

Discussion of the structure

A projection of the structure seen along the sixfold axis is shown in Fig. 1. The slightly distorted hexagonal close-packing of the chlorine atoms is immediately apparent.

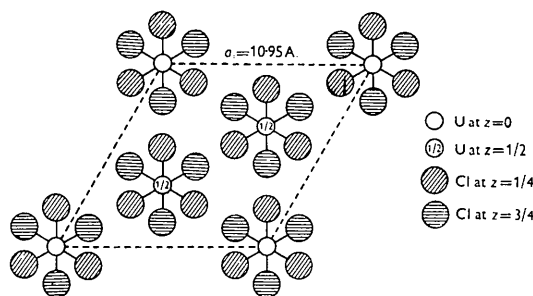


Fig. 1. The UCl_6 structure viewed along the sixfold axis. The U-Cl bonds within the UCl_6 molecules are indicated.

Fig. 1 clearly shows that UCl_6 has a typical molecular structure, being built up of individual molecules UCl_6 in a three-dimensional array. The structure thus provides a direct explanation of the observed high volatility of the substance.

The six chlorine atoms about each uranium atom

form a nearly perfect octahedron. The U-Cl distance is 2.42 Å. This distance is probably accurate to only ± 0.1 Å., since it was difficult to determine the chlorine parameters with accuracy from the powder diffraction data. The normal single-bond radius of chlorine being 0.99 Å., one finds the value 1.43 Å. for the single-bond radius of hexavalent uranium. In the preceding paper of this series (Zachariasen, 1948*b*) essentially the same single-bond radius for uranium was deduced. The metallic single-bond radius is according to Pauling (1947) for comparison 1.42 Å. This agreement represents further support for the contention of V. M. Goldschmidt and of Pauling that covalent and metallic radii are essentially the same.

The closest distance between chlorine atoms of different UCl_6 molecules is 3.85 Å.

The writer thanks Dr Sherman Fried for the UCl_6 preparation and Miss Anne Plettinger for having taken the diffraction patterns.

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The Crystal Structure of Zirconium Oxysulfide, ZrOS^*

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The crystal structure of ZrOS has been investigated by means of X-ray powder photographs and by powder spectrometry. The substance has a simple cubic lattice with $a_0 = 5.696 \pm 0.002$ Å. ($\lambda = 1.5418$ Å.) with space group T^4-P2_13 . In the resulting structure Zr shows a co-ordination number of seven, being surrounded by three sulfur atoms at 2.63 Å., one sulfur atom at 2.61 Å. and three oxygen atoms at 2.13 Å. The co-ordination polyhedron has a point-group symmetry of $C_{3v}-3m$.

Introduction

When H_2S gas was passed through a graphite tube containing ZrO_2 at 1300°C . a product which showed gradation in color from pale yellow to a dark purple resulted. The material was divided into five portions according to color, and X-ray powder patterns were photographed for the three samples corresponding to greatest interaction with H_2S . The darkest sample (no. 5) proved to be ZrS_2 , for which cell constants of

$a = 3.66$ Å. and $c = 5.79$ Å. ($\lambda = 1.542$ Å.) were found. Sample no. 3, a yellow powder, was found to be ZrOS with a few of the stronger lines of ZrO_2 appearing. The diffraction pattern of sample no. 4 showed lines of both ZrOS and ZrS_2 , the ZrOS phase having the same cell constant as in sample no. 3, where there was a slight excess of ZrO_2 . This latter observation indicates that neither ZrO_2 nor ZrS_2 are highly soluble in ZrOS , since a shift in cell constant would be expected in that case. However, our cell constants for ZrS_2 , which are lower than those reported in the literature (van Arkel, 1924; *Strukturbericht*, 1931), indicate that there may be some unreplaced oxygen in that phase.

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The structure of ZrOS

ZrOS was first prepared by Hauser (1907) and described as a light yellow powder with a density of 4.87 g.cm.⁻³. His material was prepared by passage of H₂S over Zr(SO₄)₂ at red heat. The composition ZrOS was established by chemical analysis.

Powder photographs of our product were prepared by use of filtered Cu radiation in a camera of 9.00 cm. diameter. For more accurate intensity data a record of the reflections from $\theta=0$ to $\theta=42^\circ$ was prepared by use of a Norelco Geiger-Counter X-ray Spectrometer. With the exception of a few lines which were undoubtedly due to ZrO₂, the diffraction patterns were completely indexed on the basis of a simple cubic lattice with $a_0=5.696 \pm 0.002$ A. ($\lambda=1.5418$ A.). The density 4.87 g.cm.⁻³ leads to 3.89 (4) ZrOS per unit cell. The calculated density for 4 ZrOS is 4.975 g.cm.⁻³.

