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The Crystal Structures of two Thorium Germanide Phases with Compositions Approximating to $Th_{0 \cdot 9}Ge_2$ and $ThGe_2$

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The structures of two germanium-rich thorium germanides have been found to have C-face-centred orthorhombic symmetry. One of the phases represents a new structure type; the second has the $C49(ZrSi_2)$-type structure, is isostructural with UGe_2 and is probably stoichiometric $ThGe_2$. The first structure can be derived from the second by a simple crystallographic translation of some of the component atoms. The structures are discussed in the light of their close relationship with the anti-$C38(Fe_2As)$-type phases $ThAs_2$, $ThSb_2$ and $ThBi_2$ and their similarity to the polymorphs of $ThSi_2$. The first phase is thought to have a defect structure and a composition close to $Th_{0 \cdot 9}Ge_2$.

1. Introduction

In an investigation of the phase diagram for the system Th–Ge, the phase in equilibrium with free germanium was observed to become homogeneous in arc-melted alloys at a composition between 67 and 69 at.% Ge (Brown & Norreys, 1962). It was not possible to determine the germanium content of this phase more accurately owing to the relative insensitivity towards small amounts of free germanium shown by the micrographic and X-ray powder techniques used in the examination. Measurement of the powder diffraction pattern given by this phase showed that it corresponds to the intermetallic phase described earlier as cubic $ThGe_{3 \cdot 0 \pm 0 \cdot 4}$ (Tharp, Searcy & Nowotny, 1958).

As a result of equilibrium experiments between thorium–germanium alloys and liquid bismuth, well developed crystals of two orthorhombic thorium–germanides were obtained. Powder patterns showed that one of these, crystallizing in bismuth above 650 °C., was identical with the germanium-rich phase described above. The second, crystallizing in bismuth below 650 °C., had not been previously reported in the literature.

The present investigation was made to examine the structural relationships which were expected to exist between these two phases on account of the correspondence between their cell symmetries and the similar manner of their crystallization from liquid bismuth. To facilitate description, the phases are designated as follows.

I *or* orth. $ThGe_2$(I)—the phase formed by arc-melting at 67–69 at.%. Ge and by equilibration in liquid bismuth above 650 °C.

II *or* orth. $ThGe_2$(II)—the phase formed by equilibration in bismuth below 650 °C.

2. Experimental

2·1. *Preparation of crystals*

Orth. $ThGe_2$(I) was obtained by equilibrating 10 g. of an arc-melted alloy containing $\simeq 60$ at.% Ge with 40 g. of bismuth at 700 ± 10 °C. for 48 hr. For this purpose, the reactants were sealed under vacuum in a silica capsule and simultaneously heated and shaken together to promote reaction. The alloy product was cooled, broken into lumps and transferred to an alumina crucible. Crucible and contents were resealed under vacuum in a silica capsule and heated at 700 ± 10 °C. for a month. Crystals of I varying in size from 50 to 200μ, together with free germanium, were isolated on dissolving the bismuth matrix in 50% nitric acid.

Crystals of orth. $ThGe_2$(II) were obtained by a similar procedure. In this instance, the equilibrating and crystal growing temperatures were limited to 600 ± 10 °C. The product also contained crystals of the defect C_c-type phase $ThGe_{1 \cdot 6}$ (Brown, 1961; Brown & Norreys, 1962).

2·2 *X-ray examination*

Accurate cell dimensions for the two germanides were obtained from powder patterns recorded in a Guinier-type focusing camera using Cr $K\alpha_1$ radiation (λ Cr $K\alpha_1 = 2 \cdot 2896$ Å). The specimens were prepared by crushing selected crystals together with silicon ($a_0 = 5 \cdot 4306$ Å) used as an internal standard. Powder diffraction data for the two phases are recorded in Tables 1 and 2.

For the crystal-structure determinations, Weissenberg patterns were obtained from selected crystals using zirconium-filtered Mo K radiation. The multiple-film technique was used with thin iron foil placed between successive films. Intensities were estimated by visual comparison with a standard intensity scale. Corrections were applied for Lorentz and polarization factors and, at a later stage, the structure factors were roughly corrected for absorption.

