those of the 'pseudo-cell' obtained from X-ray data by the transformation

$$a_t = a_0, \quad c_t = 2c_0 .$$

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MX₂ Compounds of Thorium and the Polymorphism of Thorium Disilicide

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The crystal structures of phases with the composition ThX_2 have been examined using X-ray powder and single-crystal techniques. Where X is Ni, Cu, Ag, Au, Zn, Cd, Al or Si (β-ThSi₂) crystal structures of the C32-type are found. Where X is Si (α-ThSi₂) or Ga, the structures are of the C_c type. Related non-stoichiometric phases are $ThSi_{1\cdot67}$ (defect C32-type), $ThGe_{1\cdot5}$ (distorted, defect C32-type) and $ThGe_{1\cdot62}$ (defect C_c type). Stoichiometric $ThGe_2$ has an A-face-centred orthorhombic structure.

Consideration of these phases suggests that their crystal structures are influenced by the atomic radius r and the valency e of the X atom. Low values of $e \cdot r$ are reflected in crystal structures of the C32-type. Si has a critical value of $e \cdot r$ and ThSi₂ is dimorphic. Ge has the highest value of $e \cdot r$ and ThGe₂ has an orthorhombic structure which may be derived from the C32 or C_c structures. The non-stoichiometric phases are formed at the boundary between two structure types.

1. Introduction

This paper describes part of an investigation into the formation of thorium intermetallic compounds. Of the compounds examined so far, those with the composition ThX_2, except $ThGe_2$, have been found to crystallize with either the $C32(AlB_2)$-type or $C_c(\alpha\text{-}ThSi_2)$-type structures. These structures are described as follows.

$C32$ type, hexagonal, $M = 1$, D_{6h}^1, $C6/mmm$.
Positions M: $1a$ $6/mmm$ $0, 0, 0$.
$\quad\quad\quad X$: $2d$ $\bar{6}m2$ $\quad \frac{1}{3}, \frac{2}{3}, \frac{1}{2}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$.

C_c-type, tetragonal, $M = 4$, D_{4h}^{19}, $I4_1/amd$.
Equivalent positions $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$
$\quad\quad M$: $4a$ $\bar{4}2m$ $\quad 0, 0, 0; 0, \frac{1}{2}, \frac{1}{4}$.
$\quad\quad X$: $8e$ mm $\quad 0, 0, z; 0, 0, \bar{z};$
$\quad\quad\quad\quad\quad\quad\quad 0, \frac{1}{2}, \frac{1}{4}+z; 0, \frac{1}{2}, \frac{1}{4}-z.$

Thorium disilicide, ThSi₂, can have either of these

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structures depending upon the temperature of preparation. In view of this dimorphism an attempt has been made to relate these two crystal structures, and to define the principles which govern the mode of crystallization of phases with the composition ThX_2.

2. Techniques of preparation and examination

2·1. General

Most intermetallic compounds of thorium are readily oxidized on heating even in vacua of 10^{-4} mm.Hg. Many of the compounds are pyrophoric in character. This instability towards oxygen, and oxygen-containing materials such as silica, introduces many difficulties into the preparation and analysis of these compounds. It is believed that there are some errors in earlier accounts of thorium and uranium compounds because the materials subjected to X-ray study had suffered changes in composition through partial oxidation. Some indication is therefore given here of the techniques adopted in the present work to prevent such oxidation.

2·2. Preparation of intermetallic compounds

Two alternative methods of preparation were used depending upon the boiling point of element X; these were

(a) Arc-melting under argon, a technique applicable where element X does not boil below 1700 °C.

(b) Reacting thorium powder with liquid element X in an evacuated and sealed glass capsule.

Those elements unsuitable for arc-melting were molten below 500 °C. At this temperature, neither the molten elements nor their compounds with thorium attacked the glass containers.

These methods were used in preference to alternatives involving prolonged heat treatment at high temperatures in continuously evacuated systems.

2·3. X-ray analysis

X-ray examinations were made throughout by powder diffraction techniques. Laue and rotation techniques were also used to determine the symmetry and cell dimensions of ThGe$_2$. Specimens of pyrophoric materials were prepared by crushing under dry paraffin and pipetting the resulting slurry into silica quills, thus preserving them from oxidation for the duration of an X-ray exposure.

