Acta Cryst. (1959). **12**, 507

The Crystal Structure of Baddeleyite (Monoclinic ZrO_2)

By J. D. McCullough and K. N. Trueblood

Department of Chemistry, University of California at Los Angeles, Los Angeles 24, California, U.S.A.

(*Received* 8 January 1959)

The structure proposed for baddeleyite by Náray-Szabó (1936) is incorrect.

Baddeleyite has the space group symmetry $P2_1/c$ with four ZrO_2 in the unit cell. The unit-cell dimensions found in the present work are:

$$a = 5{\cdot}169,\ b = 5{\cdot}232,\ c = 5{\cdot}341\ \text{Å}\ (\text{all}\ \pm 0{\cdot}008\ \text{Å}),\ \beta = 99°\ 15'\pm 10'\ .$$

The structure was determined and refined by use of Patterson and Fourier projections on the three faces of the unit cell. The seven shortest Zr–O separations in the coordination polyhedron around each zirconium range from 2·04 to 2·26 Å; since the next nearest Zr–O separation is 3·77 Å, the coordination number of zirconium is clearly seven. The structure is an interesting combination of fluorite-like layers parallel to (100) in which the oxide ions are tetrahedrally coordinated, with layers in which the oxide ions are in triangular coordination. The strong tendency to twin on (100) is explained in terms of this feature of the structure.

Introduction

The first X-ray study of baddeleyite was reported by Kathleen Yardley (Lonsdale) in 1926. Some limited spectrometer data, rotation photograph data and powder photograph data were tabulated, the space group was found to be $P2_1/c$ with 4 ZrO_2 in the unit cell, and two sets of cell constants were given. It was suggested that the structure was probably a distortion of the fluorite structure shown by CeO_2 and ThO_2 but a definite structure was not proposed. On the basis of Yardley's data, Náray Szabó (1936) proposed a structure which placed the 4 Zr in $2a$ $(0, 0, 0$ and $0, \frac{1}{2}, \frac{1}{2})$ and $2d$ $(\frac{1}{2}, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0)$ of $P2_1/c$ with the 8 oxide ions in two sets of $4e$. There are two types of Zr in this proposed structure, each with oxygen in 8-fold coordination. For Zr I, the Zr–O separations range from 2·00 to 2·39 Å and for Zr II the separations range from 1·95 to 2·65 Å. In addition to this unsatisfactory packing situation, the proposed structure does not satisfy the meager data upon which it was based.

Although the incorrectness of Náray Szabó's structure for ZrO_2 came to the attention of one of the authors several years ago in connection with the determination of the structure of ZrOS (McCullough, Brewer & Bromley, 1948), the difficulty in obtaining good single crystals of baddeleyite prevented an investigation of its structure at that time. With the kind assistance of several crystallographers, including Kathleen Lonsdale, C. Frondel and A. Pabst, suitable specimens were finally obtained from the British Museum through the courtesy of G. F. Claringbull. These specimens were small fragments which had been removed from the museum's only large crystal by Sir Lazarus Fletcher in 1893.

Crystallographic and intensity data

An X-ray examination of the specimens revealed that they were all twinned on (100). However, further fragmentation of one of the smaller pieces yielded an irregular fragment approximately 0·30 × 0·12 × 0·08 mm. which appeared to be untwinned. The longest

Table 1. *Lattice constants and axial ratios of baddeleyite*

		a	b	c	β
Present work		5·169 ± 0·008 Å	5·232 ± 0·008 Å	5·341 ± 0·008 Å	99° 15′ ± 10′
		0·9880	1	1·021	
Yardley* (1926)	(*a*)	5·21 kX.	5·26 kX.	5·375 kX.	99° 28′
	(*b*)	5·16 kX. 5·17 Å	5·21 kX. 5·22 Å	5·32 kX. 5·33 Å	
Ruff & Ebert (1929)		5·174 kX.	5·266 kX.	5·308 kX.	99° 12′
		0·975	1	1·008	
Blake & Smith (1907)		0·9905	1	1·0220	99° 28′
Dana's system of Mineralogy (1944)		0·9872	1	1·0194	99° 07½′

