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The Crystal Structure of UPt_2

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The crystal structure of UPt_2 has been determined as orthorhombic, space group *Ama*2 with a = 5·60, b = 9·68, c = 4·12 Å. The similarity between this structure and UPt_3 is shown.

Introduction

As part of an investigation into the occurrence and crystal structures of uranium compounds of the form UX_2 and UX_3 where X is Ru, Rh, Pd, Re, Os, Ir, or Pt, the platinum system compounds UPt_2 and UPt_3 were observed. The determination of the structure of UPt_3 has already been reported (Heal & Williams, 1955) and that of UPt_2 is given here.

The alloy was prepared by arc melting stoichiometric proportions on a water-cooled copper hearth under an atmosphere of purified argon. The platinum was of near-spectroscopic standard and the uranium of high purity, containing a little oxide but no aluminium. Heat-treatments were carried out on lump specimens contained in an alumina crucible enclosed in an evacuated silica capsule. Chemical analysis of the heat-treated alloy gave 68·6 at.% Pt.

Structure determination

Debye–Scherrer powder photographs were taken from crushed heat-treated alloys, these being sufficiently brittle for no appreciable cold work to be introduced during crushing. They showed sharp diffractions from UPt_2 together with some weak UPt_3 diffractions which would account for the excess platinum in the chemical analysis. It was not possible to index the powder pattern unequivocally and therefore single-crystal photographs were taken using an irregular-shaped fragment selected from crushed samples of an ingot heat-treated for 2 weeks at 1000 °C. The Laue symmetry was determined as orthorhombic. Single-crystal rotation photographs taken about the axes showed straight layer lines giving repeat distances of 5·6, 9·7, and 4·2 Å. The rotation photographs about the 9·7 and 4·2 Å axes showed a number of weak diffractions scattered over the films; all these could be explained on the basis that the fragment consisted of one large crystal, together with small pieces of adjoining crystals having a common 5·6 Å axis with the large crystal and arranged at ~44° about this axis. It was then possible to index all the single-crystal diffractions and the powder diffractions. The cell constants were modified from the powder film data to 5·60, 9·68 and 4·12 Å.

The single-crystal photographs indicated that diffractions of the type *hkl* occurred only where $k+l = 2n$ and those of the type *h*0*l* when $h = 2n$ thus suggesting space groups *Ama*2, *Amam*, or $A2_1am$. The diffractions on the zero and second layer lines of the rotation photograph about the 4·12 Å axis are similar indicating that the atoms lie on planes separated by half the cell width. Assuming that the atomic diameters of the uranium and platinum atoms are about 3·0 and 2·8 Å respectively, then two atoms cannot be placed one above the other in the 4·12 Å direction. It is probable, however, that two platinum atoms lie above one another along the 5·60 Å direction. These considerations lead to space group *Ama*2. The atomic sites are as given in *International Tables for X-ray Crystallography* (1952 No. 40). The coordinates of equivalent positions are $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2}$, with

4 U atoms in sites (b) $\frac{1}{4}, y_1, z_1;\ \frac{3}{4}, \bar{y}_1, z_1$
4 Pt atoms in sites (a) $0, 0, z_2;\ \frac{1}{2}, 0, z_2$
4 Pt atoms in sites (b) $\frac{1}{4}, y_3, z_3;\ \frac{3}{4}, \bar{y}_3, z_3$.

Satisfactory agreement between observed and calculated intensities is obtained if y_1 is made 0·17, $z_1 = 0·50$, $z_2 = 0$, $y_3 = 0·38$, and $z_3 = 0$.

Table 1. *Observed and calculated values of d spacings and intensities*

Wavelength of X-radiation used: Co $K\alpha_1 \lambda = 1·78890$ Å.

Ref.	*hkl*	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	$I_{calc.} \times 10^{-6}$
	020		4·850	—	1·75
	011		3·79	—	3·54
	120		3·66	—	0·78
	111	3·11	3·14	*vw*	1·49
1	200	2·78	2·82	*w–m*	3·23
2	031	2·53	2·56	*vs*	26·92
3	220	2·41	2·44	*m–s*	8·24
	040		2·42		0·24
4	131	2·304	2·328	*w–m*	3·81
5	211	2·240	2·240	*vs*	26·46
6	140	2·219	2·226	*w–m*	3·79
7	002	2·062	2·065	*m–s*	10·14
	022		1·896	—	0·24
8	231	1·883	1·894	*w*	1·17
9	240	1·829	1·845	*m–s*	7·62
	122		1·796	—	< 0·01
10	051	1·754	1·765	*vw*	1·32
	320		1·743	—	0·05
11	311	1·677	1·686	*vvw*	0·30
	151		1·672	—	0·31

