shell of the trivalent ion to the ns^0 shell of the pentavalent ion are responsible for the abnormally deep color. There appear, however, to be no unusual Br–Br distances in $(NH_4)_4Sb_2Br_{12}$ for the electron-transfer paths to take. Further studies on related compounds will therefore be made in an attempt to understand further the structural requirements of charge transfer, assuming this is the cause of the black color.

Acknowledgment.—The authors are indebted to Professor R. E. Rundle, who doubted the existence of the tetravalent state and who correctly predicted, shortly before his death, that, if $(NH_4)_2SbBr_6$ contained mixed Sb(III) and Sb(V) in an ordered array, it would necessarily give rise to weak reflections in the reciprocal lattice and thus render itself amenable to a detailed single-crystal X-ray structure determination.

CONTRIBUTION FROM THE NUCLEAR MATERIALS AND PROPULSION OPERATION,
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Crystal Structure of the Rhombohedral $MO_3 \cdot 3R_2O_3$ Compounds (M = U, W, or Mo) and Their Relation to Ordered R_7O_{12} Phases[1]

BY S. F. BARTRAM

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A complete three-dimensional structure analysis of the complex oxide $UO_3 \cdot 3Y_2O_3$ was carried out using single-crystal data. This structure is characteristic of a large family of rhombohedral compounds containing rare earth oxides and having an oxygen-to-metal ratio of 12:7. Bond lengths and coordination polyhedra for the atoms in this rhombohedral structure are compared with those in other known oxides. The relationship between $U_mY_{7-m}O_{12}$ compositions $(1 < m < 2.0)$ and ordered $RO_{1.71}$ phases is shown. Some conclusions are drawn as to their mode of oxidation.

Introduction

The existence of a family of rare earth–group VIb complex oxides has been reported previously.[2] These compounds have the general composition $MO_3 \cdot 3R_2O_3$ (MR_6O_{12}) where M = U, W, or Mo and R = rare earth. They crystallize in a rhombohedral structure which is closely related to the face-centered cubic fluorite structure. In order to clarify the relationship between these structures, single-crystal studies were necessary. A detailed crystal structure analysis was of additional interest because the normally volatile trioxides of U, W, and Mo show exceptional thermal stability in these rhombohedral compounds.

Crystallographic data for the compounds investigated are given in Table I. For the sake of consistency, all dimensions and indices given in the text refer to the hexagonal cell.

TABLE I

CRYSTALLOGRAPHIC DATA FOR RHOMBOHEDRAL PHASES

Compn	Rhombohedral parameters, A		Hexagonal parameters, A			Density, g/cc	
	a_0	α	a_0	c_0	c/a	Obsd	Calcd
UY_6O_{12}	6.530	99° 3′	9.934	9.364	0.943	5.91	6.00
ULu_6O_{12}	6.435	99° 9′	9.797	9.204	0.939	...	9.63
$U_2Y_5O_{12}$	6.568	99° 18′	10.01	9.36	0.935	6.88	6.83
$U_2Y_5O_{13.5}$	6.522	99° 19′	9.943	9.289	0.934	...	7.37

This rhombohedral structure is also characteristic of the ordered $RO_{1.71}$ (R_7O_{12}) phases reported for the oxides of Ce, Pr, and Tb.[3] Results obtained for the complex oxide compounds should be applicable to the ordered intermediate rare earth oxide phases. This point will be amplified in the Discussion section.

Compositional ranges for the existence of the two rhombohedral phases in the U–Y–O system should be somewhat revised from those given before.[2a] Rhombohedral 1 (rhomb 1) can exist from $U_2Y_5O_{12}$ to UY_6O_{12} (55.6 to 75.0 mole % Y_2O_3) and rhombohedral 2 (rhomb 2) occurs from $U_2Y_5O_{13.5}$ to about $U_{1.75}Y_{5.25}O_{13.1}$ (55.6 to 60 mole % Y_2O_3). The ternary phase diagram below 1700° has a two-phase region from 50 to 55.6 mole % Y_2O_3.[2b]

Experimental Section

Crystals of the $UO_3 \cdot 3Y_2O_3$ compound were formed as irregular growths on the surface of material heated in air for several days at 1500°. These crystals were pale yellowish green with no well-developed faces. Although they were very small, one was found from which satisfactory Weissenberg intensity data were collected. This crystal had an average dimension of about 0.04 mm. In spite of its angular shape, it was helpful to apply a spherical absorption parameter of $\mu R = 1.9$ to correct observed intensities for the extremely high absorptivity of this compound.

The chemical composition of these crystals could not be determined directly, but previous work by Chase[4] had conclusively proven the existence of this compound at a mole ratio of $1UO_3$: $3Y_2O_3$ when fully oxidized. Furthermore, X-ray powder dif-

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(1) (a) This paper originated from work sponsored by The Fuels and Materials Development Branch, Division of Reactor Development, U. S. Atomic Energy Commission, under Contract AT (40-1)-2847; (b) presented at The Fifth Rare Earth Research Conference, Iowa State University, Ames, Iowa, Aug 30–Sept 1, 1965.

(2) (a) E. A. Aitken, S. F. Bartram, and E. F. Juenke, *Inorg. Chem.*, **3**, 949 (1964); (b) S. F. Bartram, E. F. Juenke, and E. A. Aitken, *J. Am. Ceram. Soc.*, **47**, 171 (1964).

(3) (a) D. J. M. Bevan, *J. Inorg. Nucl. Chem.*, **1**, 49 (1955); (b) L. Eyring and N. C. Baenziger, *J. Appl. Phys., Suppl.*, **33**, 428 (1962); (c) N. C. Baenziger, H. A. Eick, H. S. Schuldt, and L. Eyring, *J. Am. Chem. Soc.*, **83**, 2219 (1961).

(4) G. A. Chase, *Acta Cryst.*, **15**, 91 (1962).

fraction patterns of 1:3 compositions, sintered under similar conditions, were identical with the single-crystal data.