3. Experimental results

Results for the preparation and examination of phases with the composition ThX$_2$ are listed in Table 1 where they are arranged according to the periodic relationships between the X elements.

3·1. Compounds with the C32-type structure

(a) Close agreement is obtained between the results for ThNi$_2$, ThCu$_2$ and ThAl$_2$ and the data quoted by Murray (1955) for these compounds.

(b) The compounds ThAg$_2$ and ThAu$_2$ were obtained by arc-melting and appear to correspond to the phases described by Raub & Engel (1943) as Th$_3$Ag$_5$ and Th$_3$Au$_5$. That these phases are in fact ThX_2 compounds is shown from a comparison of observed and calculated densities. For the thorium–silver compound $\varrho_o = 10\cdot76$ g.cm.$^{-3}$, compared with the $\varrho_{\text{X-ray}}$ values of $10\cdot95$ g.cm.$^{-3}$ for ThAg$_2$ and $10\cdot08$ g.cm.$^{-3}$ for Th$_3$Ag$_5$. The corresponding values for the thorium–gold compound are $\varrho_o = 15\cdot35$ g.cm.$^{-3}$ and $\varrho_{\text{X-ray}} = 15\cdot75$ and $14\cdot17$ g.cm.$^{-3}$ for ThAu$_2$ and Th$_3$Au$_5$ respectively.

(c) Following an investigation of the system Th–Zn, Makarov & Gudkov (1956) reported the formation of a phase ThZn$_2$ with the C32-type structure and the cell dimensions

$$a_0 = 4\cdot20, \quad c_0 = 4\cdot17 \text{ Å} .$$

These values are not in agreement with those quoted above for ThZn$_2$.

Makarov & Gudkov observed chemical attack on the silica containing vessels and in many instances the thorium–zinc alloys were covered with crystals of α-ThSi$_2$. This compound does not appear to have been present in the preparation in which crystals described as ThZn$_2$ were found. This is significant in view of the similarity between Makarov & Gudkov's cell dimensions and the cell dimensions for β-ThSi$_2$ given in this paper. It seems probable that their compound was in fact a solid solution of the type Th(Si, Zn)$_2$.

In the present investigation, ThZn$_2$ was prepared by reacting mixtures of the elements in glass capsules. Chemical attack on the containers was not detected and the compound was obtained as a homogeneous single phase from mixtures containing 66·7 at.% Zn.

Similar experiments using cadmium in place of zinc resulted in the formation of ThCd$_2$.

Table 1. *Data for* MX_2 *compounds of thorium*

Gr. VIII	Gr. IB	Gr. IIB	Gr. IIIB	Gr. IVB
—	—	—	ThAl$_2$ Hexagonal C32 $a_0 = 4\cdot388 \pm 0\cdot002$ Å $c_0 = 4\cdot162 \pm 0\cdot002$ Å	ThSi$_2$ Hexagonal C32 (β-ThSi$_2$) $a_0 = 4\cdot136 \pm 0\cdot001$ Å $c_0 = 4\cdot126 \pm 0\cdot001$ Å Tetragonal C_c (α-ThSi$_2$) $a_0 = 4\cdot135$ Å $c_0 = 14\cdot375$ Å
ThNi$_2$ Hexagonal C32 $a_0 = 3\cdot960 \pm 0\cdot003$ Å $c_0 = 3\cdot844 \pm 0\cdot004$ Å	ThCu$_2$ Hexagonal C32 $a_0 = 4\cdot387 \pm 0\cdot001$ Å $c_0 = 3\cdot472 \pm 0\cdot001$ Å	ThZn$_2$ Hexagonal C32 $a_0 = 4\cdot497 \pm 0\cdot002$ Å $c_0 = 3\cdot718 \pm 0\cdot002$ Å	ThGa$_2$ Tetragonal C_c $a_0 = 4\cdot243 \pm 0\cdot001$ Å $c_0 = 14\cdot690 \pm 0\cdot002$ Å	ThGe$_2$ A-face centred orthorhombic $a_0 = 4\cdot15 \pm 0\cdot01$ Å $b_0 = 4\cdot04 \pm 0\cdot01$ Å $c_0 = 16\cdot69 \pm 0\cdot01$ Å
Pd compounds not examined	ThAg$_2$ Hexagonal C32 $a_0 = 4\cdot837 \pm 0\cdot002$ Å $c_0 = 3\cdot353 \pm 0\cdot002$ Å	ThCd$_2$ Hexagonal C32 $a_0 = 5\cdot005 \pm 0\cdot002$ Å $c_0 = 3\cdot514 \pm 0\cdot002$ Å	No ThX_2 compound formed with In	No ThX_2 compound formed with Sn
No ThX_2 compound formed with Pt	ThAu$_2$ Hexagonal C32 $a_0 = 4\cdot740 \pm 0\cdot002$ Å $c_0 = 3\cdot402 \pm 0\cdot002$ Å	No ThX_2 compound formed with Hg	Tl compounds not examined	No ThX_2 compound formed with Pb

