The structure of baddeleyite and of prepared zirconia.

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THE crystal used in the first part of this investigation, an untwinned specimen from Ceylon in the British Museum collection, was measured goniometrically and described in detail by Dr. G. F. Herbert Smith,[1] who gave as its crystallographic constants :

Density (ρ) 5·82 (grs./c.c.). Monoclinic prismatic,

$$a:b:c = 0.9905 : 1 : 0.5110, \ \beta = 80° \ 32'.$$

Owing to the comparatively large size of the crystal and its high absorptive power it was unsuited either to the 'rotating crystal' or Laue photographic methods of X-ray examination. Reflections from the faces were observed on the Bragg ionization spectrometer and spacings measured with an accuracy of about 2 per cent. It soon became apparent that the c-axis should be doubled, the true axial ratio being

$$a:b:c = 0.9905 : 1 : 1.0220, \ \beta = 80° \ 32',$$

this double length of the c-axis being as taken by Sir L. Fletcher[2] in the original description of baddeleyite. Thus the faces recorded by Dr. Smith as (221) are really the (111) and so on. The true unit cell contains *four* molecules of ZrO_2 ($M = 122.6$). No indications were found of any larger cell.

The density of this crystal, 5·82, is higher than that of pure zirconia, which is only 5·73 (G. Hevesy, 1925) and therefore some heavier impurity, possibly HfO_2, must be present. One result of this is that the spacings calculated from the formula $a.\ b.\ c.\ \sin \beta.\ \rho = n.\ M.$ 1·65 are all consistently smaller, on an average by about 2 per cent., than the

[1] G. S. Blake and G. F. H. Smith, Min. Mag., 1907, vol. 14, p. 378, fig. 2.

[2] L. Fletcher, Min. Mag., 1893, vol. 10, p. 148.

observed spacings, owing to the fact that the presence of the impurity should have been allowed for in M, the molecular weight. A better agreement was obtained by taking $M = 128$ as a hypothetical molecular weight for $(ZrO_2 + \text{impurity})$. In the following table the observed and calculated values are compared:

Plane.		Spacing.			Comparative Intensities.					
Old indices.	New indices.	Calc. from older data.	Calc. from new ($M = 128$).	Obs.	I.	II.	III.	IV.	V.	VI.
(100)	(100)	5·06	5·14	5·10	1	20	4	10	5	2
(010)	(010)	5·18	5·26	2·61$_5$*	0	1	0	..		
(001)	(001)	2·61	5·30	2·65*	0	1	0	.		..
(021)	(011)	1·84	3·73	3·75	1	24	–	--		
(201)	(101)	1·68	3·42	1·71*	0	4	0	1	0	..
(110)	(110)	3·62	3·67	3·62	1	16	2	--	–	
(210)	(210)	2·27$_5$	2·30$_5$	2·30	1?	8	.	..	--	–
(221)	(111)	1·41	2·87$_5$	2·92	1	–	.	..	--	..
(22$\bar{1}$)	(11$\bar{1}$)	1·58	3·20	3·26	1	–	..	..	–	--

The calculated dimensions of the cell are :

$$a = 5\cdot21,\ b = 5\cdot26,\ c = 5\cdot37_5\ \text{Å.U.},\ \beta = 80° 32'.$$

The intensities given in the above table are stated in arbitrary units for each plane. In general, reflections could only be observed from planes actually present as faces on the crystal (a Rh anticathode being used), and the intensity of reflection depended to a large extent on the size and perfection of the face. This was proved by comparing reflections from the (100) and ($\bar{1}$00) faces, and also from the (110) and (1$\bar{1}$0) faces, which are very unequally developed on the specimen. The larger of each of these pairs of faces gave good sharp reflections, whereas the reflections from badly developed planes such as the (001) were small and ill defined. No weight, therefore, could be attached to any comparison of intensities of reflection from different planes, though for any one plane a comparison of intensities of different orders is legitimate and useful. In the case of planes (010), (001), and (101) (marked in the table by an asterisk) a careful search revealed no trace of odd-order reflections. The two last-named belong to the set of planes $\{h0l\}$ where l is odd ; the odd orders of the (100) plane, on the contrary, though weaker than the even orders were most decidedly present. Many attempts were made to find other reflections in the [010] zone, but this could not be done with the crystal used, and other untwinned samples of the material are very rare.