Multiple-film equiinclination Weissenberg photographs were taken with Ni-filtered Cu Kα radiation for nine layers rotating about [110] and for seven layers about [101]. The observed intensities were estimated visually using a film factor of 3.8 for Kodak No-Screen film.[5] Out of a total of 405 independent reflections possible within the sphere of reflection, 290 of these were recorded by the Weissenberg camera. Intensities of equivalent reflections appearing on various reciprocal layers were first corrected for Lorentz and polarization factors. The resulting $|F|^2$ values were then used to establish scale factors for the sets of films taken about two different axes. By merging these results, a common relative scale was established. Observed structure factors were then obtained from the averaged values.

Single crystals of $UO_3 \cdot 3Lu_2O_3$, reduced $U_mY_{7-m}O_{12}$, and oxidized $U_mY_{7-m}O_{12+x}$ ($m = 1.75$ to 2.00) were not available. Their X-ray intensities were measured from powder diffraction patterns obtained with the Philips high-angle diffractometer using Ni-filtered Cu Kα radiation and a scanning rate of 0.25°/min. In the case of $UO_3 \cdot 3Lu_2O_3$, integrated intensities were measured for 54 reflections (individual and multiple) out to about 110° (2θ). For the other two compounds a few integrated intensities were measured to provide a reference scale, and the remaining reflections were evaluated from relative peak heights. This latter method was found quite satisfactory for determination of the structural changes produced by reduction and oxidation.

The diffractometer intensities were corrected for multiplicity, Lorentz, and polarization effects. To correct for the superposition of nonequivalent reflections and the overlap of closely spaced lines, these intensities were divided according to the relative $|F|^2$ values given by the single-crystal data for $UO_3 \cdot 3Y_2O_3$. In this way, it was possible to obtain a set of observed F values for computer analysis. Without the single-crystal results, the powder diffraction patterns could not have been resolved.

Structure Determinations

I. $UO_3 \cdot 3Y_2O_3$.—This analysis was carried out for the large hexagonal cell containing three formula weights. All reflections with $-h + k + l = 3n$ were observable; hence, the possible space groups are R3, R32, R$\bar{3}$, and R$\bar{3}$m. Since this structure is a distorted fluorite arrangement, one can begin by choosing the space group which gives a set of positions best describing the cubic structure in terms of the new hexagonal cell. With the hexagonal c axis along the cubic [111] axis, the basal hexagonal plane may be drawn on a fcc (111) plane. When this is done through a layer of metal ions, the result is as illustrated in Figure 1. Using undistorted parameters for one of the metal ions at $x = {}^1/_7$, $y = {}^3/_7$, $z = 0$, the other ions should be accounted for by the space group symmetry. Using this approach, space group R32 is unsatisfactory because its (18f) general position does not fit this model. Space group R$\bar{3}$m is likewise rejected since special positions (18h), (18g), (18f) are also inadequate. Since the 18 yttrium ions are most probably equivalent, this leaves only the (18f) general position of the centrosymmetric space group R$\bar{3}$. This set of equipoints does give a correct description of the hexagonal cell as shown.

A three-dimensional electron density map was then computed using signs calculated with 18 yttrium atoms in (18f) of R$\bar{3}$ at $x = {}^1/_7$, $y = {}^3/_7$, $z = 0$ and the uranium atoms in (3a) at 0, 0, 0; etc. No assumption was made regarding the oxygen atoms although in the undistorted cell they occupy layers with the same x and y parameters as the metal ions but at $z = {}^1/_4$ and ${}^3/_4$. The oxygen atoms were quite readily located from the weak peaks which appeared in the map. They were placed in two sets of (18f) general positions with $x, y, z = 0.140, 0.440, 0.283$ and $x, y, z = 0.188, 0.044, 0.112$. After addition of these atoms to F_c, the discrepancy index R dropped from 20.3 to 18.1%.

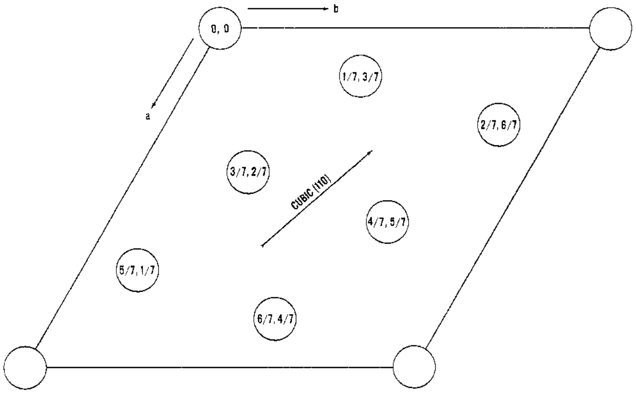

Figure 1.—Basal plane of hexagonal cell drawn through metal atoms on a fcc (111) plane. Hexagonal x and y parameters are shown.

Atomic form factors for U^{6+}, Y^{3+}, and O^{2-} were the Hartree scattering factors recently computed by Cromer, Larson, and Waber.[6] Anomalous dispersion corrections, f' and f'' values of -6.8 and $+16.0$ for U^{6+} and -0.7 and $+2.3$ for Y^{3+}, were applied to the scattering factors.

Two cycles of isotropic least-squares refinement were carried out with the Busing–Levy full-matrix, least-squares IBM 7090 computer program.[7] A weighting scheme similar to that recommended by Hughes[8] was used where $w^{1/2} = 1.0$ if $F_o < 3F(\min)_o$ and $w^{1/2} = 3F(\min)_o/F_o$ if $F_o > 3F(\min)_o$. The R factor dropped to 12.0% at this point. Final refinement in two more cycles gave an over-all $R = 11.7\%$, calculated by omitting the unobserved reflections. A three-dimensional Fourier difference map showed no significant residual electron density regions.

Details of the structural arrangement are revealed in Figure 2. Contents of the hexagonal cell from $z = 0$ to ${}^1/_2$ are shown in projection down the c axis. Ions are drawn with their proper relative sizes at their final refined positions (z parameter indicated). The atomic coordinates and thermal parameters are listed in Table II.

The anomalously low temperature factor for O(2) is not readily explained, but is probably related to the strong absorption exhibited by this compound. Structure factors calculated using these parameters are compared with observed values in Table III. Although there is a possibility that the $UO_3 \cdot 3Y_2O_3$ cell is acentric, any deviations from centrosymmetry must be very small. All attempts to settle this point by computer refinement were inconclusive.

