

## Refinement of the Crystal Structure of Ruthenium Dioxide

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Crystals of ruthenium dioxide were prepared, and powder, rotation, and Weissenberg photographs were taken. Ruthenium dioxide, which has a rutile structure, crystallizes in space group No. 136,  $P4_2/mnm$ , of the tetragonal system. The unit cell contains two formula units and the cell dimensions are  $a=4.491$ , Å,  $c=3.106$ , Å, and  $V=62.68$  Å<sup>3</sup>. The structural parameter has been determined by the use of three-dimensional X-ray data and found to be  $x=0.306 \pm 0.002$ . The final  $R$ -value was 0.071 based on a total of 235 observed, independent reflections. Ruthenium is octahedrally coordinated by oxygen; four of the six Ru—O distances are  $1.984 \pm 0.006$  Å and the other two  $1.942 \pm 0.010$  Å. The difference in bond length is quite small, only 2%, but should be regarded as significant according to the Cruickshank test. The closest Ru—Ru distance is 3.107 Å, so that there can be no significant interaction between the metal atoms.

Many oxides and fluorides crystallize with the rutile structure. As the name suggests, rutile ( $\text{TiO}_2$ ) together with cassiterite ( $\text{SnO}_2$ ) were the first members in this class to have their crystal structures investigated by X-ray methods. This was done by Vegard<sup>1</sup> as early as 1916. In the years that followed a number of metal oxides were reported to belong to this type. Among those were  $\text{RuO}_2$  and  $\text{OsO}_2$  (Goldschmidt<sup>2</sup> and Lunde<sup>3</sup>) but long before it was assumed on purely crystallographic grounds that these oxides were isomorphous with rutile.<sup>4</sup> These early crystal determinations were chiefly based on powder diffraction data, and more recently a series of reinvestigations has been carried out on compounds believed to have rutile structures, a more elaborate X-ray technique being used. It has turned out that some oxides previously reported to be of the rutile type, have a more complicated structure, e.g. in the cases of  $\text{MoO}_2$ ,  $\text{WO}_2$ , and  $\text{VO}_2$  (Magnéli,<sup>5,6</sup> Andersson<sup>6,7</sup>). Much more accurate data have also been published about rutile structures, and Baur<sup>8-10</sup> has found slightly different Me—O distances in at least  $\text{TiO}_2$  among the oxides and different Me—F distances in several of the fluorides.

This refinement was originally planned as a preliminary to an investigation of the crystal structures of some basic ruthenium salts, which was to be carried out in connection with the structure investigations of basic

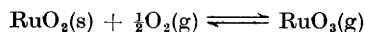
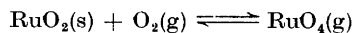
salts containing other tetra-valent metal ions, being made by Lundgren and coworkers at the University of Göteborg. It has, however, not been possible to prepare any basic ruthenium salts up to this time, and this refinement and a precision determination of the crystal structure of osmium dioxide<sup>11</sup> will therefore be published separately.

### EXPERIMENTAL

Several methods for the preparation of ruthenium dioxide are described in the literature (see Refs. 3,4,12–20). One method used was to fuse 1 g of ruthenium metal powder with 10 g of potassium hydroxide and 1 g of potassium nitrate in a nickel crucible for 15 minutes.<sup>21</sup> The red mass formed was dissolved in water and the brown solution of ruthenate ( $\text{RuO}_4^{2-}$ ) was quantitatively reduced and precipitated as the black hydrated ruthenium dioxide by adding 10 ml of ethanol. The dioxide was collected on a filter, washed and dried. The freshly precipitated dioxide could be dissolved in 6 M HCl by boiling. The dark brown solution containing  $\text{RuCl}_4$  was then transformed into the sulfate by evaporating it several times to dryness with conc.  $\text{H}_2\text{SO}_4$ . On heating the dry sulfate in a muffle furnace to 600°C  $\text{RuO}_2$  was formed.<sup>19</sup>

The simplest method, however, for the preparation of the dioxide is to heat ruthenium powder in a stream of oxygen at approximately 1000°C.<sup>17</sup> The metal becomes successively coated with the dioxide but it is difficult to know when all the metal is transformed into the dioxide.

