

Refinement of the Structure of α -TeO₂

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The structural parameters of tetragonal tellurium dioxide, α -TeO₂, space group $P4_12_12$, have been refined using three-dimensional X-ray data. Two series of reflections were initially refined separately and subsequently combined in the last stages of refinement, giving a final R value of 0.074, based on a total of 128 observed independent reflections.

Tellurium is four-fold coordinated by oxygen, the coordination polyhedron being a somewhat distorted trigonal bipyramid with bond distances Te-O_{eq} = 1.90 ± 0.02 Å and Te-O_{ax} = 2.08 ± 0.02 Å, lacking one oxygen atom in an equatorial position.

The cell dimensions of α -TeO₂, as determined by Guinier powder methods, are: $a = 4.812_2$ Å and $c = 7.615_7$ Å.

The crystal structure of the tetragonal modification of tellurium dioxide, α -TeO₂, was investigated in 1949 by Stehlik and Balák¹ and in 1961 by Leciejewicz.² The former of these two studies was carried out using only qualitatively estimated X-ray intensities, while the latter was based on 13 observed reflections obtained by neutron diffraction. Although the coordinates of the oxygen atoms can be determined with high accuracy using neutron diffraction methods, it was considered profitable, in connection with structure determinations of compounds of tellurium(IV) and tellurium(VI) at this Department, to undertake a three-dimensional refinement of the structure of α -TeO₂ with more extensive X-ray data.

INTENSITY DATA

Crystals of α -TeO₂ were prepared by dissolving metallic tellurium in concentrated nitric acid. α -TeO₂ crystallized as colourless tetragonal bipyramids, the basal planes of which had the crystallographic a - and b -axes as edges.

Two series of X-ray intensities (CuK α radiation) were collected, using Weissenberg methods with six films for each layer line. The two crystals used had the dimensions 0.09 mm \times 0.12 mm and 0.13 mm \times 0.17 mm ([110] direction \times [001] direction), the smaller being rotated about [110] and the larger about [001].

Intensity scales for visual estimation of the film data were prepared by making timed exposures of chosen reflections of the actual crystals. The different films of each layer line were scaled together using a weighting scheme, constructed in accordance with the estimated reliability of the degree of blackening of the reflexions recorded on each film.

CELL DIMENSIONS

The cell dimensions of α -TeO₂ were determined using Guinier powder methods (CuK α_1 radiation, $\lambda = 1.54050 \text{ \AA}$), with KCl as internal standard ($a_{\text{KCl}} = 6.2919_4 \text{ \AA}$ at 20°C³). 24 reflections were measured. The indexing procedure and the subsequent refinement of the cell constants were performed using the programme POWDER⁴ leading to the following results:

$$\begin{aligned} a &= 4.8122 \pm 0.0006 \text{ \AA} \\ c &= 7.6157 \pm 0.0006 \text{ \AA} \\ V &= 176.6 \text{ \AA}^3 \end{aligned}$$

A comparison between observed and calculated $\sin^2\theta$ values is given in Table 1.

Table 1. Guinier powder photograph of α -TeO₂. CuK α_1 radiation ($\lambda = 1.54050 \text{ \AA}$).

$h k l$	$10^6 \sin^2\theta$ obs	$10^6 \sin^2\theta$ calc	I obs	F calc
1 0 1	3582	3585	vw	32
1 1 0	5119	5124	s	165
1 1 1	6142	6147	w	49
1 0 2	6650	6654	vs	156
2 0 0	10241	10248	m	118
2 0 1	11280	11271	vvw	27
2 1 1	13836	13833	w	34
2 0 2	14346	14330	vvw	20
0 0 4	16381	16367	m	142
2 1 2	16913	16902	vs	135
2 2 0	20507	20496	m	121
1 1 4	21512	21491	s	127
2 1 3	22018	22016	w	40
3 1 0	25637	25620	m	104
2 0 4	26632	26615	s	112
3 0 2	27149	27150	m	106
2 2 3	29706	29702	vvw	51
3 0 3	32282	32264	vvw	48
3 2 1	34355	34329	vw	39
3 1 3	34841	34826	vw	42
2 2 4	36852	36863	m	93
1 0 6	39381	39387	s	108
3 2 3	42495	42512	vw	78
4 1 1	44573	44577	vvw	45

DATA CORRECTION AND REFINEMENT

The absorption of X-rays in α -TeO₂ is very high, the linear absorption coefficient being 1393 cm⁻¹ for CuK α radiation.⁵ This effect was corrected for using the programme DATAP2,⁶ and the correction factors varied between 12 and 82 for the [110] series and between 16 and 154 for the [001] series. Lorentz and polarization factors were calculated using the same programme.

The refinement was commenced using the coordinates given by Leciejewicz:² 4 Te and 8 O in 4(*a*) and 8(*b*), respectively, of the space group $P4_12_12$, with $x_{\text{Te}} = 0.020$ and $x_{\text{O}} = 0.142$, $y_{\text{O}} = 0.268$, and $z_{\text{O}} = 0.182$.

