in the unit cell, calculated with the values of parameters listed in Table 1, are given in Table 3.

Table 3. *Interatomic distances in* $HgSO_4.H_2O$

Atom	Neighbour	Coordination number	Interatomic distances
Hg	O(II)	2	2·44 Å
	O(II)	2	2·47
	O(III)	1	2·10
	O(H₂O)	1	2·34
S	O(I)	1	1·24
	O(II)	2	1·53
	O(III)	1	1·53
O–O distances in tetrahedron			
O(I)	O(II)	—	1·95
	O(III)	—	2·24
O(II)	O(II)	—	2·53
	O(III)	—	2·51
O–O distances in octahedron			
O(II)	O(II)	—	3·91
	O(II)	—	2·89
	O(H₂O)	—	3·09
	O(H₂O)	—	3·18
	O(III)	—	3·85
	O(III)	—	3·14

The values for the distances from mercury to the sulphate–oxygen atoms O(II) (2·44 and 2·47 Å) are nearly equal to the sum of ionic radii (2·45 Å), if the values of 1·10 Å, the generally accepted value for the radius of the mercuric ion, and 1·35 Å for oxygen are used. Distances of nearly the same length (2·40 and 2·42 Å) are found to exist also in crystals of mercurous nitrate dihydrate, between mercury and the nitrate-oxygen atoms (Grdenić, 1956).

Shorter distances between the mercury atom and the water molecule (2·34 Å) are found. It may be compared with the distances between the mercury atom and the water molecule in mercurous nitrate dihydrate (2·15 Å). A short coordination Hg–O bond has been shown to exist also in mercury diethylene oxide (2·21 Å) by Grdenić (1952), and much shorter (2·03 Å) in trichlormercury oxonium chloride (Šćavničar & Grdenić, 1955) and in mercuric oxide (Aurivilius, 1954).

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The Crystal Structure of URe₂

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The intermetallic compound URe₂ has two allotropic forms. Up to 180 °C. it has an orthorhombic structure, space group *Cmca*; above this temperature a C14 structure is formed by a simple dilation of the unit cell. The lattice parameters at 20 °C. are

$$a = 5·600, \quad b = 9·180, \quad c = 8·460 \text{ Å} .$$

For the hexagonal modification at 213 °C. $a = 5·433$, $c = 8·561$ Å. In both modifications the thermal expansion coefficients are positive along c and negative along a.

Introduction

During an investigation of the uranium–rhenium phase diagram an intermetallic compound URe₂ was observed (Brook & Hatt, 1954). An alloy of composition uranium 66·7 at.% rhenium appeared single-phased when examined microscopically and by the X-ray Debye–Scherrer powder method, whereas alloys with higher rhenium content showed free rhenium, and those of lower rhenium content free uranium. Spacing measurements indicated a negligible solubility of either rhenium or uranium in URe₂.

Structure determination

Alloys of URe₂ were prepared from uranium bar

supplied by the Atomic Energy Research Establishment, Harwell, and rhenium sponge of 99·9% purity. The sponge rhenium was first arc-melted into buttons on a water-cooled copper hearth under a purified argon atmosphere. These were then arc-melted with uranium to give alloy buttons of approximately 10 g. Heat-treatments were carried out by sealing the buttons contained in an alumina crucible inside an evacuated silica glass capsule. No chemical analyses have been made but the melting losses were less than 0·5%.

Debye–Scherrer powder photographs were taken from the crushed alloy, after a heat-treatment of two weeks at 1000 °C. followed by water quenching. The alloy was very brittle so that crushing introduced negligible cold work. A powder pattern taken with Co $K\alpha$ radiation showed 58 resolvable diffractions. These could not be indexed and so rotation single-crystal photographs were taken using an irregular shaped fragment, selected from the crushed alloy, which showed a pseudo six-fold axis of symmetry. Subsequently this was shown to consist of several grains. Attempts to obtain single grains were unsuccessful. The diffractions on the rotation photograph about one of the axes of two-fold symmetry did not lie on straight layer lines but were scattered about possible layer-line positions, indicating a repeat distance of 5·6 Å. The rotation photograph about the pseudo six-fold symmetry axis showed straight layer lines giving a repeat distance of 8·2 Å. Using these two values all the diffractions on this latter film could be indexed with an orthorhombic cell with dimensions 5·6, 9·2 and 8·2 Å. These cell constants enabled all the powder diffractions to be indexed, and the follow-