These methods all result in a more or less amorphous ruthenium dioxide, as can be seen on powder photographs. In order to obtain crystalline  $\text{RuO}_2$  it appears that chemical transport in the gas phase is necessary. According to Schäfer *et al.*,<sup>22,23</sup> who have made a very thorough investigation of the behaviour of ruthenium oxides at high temperatures, the following reversible reactions occur when  $\text{RuO}_2$  is heated in oxygen:



Crystals of  $\text{RuO}_2$  were prepared by heating ruthenium metal powder or amorphous  $\text{RuO}_2$  (obtained by the methods previously described) in a silica tube to 1100–1300°C, while oxygen gas was passed through slowly. After 5–10 h a small amount of crystalline ruthenium dioxide could be found at the cool end of the tube. The dark blue crystals were very small and mostly twinned and it proved difficult to find single crystals for the recording of Weissenberg photographs, and many of them had to be tested on the goniometer before suitable single crystals were found.

### CELL DIMENSIONS

The cell dimensions of  $\text{RuO}_2$  were determined using a Guinier camera ( $\text{CuK}\alpha_1$  radiation,  $\lambda=1.54050 \text{ \AA}$ ) with KCl as internal standard ( $a_{\text{KCl}}=6.2919_4 \text{ \AA}$  at 20°C).<sup>24</sup> Fifteen reflections were measured and the indexing procedure and the subsequent refinement were performed using the programme POWDER.<sup>25</sup> The following results were obtained:

$$\begin{aligned} a &= 4.4919 \pm 0.0008 \text{ \AA} \\ c &= 3.1066 \pm 0.0007 \text{ \AA} \\ c:a &= 0.6916 \\ V &= 62.28 \text{ \AA}^3 \end{aligned}$$

Lunde<sup>3</sup> gives the values  $a=4.51 \pm 0.02 \text{ \AA}$  and  $c=3.11 \pm 0.02 \text{ \AA}$ , and Schäfer *et al.*<sup>22</sup>  $a=4.49 \pm 0.005 \text{ \AA}$  and  $c=3.11 \pm 0.005 \text{ \AA}$ . The density as calculated from these dimensions with two formula units in the unit cell is 7.05 g/cm<sup>3</sup>;

in good agreement with the experimental value 7.2 g/cm<sup>3</sup> as found by Debray and Joly<sup>20</sup> for RuO<sub>2</sub> containing small amounts of iridium, osmium, and rhodium. A comparison between observed and calculated sin<sup>2</sup>θ values is given in Table 1.

Table 1. Guinier powder photograph of RuO<sub>2</sub>, CuKα<sub>1</sub> radiation (λ=1.54050 Å).

<i>hkl</i>	10 <sup>5</sup> sin <sup>2</sup> θ obs	10 <sup>5</sup> sin <sup>2</sup> θ calc	<i>I</i> obs	<i>F</i> calc
1 1 0	5877	5881	vs	78
1 0 1	9080	9088	vs	63
2 0 0	11755	11761	m	51
2 1 0	14699	14702	w	12
2 1 1	20852	20849	vs	63
2 2 0	23519	23523	s	66
0 0 2	24562	24589	s	71
3 1 0	29380	29403	m	49
1 1 2	30452	30470	s	54
3 0 1	32592	32610	m	63
2 0 2	36363	36351	m	41
2 1 2	39259	39291	w	7
3 2 1	44363	44372	s	40
4 0 0	47031	47045	m	47
2 2 2	48132	48112	m	51

#### INTENSITY DATA

Crystals of RuO<sub>2</sub> (about 0.1 mm in diameter) were set with [001], [010], and [110] as rotation axes and multiple film equi-inclination Weissenberg photographs were taken, CuKα radiation being used. The intensities were estimated visually. As, however, only 128 reflections (73 independent) were obtained and the absorption of X-rays is high in RuO<sub>2</sub>, the linear absorption coefficient being 993 cm<sup>-1</sup> for CuKα radiation,<sup>26</sup> it was decided to take new photographs, this time making use of MoKα radiation. Two series of Weissenberg photographs were taken, viz. *hk0*—*hk4* and *h0l*—*h5l*. One crystal was used for both recordings; it had the dimensions 0.07 mm × 0.07 mm × 0.10 mm in *a*, *b*, and *c* directions, respectively. The multiple film technique was used with six films for each layer line. Tinfoils were placed between the films as attenuators. The intensities were estimated visually using an intensity scale prepared by making timed exposures of a chosen reflection of the actual crystal.

