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The Crystal and Molecular Structure of Tetragonal Ruthenium Dioxide[1]

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Received July 16, 1965

The marked tendency of Re(III) to form metal-atom clusters[3–11] leading to essentially diamagnetic compounds suggested that compounds of other d^4 heavy transition metals having similar magnetic properties might also show evidence of metal-atom cluster formation. Like the trimeric Re(III) compounds, RuO_2 is highly colored and exhibits a very low magnetic susceptibility (203×10^{-6} c.g.s. unit/mole at 298°K.).[12] This suggested the presence of some form of strong metal–metal interaction. Although early reports[13] based only on powder diffraction data have stated that most transition metal dioxides, including RuO_2, MoO_2, and WO_2, have the rutile structure, this assignment has later been found to be erroneous in the case of MoO_2 and WO_2. These compounds adopt a *distorted* form of the basic rutile structure[14] in which the metal atoms occur in pairs with the shorter metal–metal distances being ~2.5 Å. Thus it was thought that a similar error might have been made in the case of RuO_2, and it seemed desirable to reexamine this compound by single crystal methods.

Experimental Section

Crystals of RuO_2 grown by high-temperature sublimation in a stream of oxygen were kindly supplied by Professor H. Schäfer of the University of Münster. *Anal.* Calcd. for RuO_2: Ru, 75.95. Found: Ru, 76.00, 76.05, 76.08. Precession photographs of the *h0l* and *0kl* zones established that the unit cell was tetragonal with $a = 4.491 \pm 0.007$ Å. and $c = 3.107 \pm 0.005$ Å. The only observed systematic absence was $0kl$ for $k + l \neq 2n$, which is consistent with the space groups $P4_2/mnm$ (No. 136), $P\bar{4}n2$ (No. 118), and $P4_2nm$ (No. 102).[15] There are two formula units per unit cell. The intensity data were collected and corrected in the customary manner.[16] The equi-inclination Weissenberg method and Zr-filtered Mo Kα radiation were used. Anomalous dispersion corrections to the real part of the ruthenium scattering curve were made according to the tables of Dauben and Templeton.[17]

The interesting feature of the photographs obtained in this study was the sharp division of the diffraction spots into two sets, one set having very high intensity and one set having very low intensity. The former group obeyed the condition that $h + k + l = 2n$, indicating that the ruthenium atoms formed a body-centered array and, therefore, contributed nothing to the reflections with $h + k + l \neq 2n$. The latter condition was obeyed by the spots of very low intensity. It thus seemed likely that the original assignment of the rutile structure to RuO_2 was, in this case, correct, and refinement was carried out in the space group $P4_2/mnm$. Least-square refinement of four scale factors, the oxygen x parameter, and isotropic temperature factors for each atom by the usual methods led to a conventional residual of 0.141. Similar refinement in the other possible space groups met with less success indicating that $P4_2/mnm$ is probably correct. No significant anomalies were found on the final Fourier difference map.

The final value of the oxygen x parameter was 0.302 ± 0.002, which gives Ru–O distances of 1.917 and 1.999 Å. (both ±0.008 Å.). The closest O–O contact is 2.52 Å. The previous studies[13] gave only a mean Ru–O distance of 1.97 Å. with unspecified uncertainty. The final observed (FOBS) and calculated (FCAL) structure factors are listed in Table I.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
2	0	0	47.	48.	6	1	1	40.	32.	5	2	2	0.	-0.
4	0	0	40.	49.	2	2	1	7.	-5.	6	2	2	34.	28.
6	0	0	36.	37.	3	2	1	35.	40.	3	3	2	41.	45.
2	1	0	13.	11.	4	2	1	8.	5.	4	3	2	7.	3.
3	1	0	49.	49.	5	2	1	50.	43.	5	3	2	35.	27.
4	1	0	11.	-9.	6	2	1	0.	-3.	6	3	2	0.	-3.
5	1	0	47.	42.	3	3	1	4.	-2.	4	4	2	37.	33.
6	1	0	6.	6.	4	3	1	42.	40.	5	4	2	0.	0.
3	2	0	4.	-4.	5	3	1	0.	-0.	1	0	3	49.	40.
4	2	0	42.	41.	6	3	1	43.	33.	3	0	3	40.	45.
5	2	0	0.	-0.	4	4	1	10.	-6.	5	0	3	27.	25.
6	2	0	36.	31.	5	4	1	40.	30.	1	1	3	9.	-8.
3	3	0	42.	51.	6	4	1	8.	5.	2	1	3	33.	43.
4	3	0	4.	4.	5	5	1	0.	-0.	3	1	3	5.	4.
5	3	0	36.	29.	2	0	2	43.	40.	4	1	3	35.	34.
6	3	0	7.	-3.	4	0	2	40.	42.	5	1	3	0.	0.
4	4	0	37.	37.	6	0	2	36.	34.	2	2	3	0.	-3.
5	4	0	0.	0.	1	1	2	52.	54.	3	2	3	28.	31.
5	5	0	45.	36.	2	1	2	9.	6.	4	2	3	5.	4.
3	0	1	53.	62.	3	1	2	42.	42.	5	2	3	39.	36.
5	0	1	34.	30.	4	1	2	12.	-7.	3	3	3	0.	-2.
1	1	1	19.	-18.	5	1	2	40.	37.	4	3	3	32.	33.
2	1	1	49.	62.	6	1	2	8.	5.	5	3	3	0.	-0.
3	1	1	8.	6.	2	2	2	41.	53.	4	4	3	6.	-5.
4	1	1	45.	43.	3	2	2	7.	-3.	5	4	3	33.	26.
5	1	1	0.	0.	4	2	2	39.	36.					