Table 1 (*cont.*)

Ref.	*hkl*	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{obs.}}$	$I_{\text{calc.}} \times 10^{-6}$
12	202	1·664	1·666	*vw*	1·44
13	060	1·615	1·627	*vw*	1·81
14	222	1·574	1·577	*m–s*	4·26
	042		1·569	—	0·13
15	160	1·553	1·563	*vw*	1·02
16	142	1·518	1·518	*w–m*	1·68
17	331	1·509	1·515	*vw*	0·76
18	251	1·492	1·496	*vw*	1·24
19	340	1·482	1·490	*vw*	1·00
	260		1·402	—	< 0·01
20	400	1·404	1·412	*m–s*	2·92
21	242	1·376	1·376	*m–s*	7·81
21*a*	013	1·361	1·360	*vvw*	0·43
	420		1·347	—	0·08
	322		1·331	—	0·05
21*b*	411		1·322	*vvwb*	0·11
	{113		1·322	—	< 0·12
	071}		1·312	—	0·01
22	{171	1·283	1·287	*m–sb*	3·38
	351		1·281		2·28
23	{062	1·275	1·277	*m–sb*	1·73
	033		1·268		3·26
24	162	1·248	1·239	*m*	1·06
25	{431	1·233	1·235	*sb*	6·73
	133		1·237		0·29
	213		1·227		4·18
	360		1·224		0·27
25*a*	080		1·220	*vvw*	0·28
	440		1·219	—	0·07
26	342	1·210	1·208	*vwb*	1·15
	043		1·195	—	0·15
27	271	1·195	1·197	*vwb*	3·39
	181		1·138	—	0·35
28	{262	1·165	1·163	*m–s*	< 0·01
	402		1·165		4·01
	233		1·152	—	0·26
29	422	1·132	1·133	*vvw*	0·10
30	{280	1·115	1·119	*vvw*	0·26
	370		1·114		0·03
31	{451	1·101	1·102	*w*	0·95
	313		1·100		0·10
32	{371	1·080	1·081	*mb*	3·18
	511		1·081		0·13
33	{530	1·070	1·065	*vw*	0·19
	460		1·062		1·62
34	333	1·058	1·052	*vw*	0·28
35	362	1·050	1·051	*vw*	0·05
37	004	1·032	1·033	*m*	2·24

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *b* = broad.

Table 1 lists the observed and calculated values of *d* spacings and intensities for the powder film. The intensities were calculated from the formula

$$I \propto p|F_{hkl}|^2(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$$

in the usual notation. These values give reasonably good agreement between observed and calculated intensities for the powder film. The agreement for the single-crystal diffractions is not as good; some diffractions of high calculated intensity do not appear correspondingly strong on the films. These differences may be due to insufficient refinement of the structure parameters, but it is more likely, that they are due to heavy absorption by secondary fragments adhering to the main crystal. The main use of the single-crystal photographs lay in determining the symmetry and space group from the systematic absences. Refinement of the structure was carried out with the powder data.

Discussion

For convenience of classification it may be noted that UPt_2 has a distorted Ni_2In structure. Ni_2In has a hexagonal ($\beta B8$) structure (Laves & Wallbaum, 1942), but if its orthohexagonal cell is considered the atoms can be placed in the same sites of space group *Ama*2 quoted earlier.

4 In atoms in sites (*b*) with $y = 0{\cdot}16$, $z = 0{\cdot}50$
4 Ni atoms in sites (*a*) $z = 0$
4 Ni atoms in sites (*b*) $y = 0{\cdot}33$, $z = 0$

It has been shown that UPt_2 is formed peritectically from the liquid and UPt_3 (Park & Buzzard, 1957) and a simple relationship between the two crystal structures will now be demonstrated. UPt_3 is hexagonal, *D*019, with $a = 5{\cdot}764$, $c = 4{\cdot}898$ Å and for comparison with UPt_2 it is convenient to consider the equivalent orthohexagonal cell having

$$a = 5{\cdot}764,\ b = 9{\cdot}960,\ c = 4{\cdot}898\ \text{Å}$$

with 4 uranium and 12 platinum atoms, the mean volume per atom being 17·58 (Å)³. The UPt_2 structure has a mean volume per atom of 18·6 (Å)³. In UPt_3 the atoms are arranged on two planes perpendicular

