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The Crystal Structures of $ThPb_3$, UPb_3, ThPb and UPb

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The compounds $ThPb_3$, UPb_3, ThPb and UPb have been prepared and their structures determined. Special precautions were taken to prevent oxidation during X-ray powder examination.

$ThPb_3$ and UPb_3 are cubic, but, because of the small differences between the atomic scattering factors of lead, thorium, and uranium, it has not been possible to distinguish directly whether the atomic arrangements are ordered or disordered. Evidence based upon lattice dimensions favours the ordered $L1_2$ structure.

ThPb and UPb have a simple 'face-centred tetragonal' crystal structure, which has a close geometrical relationship to the cubic structure of $ThPb_3$ and UPb_3. Possible atomic arrangements are discussed in terms of this relationship and atomic packing. It is concluded that ThPb and UPb are most appropriately described by a body-centred tetragonal structure of space group *I*4/*amd*. This structure is related to that of α-$ThSi_2$.

1. Introduction

The uranium–lead system has been investigated by Frost & Maskrey (1953) and by Teitel (1952, 1956) who agree on the existence of two compounds. These are formed as single phases in preparations containing 75 and 50 at.% lead respectively and are accordingly described as UPb_3 and UPb. Both phases are pyrophoric and are therefore difficult to study by X-rays.

In the investigation by Frost & Maskrey UPb_3 was found to have a cubic structure with a cell dimension of 4·783 Å. It was concluded that the structure was of the $L1_2$ (ordered $AuCu_3$) type. The phase UPb was found to have a more vigorously pyrophoric character than UPb_3 and satisfactory specimens for X-ray analysis could not be prepared.

The crystal structure of UPb_3 was also investigated by Ferro & Iandelli (1952) who reported a cubic structure with a cell dimension of 4·787 Å; Teitel (1952) gave the somewhat higher value of 4·791 Å. This difference was attributed to the use by Frost & Maskrey of values for the wavelength of Cu *K* radiation expressed in kX. instead of Ångström units. Investigation of the less stable UPb phase (Teitel, 1956) was made using neutron diffraction techniques on material sealed in aluminium cans under vacuum. Interpretation of the pattern of diffraction peaks from an alloy containing some UPb_3 indicated that UPb had a complex body-centred tetragonal structure with the cell dimensions

$$a_0 = 11·04,\quad c_0 = 10·6 \text{ Å} .$$

The cell contents of the phase were estimated at 24 molecules of UPb from which the calculated density of 13·7 g.cm.$^{-3}$ was obtained. No details were given of the possible space-group symmetry or the positions of the atoms for this crystal structure.

Phases in the system thorium–lead have been investigated by Weiner and by Bryner & Teitel, and preliminary results published in the compilation of uranium and thorium constitution diagrams, BMI 1300 (Rough & Bauer, 1958). Collectively, the results of these authors indicate that the system contains three compounds $ThPb_3$, $ThPb_2$ and ThPb but crystal structure data are not given. Ferro (1958) confirmed the formation of $ThPb_3$ and reported that it was isostructural with UPb_3 and that the cubic cell dimension was 4·856 Å.

In the present investigation the special technique described below was adopted to prevent oxidation during X-ray analysis.

2. Experimental details

2·1. *Method of preparation*

The uranium–lead and thorium–lead compounds were obtained by direct reaction between the elements in sealed glass capsules. Uranium and thorium were used in powder form and the lead was cut from a rod. Charges of the elements, totalling 25–50 g., were loaded into glass capsules which were evacuated to 10^{-5} mm.Hg. and then sealed. The capsules were heated in the temperature range 500–600 °C. for 3 to 7 days to form homogeneous products.

Following this treatment, the capsules were opened under paraffin to prevent oxidation of the products and samples were taken for X-ray analysis.

2·2. *X-ray examination*

In order to prevent decomposition, powder specimens for X-ray analysis were prepared and examined in an inert medium of sodium-dried paraffin. Each sample of alloy was crushed under paraffin in an

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agate mortar and the slurry which resulted from this treatment was then pipetted into silica quills of 0·3 mm. diameter filled with paraffin. In the quill, the solid phase settled rapidly to give a powder specimen which was then sealed with a quick-drying, non-aqueous glue. Such specimens could be preserved for several days without decomposition.