(d) The low-temperature polymorph of thorium disilicide, β-ThSi₂, was obtained by reacting thorium with silicon in a liquid bismuth medium. The experiments which led to the isolation and identification of this phase are described in a separate paper (Brown & Norreys, 1961a).

3·2. Compounds with the C_c-type crystal structure

(e) Good agreement was obtained between the powder diffraction data for α-ThSi₂ and the single-crystal data for this phase given by Brauer & Mitius (1942).

The structure transformation in ThSi₂ was examined by heat treatment of samples of the two forms in sealed and evacuated silica capsules. Above 1350 °C., β-ThSi₂ transformed rapidly to α-ThSi₂ and below 1250 °C., the reverse transformation occurred.

(f) Thorium powder reacted readily with gallium at 500 °C. to form a phase with the C_c-type structure. That this compound has the composition ThGa₂ was confirmed from its formation as a homogeneous single phase in mixtures containing 66·7 at.% Ga. Examination of the X-ray intensities in the powder pattern of this compound indicates that the z parameter for the Ga atom is $0·393 \pm 0·005$.

3·3. Phases with defect C32 and C_c-type structures

In addition to the stoichiometric compounds described above, there are also a number of phases with the C32 or C_c structures in which the full complement of X atoms is not attained. So far only silicon and germanium have been found to give this type of compound. Mention of these phases is relevant in the present context since they are structurally derived from the stoichiometric ThX_2 compounds.

(g) The formation of ThSi₁.₆₇ with the C32 structure has been established by arc-melting (Brown & Norreys, 1961a) and ThSi₁.₆₇ is also produced through loss of silicon, probably as SiO, on heating ThSi₂ in a continuously evacuated system. A closely similar phase which shows a monoclinic or triclinic distortion of the C32 structure cell has been found in the thorium–germanium system by Tharp, Searcy & Nowotny (1958). Present evidence from arc-melted preparations indicates that this phase has the composition ThGe₁.₅ (Brown & Norreys, 1960b). The hexagonal cell dimensions of these phases are

ThSi₁.₆₇ $a_0 = 3·986 \pm 0·001$, $c_0 = 4·228 \pm 0·001$ Å
ThGe₁.₅ $a_0 = 4·06 \ \pm 0·01$, $c_0 = 4·18 \ \pm 0·01$ Å

(the small structure distortion in this compound is ignored for present purposes).

There is an important structural difference between the defect and stoichiometric C32 phases. Thus in the defect phases, values for c/a, the axial ratio of the structure cell, are greater than unity; in the stoichiometric compounds, these values are always less than unity.

(h) In the Th–Ge system, a phase with the C_c structure has been detected and the following cell dimensions have been quoted by Tharp et al. (1958).

$$a_0 = 4·106, \quad c_0 = 14·193 \text{ Å}.$$

These authors have described the phase as α-ThGe₂ by analogy with α-ThSi₂. Inspection of the cell dimensions shows, however, that the cell volume is less than that of the disilicide whereas a volume slightly greater than that of ThGa₂ might be expected for stoichiometric ThGe₂. Evidence obtained from arc-melting thorium–germanium alloys indicates that this is a defect phase with the composition ThGe₁.₆₂ (Brown & Norreys, 1961b).