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(5) G. A. Chase, *Acta Cryst.*, **9**, 520 (1956).

(6) D. T. Cromer, A. C. Larson, and J. T. Waber, *ibid.*, **17**, 1044 (1964).

(7) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report No. ORNL-TM-305, 1962.

(8) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

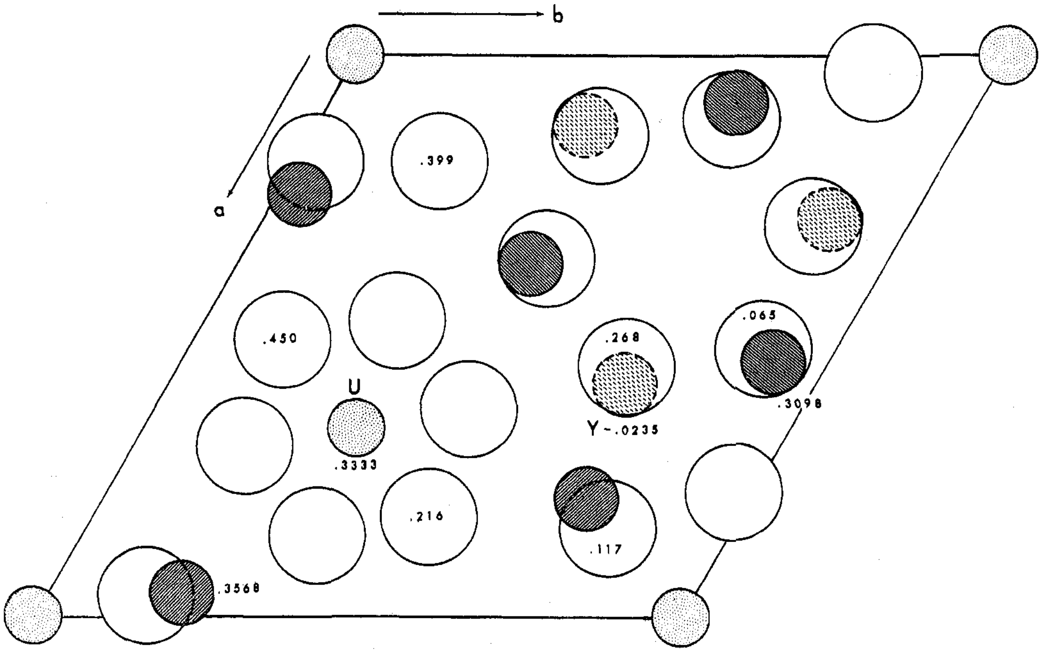

Figure 2.—The hexagonal cell ($a = b = 9.934$ A) of $UO_3 \cdot 3Y_2O_3$ from $z = 0$ to $^1/_2$ projected on the basal plane. Relative ionic sizes are shown and z parameters indicated.

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $UO_3 \cdot 3Y_2O_3$

	x	y	z	B, A^2
3 U^{6+}	0	0	0	1.248 ± 0.079
18 Y^{3+}	0.1224 ± 0.0004	0.4170 ± 0.0004	0.0235 ± 0.0004	1.005 ± 0.081
18 $O(1)^{2-}$	0.191 ± 0.003	0.032 ± 0.003	0.117 ± 0.003	0.907 ± 0.378
18 $O(2)^{2-}$	0.140 ± 0.002	0.447 ± 0.003	0.268 ± 0.003	0.461 ± 0.375

Recently, a structure analysis of this compound from neutron powder diffraction data was made by Roth.[9] His results are in good agreement with those reported here.

II. $UO_3 \cdot 3Lu_2O_3$.—Structure refinement was begun by assuming the same atomic parameters as for the yttria compound. Calculated structure factors were compared with $|I|^{1/2}$ values from powder data for 108 observed reflections of a possible 148 for $(\sin \theta)/\lambda \leq 0.475$.

Two cycles of isotropic least-squares refinement were run to obtain the best agreement between F_o and F_c values using the same weighting scheme. The discrepancy index amounted to 6.2% for the final positional and thermal parameters given in Table IV. The lower R value is partly due to the fact that the diffractometer intensities do not require an absorption correction. Also, the heavy metal ions dominate the structure more than in $UO_3 \cdot 3Y_2O_3$. Table V lists the calculated and observed structure factors for $UO_3 \cdot 3Lu_2O_3$.

As might be expected for isostructural compounds, only small changes in atomic positions were found. Table VI gives interatomic distances, bond angles, and their standard deviations for both of these compounds.

III. $U_mY_{7-m}O_{12}$ and $U_mY_{7-m}O_{12+x}$.—With these compounds the structure analysis was not so straightforward. First of all, the distribution of metal ions is not fixed by symmetry. Secondly, the number of oxygen ions introduced by low-temperature oxidation varies with the uranium content.

The marked similarity in observed intensities for $U_2Y_5O_{12}$ and UY_6O_{12} indicated no change in symmetry and only small changes in the structure. This can be achieved by placing one of the uranium ions at the origin as before and allowing the other uranium to be statistically distributed in the general position (18f) by replacing a yttrium ion. Any other arrangement of metal ions would produce more obvious intensity differences than were observed.

Low-temperature oxidation of $U_2Y_5O_{12}$ to $U_2Y_5O_{13.3}$ by oxygen diffusion does not involve a phase transformation. A maximum of four extra oxygen ions can be taken into the hexagonal cell. In order to locate these ions, an electron density map was computed using F_o values for the oxidized phase with signs derived from ionic parameters of the reduced phase. There was no difficulty finding extra peaks located on the c axis at 0, 0, z with $z \approx 0.250$. These additional oxygens were, therefore, statistically distributed in the (6c) special positions of $R\bar{3}$.

Changes in atomic positions were first roughly estimated from the observed differences in line intensities which occur at low diffraction angles. These parameters were then adjusted until best agreement between observed and calculated structure factors was obtained. The final positional parameters for $U_2Y_5O_{12}$ and U_2Y_5-

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(9) W. A. Roth, GE Research Laboratory, private communication.