The original crystals of baddeleyite ('brazilite') from Jacupiranga,

Brazil, described in 1892 by Dr. E. Hussak,[1] which are preserved in the British Museum collection, were also examined. These are much smaller (all less than $\frac{1}{2}$ mm.[3]) and were found to be twins on the planes (100), (110), and (101). Rotation photographs were taken with one of the simplest twins, using a Mo anticathode, but the resulting pictures even after exposures of upwards of 16 hours showed only a few of the more intense reflections and gave little additional information. No odd-order reflections from planes $\{h0l\}$ where l is odd could be observed, but the photograph obtained by rotation about the b-axis showed faint spots corresponding to planes (204) or (402) and (20$\bar{4}$) or (40$\bar{2}$).

Finally, the nodular fibrous zirconia from Serra de Caldas, Brazil, was examined. This was first described in 1903 by E. Hussak and J. Reitinger,[2] and was considered by them to represent perhaps a new modification of zirconia distinct from baddeleyite. They gave the density of this material as 5·538, and ZrO_2 97·19 per cent. A fragment of similar material from a specimen in the British Museum collection was crushed in an agate mortar and a powder photograph taken using $Cu(K\alpha)$ radiation. A calibration photograph was obtained by mixing the powder with calcite powder. The lines obtained on the photograph proved the identity of this material with baddeleyite, and agreed better with the data given by Dr. Smith for the large single crystal than with those of Hussak (1895). The data given by Dr. Smith were therefore used in the calculations of $\sin\theta$ (column 2 in the following table). They confirm the cell chosen and the number of molecules per cell, and lead to a length of axis $b = 5·188$ Å.U. as against 5·209 calculated from the density 5·73. The calculated density of this specimen is therefore slightly higher than for pure zirconia.

(hkl).	$\sin\theta$ calc.	$\sin\theta$ obs.	d.	Intensity.
(001)	0·1470			
(010)	0·1482			
*(100)	0·1517			
(10$\bar{1}$)	0·1931			
*(011)	0·2087	0·2096	3·667	Weak.
*(110)	0·2120			
(101)	0·2279			
*(11$\bar{1}$)	0·2434	0·2433	3·159	Very strong.

[1] E. Hussak, Neues Jahrb. Min., 1892, vol. ii, p. 141 ; Tschermaks Min. Petr. Mitt., 1895, vol. 14, p. 406.

[2] E. Hussak and J. Reitinger, Zeits. Kryst. Min., 1903, vol. 37, p. 572. 'Brazilite' and some other names have been applied to this material (Min. Mag., 1919, vol. 18, p. 375).

(khl).	sin θ calc.	sin θ obs.	d.	Intensity.
*(111)	0·2719	0·2720	2·826	Strong.
*(002)	0·2940	} 0·2944	2·611	Mod. strong.
*(020)	0·2964	}		
*(200)	0·3019	0·3033	2·535	Mod. weak.
(10$\bar{2}$)	0·3078			
(20$\bar{1}$)	0·3132			
(012)	0·3292	} 0·3301	2·329	Weak.
(021)	0·3308	}		
(120)	0·3329			
(210)	0·3363			
(11$\bar{2}$)	0·3417			
(21$\bar{1}$)	0·3464	} 0·3493	2·201	Moderate.
(102)	0·3523	}		
(12$\bar{1}$)	0·3537			
(201)	0·3570			
(121)	0·3739			
(112)	0·3822			
(20$\bar{2}$)	0·3861	} 0·3839	2·003	Mod. weak (broad).
(211)	0·3865			
*(022)	0·4175	0·4166	1·845	Mod. strong.
(21$\bar{2}$)	0·4233			
*(220)	0·4241	} 0·4255	1·807	Mod. strong.
(12$\bar{2}$)	0·4273			
(22$\bar{1}$)	0·4312			
(003)	0·4410			
(10$\bar{3}$)	0·4421			
(030)	0·4445			
(30$\bar{1}$)	0·4547			
*(300)	0·4550	} 0·4549	1·690	Moderate.
*(202)	0·4558			
(122)	0·4604			
(221)	0·4639			
(013)	0·4652	} 0·4648	1·654	Moderate.
(11$\bar{3}$)	0·4663			
(031)	0·4682			
(130)	0·4697			
(3$\bar{1}\bar{1}$)	0·4782	} 0·4783	1·607	Very weak.
(310)	0·4785	}		
(212)	0·4793			
(13$\bar{1}$)	0·4846			
(22$\bar{2}$)	0·4868			
(10$\bar{3}$)	0·4894			
(20$\bar{3}$)	0·4917			
(30$\bar{2}$)	0·4995	} 0·4999	1·538	Mod. weak.
(131)	0·4996	}		
(301)	0·5006			
(113)	0·5113	0·5100	1·507	Weak.
(21$\bar{3}$)	0·5134			
(31$\bar{2}$)	0·5210			