Clearly resolved X-ray patterns were obtained from specimens mounted in an 11·46 cm. diameter powder camera. Values of 1·5405 and 1·5443 Å were assumed for the wavelengths of Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation. The diffraction patterns of UPb and ThPb were indexed with the aid of Bunn charts for log *d versus* log *c*/*a*.

Intensities in the pattern of UPb were measured with a microdensitometer and calculated intensities were obtained from the usual expression

$$I_{hkl} \propto p|F^2|A_p(1+\cos^2 2\theta)/(\cos\theta \sin^2\theta) \,.$$

Intensities in the pattern of ThPb were estimated visually.

3. Experimental results

In general, the compounds obtained above were hard, compact and grey-black in colour. All the preparations were pyrophoric and in this respect the oxidation of UPb and ThPb was particularly violent.

UPb_3 and $ThPb_3$: These compounds were obtained as single phases in preparations containing 75 at.% lead. In each instance the compound gave the diffraction pattern of a simple face-centred cubic phase of the A_1 structure type (space group *Fm*3*m*). The structure cell dimensions calculated from measurements of the 600, 531 and 440 reflections are given in Table 1. Densities were calculated assuming that each structure cell contained one formula unit.

Table 1. *Structure cell dimensions of thorium–lead and uranium–lead phases*

Compound	Crystal structure	Cell dimensions		Calculated density
		a_0 (Å)	c_0 (Å)	(g.cm.$^{-3}$)
$ThPb_3$	Cubic	4·855 ±0·001		12·31
UPb_3	Cubic	4·7915 ±0·0002		12·93
ThPb	Tetragonal	4·545 ±0·001	5·644 ±0·003	12·51
UPb	Tetragonal	4·579 ±0·001	5·259 ±0·001	13·27

The cell dimensions quoted above are unchanged by variations in lead content on either side of the 75 at.% limit. It is evident therefore that UPb_3 and $ThPb_3$ have only narrow ranges of composition.

UPb and ThPb: These compounds were obtained as single phases in preparations containing 50 at.% lead. They gave closely similar diffraction patterns. Comparison with the patterns of $ThPb_3$ and UPb_3 suggested that the new phases had tetragonal crystal structures derived by distortion of the cubic MPb_3 structures. The patterns of the *M*Pb phases were satisfactorily indexed in the tetragonal system at approximate values for *c*/*a* of 1·15 for UPb and 1·24 for ThPb.

On this simple basis the *M*Pb compounds can be regarded as having 'face-centred tetragonal' structure cells containing four atoms at $0, 0, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, \frac{1}{2}$.

Although a simpler body-centred cell containing only two atoms can be employed to describe the *M*Pb crystal structure, the 'face-centred tetragonal' configuration is used in view of its relationship to the

Table 2. *Diffraction data for* ThPb

Alternative space groups				
I	II			
*P*4/*mmm*	*I*4/*amd*			
hkl	*hkl*	d_o	d_c	I_o
002	004	2·80 Å	2·821 Å	*w*
111	112	2·77	2·793	*vs*
200	200	2·26	2·273	*m*
202	204	1·76	1·770	*ms*
113	116	1·618	1·624	*m*
220	220	1·601	1·607	*ms*
004	008	1·408	1·411	*vw*
222	224	1·393	1·396	*vs* (diffuse)
311	312		1·393	
204	208	1·196	1·199	*w*
313	316	1·140	1·142	*m*
400	400	1·134	1·136	*w*
115	11,10	1·062	1·065	*vvw*
224	228		1·060	
402	404	1·053	1·054	*ms*
331	332		1·053	
420	420	1·015	1·016	*ms*
422	424	0·9558	0·9562	*s*

$a_0 = 4{\cdot}545,\ c_0 = 5{\cdot}644$ Å, $c_t = 2c_0,\ c_0/a_0 = 1{\cdot}24$.

