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The Structures of some Metal Compounds of Uranium*

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The compounds UAl_2, UAl_3, UAl_5, UHg_2, UHg_3, UHg_4 and USn_3 all have standard type structures, except UHg_4 and UAl_5, which are quite complex. UHg_4 appears to be a distortion of a body-centered cubic arrangement. The structure of UAl_5 remains unknown.

Compounds with aluminum

Uranium forms three compounds with aluminum. These are now known to be UAl_2, UAl_3 and UAl_5 (Kaufmann, Gordon & Palmer, 1943). The first two have common type structures, but the third is complex, and the powder data available have not been sufficient to permit a structure determination.

The structure of UAl_2

UAl_2 is face-centered cubic, $a=7{\cdot}795$ kX. We have found this spacing at compositions on both sides of the compound, indicating little solubility at room temperature. The observed density of 8·2 g.cm.$^{-3}$ (Kaufmann *et al.* 1943) indicates that there are eight UAl_2 per unit cell. The calculated density is 8·14 g.cm.$^{-3}$. Reflections with even indices are extremely weak or absent unless $(h+k+l)=4n$. There is no doubt that the uranium atoms are arranged in a diamond array.

The crystobalite structure would require U–Al distances of 1·69 A., far too short. The Cu_2Mg structure, type *C* 15 (*Strukturbericht*, 1931*a*), on the other hand, leads to very reasonable distances (Table 1). The intensity comparisons of Table 2 substantiate this structure. It can be seen that the aluminum scattering is sufficient to be an important aid in confirming the Cu_2Mg structure. The face-centered positions in this structure are:

$$8\ \mathrm{U\ in}\ 0, 0, 0;\ \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}.$$

$$16\ \mathrm{Al\ in}\ \tfrac{5}{8}, \tfrac{5}{8}, \tfrac{5}{8};\ \tfrac{5}{8}, \tfrac{3}{8}, \tfrac{3}{8};\ \tfrac{3}{8}, \tfrac{5}{8}, \tfrac{3}{8};\ \tfrac{3}{8}, \tfrac{3}{8}, \tfrac{5}{8}.$$

Table 1. *Interatomic distances in* UAl_2

About each U	4 U at 3·38 kX.	12 Al at 2·58 kX.
About each Al	6 Al at 2·76 kX.	3 U at 2·58 kX.

The structure of UAl_3

The compound UAl_3 is simple cubic,

$$a=4{\cdot}278\pm0{\cdot}01\ \mathrm{kX}.$$

The intensities of all maxima are strong, and neither intensities nor lattice constant vary with composition of the alloy at room temperature.

Table 2. *Intensity calculations for* UAl_2

	Calculated intensities		
hkl	Crystobalite	Cu_2Mg structure	Observed intensities
(111)	1470	784	*m*
(200)	0	0	0
(220)	3140	3144	*vs*
(311)	2170	3745	*vs*
(222)	100	100	0
(400)	1000	1000	*m*−
(331)	3000	1700	*m*
(420)	0	0	0
(422)	4290	4290	*s*
(333) (511)	2190	3750	*s*−
(440)	2930	2930	*m*
(531)	4570	2540	*m*
(442) (600)	0	0	0
(620)	3340	3340	*m*+
(533)	1270	2160	*m*−
(622)	160	160	*vw*
(444)	620	620	*w*+
(551) (711)	3620	2060	*m*−
(640)	0	0	0
(642)	5630	5630	*s*
(553) (731)	3220	5330	*s*+
(800)	950	950	*w*+
(733)	1560	940	*w*+
(820) (644)	0	0	0
(660) (822)	3750	3750	*m*
(555) (751)	2300	3750	*m*
(662)	110	110	0
(840)	1540	1540	*w*+
(753) (911)	4180	2520	*m*−
(842)	0	0	0
(664)	2160	2160	*m*

The volume of the unit cell requires three aluminum atoms as well as one uranium atom. The atomic positions are almost certainly those of the $AuCu_3$ structure (*Strukturbericht*, 1931*b*), i.e.

$$\mathrm{U\ at}\ 0, 0, 0;\quad 3\ \mathrm{Al\ at}\ 0, \tfrac{1}{2}, \tfrac{1}{2};\ \tfrac{1}{2}, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0.$$

The only real question concerning the structure is the possibility of disorder. In view of the constancy of lattice constants and intensity of reflections with composition, and the fact that there is no tendency for reflections of mixed indices to be reduced in intensity, the order must be quite good (Table 3). The calculated intensities in Table 3 were made without Lorentz, polarization, temperature and absorption corrections, since this is sufficient for establishing relatively high ordering.