4. Discussion

4·1. General

Ten stoichiometric ThX_2 compounds have been described of which nine have either the C32 or C_c crystal structures while the tenth has an A-face centred orthorhombic structure probably related to the other two. ThSi₂ is unique in that it is dimorphic and crystallizes with both the C32 and C_c structures. The elements which are combined with thorium are adjacent members of the periodic table and it is therefore possible that these compounds are both structurally and chemically related. Thus the Th–X interactions may be visualized as undergoing progressive alteration through the series of C32 compounds until at ThSi₂ the stability of this structure type becomes doubtful. Thereafter the C_c structure is presumed to offer a more stable atomic arrangement. The occurrence of defect silicides and germanides is significant in this respect since their formation appears to coincide with the upper limits of stability for these structure types.

Most of the above compounds have the C32 type structure. This crystal structure has been found for most of the diborides of the transition elements where there is a substantial difference between the radii of the boron and metal atoms. These borides are in fact interstitial compounds. It is to be expected therefore that the formation of $M X_2$ phases with the C32 structure would be influenced by the radius ratio of the component M and X atoms. In order to understand these influences more fully a review is given below of the principal features of this structure type with reference to β-ThSi₂ and the defect phases ThSi₁.₆₇ and ThGe₁.₅.

4·2. The C32-type crystal structure

A packing diagram for β-ThSi₂ is shown in Fig. 1. The structure consists of close-packed sheets of metal atoms, M, placed directly over each other with an intermediate layer of X atoms of smaller radius located between these sheets. A succession of such sheets normal to the hexagonal [0001] direction may be represented by the sequence

$M\,X\,M\,X\,M\,X\,M$.

This arrangement provides two interstices per metal atom and the unit hexagon shown in Fig. 1 may be regarded as containing three metal atoms and six interstices. Stoichiometric MX_2 compounds thus correspond to complete occupation of these interstices by X atoms.
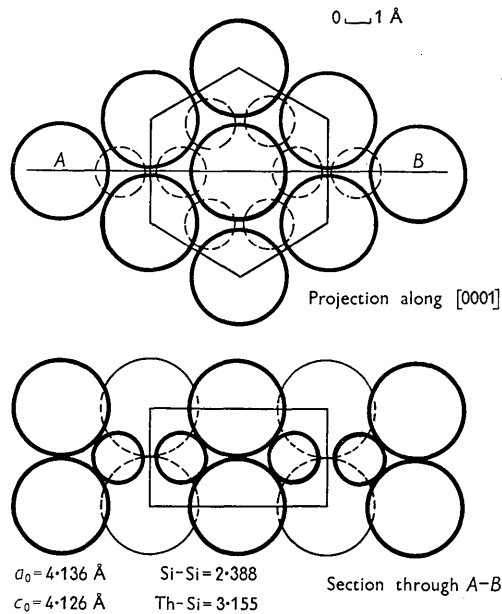

Fig. 1. Atomic packing diagram of β-ThSi$_2$.

0 ⊢—⊣ 1 Å

Projection along [0001]

$a_0 = 4\cdot136$ Å   Si–Si = 2·388
$c_0 = 4\cdot126$ Å   Th–Si = 3·155

Section through A–B

In this simple structure, the separation of the sheets of M atoms becomes the c_0 dimension and the atomic separation within these sheets, the a_0 dimension of the hexagonal cell. Calculation shows that if the radius ratio of the atomic species r_X/r_M is less than 0·527, the structure is truly interstitial and each X atom occupies the centre of a right trigonal prism formed by the contact of metal atoms in adjacent close-packed sheets. The separation of metal atoms within each sheet is equal to that between the sheets and accordingly the axial ratio of the cell, c/a, is unity. The idealized interstitial arrangement provides the following nearest neighbours:

Atom	Neighbour	Coordination number	Distance
M	M	8	$a_0\ (=c_0)$
	X	12	$a_0\ \sqrt{\tfrac{7}{12}}$
X	M	6	$a_0\ \sqrt{\tfrac{7}{12}}$
	X	3	$a_0\ \sqrt{3}$