ing systematic absences were observed: 1) hkl when $h+k=2n+1$, 2) $h0l$ when $l=2n+1$. These conditions are satisfied by space groups $Cmcm$–D_{2h}^{17} and $Cmc2_1$–C_{2v}^{12}. Oscillation photographs taken round the pseudo six-fold axis showed that the fragment consisted of several grains, all with a common 8·2 Å axis but oriented round this axis at approximately 120° intervals.

Uranium compounds of the form UX_2 often crystallize with structures of the so-called Laves phases. These tend to form when the ratio of atomic diameters of the elements is about 1·2. For U and Re this ratio is 1·16 and so its structure was expected to resemble one of the Laves phases. In order to determine the atomic sites of the present orthorhombic structure its relation to the C14, hexagonal, Laves structure was considered.

Fig. 1 shows the projection of a C14 structure on to a (0001) plane together with the orthohexagonal cell derived from it. If the atomic positions are interpreted in terms of the orthorhombic space group $Cmcm$ then these become, with respect to the equivalent positions $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$,

8 U atoms in sites (f)
 $0, y_1, z_1$; $0, \bar{y}_1, \bar{z}_1$; $0, y_1, \frac{1}{2}-z_1$; $0, \bar{y}, \frac{1}{2}+z_1$

8 Re atoms in sites (g)
 $x_2, y_2, \frac{1}{4}$; $\bar{x}_2, y_2, \frac{1}{4}$; $x_2, \bar{y}_2, \frac{3}{4}$; $\bar{x}_2, \bar{y}_2, \frac{3}{4}$

4 Re atoms in sites (c)
 $0, y_3, \frac{1}{4}$; $0, \bar{y}_3, \frac{3}{4}$

4 Re atoms in sites (a)
 $0, 0, 0$; $0, 0, \frac{1}{2}$.

Since the C14 structures have axial ratios about 1·63 then the ideal orthohexagonal cell has $a:b:c = 1:\sqrt{3}:1·63$. The actual orthorhombic cell determined for URe₂ has $a:b:c = 1:\sqrt{2·7}:1·52$, and since $a:b$ is no longer exactly $\sqrt{3}$ the hexagonal diffractions split into groups with differing multiplicities as shown in Table 1.

Table 1. *Comparison of the hexagonal diffractions with those for the orthorhombic cell when b/a deviates from $\sqrt{3}$*

Hexagonal		Orthohexagonal (distorted)	
$hkil$	p	Number of diffractions	P
$0,0,0,l$	2	Single	2
$h,h,\bar{2}h,0$	6	Double	2, 4
$h,h,\bar{2}h,l$	12	Double	4, 8
$0,k,\bar{k},0$	6	Double	2, 4
$0,k,\bar{k},l$	12	Double	4, 8
$h,k,i,0$	12	Triple	4, 4, 4
h,k,i,l	24	Triple	8, 8, 8