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Table 3. *Intensities of maxima from* UAl_3

hkl	Observed intensities: Our value	Observed intensities: (Kaufmann)	Calculated intensities
(100)	*s*	*s*	55
(110)	*s*−	*s*	102
(111)	*s*−	*s*	133
(200)	*m*−	*s*	96
(210)	*m*+	*s*	164
(211)	*m*	*m–s*	144
(220)	*w*+	*m–s*	156
(221) (300)	*w*	*m*	162
(310)	*w*	*s*	126
(311)	*m*−	*w–m*	264
(222)	*	*m*	89
(320)	*	*m–s*	108
(321)	*m*−	*w*	208
(400)	*wv*	*m–s*	55
(410) (322)	*	*m*	184
(411) (330)	*	*m*	132
(331)	*m*−	*m*	186
(420)	*w*+	*m*	100
(421)	*w*+	*w–m*	160
(332)	*	*m–s*	158
(422)	*	*w–m*	164
(500) (430)	*	*m–s*	92
(501) (431)	*w*		216

* Obscured by reflections from another phase.

Compounds with mercury

The uranium–mercury system has been given thorough study by Ahmann, Baldwin & Wilson (1945). In connection with these studies the structures of the compounds in the system have been worked out. The samples used were all prepared by Ahmann and Baldwin, and delivered to us in sealed tubes. Since the samples oxidize with great rapidity, all transfers to suitable X-ray capillaries had to be made in a dry box under an atmosphere of CO_2. Owing to the difficulty in the handling of samples, capillaries were often larger than desirable, and as a consequence the lattice constants reported below are less accurate than normal.

The structure of UHg_2

At compositions between U and UHg samples of alloys in this system were clearly two-phase, one of which was alpha-uranium (Jacobs & Warren, 1937). The other phase was UHg, an hexagonal phase with $a = 4{\cdot}98 \pm 0{\cdot}01$ kX., $c = 3{\cdot}22 \pm 0{\cdot}01$ kX. It was possible to determine the composition of the phase from X-ray data alone, and this has been confirmed by metallographic study (Ahmann *et al.* 1945).

It was not possible to demonstrate the uranium phase between UHg and UHg_2, but both above and below the composition UHg_2 the lattice constants of the compound were essentially those reported above. Probably the solubility of U and Hg in UHg_2 is small, but the atomic volumes of uranium and mercury differ by only 4 $A.^3$ so the lattice constant will not be sensitive to small changes in composition.

There is but one UHg_2 per unit cell, leading to an X-ray density of 15·29 $g.cm.^{-3}$ *v.* 15·3 observed by helium displacement (Ahmann *et al.* 1945).

The small *c* axis forbids placing mercury atoms above each other along *c*. The alteration of intensities with odd and even values of *l*, and other simple intensity comparisons, suggested the parameterless structure,

$$U \text{ at } 0, 0, 0; \quad 2\,Hg \text{ at } \pm\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}.$$

This is the AlB_2 structure, type *C*32 (*Strukturbericht*, 1937). The intensity comparison of Table 4 substantiates this structure.

The intensities were calculated using Lorentz and polarization factors, but the absorption correction was not made. Consequently only neighboring reflections in Table 4 can be compared. The agreement is sufficient to render the trial of structures with parameters unnecessary. The parameterless positions are found in the space group D^1_{6h}–$C6/mmm$ and subgroups.

Table 4. *Observed and calculated intensities for* UHg_2

hk.l	Intensities: Obs.	Intensities: Calc.	*hk.l*	Intensities: Obs.	Intensities: Calc.
(10.0)	0	46	(00.3)	0	8
(00.1)	*vvw*	227	(10.3)	*mw*	305
(10.1)	*s*	4720	(40.1)	*mw*	288
(11.0)	*s*	4676	(32.0)	0	2
(20.0)	0	8	(11.3)	0	41
(11.1)	*vw*	328	(22.2)	*ms*	608
(20.1)	*ms*	1633	(20.3)	*mw*	299
(21.0)	0	8	(31.2)	0	4
(00.2)	*w*	404	(32.1)	*ms*	612
(10.2)	0	6	(41.0)	*ms*	647
(21.1)	*ms*	1646	(41.1)	*vw*	86
(30.0)	*m*	850	(21.3)	*ms*	617
(11.2)	*ms*	1334	(40.2)	0	2
(30.1)	*vvw*	84	(50.0)	0	1
(20.2)	0	4	(30.3)	?	46
(22.0)	*m*	474	(32.2)	0	4
(31.0)	0	3	(50.1)	*m*	393
(22.1)	*vvw*	56	(33.0)	*m*	426
(21.2)	0	5	(42.0)	0	3
(31.1)	*ms*	719	(22.3)	0	73
(40.0)	0	1	(41.2)	*vs*	1986
(30.2)	*ms*	700			

The structure of UHg_3

UHg_3 is hexagonal, $a = 3{\cdot}320 \pm 0{\cdot}005$ kX., $c = 4{\cdot}878 \pm 0{\cdot}005$ kX., $c/a = 1{\cdot}47$, $z = \frac{1}{2}$, $\rho = 14{\cdot}88$ $g.cm.^{-3}$. The structure involves hexagonal closest packing, and a random structure. The composition of the phase was established by metallographic and chemical study (Ahmann *et al.* 1945).