Consideration of the Th–Th and Th–Si interatomic distances in β-ThSi$_2$ indicates that the atomic radii for thorium and silicon in this phase are 2·063 and 1·092 Å respectively. These figures give a value of 0·529 for r_{Si}/r_{Th}. This is noticeably larger than the radius ratio requirement derived above for truly interstitial packing. In ThSi$_2$, therefore, a truly inter-

stitial structure is not possible and expansion must take place either along the hexagonal [0001] or [10$\bar{1}$0] directions. The first of these alternatives leads to a crystal structure in which c/a is greater than unity, the second to a structure in which c/a is less than unity. In either case, a reduction from eight in the number of M–M nearest neighbours follows.

In the first instance, each Th atom would retain six coplanar Th atoms at a distance of a_0, while two other Th atoms would lie at the greater distances of + and $-c_0$. The compounds ThSi$_{1\cdot67}$ and ThGe$_{1\cdot5}$ display this type of configuration. Here the shortest Th–Th distances ($=a_0$) are 3·99 and 4·06 Å respectively and are sufficiently close to the value of 3·64 Å found in thorium metal to suggest the presence of metal–metal bonding within the close packed sheets. By comparison, the separations between the sheets ($=c_0$) of 4·23 Å in ThSi$_{1\cdot67}$ and 4·18 Å in ThGe$_{1\cdot5}$ indicate that Th–Th interactions in this direction are at a minimum. The sheets are presumably held by bonds formed with the defect layers of silicon or germanium atoms lying between them.

β-ThSi$_2$ and the isostructural ThX_2 compounds have the alternative packing arrangement characterized by values of c/a less than unity. In β-ThSi$_2$ c/a is 0·998. This compound therefore has a structure close to the ideal interstitial configuration. The polymorphism of ThSi$_2$ indicates, however, that at temperatures above 1350 °C. this arrangement is unstable relative to that of the tetragonal C_c structure of α-ThSi$_2$. The relationship between the C_c and $C32$ crystal structures can be seen from the model proposed below to explain the transformation in ThSi$_2$.

4·3. The mechanism proposed for the $\alpha \rightarrow \beta$ transformation in ThSi$_2$

A projection along the [010] direction of the structure cell of α-ThSi$_2$ is shown in Fig. 2. The similarities between the Th–Th coordination in α-ThSi$_2$ and in β-ThSi$_2$ can be seen from the following table:

Phase	Atom	Neighbour	Coordination number	Distance (Å)	
β-ThSi$_2$	Th	Th$_I$	2	4·126	$(=c_0)$
		Th$_{II}$	6	4·136	$(=a_0)$
α-ThSi$_2$	Th	Th$_I$	4	4·135	$(=a_0)$
		Th$_{II}$	4	4·146	$(=(a_0^2/4 + c_0^2/16)^{\frac{1}{2}})$

It is noteworthy that in both these phases, a small change in cell dimension would yield a Th–Th coordination value of eight. Thus in β-ThSi$_2$ a change in c/a from 0·998 to unity and in α-ThSi$_2$ a change in c/a from 3·478 to 3·464 ($2\sqrt{3}$) would result in equivalent crystal structures with identical coordination.

A feature of the symmetry of α-ThSi$_2$ is the division of the cell into two halves so that the upper half corresponds to the lower rotated through 90° about the tetragonal [001] direction. This division yields two
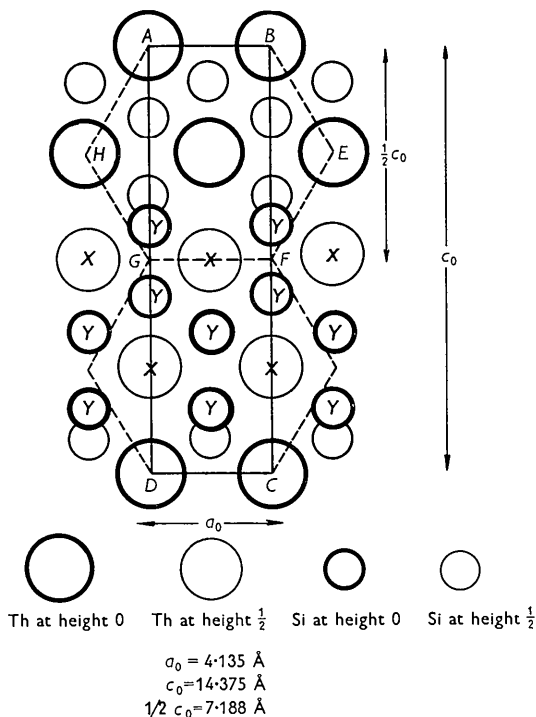
Th at height 0   Th at height ½   Si at height 0   Si at height ½