TABLE III

OBSERVED AND CALCULATED STRUCTURE STRUCTURE FACTORS FOR $UO_3{\cdot}3Y_2O_3$[a]

h	k	l	Fo	Fc
3	0	0	613	595
6	0	0	251	298
9	0	0	394	454
1	1	0	326	314
4	1	0	2257	2437
7	1	0	810	783
10	1	0	146	132
2	2	0	202	136
5	2	0	*222	115
8	2	0	1120	1024
3	3	0	*233	10
6	3	0	*205	149
9	3	0	*173	-7
1	4	0	312	546
4	4	0	829	734
7	4	0	*186	-18
2	5	0	547	479
5	5	0	336	282
3	6	0	1488	1306
6	6	0	493	533
1	7	0	*209	17
4	7	0	*186	87
2	8	0	*192	-23
3	9	0	600	701
1	10	0	301	256
1	0	1	394	460
2	0	-1	887	784
4	0	1	*242	-102
5	0	-1	*234	63
7	0	1	1565	1425
8	0	-1	485	356
10	0	1	677	735
11	0	-1	*171	114
2	1	1	546	444
3	1	-1	*245	111
5	1	1	444	458
6	1	-1	758	759
8	1	1	*198	-169
9	1	-1	*187	-50
1	2	-1	2563	2592
3	2	1	762	601
4	2	-1	879	820
6	2	1	288	273
7	2	-1	*202	10
9	2	1	180	220
1	3	1	538	586
2	3	-1	384	400
4	3	1	506	464
5	3	-1	1596	1405
7	3	1	374	517
8	3	-1	768	730
2	4	1	2000	1791
3	4	-1	283	282
5	4	1	790	656
6	4	-1	196	135
8	4	1	*175	142
1	5	-1	841	897
3	5	1	*214	-117
4	5	-1	*206	-152
6	5	1	1089	850
7	5	-1	*177	138
1	6	1	243	268
2	6	-1	271	245
4	6	1	*196	105
5	6	-1	715	747
2	7	1	760	795
3	7	-1	505	536
5	7	1	177	214
1	8	-1	198	169
3	8	1	367	352
4	8	-1	816	775
1	9	1	872	834
2	9	-1	180	160
1	0	-2	608	828
2	0	2	582	476
4	0	-2	331	352
5	0	2	451	419
7	0	-2	1418	1205
8	0	2	532	545
10	0	-2	889	898
11	0	2	0	-138
2	1	-2	297	317
3	1	2	643	493
5	1	-2	495	539
6	1	2	503	488
8	1	-2	*196	172
9	1	2	*186	197
1	2	2	1733	1776
3	2	-2	838	969
4	2	2	1053	902
6	2	-2	*210	122
7	2	2	245	190
9	2	-2	226	196
1	3	-2	997	853
2	3	2	313	-231
4	3	-2	*221	0
5	3	2	1370	1201
7	3	-2	667	716
8	3	2	576	674
2	4	-2	1772	1484
3	4	2	484	430
5	4	-2	771	744
6	4	2	337	-305
1	5	2	845	833
3	5	-2	222	143
4	5	2	350	283
6	5	-2	828	834
1	6	-2	253	-152
2	6	2	513	525
4	6	-2	194	170
5	6	2	742	649
2	7	-2	872	878
3	7	2	472	507
5	7	-2	*176	-8
1	8	2	*196	-268
3	8	-2	255	161
4	8	2	522	672
1	9	-2	854	828
2	9	2	184	166
0	0	3	1805	2359
3	0	-3	475	537
3	0	3	804	993
6	0	-3	203	-171
6	0	3	348	410
9	0	-3	410	504
9	0	3	367	429
1	1	-3	664	653
1	1	3	*248	-26
4	1	-3	1576	1761
4	1	3	1867	1739
7	1	-3	636	659
7	1	3	846	813
10	1	-3	*173	-135
10	1	3	173	233
2	2	-3	701	630
2	2	3	266	241
5	2	-3	396	307
5	2	3	337	-305
8	2	-3	1105	934
8	2	3	1086	862
3	3	-3	*226	-49
3	3	3	384	321
6	3	-3	212	229
6	3	3	*142	300
9	3	-3	*169	188
9	3	3	0	-259
1	4	-3	297	343
1	4	3	691	716
4	4	-3	865	816
4	4	3	702	666
7	4	-3	*182	71
7	4	3	*182	113
2	5	-3	0	505
2	5	3	682	658
5	5	-3	*192	102
5	5	3	433	374
3	6	-3	1184	1057
3	6	3	1318	1149
6	6	-3	409	495
6	6	3	452	488
1	7	-3	*204	156
1	7	3	266	154
4	7	-3	247	222
4	7	3	453	-291
2	8	-3	*187	-137
2	8	3	296	189
3	9	-3	0	660
3	9	3	0	573
1	10	-3	244	379
1	10	3	203	228
1	0	4	*244	-165
2	0	-4	892	975
4	0	4	397	-357
5	0	-4	237	-218
7	0	4	1402	1199
8	0	-4	310	336
10	0	4	642	633
2	1	4	779	770
3	1	-4	*233	-73
5	1	4	*218	90
6	1	-4	610	674
8	1	4	392	-320
9	1	-4	*180	-54
1	2	-4	1942	2278
3	2	4	415	360
4	2	-4	495	403
6	2	4	329	316
7	2	-4	*194	-61
9	2	4	295	210
1	3	4	799	787
2	3	-4	925	816
4	3	4	707	683
5	3	-4	1201	1246
7	3	4	480	481
8	3	-4	580	557
2	4	4	1700	1639