Discussion

Despite the somewhat high residual, there can be little doubt as to the correctness of the structure. All dimensions found in this work compare favorably with those found[18] in other dioxides known to have the rutile-type structure. Also, the pattern of intensities is such that the ruthenium atoms must be in a regular body-centered array. Thus no metal-atom clusters are present. The success of refining the oxygen atom using only those reflections for which $h + k + l \neq 2n$ seems to confirm the correctness of its location.

Since the closest Ru–Ru distance is 3.107 Å. and there is no evidence of clusters, one is left with no simple explanation of the very low susceptibility. It is not possible to account for this low susceptibility by large spin–orbit coupling effects according to the theory of Kotani[19] or even by the intermediate coupling scheme of Kamimura, *et al.*[20] However, preliminary experiments on crystalline fragments and packed powder samples of RuO_2 indicate that it has a

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[1] Supported by the United States Atomic Energy Commission.

[2] National Science Foundation Predoctoral Fellow.

[3] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1166 (1963).

[4] W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[5] F. A. Cotton and J. T. Mague, *ibid.*, 223 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

[6] F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1094 (1963).

[7] J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

[8] J. E. Fergusson and W. T. Robinson, *Proc. Chem. Soc.*, 189 (1964).

[9] F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

[10] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

[11] B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).

[12] A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, **37**, 303 (1931).

[13] P. P. Ewald and C. Hermann, "Strukturberichte, 1913–26," Akademische Verlagsgesellschaft MBH Leipzig, 1931.

[14] A. Magneli and G. Andersson, *Acta Chem. Scand.*, **9**, 1378 (1955).

[15] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1952, Vol. I.

[16] See ref. 6, for example.

[17] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 478 (1955).

[18] R. W. G. Wyckoff, "Crystal Structures," Vol. I, 2nd Ed., Interscience Publishers, New York, N. Y., 1963, p. 251.

[19] K. M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

[20] H. Kamimura, S. Koide, H. Sekiyama, and S. Sugano, *ibid.*, **15**, 1264 (1960).

very high electrical conductivity. An experimental and theoretical investigation of this is in progress.

Acknowledgments.—The use of the IBM 7094 computer at the M.I.T. Computation Center is gratefully acknowledged. We are very grateful to Professor Schäfer for his kindness in supplying the crystalline material.

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The Structure Refinement of La_2Te_3, a Th_3P_4 Type Structure[1]

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Received July 30, 1965

The thorium phosphide structure, Th_3P_4, occurs widely in the compounds of the lanthanides with tellurium, sulfur, phosphorus, bismuth, and others. The various cube edges are 8 to 10 Å., the space group is $I\bar{4}3d$, and there is only one variable parameter. This type of structure was first discussed by Meisel[2] and subsequently by Zachariasen[3] in relation to the compound Ce_2S_3. Kripyakevich[4] gave a detailed description of the structure in terms of the articulation of the polyhedra occurring in it. Carter[5] reviewed the Th_3P_4 structure from the standpoint of electrostatic energy and valence bond considerations and found that the x parameter of $^1/_{12}$, the idealized value for the single variable positional parameter, produces an unstable ionic structure in Ce_2S_3 and that a value of approximately 0.04 corresponds to a minimum in the electrostatic energy calculation. He concluded that a compound with a Th_3P_4 structure and an anion position of $^1/_{12}$ is essentially not ionic in nature, even though the bond distances obtained on the basis of this value are equal to the sum of the ionic radii.

The structure can be visualized as being made up of two kinds of anion tetrahedra surrounding a single cation. Both tetrahedra have a $\bar{4}$ axis of symmetry; one tetrahedron being large and elongated and the other being rather flat. With an anion parameter of $^1/_{12}$, the Th–P distances are all equal, but as the value drops below $^1/_{12}$, the large tetrahedron becomes longer and the flat tetrahedron smaller and less flat. The importance of this structure in the rare earth compounds prompted us to undertake a single crystal investigation to determine the exact value of the positional parameter of the 16-fold position of the ion in space group $I\bar{4}3d$; all other positions are fixed by symmetry.