The two reflection series were first refined independently, using the full matrix programme LALS.⁶ Individual scale factors for each layer line were refined as well as the atomic coordinates and isotropic temperature factors. The refinement was based on all observed data, 120 reflections in the [110] series and 85 in the [001] series. After five cycles of refinement the following *R* values were obtained: $R_{[110]} = 0.094$ and $R_{[001]} = 0.072$.

The final refinement was performed after combining the data of the two series. Absolute mean values were calculated for those structure factors occurring in both series, thus giving 128 independent reflections. Since there were as many as 43 reflections occurring in the [110] series only, a separate scale factor was used for these reflections in the refinement. Anisotropic temperature vibrations of the atoms were also included, giving 15 independent parameters, which meant that there were 8.5 observations per parameter.

The atomic scattering factors given by Cromer and Waber⁷ and the weighting function recommended by Cruickshank⁸ ($w = (a + F_{\text{O}} + cF_{\text{O}}^2 + dF_{\text{O}}^3)^{-1}$, with $a = 20$, $c = 0.01$, and $d = 0$) were used in the refinement.

Table 2. Final atomic parameters (estimated standard deviations in parentheses). The anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ^a		
Te	0.0279(4)	0.0279(4)	0	0.60(11) Å ²		
O	0.145(5)	0.262(4)	0.187(2)	1.09(51) Å ²		
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	0.013(1)	0.013(1)	0.003(1)	-0.002(1)	0	0
O	0.030(10)	0.009(8)	0.005(3)	-0.009(16)	0.003(10)	-0.009(9)

^a Obtained before the final refinement.

After five cycles of refinement, all parameter shifts became less than 0.2 % of the standard deviations and the *R* value converged to 0.074. The resulting parameters are given in Table 2, and observed and calculated structure factors are listed in Table 3.

Table 3. Observed and calculated structure factors for α -TeO₂.

H K L	F _o	F _c	cos ϕ	H K L	F _o	F _c	cos ϕ	H K L	F _o	F _c	cos ϕ	H K L	F _o	F _c	cos ϕ
0 2 0	115	118	1.000	3 5 1	32	29	-0.240	2 4 3	34	33	0.500	2 3 5	31	34	0.214
0 4 0	73	78	1.000	4 4 1	35	31	0.000	2 5 3	34	34	-0.433	2 4 5	39	36	-0.268
0 6 0	26	25	1.000	0 1 2	162	156	1.000	3 3 3	34	32	0.000	3 3 5	38	36	0.000
1 1 0	129	165	1.000	0 2 2	15	10	0.000	3 4 3	34	32	-0.302	3 4 5	30	31	0.060
1 2 0	29	24	-1.000	0 3 2	100	106	1.000	3 5 3	28	31	0.320	0 1 6	99	108	1.000
1 3 0	102	104	1.000	0 4 2	11	11	0.000	4 4 3	35	33	0.000	0 3 6	68	71	1.000
1 5 0	50	44	1.000	0 5 2	48	48	1.000	0 0 4	159	142	1.000	1 1 6	16	14	-1.000
2 2 0	118	121	1.000	1 1 2	25	20	1.000	0 1 4	15	11	0.000	1 2 6	74	83	0.998
2 4 0	67	65	1.000	1 2 2	125	135	0.996	0 2 4	114	112	1.000	1 4 6	55	54	0.999
2 5 0	23	23	-1.000	1 3 2	13	13	-0.996	0 3 4	10	10	0.000	2 3 6	60	64	0.998
3 3 0	75	65	1.000	1 4 2	62	64	0.998	0 4 4	62	64	1.000	2 4 6	14	16	-0.978
3 4 0	27	27	-1.000	1 5 2	9	8	-0.980	1 1 4	127	127	1.000	3 3 6	12	13	-1.000
3 5 0	37	33	1.000	2 2 2	16	16	-1.000	1 2 4	12	10	-0.686	0 1 7	12	9	-0.707
4 4 0	37	29	1.000	2 3 2	75	78	0.997	1 3 4	80	84	0.992	0 2 7	26	24	0.707
0 1 1	47	31	0.707	2 4 2	15	17	-0.957	1 4 4	9	9	-0.893	0 3 7	27	23	-0.707
0 2 1	31	27	-0.707	2 5 2	44	39	0.997	1 5 4	42	41	0.983	0 4 7	27	27	0.707
0 3 1	51	53	0.707	3 3 2	27	25	-1.000	2 2 4	91	93	1.000	1 1 7	11	9	0.000
0 4 1	45	48	-0.707	3 4 2	56	52	1.000	2 3 4	15	16	-0.914	1 2 7	25	24	-0.149
0 5 1	29	34	0.707	3 5 2	17	18	-0.996	2 4 4	58	53	0.999	1 3 7	33	31	0.342
0 6 1	25	33	-0.707	4 4 2	26	24	-1.000	2 5 4	15	15	-1.000	1 4 7	28	29	-0.685
1 1 1	51	49	0.000	0 1 3	12	6	0.707	3 3 4	65	60	1.000	2 2 7	25	22	0.000
1 2 1	38	34	0.597	0 2 3	24	21	0.707	3 4 4	21	20	-0.986	2 3 7	29	28	-0.255
1 3 1	34	34	-0.653	0 3 3	47	48	-0.707	0 1 5	38	30	0.707	3 3 7	23	22	0.000
1 4 1	42	45	0.369	0 4 3	41	41	0.707	0 2 5	39	36	-0.707	0 0 8	74	70	1.000
1 5 1	44	42	-0.601	0 5 3	31	33	-0.707	0 3 5	29	26	0.707	0 2 8	73	78	1.000
1 6 1	25	34	0.715	1 1 3	21	20	0.000	0 4 5	35	32	-0.707	1 1 8	80	77	1.000
2 2 1	49	49	0.000	1 2 3	42	40	-0.177	1 1 5	27	22	0.000	1 3 8	49	54	1.000
2 3 1	38	39	0.113	1 3 3	41	42	0.449	1 2 5	26	25	0.482	2 2 8	57	57	1.000
2 4 1	37	38	-0.388	1 4 3	38	39	-0.481	1 3 5	29	31	-0.472	0 1 9	6	7	0.707
2 5 1	42	39	0.536	1 5 3	38	35	0.546	1 4 5	36	35	0.589	0 2 9	16	18	-0.707
3 3 1	51	48	0.000	2 2 3	51	51	0.000	1 5 5	31	34	-0.634	1 1 9	10	8	0.000
3 4 1	39	36	0.174	2 3 3	37	37	-0.255	2 2 5	22	20	0.000	1 2 9	16	19	0.213