3	4	-4	361	378
5	4	4	650	614
6	4	-4	425	486
1	5	-4	693	835
3	5	4	303	-268
4	5	-4	249	-246
6	5	4	654	780
7	5	-4	*171	73
1	6	4	578	512
2	6	-4	236	227
4	6	4	*188	49
5	6	-4	450	597
2	7	4	708	609
3	7	-4	341	383
5	7	4	*171	230
1	8	-4	503	526
3	8	4	482	384
1	9	4	928	836
1	0	-5	882	879
2	0	5	*234	16
4	0	-5	809	874
5	0	5	591	568
7	0	-5	1146	965
8	0	5	406	362
10	0	-5	663	586
2	1	-5	232	-160
3	1	5	832	933
5	1	-5	412	451
6	1	5	240	196
8	1	-5	565	595
9	1	5	431	306
1	2	5	1499	1657
3	2	-5	935	873
4	2	5	727	719
6	2	-5	*199	-148
7	2	5	559	542
9	2	-5	0	135
1	3	-5	342	295
2	3	5	365	-296
4	3	-5	*208	-120
5	3	5	908	946
7	3	-5	535	577
8	3	5	538	551
2	4	-5	1191	1244
3	4	5	*208	125
5	4	-5	558	546
6	4	5	358	-326
1	5	5	507	463
3	5	-5	652	725
4	5	5	485	543
6	5	-5	656	650
1	6	-5	277	-339
2	6	5	644	610
4	6	-5	*184	215
5	6	5	478	451
2	7	-5	616	707
3	7	5	347	370
1	8	5	295	-251
3	8	-5	*173	49
1	9	-5	952	616
2	9	5	0	85
0	0	6	1220	1229
3	0	-6	432	403
3	0	6	685	810
6	0	-6	387	-311
6	0	6	635	670
9	0	-6	471	546
9	0	6	*176	126
1	1	-6	866	819
1	1	6	*227	-57
4	1	-6	1066	1006
4	1	6	657	1003
7	1	-6	580	515
7	1	6	590	640
2	2	-6	534	533
2	2	6	427	376
5	2	-6	719	668
5	2	6	452	-367
8	2	-6	633	590
8	2	6	718	559
3	3	-6	*209	-70
3	3	6	598	605
6	3	-6	*186	162
6	3	6	455	446
1	4	-6	*213	15
1	4	6	1207	826
4	4	-6	694	770
4	4	6	376	334
7	4	-6	0	-13
7	4	6	0	367
2	5	-6	539	564
2	5	6	429	448
5	5	-6	*179	-96
5	5	6	492	469
3	6	-6	0	707
3	6	6	831	670
1	7	-6	270	275
1	7	6	333	228
2	8	-6	247	-233
2	8	6	478	510
1	0	7	*220	106
2	0	-7	937	885
4	0	7	242	-287
5	0	-7	*203	68
7	0	7	989	727
8	0	-7	339	248
2	1	7	887	722
3	1	-7	211	-168
5	1	7	301	339
6	1	-7	865	703
8	1	7	319	-362
1	2	-7	1445	1057
3	2	7	345	237
4	2	-7	362	377
6	2	7	333	400
7	2	-7	258	-177
1	3	7	808	663
2	3	-7	910	758
4	3	7	733	701
5	3	-7	788	761
7	3	7	312	303
2	4	7	870	897
3	4	-7	366	347
5	4	7	385	440
6	4	-7	478	538
1	5	-7	644	716
3	5	7	420	-414
1	6	7	598	598
2	6	-7	*186	102
4	6	7	324	255
2	7	7	281	358
3	7	-7	0	384
1	8	-7	422	544
1	0	-8	1107	917
2	0	8	*208	-73
4	0	-8	770	895
5	0	8	0	654
7	0	-8	0	652
8	0	8	310	227
2	1	-8	308	-237
3	1	8	0	891
5	1	-8	597	534
6	1	8	0	194
1	2	8	999	911
3	2	-8	757	737
4	2	8	609	626
6	2	-8	*179	-115
7	2	8	500	613
1	3	-8	0	59
2	3	8	476	-343
4	3	-8	*187	-89
5	3	8	0	600
2	4	-8	0	728
3	4	8	*187	29
5	4	-8	330	284
1	5	8	234	242
3	5	-8	0	759
4	5	8	600	564
1	6	-8	*184	-327
2	6	8	481	566
0	0	9	697	665
3	0	-9	*196	83
3	0	9	0	684
6	0	-9	0	-195
6	0	9	0	769
1	1	-9	939	919
1	1	9	*200	-155
4	1	-9	398	530
4	1	9	0	516
2	2	-9	728	647
2	2	9	*194	38
5	2	-9	0	850
5	2	9	0	-246
3	3	-9	*185	-137
3	3	9	837	744
1	4	-9	0	-44
1	4	9	624	694
4	4	-9	470	475
4	4	9	224	169
2	5	-9	0	242
2	5	9	0	410
1	0	10	*191	125
2	0	-10	776	683
4	0	10	0	-80
5	0	-10	0	156
2	1	10	0	613
3	1	-10	*184	-83
5	1	10	0	326
1	2	-10	0	435
3	2	10	0	63
4	2	-10	320	252
1	3	10	495	416
2	3	-10	0	781
4	3	10	0	631
2	4	10	408	353
3	4	-10	0	260
1	0	-11	697	582
2	0	11	*179	21
4	0	-11	594	679
2	1	-11	*177	24
3	1	11	0	690
1	2	11	332	319
3	2	-11	558	544
1	3	-11	0	196
2	3	11	171	-159
0	0	12	209	120
1	1	-12	0	708
1	1	12	0	-93