The refinement of the structures was made with the electronic digital computer BESK using programmes made available at BESK for Fourier summations and S.F. calculations. The form factors were employed in

Table 1. *Guinier powder data for orth.* $ThGe_2$(I)

Cr K radiation $\lambda_{\alpha_1} = 2{\cdot}2896$ Å

$a_0 = 16{\cdot}642 \pm 0{\cdot}006$, $b_0 = 4{\cdot}023 \pm 0{\cdot}002$, $c_0 = 4{\cdot}160 \pm 0{\cdot}002$ Å

hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	I_0	$p\|F\|^2 \times 10^4$
200	—	0·01893	—	0·24
400	0·07579	0·07572	*m*	2·94
001		0·07572		6·03
110	0·08569	0·08568	*m*	8·19
201	—	0·09464	—	0·44
310	0·12355	0·12353	*m*	8·39
401	0·15140	0·15143	*s*	25·48
111	0·16136	0·16139	*mw*	6·45
600	0·17033	0·17037	*m*	10·54
311	0·19929	0·19925	*vs*	90·32
510		0·19925		9·18
601	0·24610	0·24608	*w*	2·79
511	0·27492	0·27497	*w*	3·06
002	0·30281	0·30284	*s*	19·82
800		0·30287		4·49
710	0·31286	0·31284	*m*	21·31
202	—	0·32177	—	0·16
020	0·32379	0·32379	*m*	18·42
220	—	0·32472	—	0·15
402	0·37860	0·37855	*m*	2·10
801		0·37858		10·90
112	0·38855	0·38852	*mw*	5·54
711		0·38855		2·10
021	0·39943	0·39950	*w*	3·87
420		0·39951		1·96
312	0·42637	0·42638	*w*	5·90
221	—	0·41843	—	0·23
910	—	0·46427	—	0·20
602	0·47324	0·47321	*mw*	7·26
10,00		0·47324		0·02
421	0·47517	0·47522	*m*	16·50

Table 2. *Guinier powder data for orth.* $ThGe_2$(II)

Cr K radiation $\lambda_{\alpha_1} = 2{\cdot}2896$ Å

$a_0 = 4{\cdot}223 \pm 0{\cdot}002$, $b_0 = 16{\cdot}911 \pm 0{\cdot}006$, $c_0 = 4{\cdot}052 \pm 0{\cdot}002$ Å

hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	I_0	$p\|F\|^2 \times 10^4$
020	—	0·01833	—	0·72
040	0·07327	0·07333	*vw*	2·19
110	0·07815	0·07808	*w*	5·59
021	0·09830	0·09814	*s*	9·20
130	0·11479	0·11474	*m*	10·11
041	—	0·15313	—	0·48
111	0·15782	0·15788	*vw*	6·10
060	0·16485	0·16499	*m*	16·93
150	0·18805	0·18807	*m*	23·44
131	0·19461	0·19454	*vs*	111·76
061	0·24473	0·24479	*mw*	20·61
151	—	0·26787	—	0·58
080	—	0·29331	—	2·76
200	0·29397	0·29397	*m*	24·88
170	—	0·29806	—	0·14
220	—	0·31230	—	0·58
002	0·31922	0·31922	*m*	23·14
022	—	0·33755	—	0·54
240	—	0·36730	—	1·97
081	0·37312	0·37312	*mw*	16·76
171	—	0·37786	—	2·81
221	0·39207	0·39211	*mw*	14·76
042	—	0·39255	—	1·85
112	—	0·39730	—	4·94
132	0·43389	0·43396	*vw*	7·92
190	0·44476	0·44477	*mw*	16·80
241	—	0·44710	—	0·47
010,0	—	0·45830	—	0·32
260	0·45884	0·45896	*w*	14·61
062	0·48429	0·48421	*w*	13·68

exponential form using coefficients given for thorium in the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) and for germanium by Thomas & Umeda (1957). The real part of the anomalous dispersion correction was applied to the form factors for each type of atom. The values used were those given by Dauben & Templeton (1955) of -7 and $+0{\cdot}2$ electrons for thorium and germanium respectively. The refinement of the temperature and scale factors was made by means of a least-squares programme. The standard deviations of the atomic parameters were calculated using Cruickshank's formula (1949).