* Yardley's lattice constants were based on the axial ratios of Blake & Smith. Two sets were given. Set (*b*), when converted to Å, is in excellent agreement with the results of the present work. The observed spacings reported by Yardley [$d(100) = 5{\cdot}10$ kX., $d(010) = 5{\cdot}23$ kX., $d(001) = 5{\cdot}30$ kX.] lead to lattice constants of $a = 5{\cdot}17$ Å, $b = 5{\cdot}24$ Å and $c = 5{\cdot}37$ Å.

direction in the fragment was approximately along the *c* axis.

Precession photographs of the *h*0*l*, *h*1*l*, *h*2*l*, 0*kl*, 1*kl*, and 2*kl* nets and Weissenberg photographs of the *hk*0 net were prepared with Mo *K* radiation. The intensity data consisted of series of timed exposures of the *h*0*l* and 0*kl* nets taken with the precession camera and of timed multiple film sets of the *hk*0 net taken with the Weissenberg camera. The lattice constants given in Table 1 were obtained by averaging measurements from the various zero level precession photographs. CeO_2 ($a = 5{\cdot}411 \pm 0{\cdot}001$ Å) was used as a reference standard in calibrating the precession camera. The diffraction data are all consistent with the earlier cell and space group assignment (Yardley, 1926).

The intensities were estimated visually by use of an intensity strip consisting of a series of timed exposures of a selected diffraction spot. The irregular and varying shape of the diffraction spots caused some trouble in estimating the intensities but the correlation from one film to another was, in general, good. The intensity data from the precession photographs were corrected by use of a Waser chart (Waser, 1951) to give values of $k|F^2|$. The data from the Weissenberg photographs were corrected by the usual *Lp* factors.

Determination and refinement of the structure

A Patterson projection on (100) indicated Zr parameters of $y = 0{\cdot}040$ and $z = 0{\cdot}210$. Consideration of the *h*00 intensities indicated that the *x* parameter of Zr was $\pm 0{\cdot}225$ or $\pm 0{\cdot}275$. The calculation of a few *hk*0 and *h*0*l* structure factors showed that $x = 0{\cdot}275$ was a satisfactory trial parameter. With these Zr positional parameters and an isotropic temperature factor of $B = 1{\cdot}00$ Å^2 for Zr as the only input, F_o and $(F_o - F_c)$ Fourier syntheses on (100), (010) and (001) were prepared. These clearly indicated the oxygen positions:

	x	*y*	*z*
O_I	0·04	0·36	0·36
O_{II}	0·49	0·78	0·49

The essential correctness of these oxygen positions was indicated by the drop of the *R* value for each projection from approximately 0·18 to approximately 0·14 when these atoms were included in the structure factor calculations. The structure was refined by means of observed, calculated and difference Fourier syntheses on the three faces of the unit by methods described elsewhere (Sparks, Prosen, Kruse & Trueblood, 1956). Parameter values from the separate syntheses were averaged at each stage of the refinement. The maximum difference for any pair of Zr parameters was 0·0003 while the maximum difference for oxygen was 0·014. Because of the nearness of the O_{II} parameters to the values $x = \frac{1}{2}$, $y = \frac{3}{4}$, $z = \frac{1}{2}$, the peaks from pairs of these atoms overlap on the (010) and (001) syntheses (see Figs. 1 and 2). However, the overlap on the (001) syntheses did not interfere with the determination of the *x* parameter of O_{II}; in fact the curvature $\partial^2\varrho/\partial x^2$ at the peak maximum is increased by this overlap. It is thus possible to get one (but only one) clear determination of each of the O_{II} parameters.

Initially an isotropic temperature factor of $B = 2{\cdot}00$ Å^2 was assigned to each oxygen atom, while that for Zr was kept at 1·00 Å^2. After the second cycle, the isotropic temperature factor for O_{II} was adjusted to 1·40 Å^2 by comparison of corresponding peaks on the observed and calculated syntheses. No further adjustment was needed later. The temperature factors for Zr and O_I required no adjustment from the values of 1·00 Å^2 and 2·00 Å^2 respectively.