$$a_0 = 4 \cdot 135 \text{ Å}$$
$$c_0 = 14 \cdot 375 \text{ Å}$$
$$\tfrac{1}{2} c_0 = 7 \cdot 188 \text{ Å}$$

Fig. 2. Tetragonal structure cell of α-ThSi₂ projection along [010] direction.

sub-cells with the dimensions

$$a_0 = 4 \cdot 135, \quad \tfrac{1}{2}c_0 = 7 \cdot 188 \text{ Å} .$$

The ratio, $\tfrac{1}{2}c/a = 1 \cdot 739$, is close to $\sqrt{3}$, a critical value capable of giving hexagonal symmetry to the structure cell. Thus in Fig. 2, the condition that $ABEFGH$ should be a hexagon is given by $AG/AB = \sqrt{3}$.
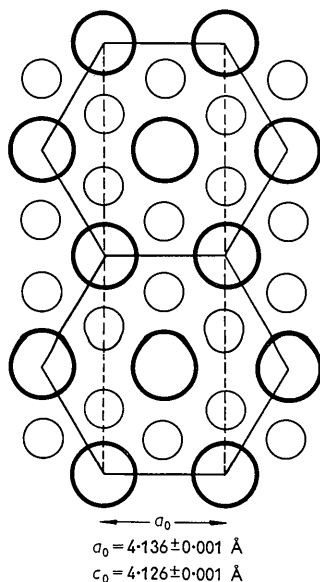

$$a_0 = 4 \cdot 136 \pm 0 \cdot 001 \text{ Å}$$
$$c_0 = 4 \cdot 126 \pm 0 \cdot 001 \text{ Å}$$

Fig. 3. Hexagonal structure cell of β-ThSi₂ projection along [0001] direction.

Whilst these geometrical relationships suggest that α-ThSi₂ might transform to a hexagonal modification, a rearrangement of some thorium and silicon atoms is clearly necessary to effect the change in structure. In Fig. 2, thorium atoms, X, depicted as lying within the cell at height $\tfrac{1}{2}$, and silicon atoms, Y, at height 0 are moved along the [110] direction through a distance $a_0/\sqrt{2}$. This translation brings all thorium atoms to height 0 and silicon atoms to height $\tfrac{1}{2}$ between them.

Comparison of the measured cell dimensions of the two polymorphs indicates that within the limits of experimental error, the repeat distance in the tetragonal [100] direction is unchanged by the transformation. However, contractions occur in the (001) repeat distance, which is reduced from 14·375 to 14·326 Å to fulfill the condition that $AG/AB = \sqrt{3}$, and also in the (010) repeat distance which is altered from 4·135 to 4·126 Å. The result is the hexagonal structure shown in Fig. 3. The Th–Si interatomic distance of 3·161 Å found in α-ThSi₂ is comparable with 3·155 Å, the value of this distance in β-ThSi₂.

4·4. *The influence of size factor and valency in* ThX_2 *compounds*

From the above, it appears that the polymorphism of ThSi₂ is associated with the relatively small atomic radius of the silicon atom. This small atomic radius permits an approach to a close-packed configuration in the alternative structures which become equivalent in terms of atomic coordinations. A further influence of the radius ratio r_X/r_M can be seen from a comparison of the cell dimensions for the ThX_2 compounds of Group IB and IIB elements given in Table 1.

For the compounds ThCu₂, ThAu₂ and ThAg₂, containing Group IB elements whose Goldschmidt radii increase in the order $r_{Cu} < r_{Au} < r_{Ag}$, a_0 increases and c_0 decreases in the same order. Similarly for the compounds of Group IIB elements, in which $r_{Zn} < r_{Cd}$, the a_0 and c_0 dimensions are respectively greater and less for ThCd₂ than for ThZn₂.