2·3. *Determination of the crystal structures*

For the examination of orth. $ThGe_2$(I), the crystal used was a near-cylindrical fragment (mean radius 86μ) in which the cylinder axis corresponded to the [010] crystal axis. Layer-line patterns for $0 \le k \le 3$ demonstrated systematic absences for *hkl* reflections when $h+k=2n+1$. The intensity distribution in the *hkl* reflections followed closely that in the $h,k+2,l$ reflections and it was concluded that the atoms occupy special positions along the [010] axis.

From the above observations and the location of peaks in the Patterson section $P(x0z)$ computed from S.F. data given by 360 independent $h0l$ and hll reflections, it was concluded that the thorium atoms are in the positions $4(g)$ ($x_{\text{Th}} \simeq 0{\cdot}144$) and the germanium atoms in the positions $4(h)$ ($x_{\text{Ge}} \simeq 0{\cdot}296$), $2(b)$ and $2(d)$ of the space group *Cmmm*–(D_{2h}^{19}). The structure was refined by successive difference syntheses using 180 $h0l$ S.F.s corrected for absorption in a cylindrical specimen with $\mu R = 9$.

For the structure determination of orth. $ThGe_2$(II) a nearly cylindrical crystal (mean radius 30μ), with the cylinder axis coincident with the [001] crystal axis, was used to obtain the layer line patterns $0 \le l \le 3$. Systematic absences were observed for *hkl* reflections when $h+k=2n+1$ and for $h0l$ when $l=2n+1$. From the closely similar intensity distributions in the *hkl* and $hkl+2$ reflections, it was inferred that the atoms occupy special positions along the [001] axis. The highest symmetry fullfilling these conditions is *Cmcm*–(D_{2h}^{17}).

UGe_2 has the $C49$ ($ZrSi_2$)-type structure in which the atoms U, Ge_{I} and Ge_{II} all occupy the positions $4(c)$ of the space group *Cmcm* (Makarov & Bykov, 1959). It seemed probable that II would be isostructural with UGe_2 and the structure was refined on this assumption using 180 $hk0$ S.F.s corrected for absorption in a cylindrical specimen with $\mu R = 2{\cdot}9$. In the difference syntheses, shifts in the atomic parameters became smaller than the standard deviations when the observed S.F.s of ten of the strongest low angle reflections were set equal to the calculated values.

Note that $ThGe_2$(I) was previously reported (Brown, 1961) and was described as *A*-face-centred orthorhombic. This orientation was chosen in order to demonstrate dimensional similarities with α-$ThSi_2$. In the present paper, however, the compounds described have been assigned axes in accordance with the standard settings given in the 1952 edition of the *International Tables*.

3. Results

Final structure data for the two germanides are given in Table 3. Details of the nearest-neighbour coordinations obtained from these results are listed in Table 4.

Table 3. *Structure data for orth.* $ThGe_2$ *phases*

Orth. ThGe(I). Space group *Cmmm*–(D_{2h}^{19})
$a_0 = 16{\cdot}642 \pm 0{\cdot}006$, $b_0 = 4{\cdot}023 \pm 0{\cdot}002$, $c_0 = 4{\cdot}160 \pm 0{\cdot}002$ Å;
$U = 278{\cdot}52$ Å^3

Atomic positions and parameters (x)		$\sigma(x)$	Temperature factor B
Th in 4(g)	0·1396	0·0002	Isotropic and general = 0·57 Å^2
Ge in 4(h)	0·3005	0·0006	
in 2(d)			
in 2(b)			

Reliability coefft. for 180 $h0l$ reflections $R = 0{\cdot}17$.*

Orth. ThGe(II). Space group *Cmcm*–(D_{2h}^{17}). *C*49-type structure
$a_0 = 4{\cdot}223 \pm 0{\cdot}002$, $b_0 = 16{\cdot}911 \pm 0{\cdot}006$, $c_0 = 4{\cdot}052 \pm 0{\cdot}002$ Å;
$U = 289{\cdot}37$ Å^3

Atomic positions and parameters (y)		$\sigma(y)$	Temperature factor B
Th in 4(c)	0·1037	0·0001	Isotropic and general = 0·41 Å^2
Ge_I in 4(c)	0·7490	0·0003	
Ge_{II} in 4(c)	0·4512	0·0006	

For 180 $hk0$ reflections $R = 0{\cdot}12$*

* Tables of observed and calculated S.F.s for the two structures can be obtained from this Institute on request.