At the sixth cycle of refinement there was little change in the parameters and in the *R* values. The final parameters are listed in Table 2 with their standard deviations estimated by Cruickshank's method (Cruickshank, 1949). The structure factors calculated by use of the final positional and isotropic thermal parameters are compared with the observed values in Table 3. Special consideration was given to the atomic scattering factors used in the structure factor calculations. The HfO_2 content of the specimen of baddeleyite used was estimated as 2 mol.% from the observed density 5·82 g.cm.$^{-3}$ (Blake & Smith,

Table 2. *Final positional parameters in baddeleyite*

Atom	Projection	*x*	σ*x*	*y*	σ*y*	*z*	σ*z*
Zr	(100)			0·0405	0·0010	0·2090	0·0010
	(010)	0·2757	0·0013			0·2087	0·0012
	(001)	0·2758	0·0006	0·0404	0·0006		
	Average	0·2758		0·0404		0·2089	
O_I	(100)			0·347	0·004	0·350	0·010
	(010)	0·067	0·008			0·341	0·008
	(001)	0·070	0·009	0·338	0·006		
	Average	0·069		0·342		0·345	
O_{II}	(100)			0·758	0·007	0·479	0·009
	(010)	*				*	
	(001)	0·451	0·003	*			
		0·451		0·758		0·479	

* Parameter not determined because of overlap of O_{II} peaks.