[a] Listed values are 10 times absolute scale. Reflections indicated by an asterisk were less than minimum; those having F_o = 0 were not recorded on film.

TABLE IV

POSITIONAL AND THERMAL PARAMETERS FOR $UO_3{\cdot}3Lu_2O_3$

	x	y	z	B, A²
3 U^{6+}	0	0	0	0.350 ± 0.222
18 Lu^{3+}	0.1190 ± 0.0005	0.4161 ± 0.0005	0.0252 ± 0.0004	0.839 ± 0.177
18 $O(1)^{2-}$	0.194 ± 0.007	0.028 ± 0.006	0.118 ± 0.006	1.88 ± 1.29
18 $O(2)^{2-}$	0.141 ± 0.006	0.450 ± 0.007	0.269 ± 0.006	1.96 ± 1.14

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $UO_3{\cdot}3Lu_2O_3$[a]

h	k	l	Fo	Fc
3	0	0	834	770
6	0	0	*527	-121
1	1	0	*527	-195
4	1	0	3675	3807
7	1	0	1397	1388
2	2	0	*527	-193
5	2	0	*527	-463
3	3	0	589	-517
6	3	0	*527	-51
1	4	0	*527	562
4	4	0	1294	1300
2	5	0	676	631
3	6	0	2059	2066
1	7	0	*527	-285
1	0	1	*527	62
2	0	-1	839	793
4	0	1	950	-837
5	0	-1	*527	-396
7	0	1	2218	2310
2	1	1	*527	12
3	1	-1	*527	-341
5	1	1	*527	313
6	1	-1	1221	1118
1	2	-1	3898	4270
3	2	1	942	828
4	2	-1	986	1111
6	2	1	*527	-94
1	3	1	695	646
2	3	-1	*527	2
4	3	1	*527	358
5	3	-1	2218	2297
2	4	1	2882	3033
3	4	-1	*527	-80
5	4	1	1031	1072
1	5	-1	1577	1480
3	5	1	*527	-730
4	5	-1	745	-547
1	6	1	*527	-129
2	6	-1	*527	296
1	0	-2	864	816
2	0	2	*527	119
4	0	-2	*527	173
5	0	2	*527	141
7	0	-2	2018	2074
2	1	-2	*527	-426
3	1	2	527	489
5	1	-2	527	386
6	1	2	527	704
1	2	2	3100	3347
3	2	-2	1357	1391
4	2	2	1236	1283
6	2	-2	*527	-351
1	3	-2	819	734
2	3	2	1151	-1065
4	3	-2	*527	-381
5	3	2	2018	2046
2	4	-2	2473	2606
3	4	2	*527	113
1	5	2	1136	1262
3	5	-2	*527	43
1	6	-2	945	-907
2	6	2	645	700
0	0	3	3692	3869
3	0	-3	*527	506
3	0	3	1306	1327
6	0	-3	946	-926
6	0	3	*527	506
1	1	-3	854	790
1	1	3	929	-882
4	1	-3	2849	2864
4	1	3	2849	2819
2	2	-3	763	571
2	2	3	*527	-197
5	2	-3	*527	407
5	2	3	1317	-1232
3	3	-3	854	-867
3	3	3	*527	358
1	4	-3	*527	30
1	4	3	883	1025
4	4	-3	1380	1406
4	4	3	976	1083
2	5	-3	645	693
2	5	3	912	758
1	0	4	709	-677
2	0	-4	1276	1358
4	0	4	1343	-1362
5	0	-4	731	-755
7	0	4	1828	1829
2	1	4	833	906
3	1	-4	833	-821
5	1	4	*527	39
6	1	-4	1178	1121
1	2	-4	3415	3436
3	2	4	*527	340
4	2	-4	*527	632
1	3	4	1001	950
2	3	-4	1186	1064
4	3	4	847	942
5	3	-4	1866	1941
2	4	4	2492	2512
3	4	-4	*527	234
1	5	-4	1302	1357
3	5	4	1178	-1131
1	6	4	745	718
1	0	-5	1148	1203
2	0	5	527	-473
4	0	-5	1289	1199
5	0	5	645	598
2	1	-5	833	-930
3	1	5	1540	1363
5	1	-5	*527	386
6	1	5	1020	274
1	2	5	2695	2669
3	2	-5	1317	1376
4	2	5	1020	1051
1	3	-5	*527	141
2	3	5	1262	-1256
4	3	-5	589	-542
2	4	-5	2006	2000
3	4	5	*527	-55
1	5	5	*527	644
1	6	-5	1050	-1181
0	0	6	2225	2068
3	0	-6	*527	212
3	0	6	1230	1232
1	1	-6	1394	1351
1	1	6	912	-866
4	1	-6	1624	1661
4	1	6	1624	1634
2	2	-6	745	706
2	2	6	*527	2
3	3	-6	833	-779
3	3	6	882	972
1	4	-6	*527	-312
1	4	6	1178	1293
1	0	7	*527	-325
2	0	-7	1455	1416
4	0	7	1178	-1073
2	1	7	1110	1218
3	1	-7	874	-819
1	2	-7	1727	1518
3	2	7	*527	83
1	3	7	954	902
2	3	-7	1532	1444
1	0	-8	1559	1370
2	0	8	589	-476
2	1	-8	719	-715
1	2	8	1207	1189

[a] Listed values are 10 times absolute scale. Reflections indicated by an asterisk were less than minimum.

$O_{13.3}$ are given in Table VII with their respective discrepancy index values. The higher R values for both of these structures may be attributed to the uncertainty in composition as well as the inherently poorer quality of the X-ray diffraction data.

Discussion

Structure of the Rhombohedral Phases.—Solid solutions of UO_{2+x} and Y_2O_3 have long been known to be face-centered cubic with a degree of anion deficiency which depends upon the uranium content and the oxygen partial pressure.[10] When the number of oxygen vacancies becomes too large, a structural rearrangement takes place to give a phase of rhombohedral symmetry.

The c axis of the hexagonal cell lies along the threefold [111] axis of the face-centered cube. The stacking arrangement of the metal ions remains essentially the same, except for a slight displacement of the yttrium ions out of the fcc (111) planes and an ordering of the uranium ions at the rhombohedral cell origin. Oxygen ions are missing in rows along the hexagonal axis occupied by uranium ions; the remaining oxygens shift toward these vacant sites.

The ideal fluorite structure is characterized by MO_8 coordination cubes, as in UO_2 and the rare earth dioxides. In rhombohedral $UO_3{\cdot}3Y_2O_3$, the uranium ions are octahedrally coordinated with all U–O distances equal to 2.07 A. These octahedra alternate along the hexagonal c axis with similar octahedra not containing a uranium ion. No other reported oxide of uranium possesses this type of coordination with six primary bonds of equal strength except δ-UO_3.[11] This coordination around the uranium ion may account for the remarkable thermal stability of the rhombohedral phase. All other uranium(VI) oxides are characterized by UO_2^{2+} groups or U–O–U–O chains in which there are two strong U–O bonds and several much weaker secondary bonds.

In the reduced rhombohedral phase, the uranium in random yttrium sites is coordinated to six oxygen atoms forming a highly distorted octahedron. Upon oxidation the uranium coordination number increases to seven.