Though no extensive studies have been made, no tendency to form a superlattice at the composition UHg_3 has been observed. This seems strange, since the composition of the compound appears to be fairly definite. We have not found an appreciable change in the lattice constant with composition of the alloy, and on either side of the compound a second phase appears upon relatively small composition changes. Since the atomic volumes of uranium and mercury are nearly equal, it may be that the lattice constant is very insensitive to composition changes. It is noteworthy that the axial ratio is far from ideal for hexagonal closest packing, corresponding to a compression along *c*.

Table 5 compares estimated and observed intensities. The latter are very rough; all functions of angle alone were omitted. The absences and general trend of the intensities are sufficient, however, to indicate a random distribution of the uranium atoms over the position of hexagonal closest packing.

Table 5. *Intensity data for* UHg_3

	Intensities			Intensities	
hk.l	Obs.	Calc.	*hk.l*	Obs.	Calc.
(00.1)	0	0	(21.1)	*s*	72
(10.0)	*w*	12	(21.2)	*w*	24
(10.1)	*vs*	36	(11.4)	*m*	48
(00.2)	*w*−	8	(30.0)	*w*	24
(10.2)	*w*	12	(30.1)	0	0
(11.0)	*m*	24	(20.4)	*vw*	12
(11.1)	0	0	(00.5)	0	0
(00.3)	0	0	(10.5)	*m*	36
(20.0)	*vw*	6	(21.3)	*s*	72
(10.3)	*s*	36	(30.2)	*m*	48
(20.1)	*s*	36	(22.0)	*w*+	24
(11.2)	*s*+	48	(22.1)	0	0
(20.2)	*w*+	12	(30.3)	0	0
(00.4)	*w*−	8	(21.4)	*m*	24
(10.4)	*w*	12	(11.5)	0	0
(21.0)	*w*	12	(20.5)	*s*−	36
(11.3)	0	0	(31.0)	?	12
(20.3)	*m*	36	(31.1)	*vs*	72

The structure of UHg_4

The phase UHg_4 appears in samples whose overall mercury content exceeds UHg_3 materially. Above this composition free mercury appears. The composition of the compound has been established by chemical and metallographic study (Ahmann *et al.* 1945).

The X-ray powder diagram consists of an intense set of reflections from a body-centered cubic lattice, $a=3{\cdot}62$ kX., together with numerous, very weak reflections which are not related simply to the pseudo-unit. These extra reflections are too weak to be measured with accuracy, so the structure remains uncertain. However, to a first approximation the structure is a body-centered cubic array of atoms, $z=2$ for the pseudo-unit. The density on this basis is 14·5 g.cm.$^{-3}$.

Atomic volumes in the U–Hg *system*

The atomic volumes of U and Hg can be calculated from the unit cells of UHg_2 and UHg_3, assuming them to be equal in the two compounds. They are 20·8 and 24·1 A.^{3} for uranium and mercury respectively, *v.* 20·7 for alpha-uranium (Jacobs & Warren, 1937), 24·4 for liquid mercury and 23·4 for crystalline mercury (Mehl & Barrett, 1939). (The atomic volume of crystalline mercury was corrected to 25° C. by taking the linear coefficient of expansion equal to 35×10^{-6}.)

The observed volume of UHg_4 is 118·8 A.^{3}, using the lattice constant of the pseudo-unit, while the expected value is 117·3 A.^{3} on the basis of the atomic volume above. These values are well within the experimental error of each other. It appears that atomic volumes in this system are strictly additive in spite of the diversity of structures involved.

Compounds with tin

Uranium apparently forms at least three compounds with tin. They are all exceedingly pyrophoric and difficult to handle. Moreover, they are brittle, and X-ray reflections are generally very broad and characteristic of highly strained samples. Annealing temperatures are quite high, and the samples are so easily oxidized as to make annealing very difficult. As a consequence, only one compound has been located definitely. It is USn_3, with the $L1_2$ structure, like that of UAl_3 above. The lattice constant observed is $a=4{\cdot}62$ kX., $\rho=9{\cdot}95$ g.cm.$^{-3}$.

We have observed no tendency towards a random structure in USn_3. Owing to the nature of the samples it has been hard to establish the solubility limits of uranium and tin in the compound, but they appear to be fairly small.

Method of investigation

All results reported above are from powder data made with samples sealed in thin-walled glass capillaries. Powder cameras of 5·73 cm. radius were used. Radiation was Cu $K\alpha$, and the Siegbahn wave-length, $\lambda=1{\cdot}539$ kX., was used in reporting lattice constants.

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