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. Satisfactory agreement with observed values were obtained with $y_1=\frac{1}{3}$, $z_1=\frac{1}{16}$, $x_2=\frac{1}{4}$, $y_2=\frac{1}{12}$, $y_3=-\frac{1}{6}$. No detailed refinement of these parameters has been undertaken but they are probably correct to ±0·01. Observed and calculated values of intensities and d spacings are given in Table 2.
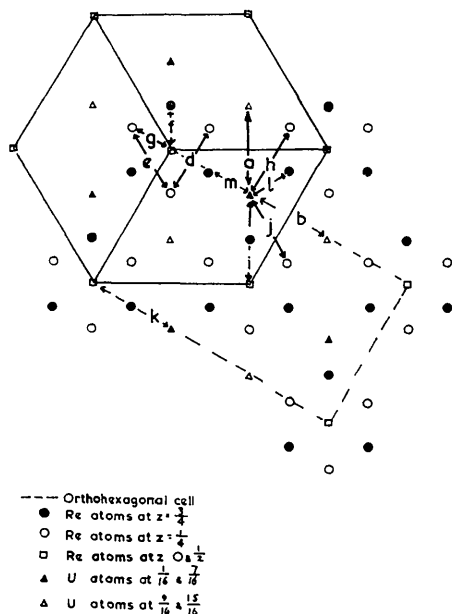

Fig. 1. Projection of the atoms of a URe₂ C14 structure on to a (0001) plane. The letters refer to the interatomic distances given in Fig. 3.

Table 2. *Observed and calculated values of d spacings and intensities for the orthorhombic modification of* URe$_2$ *at* 20 °C.

Wavelength of X-radiation used Co $K\alpha_1$, $\lambda = 1\cdot78890$ Å

Ref. No.	hkl	d_o	d_c	I_o	$I_c \times 10^{-6}$
	002	—	4·230 Å	—	0·4
	111	—	4·162	—	<0·1
	021	—	4·032	—	<0·1
	112	—	3·168	—	1·7
	022	—	3·110	—	0·8
1	200	2·786 Å	2·800	w	14·1
2	130	2·664	2·691	m	22·3
3	113	2·419	2·431	m–s	49·5
4	{ 023	2·388	2·404	m	{ 24·4
	220		2·391		5·6
5	202	2·325	2·333	m	39·8
6	{ 040	2·286	2·295	s	{ 4·1
	221		2·299		63·0
7	132	2·257	2·271	m–s	72·7
8	041	2·206	2·215	m	31·3
9	004	2·111	2·116	w–m	16·9
10	222	2·072	2·081	w–m	10·2
11	042	2·012	2·017	w	4·7
12	114	1·931	1·935	w–m	7·2
12a	024		1·921	w	3·6
	223	—	1·824	—	0·8
	311	—	1·788	—	<0·1
	310	—	1·780	—	<0·1
	240	—	1·774	—	<0·1
	150	—	1·743	—	<0·1
	241	—	1·737	—	<0·1
	151	—	1·707	—	<0·1
	204	—	1·687	—	0
	134	—	1·661	—	0
	242	—	1·637	—	0·3
	152	—	1·612	—	0·3
13	{ 330	1·586	1·593	w–m	{ 5·9
	115		1·595		2·5
	224	—	1·584	—	0·4
14	{ 060	1·528	1·529	m–s	{ 3·0
	313		1·535		13·8
15	243	1·496	1·502	w–m	13·3
16	332	1·486	1·491	s	22·2
17	153	1·479	1·484	m	12·8