The Y–O and Lu–O bond lengths agree very well with those reported for their respective bcc oxides. The highly distorted octahedron of oxygen ions surrounding the yttrium shown in Figure 3 is a view along the b axis in Figure 2 of the ions designated. The four O(2) ions are shared between two yttrium polyhedra while the two O(1) ions are shared by yttrium and

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(10) (a) F. Hund, U. Peetz, and G. Kottenhahn, *Z. Anorg. Allgem. Chem.*, **278**, 184 (1955); (b) J. Anderson, I. Ferguson, and L. E. J. Roberts, *J. Inorg. Nucl. Chem.*, **1**, 340 (1955); (c) I. Ferguson and P. Fogg, *J. Chem. Soc.*, 726, 3679 (1957).

(11) H. R. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.*, **18**, 154 (1961).

TABLE VI

INTERATOMIC DISTANCES[a] AND ANGLES WITH STANDARD DEVIATIONS

	$UO_3 \cdot 3Y_2O_3$			$UO_3 \cdot 3Lu_2O_3$	
Ions	Distances, A	Angle, deg	Ions	Distances, A	Angle, deg
O(1′)-U-O(1″)	2.07, 2.07	85.2 ± 0.6	O(1′)-U-O(1″)	2.13, 2.13	84.4 ± 0.7
O(1″)-U-O(1‴)	2.07, 2.07	94.8 ± 0.8	O(1″)-U-O(1‴)	2.13, 2.13	95.6 ± 0.8
O(1)-Y-O(2′)	2.40, 2.30	104.0 ± 0.5	O(1)-Lu-O(2′)	2.27, 2.22	104.2 ± 0.5
O(1)-Y-O(2‴)	2.40, 2.28	80.5 ± 0.5	O(1)-Lu-O(2‴)	2.27, 2.25	82.8 ± 0.5
O(1′)-Y-O(2″)	2.32, 2.30	160.0 ± 0.3	O(1′)-Lu-O(2″)	2.25, 2.23	160.5 ± 0.3
O(2)-Y-O(2′)	2.17, 2.30	106.3 ± 0.8	O(2)-Lu-O(2′)	2.20, 2.22	104.7 ± 0.8
O(2′)-Y-O(2‴)	2.30, 2.28	77.0 ± 0.8	O(2′)-Lu-O(2‴)	2.22, 2.25	77.0 ± 0.8
O(1)-O(1‴)	3.05 ± 0.03		O(1)-O(1‴)	3.15 ± 0.03	
O(1)-O(2″)	2.87 ± 0.02		O(1)-O(2″)	2.72 ± 0.02	
O(1)-O(2‴)	3.02 ± 0.02		O(1)-O(2‴)	2.98 ± 0.02	
O(1′)-O(1″)	2.81 ± 0.02		O(1′)-O(1″)	2.86 ± 0.02	
O(1′)-O(2)	3.22 ± 0.03		O(1′)-O(2)	3.23 ± 0.03	
O(1′)-O(2′)	3.32 ± 0.02		O(1′)-O(2′)	3.23 ± 0.02	
O(2)-O(2″)	2.80 ± 0.02		O(2)-O(2″)	2.71 ± 0.02	
U-Y	3.70 ± 0.03		U-Lu	3.64 ± 0.03	
Y-Y′	3.54 ± 0.02		Lu-Lu′	3.47 ± 0.02	
Y-Y″	3.64 ± 0.03		Lu-Lu″	3.55 ± 0.03	

[a] The standard errors in the metal–oxygen distances are all 0.02 A.

TABLE VII

POSITIONAL PARAMETERS AND *R* VALUES

	$U_2Y_5O_{12}$				$U_2Y_5O_{13.3}$		
	x	y	z		x	y	z
3 U^{5+}	0	0	0	3 U^{6+}	0	0	0
3 U^{4+} + 15 Y^{3+}	0.126	0.418	0.018	3 U^{6+} + 15 Y^{3+}	0.134	0.419	0.017
18 $O(1)^{2-}$	0.210	0.043	0.110	18 $O(1)^{2-}$	0.222	0.035	0.100
18 $O(2)^{2-}$	0.138	0.442	0.256	18 $O(2)^{2-}$	0.133	0.437	0.253
	R = 14.0%			4 $O(3)^{2-}$	0	0	0.265
					R = 11.9%		

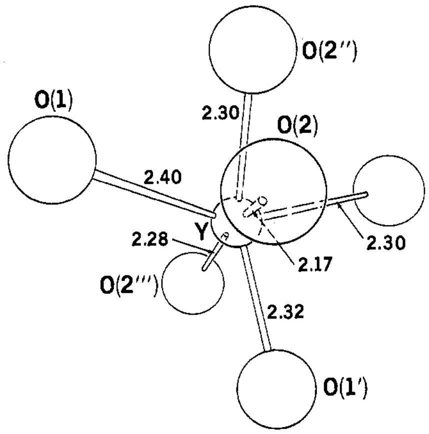

Figure 3.—A view of the yttrium coordination polyhedron perpendicular to the hexagonal *c* axis. Atom designations are the same as in Table VI.

uranium polyhedra. These polyhedra are joined together at their corners. This is in contrast to the bcc (C-type) rare earth oxide structure in which the polyhedra are linked together at both edges and corners. Here again, the rhombohedral structure is a more stable arrangement.