(hkl).	$\sin\theta$ calc.	$\sin\theta$ obs.	d.	Intensity.
(311)	0·5221	0·5222	1·472	Weak.
(023)	0·5313	0·5314	1·447	Very weak.
(12$\bar{3}$)	0·5323			
(032)	0·5330			
(2$\bar{3}$0)	0·5373			
(13$\bar{2}$)	0·5407			
(32$\bar{1}$)	0·5427			
(320)	0·5430			
(23$\bar{1}$)	0·5437			
(222)	0·5437			

It is difficult to be certain as to the indices of the planes giving some of the observed lines. The planes observed on the spectrometer are marked by an asterisk, though it must be remembered, of course, that, owing to the varying amounts of impurity present, the spacings from different samples of baddeleyite cannot be expected to agree very closely. The line for which $\sin\theta = 0\cdot4255$ may be due to any or all of the three planes (21$\bar{2}$) (220) (12$\bar{2}$), but the large spectrometer reflection observed from (220) renders it highly probable that the latter is the main contributing plane. Similarly, the line 0·4549 is probably due to the planes (300) and (202), although the possibility of a contribution from (30$\bar{1}$) cannot be definitely eliminated. However, on the whole it may be stated that the powder lines are in substantial agreement with the space-group C_{2h}^5, for which odd-order reflections from planes $\{h0l\}$ where l is odd and from (010) would be absent.[1]

It is significant that, contrary to expectation, the powder photographs from two separate specimens of artificially prepared zirconia were almost identical with those from the natural oxide. A sample from the firm of Kahlbaum gave the value $b = 5\cdot193$ Å.U., again showing a slightly high value of the density. The photographs, with the exception of one line, fitted the monoclinic lattice very well, and could not be made to agree with a tetragonal lattice of any axial ratio whatever.

The data given by A. E. Nordenskiöld[2] describing artificially prepared crystals of zirconia as tetragonal, with an axial ratio $a:c = 1:1\cdot0061$, are certainly not applicable to either of the samples used in the present

[1] P. Niggli, Geometrische Kristallographie des Diskontinuums, Leipzig, 1919; also W. T. Astbury and K. Yardley, Phil. Trans. Roy. Soc. London, Ser. A, 1924, vol. 224, p. 221.

[2] A. E. Nordenskiöld, Öfvers. K. Vetens.-Akad. Förh. Stockholm, 1861, vol. 17 (for 1860), p. 450; Ann. Phys. Chem. (Poggendorff), 1861, vol. 114, p. 625. W. Florence (Neues Jahrb. Min., 1898, vol. ii, p. 126), who also prepared crystals of zirconia in borax beads, suggested that these might be monoclinic.

investigation. His measurements were made on microscopically small crystals showing only the forms {110}, {111}, and (201). The only line on the photographs that does not also appear on the photograph of natural zirconia is a weak line between the (11$\bar{1}$) and (111) lines corresponding to a spacing of 2·876 Å.U. This may be due to an impurity or it may indicate a larger cell than that taken as unit for baddeleyite. However, no other such indications were found, so that to a first approximation the structures of baddeleyite and of artificially prepared zirconia may be considered as identical.