Table 3. *Comparison of observed and calculated structure factors for baddeleyite*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	64.5	-84.7	3	0	2-	80.2	-97.0	1	4	0	18.7	-20.8
0	0	4	39.4	40.7	2	0	2-	58.3	68.6	2	4	0	27.6	-30.0
0	0	6	10.9	6.0	1	0	2-	29.6	31.6	3	4	0	10.2	9.4
0	1	1	36.2	38.1	1	0	2	48.0	-52.7	4	4	0	26.8	23.0
0	1	2	< 7.8	-3.0	2	0	2	87.3	108.2	5	4	0	16.0	-14.6
0	1	3	61.7	-70.7	3	0	2	7.4	6.2	6	4	0	13.6	-9.3
0	1	4	< 7.3	5.8	4	0	2	54.3	-54.2	7	4	0	20.6	21.0
0	1	5	53.5	54.4	5	0	2	24.4	19.5	8	4	0	< 5.2	3.1
0	1	6	21.8	-16.3	6	0	2	44.4	34.7	9	4	0	6.8	-9.1
0	1	7	37.0	-32.6	6	0	4-	23.4	19.9	10	4	0	< 5.6	-0.7
0	2	0	57.9	66.7	5	0	4-	43.6	-43.8	1	5	0	47.1	-50.2
0	2	1	33.9	-35.3	4	0	4-	< 8.5	2.8	2	5	0	17.9	16.7
0	2	2	73.8	-88.5	3	0	4-	56.0	60.8	3	5	0	48.6	48.4
0	2	3	31.1	31.5	2	0	4-	< 7.6	-5.3	4	5	0	27.0	-24.4
0	2	4	26.0	25.3	1	0	4-	72.3	-85.4	5	5	0	18.7	-17.4
0	2	5	13.2	-11.5	1	0	4	41.3	40.0	6	5	0	24.3	29.4
0	2	6	8.3	-5.2	2	0	4	54.3	-51.1	7	5	0	13.6	15.2
0	3	1	9.9	11.3	3	0	4	39.0	-32.8	8	5	0	22.7	-24.1
0	3	2	25.6	-23.3	4	0	4	44.1	38.5	9	5	0	< 5.6	-1.5
0	3	3	28.2	-26.6	5	0	4	12.5	9.3	10	5	0	13.0	9.2
0	3	4	39.9	37.9	5	0	6-	21.3	21.1	1	6	0	8.0	7.2
0	3	5	37.9	33.9	4	0	6-	32.4	27.4	2	6	0	5.1	-3.2
0	3	6	26.3	-24.4	3	0	6-	42.7	-41.1	3	6	0	4.3	3.8
0	4	0	42.8	43.5	2	0	6-	< 8.1	-5.6	4	6	0	< 4.5	-0.2
0	4	1	60.4	-65.9	1	0	6-	51.2	47.3	5	6	0	< 4.8	-2.8
0	4	2	21.2	-21.0	1	0	6	49.0	-42.8	6	6	0	< 5.2	-1.7
0	4	3	35.1	34.5	2	0	6	19.4	15.0	7	6	0	< 5.6	-1.4
0	4	4	23.0	20.4	3	0	6	38.7	30.4	8	6	0	< 5.6	0.7
0	4	5	< 7.5	-8.0	1	1	0	32.2	-32.0	9	6	0	< 5.6	-1.9
0	4	6	< 5.7	0.4	2	1	0	17.4	-16.1	1	7	0	37.4	-35.7
0	5	1	< 7.8	3.6	3	1	0	19.1	20.4	2	7	0	11.7	11.1
0	5	2	34.5	-31.5	4	1	0	27.6	-26.5	3	7	0	22.7	22.9
0	5	3	14.3	-12.3	5	1	0	7.6	-7.2	4	7	0	18.7	-20.8
0	5	4	38.1	35.0	6	1	0	< 4.2	3.2	5	7	0	24.0	-25.4
0	5	5	9.6	9.6	7	1	0	6.4	6.2	6	7	0	21.7	23.0
0	6	0	< 3.8	1.4	8	1	0	7.8	-10.3	7	7	0	5.6	7.4
0	6	1	48.5	-44.6	9	1	0	< 5.6	0.9	8	7	0	12.3	-10.8
0	6	2	8.9	-7.0	10	1	0	6.8	5.6	1	8	0	< 4.8	-0.6
0	6	3	36.8	27.9	11	1	0	< 5.6	-0.4	2	8	0	13.6	17.6
0	6	4	5.6	-3.7	1	2	0	4.0	-2.8	3	8	9	8.8	-8.6
0	7	1	< 5.7	0.5	2	2	0	73.6	-97.8	4	8	0	9.1	-9.6
0	7	2	16.3	-14.0	3	2	0	34.9	39.2	5	8	0	8.5	8.1
0	8	0	13.6	-14.1	4	2	0	44.3	43.6	6	8	0	< 5.6	4.9
0	10	0	21.3	-20.1	5	2	0	34.0	-32.0	7	8	0	< 5.6	-4.3
1	0	0	23.0	-22.6	6	2	0	20.6	-18.0	8	8	0	< 5.6	-1.8
2	0	0	60.8	-73.7	7	2	0	27.9	24.8	1	9	0	18.7	-21.0
3	0	0	38.0	38.2	8	2	0	13.0	11.5	2	9	0	< 5.6	4.8
4	0	0	54.8	60.3	9	2	0	21.7	-23.8	3	9	0	18.3	17.6
5	0	0	48.3	-45.1	10	2	0	< 5.6	2.0	4	9	0	12.3	-12.2
6	0	0	36.8	-29.6	11	2	0	10.7	7.5	5	9	0	7.8	-9.0
7	0	0	38.7	30.6	1	3	0	57.8	-67.2	6	9	0	8.8	6.3
8	0	0	4.9	5.0	2	3	0	23.4	23.7	1	10	0	< 5.6	3.5
9	0	0	27.3	-26.1	3	3	0	33.8	34.3	2	10	0	13.6	14.1
10	0	0	< 5.6	-1.0	4	3	0	17.9	-19.0	3	10	0	5.6	-4.7
11	0	0	21.0	11.3	5	3	0	28.1	-27.9	4	10	0	12.3	-8.2
12	0	0	4.9	-3.2	6	3	0	30.0	24.7	5	10	0	10.9	6.7
7	0	2-	40.6	-33.1	7	3	0	5.8	6.2	1	11	0	< 5.6	-3.9
6	0	2-	< 8.5	3.0	8	3	0	17.4	-19.2	2	11	0	< 5.6	2.1
5	0	2-	48.7	50.0	9	3	0	< 5.6	-2.4	3	11	0	< 5.6	2.8
4	0	2-	30.1	-29.9	10	3	0	12.3	8.9					