Table 3. *Diffraction data for* UPb

Alternative space groups					
I	II				
*P*4/*mmm*	*I*4/*amd*				
hkl	*hkl*	d_o	d_c	I_o	I_c
111	112	2·74 Å	2·76 Å	100	100
002	004	2·61	2·63	27	20
200	200	2·28	2·29	78	40
202	204	1·72	1·73	70	70
220	220	1·613	1·619	53	30
113	116	1·539	1·541	36	60
311	312	1·393	1·396	100	100
222	224	1·376	1·378	55	50
004	008	1·313	1·315	3	5
400	400	1·143	1·146	13	20
204	208	1·134	1·140	10	40
313	316	1·115	1·117	40	80
331	332	1·056	1·058	40	40
402	404	1·049	1·050	36	40
420	420	1·023	1·024	55	60
224	228	—	1·021		
115	11,10	—	1·000	—	1
422	424	0·9538	0·9541	90	100
333	336	0·9189	0·9191	30	50

$a_0 = 4{\cdot}579,\ c_0 = 5{\cdot}259$ Å, $c_t = 2c_0,\ c_0/a_0 = 1{\cdot}15$.

MPb_3 structure from which it is derived. This similarity forms the basis of the discussion of possible atomic arrangements given below.

Cell dimensions for these compounds obtained from measurements of the 315, 424 and 440 reflections are given in Table 1. Densities were calculated assuming that each unit cell contained two formula units.

Diffraction data for the first nineteen reflections in the X-ray powder patterns of ThPb and UPb are given in Tables 2 and 3.

4. Discussion

There are only small differences in X-ray scattering power between lead on the one hand and thorium and uranium on the other. X-ray patterns of compounds formed between these elements are virtually those of a single atomic species. Accordingly, the cell dimensions and space groups assigned to the compounds in Section 3 refer to simplified crystal structures in which the atomic arrangements of the true structure cells cannot be determined directly. It is, however, possible to discuss the probable atomic arrangements in the light of packing considerations and analogies with known and established structures. Such considerations are reviewed below.

4·1. *The crystal structure of* $ThPb_3$ *and* UPb_3

The above results confirm previous reports that both these compounds have a cubic structure which gives the pattern of a face-centred cubic lattice. The measured cell dimensions are in good agreement with the results quoted by Ferro (1958) and Teitel (1952).

The diffraction effects observed for these compounds can be explained equally well by a disordered face-centred cubic structure or by a fully ordered atomic arrangement of the $L1_2$ ($AuCu_3$) structure type (see Fig. 1). In this connection Coffinberry & Ellinger (1955) describe the isostructural compound $PuPb_3$ as having a disordered face-centred cubic structure. The difference between the scattering powers of Pu and Pb, however, is again too small to permit detection of an ordered superlattice, should one exist, and their conclusion is based upon intensity measurements for yet another isostructural phase, $InPu_3$.

By comparison, the $L1_2$ crystal structure has been established for the related compounds UAl_3, UGa_3, USi_3, UGe_3, USn_3 (Frost & Maskrey, 1953) and for $PuGe_3$ and $PuSn_3$ (Coffinberry & Ellinger, 1955), where the differences between the scattering powers of the pairs of elements are sufficient for superlattice reflections to be detected. On this basis it is reasonable to assume that $ThPb_3$, $PuPb_3$ and UPb_3 also have the $L1_2$ structure.

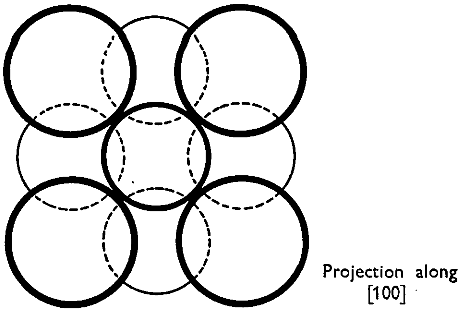

Fig. 1. $L1_2$ crystal structure of MPb_3.

In view of the different values which have been reported for the cell dimension of UPb_3, the diffraction data published for this compound by Maskrey & Frost have been analyzed. Calculations show that their value of 4·783 Å is a correct result and not one which arises from the use of incorrect figures for the wavelength of Cu K radiation as suggested by Teitel. It seems reasonable to conclude that real differences in structure cell dimension exist for different preparations of UPb_3 and that these are not attributable to variations in composition. The differences, roughly 0·2% of a_0, are comparable with those observed between the ordered and disordered crystal structures of $AuCu_3$. This comparison is interesting in view of the high temperatures, in excess of 1000 °C., used by Frost & Maskrey to anneal their samples of UPb_3.