A survey of the indices of the reflections shows no systematic absences among those of the general (*hkl*) type; thus the lattice is primitive. For the principal zones the only systematic absences are *h0l* reflections having *h+l* odd together with the equivalent type *0kl* with *k+l* odd. The possible space-groups are *P*<sub>2</sub><sup>1</sup>*nm* (No. 102), *P*4*n*2 (No. 118), and *P*4<sub>2</sub>/*mnm* (No. 136).<sup>26</sup> The unit cell contains two formula units. Since the rutile structure is reported<sup>8</sup> to belong to *P*4<sub>2</sub>/*mnm* with the metal atoms situated in 2(*a*): 0,0,0; ½,½,½, and the four oxygen atoms in 4(*f*): *x,x,0*; *x̄,x̄,0*; ½+*x*,½-*x*,½; ½-*x*,½+*x*,½, this

Table 2. Observed and calculated structure factors for RuO<sub>2</sub>.

H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>					
0	2	0	59	51	1	1	0	77	78	1	1	8	11	11	3	11	0	10	10	4	7	5	13	13
0	4	0	46	47	1	2	0	12	12	1	3	8	9	10	3	4	1	36	38	4	4	6	16	15
0	6	0	36	35	1	3	0	48	49	2	2	0	58	66	3	6	1	26	30	4	6	6	13	12
0	8	0	16	19	1	4	0	9	-9	2	3	0	4	-4	3	8	1	18	18	4	5	7	11	10
0	10	0	16	18	1	5	0	42	40	2	4	0	40	41	3	10	1	15	16	5	5	0	30	32
0	12	0	11	9	1	7	0	24	26	2	6	0	26	29	3	3	2	43	43	5	7	0	20	19
0	1	1	69	63	1	9	0	16	19	2	8	0	23	25	3	5	2	23	25	5	9	0	16	15
0	3	1	59	63	1	11	0	11	13	2	10	0	13	13	3	7	2	24	25	5	11	0	11	11
0	5	1	29	30	1	1	1	23	-18	2	12	0	12	10	3	9	2	16	16	5	6	1	21	21
0	7	1	27	30	1	2	1	57	63	2	2	1	6	-6	3	11	2	11	10	5	8	1	20	20
0	9	1	18	19	1	3	1	6	6	2	3	1	38	40	3	4	3	29	30	5	10	1	11	10
0	11	1	10	11	1	4	1	41	42	2	4	1	5	5	3	6	3	24	25	5	5	2	26	29
0	0	2	76	71	1	6	1	28	30	2	5	1	40	40	3	8	3	14	15	5	6	1	21	21
0	2	2	41	41	1	8	1	22	24	2	7	1	23	23	3	10	3	12	13	5	9	2	15	14
0	4	2	39	40	1	10	1	14	14	2	9	1	18	18	3	3	4	29	30	5	6	3	18	18
0	6	2	27	32	1	12	1	11	10	2	11	1	11	13	3	5	4	17	19	5	8	3	16	17
0	8	2	17	18	1	1	2	53	54	2	2	2	53	51	3	7	4	18	19	5	10	3	8	8
0	10	2	15	17	1	2	2	7	7	2	4	2	37	35	3	9	4	12	12	5	5	4	21	22
0	12	2	10	9	1	3	2	44	41	2	6	2	26	26	3	4	5	22	21	5	7	4	14	13
0	1	3	45	39	1	4	2	7	-7	2	8	2	23	23	3	6	5	18	17	5	9	4	10	11
0	3	3	46	42	1	5	2	35	35	2	10	2	11	12	3	8	5	10	10	5	6	5	15	13
0	5	3	23	24	1	7	2	21	24	2	3	3	33	30	3	3	6	23	19	5	6	5	13	12
0	7	3	22	25	1	9	2	17	17	2	5	3	31	32	3	5	6	14	12	5	5	6	17	14
0	9	3	14	16	1	11	2	9	12	2	7	3	17	19	3	7	6	12	12	5	7	6	9	9
0	11	3	7	9	1	1	3	8	-7	2	9	3	13	15	3	4	7	13	12	6	6	0	22	22
0	0	4	43	40	1	2	3	46	41	2	11	3	9	11	3	6	7	11	11	6	8	0	16	14
0	2	4	29	27	1	4	3	32	32	2	2	4	38	33	4	4	0	33	34	6	10	0	12	12
0	4	4	29	28	1	6	3	23	25	2	4	4	26	26	4	6	0	26	27	6	7	1	21	19
0	6	4	24	24	1	8	3	17	20	2	6	4	21	20	4	8	0	18	19	6	9	1	12	13
0	8	4	15	14	1	10	3	11	12	2	8	4	16	17	4	10	0	13	14	6	6	2	19	20
0	10	4	12	13	1	1	4	34	33	2	10	4	8	9	4	4	1	6	-6	6	8	2	15	13
0	1	5	25	25	1	2	4	4	3	2	3	5	24	20	4	5	1	28	29	6	10	2	12	11
0	3	5	30	27	1	3	4	30	28	2	5	5	23	22	4	7	1	24	23	6	7	3	16	16
0	5	5	17	17	1	5	4	25	26	2	7	5	13	14	4	9	1	17	16	6	9	3	11	11
0	7	5	16	17	1	7	4	17	16	2	9	5	13	11	4	11	1	9	10	6	6	4	16	16
0	9	5	10	11	1	9	4	13	13	2	2	6	26	21	4	4	2	32	31	6	8	4	11	10
0	0	6	27	24	1	2	5	28	26	2	4	6	17	16	4	6	2	23	24	6	7	5	13	11
0	2	6	20	17	1	4	5	23	22	2	6	6	14	13	4	8	2	16	17	6	6	6	12	10
0	4	6	19	18	1	6	5	19	17	2	8	6	12	12	4	10	2	11	13	7	7	0	18	17
0	6	6	17	15	1	8	5	13	14	2	3	7	12	12	4	5	3	23	24	7	9	0	11	12
0	8	6	8	9	1	1	6	22	20	2	5	7	14	13	4	7	3	18	19	7	8	1	12	12
0	1	7	17	14	1	3	6	20	17	2	2	6	11	11	4	9	3	12	13	7	7	2	16	16
0	3	7	18	16	1	5	6	18	16	2	4	8	10	9	4	4	4	22	23	7	9	2	10	11
0	5	7	11	10	1	7	6	11	12	3	3	0	48	51	4	6	4	19	19	7	8	3	9	10
0	0	8	16	13	1	2	7	20	15	3	5	0	25	28	4	8	4	13	13	7	7	4	11	12
0	2	8	9	9	1	4	7	13	13	3	7	0	25	27	4	10	4	10	10	8	8	0	13	14
0	4	8	10	10	1	6	7	11	10	3	9	0	16	17	4	5	5	17	16	8	8	2	11	13