The only absences noted were $4n0$ with n even, and 100. Only the latter has significance in the space-group assignment, and since possible reflections of 300, 500 and 700 would be obscured by 221, 430 and 632 respectively, it was assumed that the absence 100 indicates the general absence of $n00$ with n odd. The space group is accordingly T^4-P2_13 or O^2-P4_23 , the latter being improbable since it does not provide three sets of four equivalent points.

The complete absence of 400 requires that

$$f_{Zr} \cos 8\pi X_{Zr} + f_S \cos 8\pi X_S + f_O \cos 8\pi X_O \cong 0.$$

Since f_{Zr} is over twice the sum of f_S and f_O for most of these reflections, the above requirement limits X_{Zr} to values near $m/16$ with m odd. The maximum uncertainty in X_{Zr} caused by variation of X_S and X_O through all possible values amounts to only ± 0.02 . Since all of the positions $m/16$ (m odd) offer the same possibilities, the value 0.31 was arbitrarily chosen as a starting point.

The sulfur atoms were located next on the basis of packing considerations. If S-S separations under 3.60A. are considered improbable, X_S is restricted to the four ranges: (1) 0.00 ± 0.07 , (2) 0.25 ± 0.07 , (3) 0.50 ± 0.07 and (4) 0.75 ± 0.07 . In the first of these possibilities the Zr-S separation is less than 2.58 A. (the value found by van Arkel in ZrS₂) except in the region 0.05-0.07. An attempt to carry this possibility further, however, shows that it does not permit the location of the oxygen atoms except at positions yielding Zr-O and S-O separations considerably less than 2.1 and 2.9 A. respectively. The second range (0.25 ± 0.07) is ruled out because it would require Zr-S separations of less than 1.3 A., which is considerably less than the expected value. The third range (0.50 ± 0.07) leads to Zr-S separations which are satisfactory only if X_S is at the extreme upper end of the range. This leads to the structure finally accepted as correct. In the fourth range (0.75 ± 0.07) values of X_S below 0.76 are ruled out because of the small Zr-S separation which would result. With $X_S > 0.75$ there

are no positions left for oxygen which do not lead to improbable (short) Zr-O and S-O separations.

Taking X_{Zr} at approximately 0.31, X_S is thus seen

Table 1. Comparison of calculated and observed intensities for ZrOS

<i>hkl</i>	$\sin^2 \theta$	Intensities		
		Powder photo	Spectrometer	Calculated
110	0.0364	<i>m</i>	55	50
111	0.0543	<i>s</i>	120	160
200	0.0736	<i>m</i>	20	34
210	0.0916	<i>s</i>	98	104
211	0.1097	<i>s</i>	85	85
220	0.1472	<i>m</i>	32	62
221	0.1653	<i>ms</i>	40	61
310	0.1839	<i>ms</i>	40	60
311	0.2015	<i>mw</i>	15	30
222	0.2195	<i>w</i>	3	4
320	0.2388	<i>m</i>	18	23
321	0.2579	<i>s</i>	50	55
400	—	Nil	Nil	0.01
410	0.3125	<i>s</i>	41	49
322				
411	0.3303	<i>vw</i>	6	4
330				
331	0.3498	<i>mw</i>	8	4
420	—	Nil	Nil	0.9
421	0.3856	<i>ms</i>	16	23
332	0.4053	<i>mw</i>	Limit of instrument	9
422	0.4409	<i>ms</i>		11
430	0.4592	<i>ms</i>	16	
510	0.4775	<i>s</i>		45
431				
511	0.4953	<i>m</i>		10
333				
520	0.5319	<i>ms</i>		24
432				
521	0.5497	<i>mw</i>		18
440	—	Nil		0.0
522	0.6046	<i>w</i>		5
441				
530	0.6225	<i>w</i>		3
433				
531	0.6413	<i>w</i>		6
600	0.6598	<i>w</i>		8.5
442				
610	0.6872	<i>w</i>		8.5
611	0.6962	<i>s</i>		19
532				
620	0.7318	<i>ms</i>		12
621	0.7509	<i>s</i>		27
540				
443	0.7689	<i>s</i>		34
541				
533	0.7874	<i>ms</i>		21
622	0.8066	<i>vw</i>		2
630	0.8239	<i>s</i>		35
542				
631	0.8429	<i>s</i>		22
444	0.8772(α_1)	<i>ms</i>		18
632	0.8962(α_1)	<i>ms</i>		22
710	0.9142(α_1)	<i>ms</i>		10
550				
543	0.9324(α_1)	<i>s</i>		22
711				
551	—	Nil		1
640	0.9692(α_1)	<i>vs</i>		35
720				
641				