With these considerations in mind, it is suggested that UPb_3 can undergo an order–disorder transition comparable to that observed in $CuAu_3$. Values of cell dimensions quoted for UPb_3 by Frost & Maskrey and by Ferro are accordingly attributable to a more-or-less random distribution of U and Pb atoms while the results reported by Teitel and in the present investigation probably correspond to an ordered atomic arrangement.

It is possible that order–disorder transitions can also occur in the phases $PuPb_3$ and $ThPb_3$ but further investigation is required to establish this point.

4·2. *The crystal structure of* ThPb *and* UPb

X-ray analysis shows that these two compounds are isostructural and have a simple 'face-centred tetragonal' crystal structure. The X-ray-diffraction data for UPb obtained in the present investigation cannot be reconciled with the neutron-diffraction data published by Teitel. In view of the simplicity of the X-ray diffraction pattern of UPb and its analogy with ThPb, it seems possible that Teitel's results are in error because of some fault in the quality of the sample used in his examination.

The structures of UPb and ThPb may be derived from those of UPb_3 and $ThPb_3$ by a simple tetragonal distortion. Thus the tetragonal a_0 and c_0 dimensions are obtained from the cubic structure cell by appropriate expansions along the [001] and contractions along the [100] and [010] directions. In addition, it is noteworthy that the separation of the planes of closest packing is substantially the same in the MPb and the corresponding MPb_3 compounds. This is demonstrated by values for the 111 interplanar spacing of 2·76 Å for UPb and UPb_3 and 2·79 Å for ThPb and $ThPb_3$.

Table 4. *Details of coordination in structure proposed for MPb phases*

Coordination of M atom		Coordination of Pb atom		Interatomic distances		
Neighbour	C.N.	Neighbour	C.N.	In terms of tetragonal cell dimensions	Found in ThPb	Found in UPb
Pb_I	4	M_I	4	$a_0/\sqrt{2}$	3·214 Å	3·238 Å
Pb_{II}	4	M_{II}	4	$(a_0^2+c_0^2)^{\frac{1}{2}}/2$	3·622	3·487
M	4	Pb	4	$(a_0^2+c_0^2)^{\frac{1}{2}}/2$	3·622	3·487

These structural relationships provide a basis for discussing the probable atomic arrangement in the MPb structure cell. Thus the ordered $L1_2$ structure of the MPb_3 phases can be used as a starting point to derive an ordered atomic arrangement in the MPb phases. Two of the simplest and most likely alternatives are as follows.

(I) *The* $L1_0$ (AuCuI) *crystal structure*, space group *P4/mmm*: This structure is obtained directly from the $L1_2$ structure by substituting M atoms for the Pb atoms with coordinates $\frac{1}{2}, \frac{1}{2}, 0$.

Simple packing considerations suggest that the distortion associated with such a substitution should lead to a structure cell in which the tetragonal a_0 dimension is greater than the c_0 dimension. Crystal structures with axial ratios less than unity are therefore to be expected and most compounds with the $L1_0$ structure, including the ordered AuCuI phase, do in fact have axial ratios in the range 0·8–0·95. In contrast, ThPb and UPb have axial ratios greater than unity; they are therefore not likely to have this atomic configuration.

(II) *The tetragonal structure*, space group *I4/amd*: This structure is shown in projection in Fig. 2. M and Pb atoms occupy equivalent positions and Table 4 gives details of their coordination.

The atomic arrangement may be regarded as a sequence of layers stacked in a manner derived directly from the $L1_2$ crystal structure. Each layer has the composition MPb and a rock-salt configuration of M and Pb atoms. The layers are stacked in a sequence

$$A_1\,B_1\,A_2\,B_2\,A_1\,\ldots$$

so that alternate layers $A_1\,A_2\,A_1\,\ldots$ constitute a simple rock-salt lattice with tetragonal distortion.

The distortion arises from the interpenetration of lattices A and B. The separation of successive layers A–B etc., depends upon contact between the atoms with the greater atomic radius as shown in Fig. 2. This interatomic distance is $(a_0^2+c_0^2)^{\frac{1}{2}}/2$ and values for the expression calculated from the cell dimensions of ThPb and UPb, are given in Table 4.