The above correlation is only observed within a given group of the periodic table and is not applicable to the series of ThX_2 compounds with the $C32$ structure as a whole. This suggests that valency considerations may also influence coordination in these compounds. In Table 2, the X elements are listed according to the magnitude of the product $e.r$, where e is the formal valency and r the atomic radius. For the compounds with the $C32$ structure values of r_X are obtained from calculations of Th–Th and Th–X interatomic distances. The particularly large radii of silver and cadmium appear to be compensated by their small valencies so that these atoms can occupy the 'interstices' in the $C32$ structure. ThSi₂ may be regarded as occupying the position of equilibrium between the $C32$ and C_c structure groups owing to the combination in the silicon atom of small atomic radius and large formal valency. By comparison gallium has intermediate valency and large atomic radius and ThGa₂

Table 2.

MX_2 compound	Interatomic distances		Atomic radii		Formal valency of X atom		Structure type
	Th–Th $=c_0$	Th–X $=(a_0^2/3+c_0^2/4)^{\frac{1}{2}}$	r_{Th}	r_X	e_X	$e_X \cdot r_X$	
ThCu$_2$	3·472 Å	3·071 Å	1·736	1·335	1	1·34	
ThAu$_2$	3·402	3·221	1·701	1·520	1	1·52	
ThAg$_2$	3·353	3·256	1·677	1·579	1	1·58	
ThNi$_2$	3·844	2·987	1·922	1·065	2	2·13	C32
ThZn$_2$	3·718	3·194	1·859	1·335	2	2·67	
ThCd$_2$	3·514	3·383	1·757	1·626	2	3·24	
ThAl$_2$	4·162	3·242	2·081	1·161	3	3·48	
β-ThSi$_2$	4·126	3·155	2·063	1·092*	4	4·37	
α-ThSi$_2$	—	—	—	1·092	4	4·37	C_c
ThGa$_2$	—	—	—	1·53†	3	4·59	
ThGe$_2$	—	—	—	1·39†	4	5·56	A-face centred orthorhombic

* r_{Si} found in hexagonal USi$_2$ = 1·093 Å (Brown & Norreys, 1960b).
† r_{Ga} and r_{Ge} values are approximate and are quoted for 12 co-ordination.

crystallizes with the C_c structure only. Germanium, which has the highest value for $e.r$, does not form a stoichiometric ThX_2 phase with either the $C32$ or C_c structures. Although the face-centred orthorhombic structure found for ThGe$_2$ (Brown & Norreys, 1961b) is dimensionally related to the polymorphs of ThSi$_2$, further investigation is necessary to establish whether this compound is structurally related to the series of ThX_2 compounds as a whole.

The formation of the defect phases provides a further example of the operation of size factor and valency. Thus ThSi$_{1.67}$ and ThGe$_{1.5}$, which are more stable than β-ThSi$_2$, combine reduced valency and volume requirements for the interstitial atom compared with those for silicon in the stoichiometric disilicide. Compared with ThGe$_{1.5}$ (60 at.% Ge), the phase ThGe$_{1.62}$ (61·9 at.% Ge) has a defect C_c structure corresponding to the slightly increased $e.r$ requirements of the additional germanium atoms.

5. Concluding remarks

The close association of $C32$ and C_c crystal structures is not restricted to compounds of thorium alone. Thus uranium forms USi$_2$ (Brown & Norreys, 1961b), UGa$_2$ (Makarov & Levdik, 1956) and UHg$_2$ (Rundle & Wilson, 1949) with the $C32$ type structure. In addition USi$_{1.67}$ has the defect $C32$ structure and USi$_{1.88}$ the defect C_c structure (Brown & Norreys, 1961b), provid-

ing a correlation between the U–Si and Th–Ge systems. Whilst only a qualitative consideration of the relationships between structures and compositions has been presented here, it is believed that were the investigation extended to include other MX_2 compounds of actinide and lanthanide elements an approach to a more quantitative treatment could be made.

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