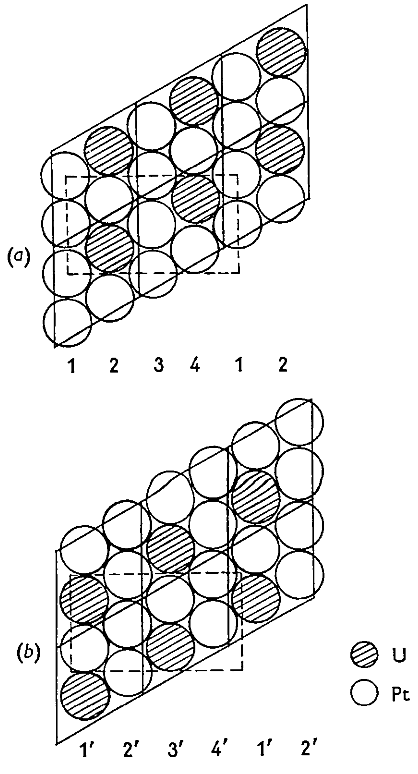

Fig. 1. UPt_3 atoms on planes $z = \frac{1}{4}$ and $z = \frac{3}{4}$.

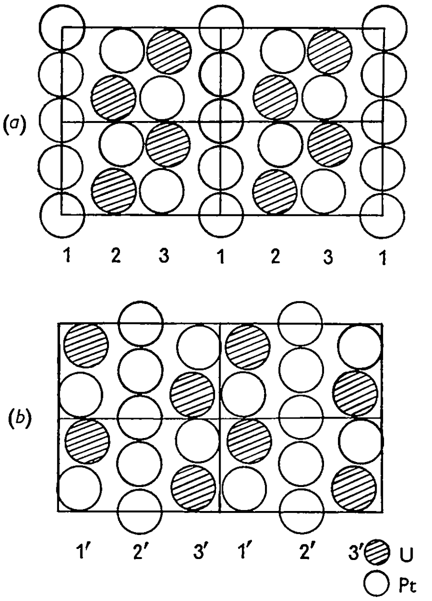

Fig. 2. UPt_2 atoms on planes $z = 0$ and $z = \frac{1}{2}$.

to c as shown in Figs. 1(*a*) and (*b*). The atoms in UPt_2 are also arranged on two planes perpendicular to c as shown in Figs. 2(*a*) and (*b*).

UPt_3 can be converted to UPt_2 by removing the rows of atoms 3 from Fig. 1(*a*) thus allowing rows 2 and 4 to move closer together to give the packing of Fig. 2(*a*). Similarly by removing rows 2′ from Fig. 1(*b*) rows 3′ and 1′ move closer together. If these two planes are then moved $\mathbf{b}/6$ relative to each other, the UPt_2 packing sequence is obtained. These changes remove 4 Pt atoms from the UPt_3 orthohexagonal cell leaving 4 uranium and 8 platinum atoms as required for the UPt_2 structure.

The similarity between the two structures suggests that nucleation of UPt_2 on UPt_3 and of the rearrangement from UPt_3 to UPt_2 by diffusion will be comparatively easy, and therefore the reaction to equilibrium should be correspondingly rapid.

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The Lattice Energies of Alkaline Earth Fluorides

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The lattice energies U_0 of the alkaline earth fluorides CaF_2, SrF_2, and BaF_2 have been derived by term-by-term theoretical calculation. The results have been compared with 'experimental lattice energies' U obtained from thermodynamic data using the Born-Haber cycle. The values of U_0 and U are respectively for CaF_2 610, 617, for SrF_2 582, 584, and for BaF_2 550, 549 kcal/mole at 0 °K. The small discrepancies in the case of CaF_2 and SrF_2 have been attributed to some deformation and interpenetration of the ions in the crystals.

1. Introduction

This communication reports calculations of lattice energies of the alkaline earth fluorides CaF_2, SrF_2, and BaF_2. Theoretical values for the lattice energies have been computed on the basis that the compounds are ionic crystals with a van der Waals potential. The underlying theory is that of Born & Mayer (1932), and the method used is similar to that employed by Morris (1958) for alkali monosulphides. The results are presumably more accurate than those previously obtained, using approximation equations, by Sherman (1932), Yatsimirskii (1951), Morris (1957), and others.

The theoretically calculated lattice energies have been compared with 'experimental' values derived from thermodynamic data by means of the Born–Haber cycle.

2. Theoretical calculation of lattice energies

The lattice energy per mole at 0 °K. of an ionic crystal