It will be noticed both from the spectrometer and powder observations that in the case of planes such as (100), (011), (110), (021), &c., from which first-order reflections were found, those reflections were very weak compared with the second orders (200), (022), (220), (420), &c. Also the reflections from general planes with 'all odd' indices, (11$\bar{1}$), (113), (311), &c., are considerably stronger than those from planes with 'mixed' indices. This indicates a nearly face-centred arrangement of the Zr^{++++} ions, which are the chief scattering centres, their maximum scattering power being 36 as compared with 10 for the O^{--} ions. The comparatively large intensity of the (400) indicates that in the [100] direction, at any rate, the O-ions interleave the Zr. J. A. Wasastjerna [1] pointed out that the negative O^{--} ion would be expected to have a much larger radius than the neutral O atom, and calculated from ionic refractions that the 'ionic radius' of O^{--} should be about 1·32 Å.U. W.L. Bragg also found that in a number of substances the distance apart of the O-ion centres is approximately twice this value, and he and G. B. Brown have used this fact in the elucidation of the structure of chrysoberyl.[2] More recently L. Vegard [3] has given a further verification in the cases of anatase, cassiterite, rutile, zircon, and the scheelite group of crystals. The cubic crystals of ThO$_2$, UO$_2$, and CeO$_2$, whose structures most probably conform to the fluorite arrangement, have cube edges $a = 5·61, 5·47$, and 5·41 Å.U. respectively.[4] In these cases, therefore, the distances apart of the O centres are 2·80$_5$, 2·73$_5$, 2·70$_5$ Å.U. respectively, and each heavy metallic ion may be visualized as occupying the small space between eight large O-ions arranged cubically about it. It is significant that

[1] J. A. Wasastjerna, Comm. Phys.-Math. Soc. Sci. Fennicae, 1923, vol. 1, no. 38, p. 20.

[2] W. L. Bragg and G. B. Brown, Proc. Roy. Soc. London, Ser. A, 1926, vol. 110, p. 34.

[3] L. Vegard, Phil. Mag., 1926, ser. 7, vol. 1, p. 1151.

[4] V. M. Goldschmidt and L. Thomassen, Vidensk. Skrifter, I. Mat.-naturvid. Kl., Kristiania, 1923, no. 2, p. 5. [Min. Abstr., vol. 2, p. 206.]

in the case of monoclinic zirconia the three axial lengths, taking $\rho = 5\cdot73$, are $5\cdot16$, $5\cdot21$, and $5\cdot32$ Å.U. respectively, that is, each about twice the diameter of the O-ion. This fact, together with that of the face-centred arrangement of the Zr-ions, certainly indicates that the whole structure is similar to a distorted fluorite arrangement. The co-ordinates of the Zr-ions would be:

$$(xyz)\,(\tfrac{1}{2} - x, \tfrac{1}{2} + y, \bar{z})\,(x, \tfrac{1}{2} - y, \tfrac{1}{2} + z)\,(\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} - z),$$

where x, y, z are all small. Similarly, but with different small values of the parameters, the O co-ordinates would be:

$$(\tfrac{3}{4} + l, \tfrac{3}{4} + m, \tfrac{1}{4} + n)\,(\tfrac{3}{4} - l, \tfrac{1}{4} + m, \tfrac{3}{4} - n)\,(\tfrac{3}{4} + l, \tfrac{3}{4} - m, \tfrac{3}{4} + n)\,(\tfrac{3}{4} - l, \tfrac{1}{4} - m, \tfrac{1}{4} - n)$$
$$(\tfrac{1}{4} + u, \tfrac{3}{4} + v, \tfrac{1}{4} + w)(\tfrac{1}{4} - u, \tfrac{1}{4} + v, \tfrac{3}{4} - w)(\tfrac{1}{4} + u, \tfrac{3}{4} - v, \tfrac{3}{4} + w)(\tfrac{1}{4} - u, \tfrac{1}{4} - v, \tfrac{1}{4} - w).$$

The observed data are too few to allow of any exact determination of these small parameters.

A recent note by W. P. Davey[1] states that powder photographs of different samples of zirconia showed the existence of at least two crystalline forms. In the case of the first ' the strong lines of the pattern taken alone ' showed a face-centred cubic lattice, $a = 5\cdot098$ Å.U., leading to a probable fluorite arrangement of ions. The second type of pattern indicated a triangular close-packed lattice, $a = 3\cdot598$ Å.U., $c/a = 1\cdot633$, the structure being closely related to that of the face-centred cube. The second crystalline form is not indicated at all by the results given in the present paper, but the first form (the ' face-centred cubic lattice ') is probably the same as the approximately face-centred monoclinic lattice here described, since there were apparently some weaker lines on the photograph which did not agree with a cubic lattice.

[1] W. P. Davey, Bull. Amer. Physical Soc., 1926, vol. 1, no. 9, p. 25.