1907) and the densities of pure HfO_2 and ZrO_2 which are 9·67 g.cm.$^{-3}$ and 5·73 g.cm.$^{-3}$ respectively (Hevesy & Bergland, 1924). The atomic scattering factors for Zr^{+4} and Hf^{+4} (Thomas & Umeda, 1957) were corrected for dispersion (Dauben & Templeton, 1955) and a synthetic atomic scattering factor curve for a mixture 98 at.% Zr^{+4} and 2 at.% Hf^{+4} was prepared. The McWeeny atomic scattering factors for oxygen (McWeeney, 1951) were corrected to oxide ion by addition of the difference between the oxygen and oxide ion scattering factors of James & Brindley (1931). The values of the index

$$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$$

based on the final parameters are 11·9 for the *hk*0 data, 13·5 for the *h*0*l* data and 12·0 for the 0*kl* data.

Description of the structure

The structure of baddeleyite is shown in Figs. 1 and 2 and the observed interatomic distances and angles are given in Tables 4 and 5 respectively. There are two especially interesting features of the structure. One is the sevenfold coordination of Zr. The Zr–O distances in the coordination polyhedron vary from 2·04 Å to 2·26 Å, a much shorter range than those involved in the previously reported structure. That the coordination number is clearly seven is shown by the fact that the next nearest Zr–O separation is 3·77 Å. The coordination polyhedron of Zr is indicated in Fig. 1 and in somewhat idealized form in Fig. 3. As indicated in Fig. 3, the coordination polyhedron about Zr may be visualized as being derived from a cube. In this view four oxide ions are at the base and one at one of the upper corners; the remaining two are at the midpoints of the cube edges connecting the unoccupied corners. If the last three oxide ions are moved as indicated by the arrows, their distances from Zr (at

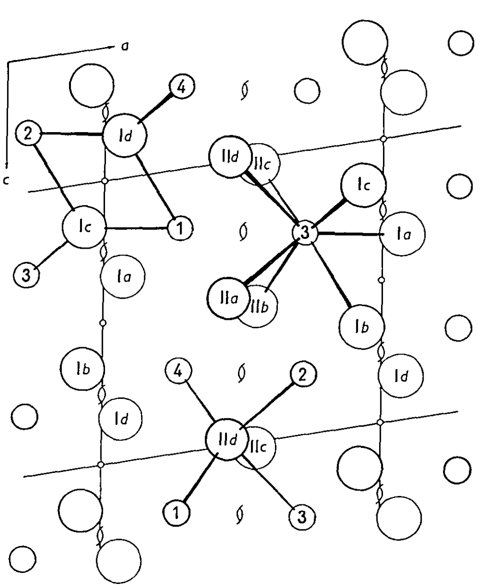

Fig. 1. Projection of the structure of baddeleyite on (010).

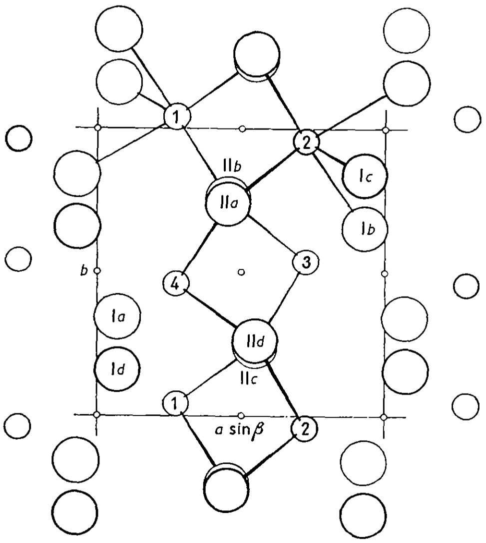

Fig. 2. Projection of the structure of baddeleyite on (001)