To check the results of the refinement, a three-dimensional Fourier difference synthesis was calculated, using the programme DRF.⁶ No significant disagreement could be detected in the maps, but a slight disturbance corresponding to an electron density of 4 e/Å³ was, however, observed near the centre of the tellurium atom. This must be due to diffraction effects and to termination errors in the Fourier summations caused by the low number of reflections available in the small unit cell.

Table 4. Essential distances and angles in the structure of α -TeO₂ (estimated standard deviations in parentheses).

Te-O ₁ = Te-O ₂	1.903(20) Å
Te-O ₃ = Te-O ₄	2.082(23)
Te-Te (4 ×)	3.740(1)
Te-Te (2 ×)	3.827(1)
Te-Te (4 ×)	4.070(2)
O ₁ -O ₂	2.959(36)
O ₁ -O ₃ = O ₂ -O ₄	2.686(22)
O ₁ -O ₄ = O ₂ -O ₃	2.775(22)
O ₃ -O ₄	4.144(45)
O ₁ -Te-O ₂	102.0(1.3)°
O ₃ -Te-O ₄	168.5(1.3)°
O ₁ -Te-O ₃ = O ₂ -Te-O ₄	84.6(1.1)°
O ₁ -Te-O ₄ = O ₂ -Te-O ₃	88.1(0.5)°
Te-O-Te	139.5(1.2)°

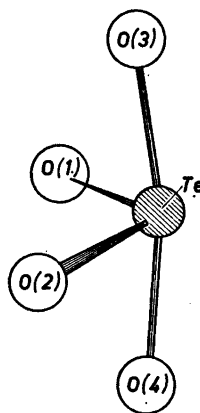


Fig. 1. A schematic picture of the TeO₄ unit in the structure of α -TeO₂.

DESCRIPTION OF THE STRUCTURE

Interatomic distances and angles, calculated with the programme DISTAN,⁶ are given in Table 4.

The basic unit of the structure is built up from four oxygen atoms coordinated to one tellurium atom to form a trigonal bipyramid with one of the equatorial positions unoccupied (*cf.* Table 4 and Fig. 1). This configuration has been found in other Te(IV) compounds (*cf.* β -TeO₂^{9,10}, Te₂O₄ · HNO₃,¹¹ and Te(C₆H₄O₂)₂¹²). As pointed out in the discussion of the structure of Te(C₆H₄O₂)₂,¹² the equatorial bonds may be considered to be formed by combination of the 5s, 5p_x, and 5p_y orbitals of the tellurium atom while the axial bonds involve the 5p_z orbital only.*

The structure of α -TeO₂ may be described in terms of a three-dimensional network built up from the TeO₄ units, each oxygen atom being shared by two units, and bonded in the equatorial position to one tellurium atom and in the axial position to another.

Leciejewicz² has discussed similarities between the structure of α -TeO₂ and those of α -cristobalite and rutile. The electronic configuration of tellurium in α -TeO₂ in accordance with the findings presented in this paper, is, however, essentially different from that of the central atom in α -cristobalite on the one hand, and in rutile, on the other.

The structure of β -TeO₂ consists of infinite two-dimensional sheets^{9,10} formed from Te₂O₆ units. A detailed comparison between the structure of α -TeO₂ and β -TeO₂ is given by Beyer,¹⁰ and is in complete agreement with the present results.

* The Te—O bond distances and angles in α -TeO₂ given in the discussion of Te(C₆H₄O₂)₂ were calculated before the final refinement, but are the same within the standard deviations as the final values given in Table 4 of this paper.

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