18	062	1·434	1·437	w–m	9·8
19	006	1·407	1·411	w	1·0
20	400	1·395	1·400	m–s	13·9
21	{ 314	1·378	1·384	s	{ 2·9
	225		1·381		27·6
22	{ 045	1·357	1·362	mb	{ 13·0
	244		1·359		2·7
	116		1·353		2·4
23	{ 026	1·338	1·348	s	{ 1·1
	154		1·346		2·5
	260		1·343		24·0
	420	—	1·339	—	<0·1
	402	—	1·329	—	<0·1
	421	—	1·323	—	<0·1
	350	—	1·309	—	<0·1
	351	—	1·294	—	<0·1
	262	—	1·279	—	<0·1
	422	—	1·277	—	<0·1
	170	—	1·276	—	<0·1
	171	—	1·262	—	<0·1
	206	—	1·259	—	<0·1
	352	—	1·250	—	<0·1
	136	—	1·248	—	<0·1
	315	—	1·243	—	0·5
	172	—	1·221	—	<0·1
	245	—	1·225	—	0·5
24	{ 226	1·212	1·214	m	10·3
	155		1·214		0·5
25	423	1·207	1·210	m	7·5
25a	046	1·202	1·201	w	5·1
25b	440		1·195	vw	1·2
26	353	1·186	1·187	m	7·4
27	441	1·182	1·184	m–s	10·0
28	{ 117	1·166	1·172	w–m	2·4
	027		1·169		1·2
	404		1·167		6·2
29	173	1·161	1·162	w–m	6·6
30	{ 442	1·147	1·150	wb	2·0
	080		1·148		0·6
31	{ 081	1·132	1·137	mb	2·4
	264		1·133		12·4
	424		1·132		1·8
31a	{ 316	1·114	1·117	vw	1·5
	354		1·113		1·7
	510	—	1·111	—	<0·1
	246		1·104		1·4
31b	{ 082	1·104	1·108	vw	1·0
	511		1·103		<0·1
	174		1·093		1·6
31c	{ 156	1·091	1·097	vw	1·4
	443		1·100		0·2
32	{ 227	1·078	1·078	w–m	2·2
	512		1·075		0·1
	370	—	1·073	—	<0·1
32a	{ 371	1·064	1·065	w	<0·1
	083		1·063		<0·1
	280		1·062		<0·1
32b	{ 336	1·055	1·056	vw	<0·1
	281		1·053		<0·1
33	530	1·051	1·052	w–m	2·2
	066	—	1·036	—	<0·1
34	{ 118		1·033	m–s b	5·6
	028	1·032	1·033		2·8
	460		1·032		2·4
	513		1·035		6·1
	282	—	1·029	—	0·1
35	532	1·020	1·021	m–s	10·8
36	{ 317		1·009	s	11·2
	190	1·003	1·003		2·6
	373		1·003		6·5
	462		1·003		11·2
37	{ 247		0·9940	s	2·2
	157	0·9938	0·9949		2·2
	406		0·9938		5·5
	283		0·9938		6·4
38	138	0·9842	0·9845	w–m	4·8
39	{ 192	0·9759	0·9763	s	9·9
	445		0·9763		16·2
39a	266	0·9727	0·9721	m	10·8