arrangement was tried first. This met with success, ( $R=0.071$ ), and as 4(c) of space-group  $P4_2nm$  can be shown to be equivalent with 4(f) of  $P4_2/mnm$  in this case, space-group  $P4_2/mnm$  is certainly correct.

## DATA CORRECTION AND REFINEMENT

The intensities were corrected for polarization and Lorentz' effects using the programme "General data reduction", written by Abrahamsson and Larsson<sup>27</sup> for the computer SAAB D21. No correction for absorption was applied, since the crystal used was small and since the linear absorption coefficient for MoK $\alpha$  radiation<sup>26</sup> is only 114 cm<sup>-1</sup>.

Since the oxygen parameter in several rutile compounds is reported to have values about 0.300 the refinement was started with  $x=0.300$  for oxygen in 4(*f*) of space-group  $P4_2/mnm$ . First the two reflection series were refined separately on the computer SAAB D21 at Göteborgs Datacentral, using the programme SFLS, written by Aleby and Abrahamsson.<sup>27</sup> Individual scale factors for each layer line, the atomic coordinates, and isotropic temperature factors were refined, making use of all the observed data *viz.* 313 reflections in the [100] series and 171 reflections in the [001] series. When, after eight cycles, the residuals were  $R_{[100]}=0.121$  and  $R_{[001]}=0.123$ , the data of the two series were combined and the refinement was continued with the 235