High values for σ and R were traced to discrepancies between the calculated and observed S.F.s for reflections in a limited number of zones. It was noted that in the difference maps 'four-leaf clover' patterns of positive and negative 'electron density' were centred on the Th and Ge positions. These might be taken to indicate the occurrence of anisotropic thermal vibrations. However, in each instance, these areas were oriented parallel to the cell axes and in view of the shape and orientation of the crystals, they might

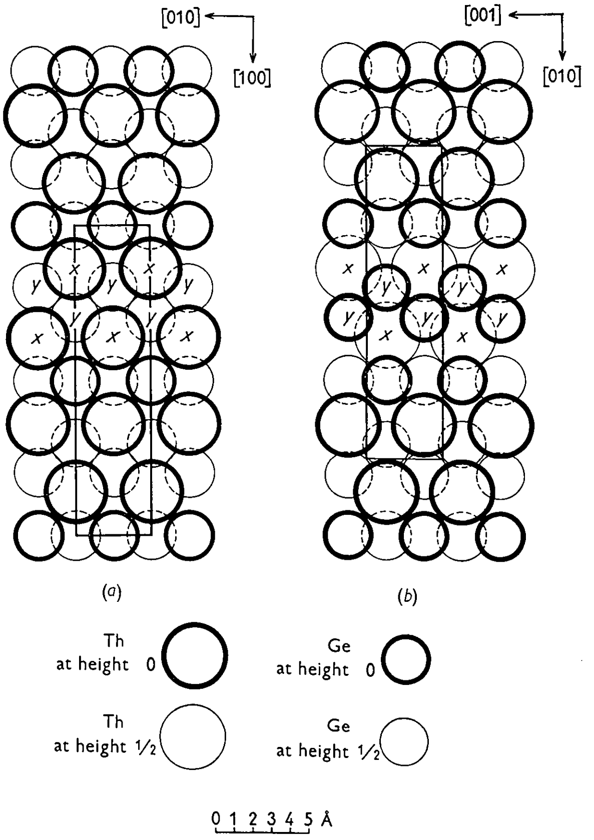

Fig. 1. (*a*) Projection of orth. $ThGe_2$(I) on (001). (*b*) Projection of orth. $ThGe_2$(II) on (100).

Table 4. *Nearest neighbour interatomic distances in orth.* $ThGe_2$ *phases*

With the exception of the Th–Th distances only values less than 3·5 Å have been quoted

		Orth. $ThGe_2$(I)		Orth. $ThGe_2$(II)		Distances shown
Atom	Neighbour	C.N.	distance	C.N.	distance	in Figs. 2 and 3
Th	Th	2	$4{\cdot}02_3$ Å	2	$4{\cdot}05_2$ Å	P_1
		2	$4{\cdot}16_0$	2	$4{\cdot}22_3$	P_2
		2	$4{\cdot}18_9$	2	$4{\cdot}05_1$	
		1	$4{\cdot}64_6$	—	—	
	Ge″	4	$3{\cdot}06_0$	4	$3{\cdot}07_0$	d
	Ge′	2	$3{\cdot}07_2$	2	$3{\cdot}21_0$	d_1'
		2	$3{\cdot}11_8$	2	$3{\cdot}24_0$	d_1''
Ge′	Ge′	4	$2{\cdot}89_4$	4	$2{\cdot}92_3$	$(p_1^2+p_2^2)^{1/2}/2$
	Th	4	$3{\cdot}07_2$	2	$3{\cdot}21_1$	d_1'
		4	$3{\cdot}11_8$	2	$3{\cdot}24_0$	d_1''
Ge″	Ge″	2	$2{\cdot}62_1$	2	$2{\cdot}61_4$	d_2
	Th	4	$3{\cdot}06_0$	4	$3{\cdot}07_0$	d

Ge′ refers to Ge atoms 2(b) and 2(d) in I and Ge_I atoms 4(c) in II.
Ge″ refers to Ge atoms 4(h) in I and Ge_{II} atoms 4(c) in II.

equally be attributed to an absorption effect. In view of the difficulties entailed in improving the absorption corrections no further refinement was attempted.

4. Discussion

4·1. *Description of the structures*

Projections of the structures of I and II are shown in Figs. 1(*a*) and (*b*) respectively. In both structures, each Th atom is coordinated by eight Ge atoms located at the corners of an antiprism as shown in Fig. 2. The antiprism shows distortion from ideal symmetry; the base is a rectangle with the dimensions p_1 and p_2 (the short orthorhombic cell dimensions) and the top is a square of side $(p_1^2+p_2^2)^{\frac{1}{2}}/2$.