to be approximately 0.57. The oxygen atoms were then located as follows. There must be one of each kind of atom along the body diagonal of the unit cube. Keeping Zr-O greater than 2.1 Å. and S-O greater than 2.9 Å. leaves only the range from -0.14 to 0.10 open to oxygen. The portions of this range from -0.14 to -0.08 and from -0.06 to 0.10 are ruled out because they lead to S-O separations off the body diagonal which are less than 2.9 Å. By taking $X_O = \frac{1}{2} - X_S$, i.e. -0.07 or 0.93, all of the nearest approaches of O to S are equalized at the reasonable value 2.96 Å.

Minor adjustments in the above parameters were made in order to give better agreement between calculated and observed intensities. The values finally taken are

$$X_{Zr} = 0.307, \quad X_S = 0.572, \quad X_O = 0.928.$$

Intensities calculated by use of the above parameters and the equation

$$I_{hkl} = K p_{hkl} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} (F_{hkl})^2$$

are shown in Table 1, together with the visually estimated intensities from a powder photograph and the intensities observed on a record prepared on a Norelco Geiger-Counter X-ray Spectrometer.

The general agreement between calculated and observed intensities supports the correctness of the structure reported.

Discussion of the structure

An interesting feature of the resulting structure (Fig. 1) is the co-ordination number, seven, for zirconium. Each zirconium atom is surrounded by four sulfur atoms and three oxygen atoms. The sulfur atoms form an elongated tetrahedron with one Zr-S separation of 2.61 Å. and three of 2.63 Å. The oxygen atoms form an equilateral triangle about zirconium in such a way that there is an oxygen atom in each of the elongated faces of the sulfur tetrahedron. The zirconium atom is just slightly out of the plane of the oxygen triangle at a distance of 2.13 Å. from each oxygen atom. The result may be looked upon as a distorted octahedron consisting of three sulfur atoms and three oxygen atoms with the fourth sulfur atom above the center of that face of the octahedron determined by the oxygen atoms. From this point of view, the co-ordination of zirconium is quite similar to that found in the hepta-

fluorozirconate ion in crystals of K_3ZrF_7 , (Hampson & Pauling, 1938).

The observed Zr-S separation of 2.62 Å. differs by a reasonable amount from that of 2.58 Å. found in ZrS_2 (van Arkel, 1924; *Strukturbericht*, 1931) in which the co-ordination number is six. Also the observed Zr-O separation of 2.13 Å. differs in the right direction

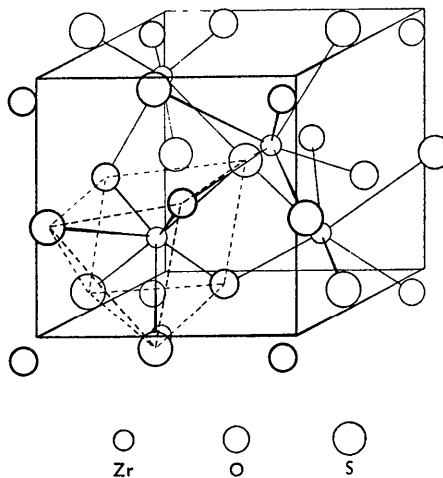


Fig. 1. The structure of ZrOS.

from that of 2.20 Å. found for co-ordination number eight in the cubic modification of ZrO_2 (Passerini, 1930; *Strukturbericht*, 1937). The stable monoclinic form of ZrO_2 shows Zr-O separations from 1.95 to 2.65 Å. with an average of 2.3 Å. (Náray-Szabó, 1936). The observed S-S and S-O separations of 3.59 and 2.96 Å. are both shorter than the sum of the radii (3.68 Å. for S-S and 3.24 Å. for S-O) owing to the sharing of edges between the co-ordination polyhedra.

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