Table 4. *Interatomic distances in baddeleyite in* Å

$\sigma(\text{Zr–O}) = 0{\cdot}05$ Å $\sigma(\text{O–O}) = 0{\cdot}07$ Å

(*a*) Zr–O distances in the Zr coordination polyhedron

Zr	O	Distance	Zr	O	Distance
3	I*a*	2·04	3	IIc	2·16
3	Ic	2·10	3	II*a*	2·18
3	I*b*	2·15	3	II*b*	2·26
			3	II*d*	2·26

(*b*) Zr–O distances in the O_I coordination triangle

Zr	O	Distance
1	Ic	2·04
3	Ic	2·10
2	Ic	2·15

(*c*) Zr–O distances in the O_{II} coordination tetrahedron

Zr	O	Distance	Zr	O	Distance
1	II*d*	2·26	3	II*d*	2·26
2	II*d*	2·18	4	II*d*	2·16

(*d*) O–O packing distances within a given Zr coordination polyhedron. Shared edges are indicated by (*s*) and unshared edges by (*u*)

I*a*	I*b*	(*s*)	2·52	I*b*	II*a*	(*s*)	2·56
I*a*	Ic	(*u*)	2·85	Ic	II*d*	(*s*)	2·56
I*b*	Ic	(*u*)	2·83	II*a*	II*b*	(*s*)	2·75
I*a*	II*b*	(*u*)	3·03	II*a*	II*d*	(*s*)	2·75
I*a*	IIc	(*u*)	2·99	II*b*	IIc	(*s*)	2·67
I*b*	II*b*	(*u*)	2·95	IIc	II*d*	(*s*)	2·59

(*e*) Shortest distances from Zr to O outside the coordination polyhedron

Zr	O	Distance	Zr	O	Distance
3	I*d*	3·77	3	II*b*′	4·02
3	I*d*′	3·77	3	IIc′	4·07
3	Ic′	3·91			

Table 5. *Angles in baddeleyite*

$\sigma \sim 2°$

(*a*) Within the Zr coordination polyhedron

O	Zr	O	Angle	O	Zr	O	Angle
I*a*	3	I*b*	74°	Ic	3	II*d*	72°
I*a*	3	Ic	87	II*a*	3	II*b*	76
I*b*	3	Ic	84	II*a*	3	II*d*	74
I*a*	3	II*b*	89	II*b*	3	IIc	74
I*a*	3	IIc	91	IIc	3	II*d*	72
I*b*	3	II*a*	73				
I*b*	3	II*b*	84				

(*b*) Within the O_I coordination triangle

Zr	O	Zr	Angle
1	Ic	3	145°
1	Ic	2	106
2	Ic	3	109

(*c*) Within the O_{II} coordination tetrahedron

Zr	O	Zr	Angle
1	II*d*	2	104°
1	II*d*	3	100
1	II*d*	4	132
2	II*d*	3	102
2	II*d*	4	107
3	II*d*	4	109

the cube center) are more nearly equalized but still averaged somewhat less than the Zr–O distances for the four oxide ions at the cube corners. This description of the Zr coordination polyhedron is somewhat idealized, as an examination of the tabulated distances and angles will show, but it does give a fairly close approximation to the structure.

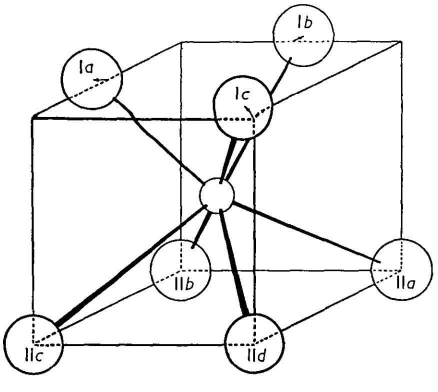

Fig. 3. The Zr coordination polyhedron in baddeleyite (idealized).