Table 3. Final atomic parameters and isotropic temperature factors (estimated standard deviations in parentheses).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ru	0	0	0	0.384(12) Å <sup>2</sup>
O	0.3058(16)	0.3058(16)	0	0.517(8) Å <sup>2</sup>

independent reflections until the shifts were sufficiently small, the *R*-value now being 0.076. As the form factor range in the programme used was not sufficient, a second refinement was later performed using the programme LALS<sup>28</sup> and the computer IBM 360/50 at Göteborgs Datacentral. After five cycles the *R*-value had decreased to 0.071. In both refinements the weights were assigned according to Hughes,<sup>29</sup> and the atomic form factors for the neutral atoms were taken from Cromer and Waber.<sup>30</sup> The observed and calculated structure factors are given in Table 2. The final parameters obtained are listed in Table 3. A refinement based on the data taken with CuK $\alpha$  radiation was also performed, resulting in  $x=0.308\pm 0.004$  with  $R=0.100$ .

Table 4. Distances and angles (estimated standard deviations in parentheses).

(Ru—O) <sub>1</sub>	(2 ×)	1.942(10) Å
(Ru—O) <sub>2</sub>	(4 ×)	1.984(6)
(Ru—Ru) <sub>1=c</sub>	(2 ×)	3.107(1)
(Ru—Ru) <sub>2</sub>	(8 ×)	3.536(1)
(O—O) <sub>1</sub>	(2 ×)	2.468(16)
(O—O) <sub>2</sub>	(8 ×)	2.776(7)
(O—O) <sub>3=c</sub>	(2 ×)	3.107(1)
(O—Ru—O) <sub>1</sub>		76.9(0.4)°
(O—Ru—O) <sub>2</sub>		90.0(0.1)
(O—Ru—O) <sub>3</sub>		103.1(0.4)

As a check on the results of the refinement, three-dimensional Fourier and difference syntheses were calculated using the programme DRF.<sup>28</sup> No disagreement could be detected, the highest peaks on the difference Fourier map being less than 2 % of the highest peaks on the Fourier map.

Interatomic distances and angles were calculated with the programme DISTAN<sup>28</sup> and the essential values are given in Table 4.

#### DISCUSSION AND COMPARISON WITH PREVIOUS WORK

It has thus been established that ruthenium dioxide has a rutile structure. As the shortest Ru—Ru distance is 3.107 Å there can be no significant metal-metal interaction.

Ruthenium is octahedrally coordinated by the oxygen atoms, four Ru—O distances being somewhat longer than the other two. The difference is only 2 %, but according to Cruickshank<sup>31</sup> it should be considered as significant. On this point it is interesting to compare with other compounds having a rutile structure. Baur<sup>8-10</sup> has found differences in the Me—O lengths for several other dioxides, but only for TiO<sub>2</sub> was this difference considered significant. In this case, however, four Ti—O distances were found to be about 2 % shorter than the other two, *viz.* 1.944 ± 0.004 Å (4 ×) and 1.988 ± 0.006 Å (2 ×). The bonding in RuO<sub>2</sub> and in TiO<sub>2</sub> should thus be different. It is, however, necessary to be very careful, when drawing conclusions based on the difference in bond lengths, when the deviations are so small as in these cases.

This investigation was made in 1964—1965, except for the last refinement on IBM 360/50, which was performed in 1968. When the manuscript of this paper was being written up, the author became aware of the fact that a crystal structure determination of RuO<sub>2</sub> had been published in 1966 by Cotton and Mague.<sup>32</sup> It seems, however, that the primary object with their investigation was to find out if substantial metal-metal interaction occurred in RuO<sub>2</sub>, rather than to aim at the highest possible accuracy. They found the cell dimensions to be  $a=4.491 \pm 0.007$  Å and  $c=3.107 \pm 0.005$  Å, which is in good agreement with those published here. Their values of the oxygen parameter ( $x=0.302 \pm 0.002$ ) and the Ru—O distances [(Ru—O)<sub>1</sub> = 1.917 ± 0.008 Å and (Ru—O)<sub>2</sub> = 1.999 ± 0.008 Å], however, differ somewhat from those obtained in this work. It is easily ascertained by means of the parameter that also according to this investigation, four Ru—O distances are longer than the other two, although the difference now amounts to about 4 %. Cotton and Mague based their investigation on 64 independent, non-zero reflections, whereas this work was based on 235 ones. Their final *R*-value was also higher (*R* = 0.141) than that found here. The author therefore considers the Ru—O distances in this work to be the more correct ones.

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