Relationship between Structure and Composition.—The existence of a rhombohedral structure over a range of $UO_{2+x}:Y_2O_3$ compositions is possible by the partial substitution of uranium for yttrium ions in the (18f) general positions. Chemical and crystallographic evidence now indicate that the $U_mY_{7-m}O_{12}$ phase can exist over the range $1 \leq m \leq 2$. The limiting reduced composition becomes $U_2Y_5O_{12}$ at a mole ratio of $4UO_{2.25} \cdot 5Y_2O_3$ (55.6 mole % Y_2O_3). The uranium ion at the origin can be assumed to be in the pentavalent oxidation state, while the uranium ion randomly distributed in the yttrium sites is tetravalent. The structure analysis was carried out for this limiting composition although the actual composition was close to $2UO_{2.30} \cdot 3Y_2O_3$ (60 mole % Y_2O_3). Oxidation of these compositions can be expressed in the following way

$$\begin{tikzcd}
U^{5+}(1U^{4+}, 5Y^{3+})O_{12} \arrow[d, "1.5O"] & U^{5+}(0.75U^{4.32+}, 5.25Y^{3+})O_{12} \arrow[d, "1.1O"] \\
U^{6+}(1U^{6+}, 5Y^{3+})O_{13.5} & U^{6+}(0.75U^{6+}, 5.25Y^{3+})O_{13.1}
\end{tikzcd}$$

It was assumed that the final valence state of the uranium was 6+; hence, the large hexagonal cell could contain 1.33 × 3 = 4 additional oxygens. These extra ions were found in the three-dimensional Fourier map near the ideal positions they would occupy in the fcc fluorite structure. Structure factor calculations carried out on the basis of 4 oxygen atoms randomly distributed in the (6c) position (0, 0, z) confirmed this arrangement. The change in oxidation state has also been corroborated by low-temperature oxidation studies.[2b]

The z parameter of the extra oxygen ions could not be accurately determined from the powder diffraction data, but best agreement was indicated for $z \approx 0.265$. The distance from the metal ions in the general (18f) position to this extra oxygen is 2.40 A. Its oxygen neighbors are very near, being only 2.56 A away. In order to accommodate these extra oxygens in the structure, there must be a slight relaxation around their lattice sites.

For the uranium at the cell origin, the coordination number increases to 7 or 8 with the extra U–O bonds being perpendicular to opposite faces of the octahedron at a distance of 2.46 A. At temperatures above 1000°, the structure rearranges to the normal fluorite structure.

Ordered rare earth oxide phases of composition $RO_{1.71}$ are isostructural with $UO_3 \cdot 3Y_2O_3$. Their narrow composition limits are fixed by the oxygen-to-metal ratio of 12:7. This phase can form only with Ce, Pr, and Tb because they have both trivalent and tetravalent oxidation states. In terms of these valences, this phase should be written $(M^{4+})_3(M^{3+})_4O_{12}$. However, since the crystal structure requires one metal ion to be located at the origin, it is apparent that this arrangement must be stabilized by electron transfer. Although it would be impossible by X-ray diffraction to determine whether an M^{3+} or M^{4+} ion is located at the origin, analogy with $U_2Y_5O_{12}$ suggests that it is the site of an M^{4+} ion. Structurally, then, the composition is $M^{4+}(2M^{4+}, 4M^{3+})O_{12}$ where electron exchange produces equivalency in the 18-fold general position of the hexagonal unit cell.

TABLE VIII

CHANGE IN c/a RATIO WITH COMPOSITION

Compd	c/a	Compd	c/a
$U_2Y_5O_{12}$	0.935	$U_2Y_5O_{13.5}$	0.934
$CeO_{1.71}$	0.936	$CeO_{1.78}$	0.926
$PrO_{1.71}$	0.932	$PrO_{1.78}$	0.918

Further oxidation of $PrO_{1.71}$ and $CeO_{1.71}$ leads to another stable phase of composition $MO_{1.78}$. In terms of ions, this could be written $(M^{4+})_4(M^{3+})_3O_{12.5}$. If this oxidation takes place without rearrangement, the rhombohedral structure would contain $M^{4+}(3M^{4+}, 3M^{3+})O_{12.5}$ and 1.5 additional oxygen atoms would have randomly entered the (6c) special positions of the hexagonal cell. That this is probably the case can be inferred from the changes in the lattice parameters which have been reported.[12] Comparison of hexagonal c/a ratios are given in Table VIII. Although the number of oxygens added to the rare earth oxides is less than that for the mixed uranium–yttrium compound, they produce a greater contraction of the c axis. The formation of RO_7 polyhedra probably causes more rearrangement in these oxides than is the case for the seven-coordination around the uranium ions. A continuation of this oxidation process in similar steps might be expected to produce the following stable compositions

$$M^{4+}(4M^{4+}, 2M^{3+})O_{13} = (MO_{1.86})$$

$$M^{4+}(5M^{4+}, 1M^{3+})O_{13.5} = (MO_{1.93})$$

but neither of these stoichiometries has been reported as a stable phase. This can probably be accounted for by the fact that the addition of more oxygen, along the hexagonal c axis, further contracts the lattice in this direction to produce eightfold coordination around the M^{4+} ions at the origin. This configuration is unstable because an MO_8 group normally exists as a regular cube. Also, adding more oxygen rapidly increases the repulsion between neighboring oxygens, causing a structural rearrangement to occur. The short O–O distances in rhombohedral $U_2Y_5O_{13.3}$ after low-temperature oxidation make this a metastable compound which transforms to face-centered cubic above 1000°.

Acknowledgment.—The author is grateful to Dr. J. M. Stewart of The University of Maryland for the X-ray 63 system of computer programs used in the solution of this problem.

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[12] L. Eyring and B. Holmberg, "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, pp 46–57.

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Phase Relationships in the Rare Earth Sesquioxides at High Pressure[1,2]

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Phase relationships in the rare earth sesquioxides have been studied at pressures from 15 to 60 kbars at 550, 1000, and 1450°. No measurable shift is observed in the boundary between the hexagonal (A) and monoclinic (B) phases, but stability of the monoclinic phase relative to the cubic phase is enhanced by increased pressure as well as higher temperature. The C–B phase transformations are shown to be reversible. Lattice parameters are given for 11 monoclinic sesquioxides—Y_2O_3 and Sm_2O_3 through Lu_2O_3. The entropy increase involved in the transformation from the cubic to monoclinic structure is estimated to be 1.5 eu.

The rare earth sesquioxides were first investigated systematically by Goldschmidt and his co-workers[3] in 1925. The great similarity in the chemical properties of the individual lanthanides had effectively prevented the isolation of sufficiently pure samples for any de-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[3] V. M. Goldschmidt, F. Ulrich, and T. Barth, *Skrifter Norske Videnskaps-Akad. Oslo, I: Mat. Naturv. Kl.*, No. 5 (1925).