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

High temperature modification

The room-temperature structural work indicated the possibility that the orthorhombic form of URe$_2$ had transformed from a hexagonal C14 structure while cooling. To check this prediction several photographs were taken with a Unicam high-temperature camera. The furnace thermo-couples were not calibrated throughout the range of temperature investigated, but exposures made with a super-purity aluminium

Table 3. *Observed and calculated values of d spacings and intensities for the* C14 *hexagonal modification of* URe₂ *at* 655 °C.

Wavelength of X-radiation used Cu $K\alpha_1$, $\lambda = 1.54050$ Å.

Ref. No.	hkl	d_o	d_c	I_o	$I_c \times 10^{-6}$	Ref. No.	hkl	d_o	d_c	I_o	$I_c \times 10^{-6}$
	101	—	4.12 Å	—	<0.1		312	—	1.246	—	<0.1
	002	—	4.36	—	<0.1	24a	215	1.237	1.242	vw	0.8
	102	—	3.19	—	0.7	25	206	1.231	1.233	m	3.1
3	110	2.68 Å	2.70	w–m	10.2	25a	107	1.195	1.199	vw	0.8
4	103	2.44	2.46	m–s	18.3	26	313	1.184	1.186	s	4.4
5	200	2.32	2.35	w–m	3.3	26a	400	1.169	1.172	vw	0.4
6	112	2.28	2.30	s	27.3	27	401	1.158	1.161	m–s	3.1
7	201	2.25	2.26	s	22.2	28	224	1.147	1.149	m–s	4.0
8	004	2.17	2.18	w–m	3.9	29	402	1.129	1.132	w	0.7
9	202	2.05	2.07	m	3.7	29a	216	1.119	1.122	w	1.1
10	104	1.96	1.98	w–m	2.4	30	314	1.114	1.116	w	1.3
	203	—	1.82	—	0.3	31	207	1.098	1.097	w	0.8
	210	—	1.78	—	<0.1		403	—	1.085	—	<0.1
	211	—	1.73	—	<0.1	31a	008	1.090	1.086	vvw	0.2
	212	—	1.64	—	0.2		320	—	1.074	—	<0.1
13	105	1.62	1.63	vw	0.8		321	—	1.066	—	<0.1
	204	—	1.59	—	0.1		306	—	1.062	—	<0.1
14	300	1.552	1.560	w–m	1.9	32	108	1.060	1.057	w	2.2
16	213	1.507	1.512	s	8.6		322	—	1.043	—	<0.1
18	302	1.465	1.468	s	7.3		404	—	1.030	—	<0.1
19	006	1.446	1.448	w	1.0	32a	410	1.020	1.023	w	1.8
20	205	1.393	1.399	s	8.2		217	—	1.016	—	<0.1
20a	106	1.381	1.383	vw	0.7	33	{ 118 / 323 }	1.007	{ 1.009 / 1.007 }	m–s	{ 2.3 / 4.9 }
21	214	1.369	1.373	w–m	1.7	34	412	0.9941	0.9955	s	8.4
22	220	1.349	1.351	s	8.5	35	226	0.9888	0.9856	m–s	4.7
	310	—	1.299	—	<0.1	36	{ 405 / 316 }	0.9721	{ 0.9709 / 0.9673 }	s	{ 7.6 / 1.4 }
	222	—	1.290	—	<0.1						
	311	—	1.284	—	<0.1						
	116	—	1.276	—	<0.1						

specimen mounted similarly to the URe₂ specimen indicated that they were reading 40° low in the temperature range 100 to 200 °C. Temperatures in this range have been corrected for this error and are probably correct to ± 10° whereas above 200 °C. the same error has been assumed but the accuracy will not be as great.

The URe₂ powder was sealed in a silica quill after evacuating to a pressure of the order 10^{-2} mm.Hg. X-ray photographs were taken at 20, 151, 210, 340, 555 and 655 °C. Before each exposure the powder was maintained at the temperature for 2 hr. Traces of UO₂ appeared after 5 hr. at 655 °C.

Up to 151 °C. the diffractions corresponded to the orthorhombic version of URe₂ already described. At 210 °C. and above a new set of diffractions appeared which could all be indexed on a hexagonal cell. The systematic absences and line intensities are consistent with the space group and atomic sites of the C14 hexagonal Laves phase, as given in *International Tables for X-ray Crystallography* (1952).

Space group $P6_3/mmc$–D_{6h}^4.

4 U atoms in sites (f)

$\frac{1}{3}, \frac{2}{3}, z;\ \frac{2}{3}, \frac{1}{3}, \bar{z};\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z;\ \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z$

with $z = \frac{1}{16} \pm 0.01$

6 Re atoms in sites (h)

$x, 2x, \frac{1}{4};\ 2\bar{x}, \bar{x}, \frac{1}{4};\ x, \bar{x}, \frac{1}{4};\ \bar{x}, 2\bar{x}, \frac{3}{4}$
$2x, x, \frac{3}{4};\ \bar{x}, x, \frac{3}{4}$

with $x = -\frac{1}{6} \pm 0.01$

2 Re atoms in sites (a)

$0, 0, 0;\ 0, 0, \frac{1}{2}$.

The diffraction data are listed in Table 3 and show good agreement between observed and calculated values of intensities and d spacings. Lattice parameters of both modifications and their variation with temperature are given in Table 4.

Table 4. *Cell dimensions at various temperatures*

	Temp. (°C.)	Lattice parameter (Å)			Cell Vol. (Å³)
		a	b	c	
Orthorhombic	20	5.600	9.178	8.463	435
	151	5.555	9.180	8.512	434
		a	$a\sqrt{3}$	c	
Hexagonal	213	5.433	9.410	8.561	438
	340	5.420	9.389	8.590	437
	655	5.405	9.363	8.682	441

The above cell parameters are correct to ± 0.003 Å.