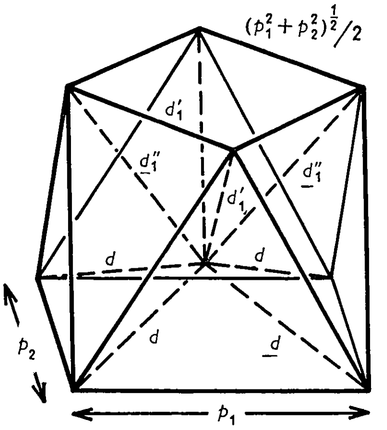

Fig. 2. Antiprismatic coordination of thorium by germanium in $ThGe_2$ phases.

The antiprisms are associated in layers normal to the long cell dimension in each structure and a pair of these layers, coupled as shown in Fig. 3, forms a unit common to both structures. Within each pair, the upper layer is displaced relative to the lower by half the repeat distance in the direction of the p_1 dimension. In consequence, the separation of the layers is determined by contact between the Ge atoms at the base corner of the polyhedra. It is noteworthy that within the limits of experimental error this Ge–Ge distance (d_2 in Fig. 3) is the same in both structures. The Th atom within each antiprism is displaced towards the 'base corner' Ge atoms and the resulting Th–Ge distance (d in Fig. 2) is only slightly different in the two structures. These separations may be regarded as originating in the packing of spherical atoms with radii approximating to the Goldschmidt C.N. 8 value for thorium of 1·76 Å and the C.N. 6 value for germanium of 1·33 Å. The separations d_1' and d_1'' between the Th and the Ge atoms at the top corners of the polyhedra are very different in the two structures and cannot be explained in terms of a simple packing of spheres.

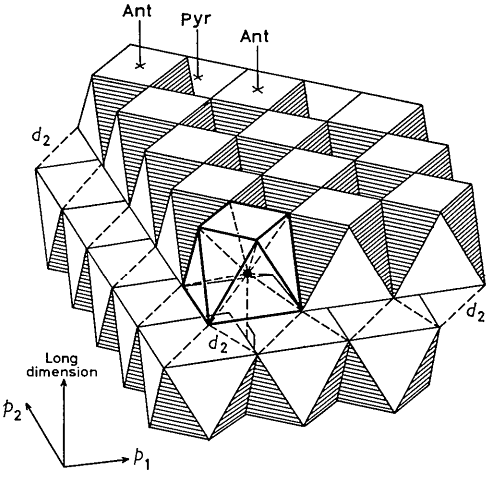

Fig. 3. Double layers of antiprismatic polyhedra in orth. $ThGe_2$ phases.

In the layers, antiprisms alternate with pyramidal spaces, the top of each antiprism being congruent with the base of the adjacent pyramid. The structures may be regarded as constituted of successive paired layers, superimposed so that the top faces of the antiprisms in one layer coincide either with the antiprism tops or the pyramid bases in the layer below. Structure I corresponds to the first, and structure II to the second of these alternatives. In both structures, the Th–X coordination is $4+2+2$.

4·2. *Similarities between the digermanide and C38 structures*

It is of considerable interest to note the close correspondence between the orthorhombic digermanide structures described above and those of the tetragonal phases $ThAs_2$, $ThSb_2$ and $ThBi_2$ (Ferro, 1955, 1956, 1957). These phases have the anti-*C*38 (Fe_2As)-type structure in which each Th is again coordinated by eight X atoms at the corners of a distorted antiprism. Layers of prisms, normal to the long cell dimension, are paired as shown in Fig. 4. Pairs of layers are then superimposed as in the *C*49-type structure of II.

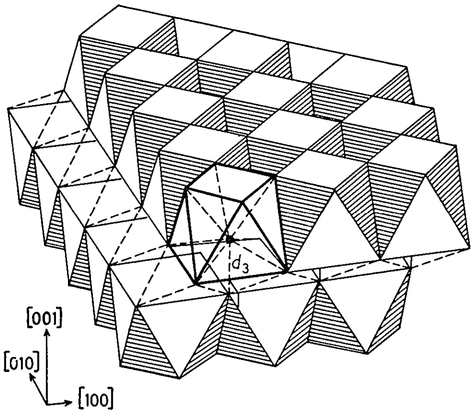

Fig. 4. Double layers of antiprismatic polyhedra in tetragonal *C*38-type structures.