Experimental Section

Samples for this determination were obtained from specimens which had been previously prepared during the investigation of the lanthanum–tellurium phase diagram.[6] Several crystals of irregular shape were selected from reacted batches of desired analyzed composition. The crystal used for data collection had dimensions of 0.11 mm. and 0.037 mm. at its widest and narrowest limits. The lattice constant for La_2Te_3 had previously been determined from powder diffraction data as 9.619 Å., and the value obtained from a Weissenberg film was in agreement with it. Flahaut[7] reports a value of 9.627 Å. for this composition. The crystal was mounted on a single crystal orienter and the diffraction data were collected using Zr-filtered Mo radiation with a scintillation counter and pulse height discrimination. The linear absorption coefficient of La_2Te_3 for Mo Kα is 262 cm.$^{-1}$ and $\mu R = 1.8$ when an average radius of 0.07 mm. is used for this crystal; no absorption corrections were made on the measured intensities.

There are $5^1/_3$ formula weights of La_2Te_3 in the unit cell and $10^2/_3$ sites of the equipoints 12(a) of $I\bar{4}3d$ are occupied by La, while Te is in 16(c), xxx; the single, variable, positional parameter and two isotropic temperature factors were determined using a full-matrix least-squares procedure with unit weights assigned to the structure factors. A test with two anisotropic temperature factors for La indicated essentially spherical symmetry. Approximately 100 general *hkl* reflections were collected because they overdetermine the problem sufficiently. The atomic scattering factors for lanthanum and tellurium were corrected for dispersion. The final discrepancy coefficient is 0.040 for the observed reflections listed in Table I, and Table II lists the parameters of the structure. The discrepancy factor, R, was

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR La_2Te_3

h	k	l	F_{obs}	$\lvert F_{cal}\rvert$	h	k	l	F_{obs}	$\lvert F_{cal}\rvert$	h	k	l	F_{obs}	$\lvert F_{cal}\rvert$
4	0	0	75	75	3	2	1	765	799	5	5	2	585	576
12	0	0	562	536	5	2	1	159	161	7	5	2	493	463
16	0	0	275	302	7	2	1	480	507	11	5	2	227	214
3	1	0	1052	1123	9	2	1	611	646	8	6	2	167	172
5	1	0	159	148	11	2	1	171	195	7	7	2	372	358
7	1	0	281	266	4	3	1	530	560	11	7	2	272	273
9	1	0	215	214	6	3	1	367	379	6	3	3	587	468
13	1	0	303	283	8	3	1	224	218	10	3	3	196	203
2	2	0	151	145	12	3	1	380	376	5	4	3	261	266
4	2	0	590	588	5	4	1	643	651	7	4	3	487	514
10	2	0	159	156	7	4	1	241	237	9	4	3	325	326
12	2	0	243	233	9	4	1	182	194	6	5	3	292	294
5	3	0	317	303	11	4	1	276	271	8	5	3	172	194
7	3	0	125	118	6	5	1	253	275	10	5	3	388	390
11	3	0	168	162	8	5	1	546	542	7	6	3	405	422
13	3	0	225	208	10	5	1	247	223	9	6	3	190	182
4	4	0	165	161	7	6	1	212	189	8	7	3	443	449
6	4	0	440	436	11	6	1	292	297	10	7	3	334	353
8	4	0	365	362	8	7	1	181	177	9	8	3	296	293
10	4	0	296	281	10	7	1	193	166	4	4	4	942	1069
12	4	0	220	226	9	8	1	153	149	8	4	4	404	414
7	5	0	490	494	11	8	1	249	249	12	4	4	381	361
9	5	0	485	516	4	2	2	722	733	7	5	4	245	263
11	5	0	241	243	8	2	2	521	507	9	5	4	281	286
6	6	0	512	520	12	2	2	323	320	8	6	4	285	281
12	6	0	218	196	3	3	2	535	529	6	5	5	567	585
9	7	0	263	264	5	3	2	597	594	7	6	5	227	248
11	7	0	379	364	7	3	2	304	284	8	6	6	495	524
8	8	0	777	768	11	3	2	250	232	9	7	6	370	367
2	1	1	192	197	13	3	2	276	272	9	9	6	316	316
6	1	1	833	824	6	4	2	447	419					
10	1	1	487	472	10	4	2	506	475					

TABLE II

POSITIONAL AND TEMPERATURE PARAMETERS OF La_2Te_3

Atom	x	$\sigma(x)$	B, Å.^{2}	$\sigma(B)$
La	. . .		1.20	0.08
Te	0.0748	0.0002	0.96	0.08

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 62-237.

[2] K. Meisel, *Z. anorg. allgem. Chem.*, **240**, 300 (1939).

[3] W. H. Zachariasen, *Acta Cryst.*, **2**, 57 (1949).

[4] P. I. Kripyakevich, *Sov. Phys. Cryst.*, **7**, 556 (1963).

[5] F. L. Carter, Proceedings, Fourth Rare Earth Conference, Phoenix, Ariz., 1964; to be published.

[6] T. H. Ramsey, H. Steinfink, and H. J. Weiss, *Inorg. Chem.*, **4**, 1154 (1965).

[7] J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golobi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).