Another interesting feature of the structure is the alternation of fluorite-like layers containing O_{II} ions in tetrahedral coordination with layers which contain O_I ions in triangular coordination. These layers are parallel to (100) and are approximately $a/2$ in thickness. In the O_{II} coordination tetrahedron, the Zr–O_{II} distances range from 2·16 Å to 2·26 Å with an average of 2·22 Å while the central angles at O_{II} range from 100° to 132° with an average of 109°. In the O_I coordination triangle, the Zr–O_I distances are 2·04 Å, 2·10 Å and 2·15 Å with an average of 2·10 Å and the central angles at O_I have the values 106°, 109° and 145°. According to the electrostatic valence rule (Pauling, 1929), the ratio of the strength of the Zr–O_I bonds to the strength of the Zr–O_{II} bonds is $\frac{2}{3}:\frac{1}{2} = 4:3$. The difference of 0·12 Å in the corresponding average separations is therefore reasonable. In the O_I coordination triangle, the O_I ion is only $0{\cdot}09 \pm 0{\cdot}07$ Å from the plane of the Zr ions; hence the coordination appears to be planar within the limit of error. Pairs of these triangles share Zr–Zr edges as shown in Fig. 1, in a manner similar to the situation in rutile. However, analogy with rutile does not extend much beyond this.

It is also of interest to examine the sharing of edges and corners of the Zr coordination polyhedra in the light of the principles determining the structures of ionic crystals (Pauling, 1929). According to these principles, we should expect the O–O separations to be in the following order of increasing length: O_I–O_I shared edge < O_I–O_{II} shared edge < O_{II}–O_{II} shared edge < unshared edges. An inspection of the O–O distances in Table 4(*d*), in which the sharing of edges is indicated, will show that these expectations are fulfilled. The corners of the Zr coordination polyhedra occupied by O_I ions are shared between three such polyhedra. At these sites, the value of $\Sigma s = \Sigma z/v = 3(4/7) = 12/7$. This is to be compared with -2, the charge on the oxide ion. The corners occupied by O_{II} ions are shared between four polyhedra, so that $\Sigma s = 4(4/7) = 16/7$ which is again to be compared with -2. Thus there are deviations from the electrostatic valence rule amounting to $\pm 2/7$ at each corner of the Zr coordination polyhedron. Shortening of the Zr–O_I distances relative to the Zr–O_{II} distances may be a result of this electrostatic imbalance.

The Zr–O separations in the present structure may be compared with the value 2·13 Å in ZrOS (McCullough, Brewer & Bromley, 1948) and the values of 2·15 Å and 2·29 Å found in zircon (Krstanović, 1958). In zircon, Zr has four oxide ions at 2·15 Å in a flattened tetrahedron and four at 2·29 Å in an elongated tetrahedron which is rotated 90° with respect to the first one. The Zr–O separation in the unstable cubic modification of ZrO_2 is 2·20 Å (Passerini, 1930; *Strukturbericht*, 1937). This modification of ZrO_2 has the fluorite structure with Zr in eightfold coordination. In this structure the oxide ion contacts all have the unusually short value of 2·53 Å. This is probably an important factor in the instability of the cubic modification of ZrO_2 at room temperature.

The twinning

As mentioned earlier, the fragments of baddeleyite showed twinning on (100). In Dana's System of Mineralogy, 7th Edition (1944) it is stated that untwinned crystals are rare. Twinning on (100) is stated to be common and often polysynthetic. This twinning habit is readily explained in terms of the reported structure. In the transition from the fluorite-like layers to the O_I layers, the latter may be oriented in either of two directions on the plane of Zr ions. In the orientation usually followed the crystal symmetry is preserved. In the other orientation, the growth is such that it is a reflection of the previous structure in a plane parallel to (100). At the twinning plane there would be little distortion of the Zr coordination polyhedra since a 180° rotation of the triangular group of O_I ions about an axis approximately perpendicular to the base of four O_{II} ions is involved. The polyhedron thus formed would differ only slightly from the original one.

The authors acknowledge, with thanks, the assistance of those crystallographers who helped in the search for baddeleyite specimens. We are especially grateful to the British Museum of Natural History and to Dr Claringbull for the specimens used in this study and to Prof. Pauling for his interest and helpful discussion. We are also indebted to the Numerical Analysis Research Project of the U. C. L. A. Department of Mathematics for the use of SWAC and other computing facilities, and to the Office of Naval Research for their support of these facilities.

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