The constitution of the layers in the $C38$ structure is identical with that found in the orthorhombic digermanides. In this instance, however, within each of the paired layers, the displacement of one layer relative to the other is $a_0/\sqrt{2}$ in the [110] direction. The fourfold symmetry of the antiprism is thus retained in the [001] direction and the structure is tetragonal with $p_1=p_2=a_0$ and $d_1'=d_1''$. The repeat unit in the direction of the fourfold axis consists of a pair of antiprism layers, whereas in the corresponding [010] direction of II, the unit consists of two pairs of layers.

As a result of this displacement, thorium atoms in the upper layer are located at a distance d_3 from, and directly above, X atoms in the layer below. The Th–X coordination in the $C38$ structures is accordingly $4+1+4$. Cell dimensions and Th–X interatomic distances in $ThAs_2$ are given below for comparison.

$ThAs_2$: $c_0=8{\cdot}575$ Å, $a_0=4{\cdot}086$ Å, $U=143{\cdot}16$ Å^3;
Th-4 As at 2·97 Å (d); Th-1 As at 3·09 Å (d_3);
Th-4 As at 3·15 Å (d_1).

4·3. *Similarities between the digermanide and $C32$ and C_c structures*

The relationship between the two digermanide structures as described in section 4·1 can also be interpreted in terms of atomic displacements with reference to the projections in Figs. 1 (*a*) and (*b*). Thus the geometry of I can be derived from that of II by translating thorium atoms X and germanium atoms Y through a distance $(a_0^2+c_0^2)^{\frac{1}{2}}/2$ in the [101] direction. This is closely similar to the relationship proposed to explain the transformation between the high- and low-temperature modifications of $ThSi_2$ (Brown, 1961). In this connection I corresponds structurally to the $C32$-type phase, β-$ThSi_2$, while II is comparable with the C_c-type phase α-$ThSi_2$. Thorium atoms in the (200) planes of the α-$ThSi_2$ and II crystal structures are moved into the (001) planes of β-$ThSi_2$ and I by the translation. As a result, the repeat distances are slightly shorter, and the atomic packing more compact in the [001] directions of these last two structures than in the corresponding [100] directions of α-$ThSi_2$ and II.

There are, however, differences between the orthorhombic digermanide structures on the one hand and the modifications of $ThSi_2$ on the other which indicate that I and II need not necessarily be polymorphs of $ThGe_2$. The cell volume of the room-temperature modification, β-$ThSi_2$, is very slightly smaller than that of α-$ThSi_2$. By contrast II, the phase which is formed only below 650 °C., has an appreciably larger cell volume than I. The volume difference ($\simeq 4\%$ of U_{II}) is rather more than would be expected from a rearrangement of the atomic packing and suggests that I has a smaller cell content than II. In view of the germanium content of the arc-melted alloys in which I occurs as a single phase, its real composition may be $Th_{0{\cdot}9}Ge_2$ (69 at.% Ge). Phase II, which is isostructural with UGe_2, most probably has the stoichiometric composition $ThGe_2$. In this event, I and II show a relationship similar to that found between the defect and stoichiometric phases $ThSi_{1{\cdot}67}$ and β-$ThSi_2$ (Brown, 1961).

5. Concluding remarks

The orthorhombic phases I and II are seen to provide a link between the ThX_2 phases with the $C32$ and C_c structures and the $C38$-type phases $ThAs_2$, $ThSb_2$ and $ThBi_2$. The $C32$ and C_c structures yield Th–X coordinations of 12 and $8+4$ respectively. An increase in the radius ratio r_x/r_{Th}, or a change in some other factor leading to a comparable change in atomic packing, can accordingly result in the coordination of the C_c structure being preferred to that of the $C32$ configuration. The orthorhombic structures I and II, in which there are $4+2+2$ nearest Ge neighbours, clearly represent a further step in this progressive reduction of Th–X coordination. In the $C38$ structures the coordination rises again to $4+1+4$. The overall series of coordination changes in the ThX_2 compounds considered so far can therefore be represented by the sequence $C32 \rightarrow C_c \rightarrow C49 \leftarrow C38$.

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