In ThPb this interatomic distance is 3·62 Å which is in close agreement with the Th–Th distance of 3·60 Å found in the crystal structure of thorium. The value for the Pb–Pb distance in the lead structure is 3·50 Å. In UPb the distance $(a_0^2+c_0^2)^{\frac{1}{2}}/2$ is 3·49 Å. This is closer to the observed Pb–Pb distance than to the generally quoted U–U distance of 3·0 Å. Given that in ThPb and UPb, $r_{Th} > r_{Pb} > r_U$, the packing in the proposed structure thus gives good agreement with the observed atomic radii of these elements.

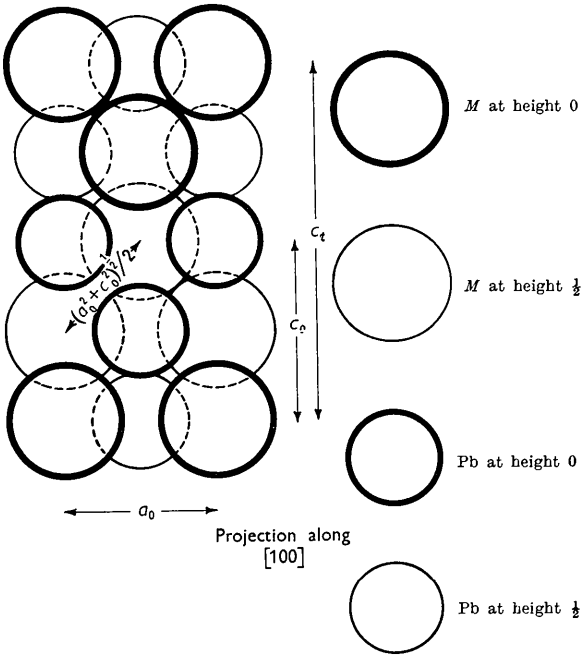

Fig. 2. Proposed structure of MPb.

The proposed structure has the space group *I4/amd*. The compound α-$ThSi_2$ (Brauer & Mitius, 1942) also has this space group. The silicide configuration may be obtained from that of the MPb phases on replacing each lead atom by a pair of silicon atoms aligned parallel to the tetragonal [001] direction. The positions of the M atoms are unaltered.

From the above considerations of atomic packing and structure relationships, it is most probable that ThPb and UPb have structures with the space group *I4/amd* and the following atomic positions

$$\begin{aligned} 4M \text{ at } & 0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\\ & \tfrac{1}{2},0,\tfrac{1}{4};\ 0,\tfrac{1}{2},\tfrac{3}{4}.\\ 4\,\text{Pb at } & \tfrac{1}{2},\tfrac{1}{2},0;\ 0,0,\tfrac{1}{2};\\ & 0,\tfrac{1}{2},\tfrac{1}{4};\ \tfrac{1}{2},0,\tfrac{3}{4}. \end{aligned}$$

The true cell dimensions a_t and c_t are derived from those of the 'pseudo-cell' obtained from X-ray data by the transformation

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

The author would like to express his thanks to Mr J. A. Champion for his valuable help in the preparation of the compounds.

References

Brauer, G. & Mitius, A. (1942). *Z. anorg. Chem.* **249**, 325.

Coffinberry, A. S. & Ellinger, F. H. (1955). U.S.A. Rep. A/Conf., 8/P/826.

Ferro, R. (1958). *Acta Cryst.* **11**, 737.

Frost, B. R. T. & Maskrey, J. T. (1953). *J. Inst. Met.* **82**, 171.

Iandelli, A. & Ferro R. (1952). *Ann. Chim. Appl.* (*Rome*), **42**, 598.

Rough, A. F. & Bauer, A. A. (1958). Battelle Memorial Institute, Report No. BMI 1300, 114.

Teitel, R. J. (1952). *J. Met.* **4**, 397.

Teitel, R. J. (1956–57). *J. Inst. Met.* **85**, 409.

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MX_2 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-$ThSi_2$) crystal structures of the $C32$-type are found. Where X is Si (α-$ThSi_2$) 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 $e.r$ are reflected in crystal structures of the $C32$-type. Si has a critical value of $e.r$ and $ThSi_2$ is dimorphic. Ge has the highest value of $e.r$ and $ThGe_2$ 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 $C_c(\alpha$-$ThSi_2)$-type structures. These structures are described as follows.

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

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

Thorium disilicide, $ThSi_2$, can have either of these 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.

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