Discussion

The hexagonal high-temperature modification of URe₂ transforms on cooling to an orthorhombic structure, at a temperature which lies between 210 and 151 °C. with a 2.0% expansion in the a direction and contractions of 2.4 and 0.35% in the b and c directions respectively. The original hexagonal grain transforms

into several orthorhombic domains each having one of the three orthohexagonal orientations, thus producing a macroscopic pseudo hexagonal grain. The transformation may be termed martensitic since it consists of a simple dilation of the unit cells without breaking the atomic bonds.
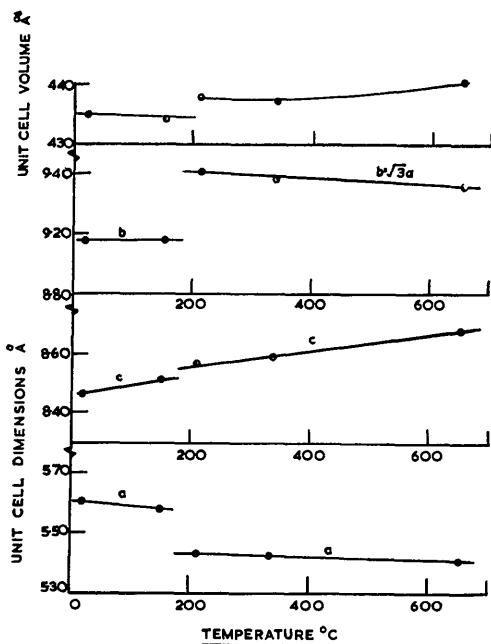

Fig. 2. Variation of cell dimensions and volume with temperature.
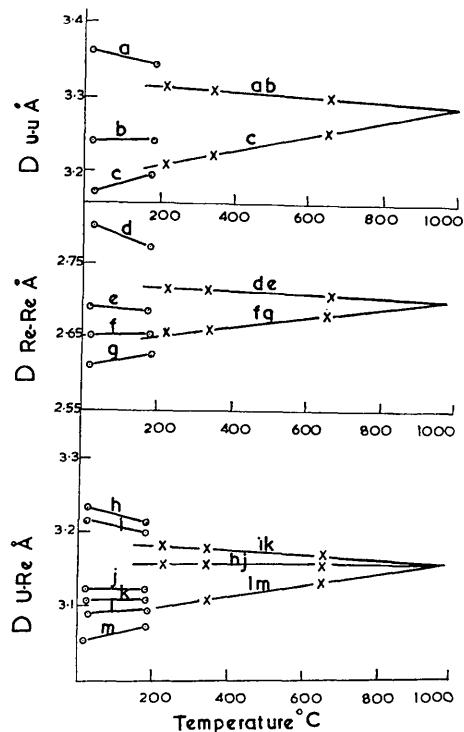

Fig. 3. Variation of interatomic distances with temperature. The interatomic distance c is that between uranium atoms vertically above one another; the others are as shown in Fig. 1.

The anisotropic thermal expansion of both modifications are shown in Fig. 2 and the variation in near neighbour atomic distances in Fig. 3. The latter shows that the extrapolated curves intersect at approximately 1000 °C. when all U–U distances are equal to 3·29, Re–Re 2·69 and U–Re 3·15 Å. At this temperature the C14 structure would have the ideal axial ratio of 1·63. As the temperature falls, the distance between planes of atoms perpendicular to the c direction decreases, whereas distances in these planes increase. During the transformation those interatomic distances which contracted while cooling undergo small changes in length but those which expanded undergo relatively large ones. This suggests that the origin of the transformation is that on cooling the strain in the {000l}

planes produced by the thermal expansion reaches a maximum value at ∼ 180 °C. and is relieved by disrupting the {000l} hexagonal atomic arrangement. Conversely, on heating, the atoms have sufficient energy at 180 °C. to take on the more symmetrical arrangement.

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