist; however, they decompose so fast in air that X-ray diffraction patterns can only be made under special precautions.*

The compound ScRu with *B*2 (CsCl) type is known but no space is provided for it in Table 4. It is the only equiatomic compound with an element of the Fe group. In general, elements not listed in Table 4 do not form monocompounds with Sc, Y or rare-earth metals; they may not form any Sc, Y and rare-earth compounds at all, as for example the transition metals of the fourth, fifth and sixth groups. Exceptions are alloys of Y and rare earth metals between themselves. In many cases, in agreement with the Darken & Gurry plots (Waber, Gschneidner, Larson & Prince, 1963), complete solid solubility is observed, but intermediate compounds are found with LaY, CeY, PrY, NdY, NdTm, and others which all crystallize with the Sm structure, a nine-layer stacking variation of the f.c.c. or h.c.c. structure. (See *e.g.* Spedding, Valletta & Daane, 1962). However, the composition of these Sm type phases varies from system to system; they are equatomic compounds in some cases but not all. The occurrence of these phases has been connected with a small value of the magnetic dipole–dipole interaction energy (Gschneidner in Spedding & Daane, 1961).

Summarizing, it is possible to find some general rules which correctly describe the formation of these phases; however, many of the experimental data cannot be explained. Simple ideas on crystal structure formation using size effects, number of valence electrons, *etc.*, are just not sufficient to to explain all aspects of the occurrence of these phases and their structures.

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* Unpublished studies.

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PARTHÉ, E. (1961). *Z. Kristallogr.* **115**, 52. (In Fig. 6 are compared space-filling curves for FeSi (*B*20), FeB (*B*27), CrB (*B*33) and NaCl (*B*1) structure types. The curve for the CsCl (*B*1) structure type is very similar to the curve for FeSi type with discontinuity points at the same ε values of 0·731 and 1·365, however, altogether vertically shifted to slightly higher space-filling values.)

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Comparison of Scattering Factors Computed from Four Different Atomic Models*

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Scattering factors computed from four different atomic models are compared at various values of sin θ/λ throughout most of the Periodic Table. The differences are discussed in relation to the differences in the atomic models.

Introduction

Scattering factors calculated from four different atomic models are now available for nearly all atoms. These models are the Thomas–Fermi–Dirac (TFD), which is the familiar statistical model including exchange; the non-relativistic Hartree (H) without exchange (Cromer, Larson & Waber, 1963, 1964); the Hartree–Fock–Slater (HFS), similar to Hartree but including Slater's approximate exchange correction (Hanson, Herman, Lea & Skillman, 1964); and the Dirac–Slater (DS), the relativistic equivalent of the HFS model (Cromer & Waber, 1964, 1965).

Differences between these scattering factors have been plotted *versus* Z (atomic number) for various values of sin θ/λ. These differences are briefly discussed in relation to the differences in the atomic models. A large number of sets of differences were initially calculated and plotted with the use of a computer. The various scattering curves were fitted to analytic functions to facilitate entry of all the information into the computer. A representative few have been selected for the present discussion.

As a general rule, differences in scattering factors at low values of sin θ/λ arise because of differences in

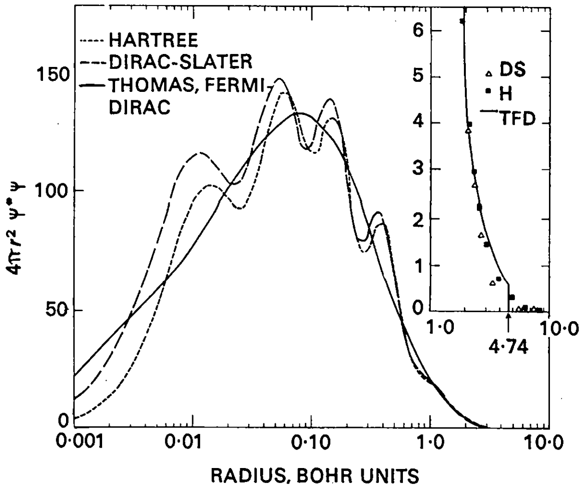

Fig. 1. Radial electron density plots for three different models of the Hg atom. The inset shows the details at large radii.

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