

The OD-Structure of $\text{Zr}(\text{OH})_2\text{CrO}_4$

WANDA MARK

Department of Inorganic Chemistry, Chalmers University of Technology and The University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of $\text{Zr}(\text{OH})_2\text{CrO}_4$ has been determined by single crystal X-ray methods. The structure consists of ordered layers the stacking of which is disordered in the c direction.

The space group of the superposition structure is $I4_1/amd$ with $a = 6.868 \text{ \AA}$, $c = 29.026 \text{ \AA}$, and $Z = 12$. A final R value of 0.093 was obtained with full matrix least squares calculation based on 375 independent reflexions.

The ordered layers in the true structure have the dimensions $a = b = 13.735 \text{ \AA}$, the structure belonging to the family represented by the OD-groupoid:

$$P m m (n)_{1,1,2} \quad \begin{matrix} 1 & 1 \\ \left\{ \begin{matrix} 1 & 1 & \left(\frac{\bar{4}}{4_4} \right) \\ & \frac{2_{1/2}}{n_{1/4,2}} & \frac{2}{n_{1/4,2}} \end{matrix} \right\} \end{matrix}$$

Infinite nets of composition $[\text{Zr}_3(\text{OH})_6\text{CrO}_4]_n^{4n+}$ are held together in the c direction by chromate groups, the zirconium atoms being joined by double oxygen bridges. Zirconium exhibits both eightfold (dodecahedral) and sevenfold (pentagonal bipyramidal) oxygen coordination. The Zr-O distances range between 2.12 and 2.27 \AA with an average distance of 2.19 \AA in the Zr-O₈ dodecahedron and of 2.14 \AA in the Zr-O₇ arrangement.

An investigation of the crystal structures of different phases appearing in the $x\text{ZrO}_2 \cdot y\text{CrO}_3 \cdot z\text{H}_2\text{O}$ system was started some years ago by Lundgren. The principal features of the crystal structure of $4\text{ZrO}_2 \cdot 5\text{CrO}_3 \cdot 5\text{H}_2\text{O}$ were published.¹ The present paper deals with the crystal structure of $\text{ZrO}_2 \cdot \text{CrO}_3 \cdot \text{H}_2\text{O}$, whereas the somewhat modified structure of $4\text{ZrO}_2 \cdot 5\text{CrO}_3 \cdot 5\text{H}_2\text{O}$ will be described in a later paper.

EXPERIMENTAL

An amorphous zirconium chromate was prepared according to a method described in 1929 by Briggs² and was dissolved in an aqueous solution of CrO_3 . Mixtures with various Zr : Cr mol ratios were sealed in Pyrex glass tubes and heated to different temperatures in the range 100–190°C for about ten days. In the temperature range 100–130°C only red crystals of $4\text{ZrO}_2 \cdot 5\text{CrO}_3 \cdot 4\text{H}_2\text{O}$ were obtained, regardless of the

value of the Zr : Cr mol ratio. If the temperature was raised to 140°C or more, small yellow crystals of $\text{ZrO}_2 \cdot \text{CrO}_3 \cdot \text{H}_2\text{O}$ were obtained from dilute mixtures with comparatively higher Zr : Cr mol ratios than mixtures from which $4\text{ZrO}_2 \cdot 5\text{CrO}_3 \cdot 4\text{H}_2\text{O}$ was obtained at the same temperature. As will be seen later, the formula $\text{Zr}(\text{OH})_2\text{CrO}_4$ for $\text{ZrO}_2 \cdot \text{CrO}_3 \cdot \text{H}_2\text{O}$ is more consistent with the structure of this product and is therefore used in the following.

The water content in $\text{Zr}(\text{OH})_2\text{CrO}_4$ was determined by Penfield's³ method, the chromium content by atomic absorption spectroscopy and the zirconium content as $\text{ZrO}_2 + \text{Cr}_2\text{O}_3$ after heating the compound to 1200°C in a Mettler Recording Thermo-analyzer. The density was determined from the loss of weight in benzene. The following results were obtained:

	% Cr	% ($\text{ZrO}_2 + \text{Cr}_2\text{O}_3$)	% H_2O	density (g cm^{-3})
Found	21.6	82.9	7.6	3.43
Calculated for $\text{Zr}(\text{OH})_2\text{CrO}_4$	21.6	82.6	7.5	3.51 (<i>cf.</i> below)

CRYSTAL DATA

$\text{Zr}(\text{OH})_2\text{CrO}_4$ crystallises as small, thin square plates with tetragonal symmetry. The cell dimensions were determined accurately from Guinier powder photographs taken with $\text{CuK}\alpha_1$ radiation using lead nitrate as internal standard ($a = 7.8566 \text{ \AA}$ at 21°C).⁴ With the aid of preliminary cell dimensions obtained from Weissenberg photographs, 44 lines were indexed and a subsequent refinement of the cell parameters based on these lines gave the following results:

$$\begin{aligned} A = B &= 6.8677 \pm 0.0003 \text{ \AA}^* \\ C &= 29.0256 \pm 0.0017 \text{ \AA} \\ V &= 1369.0 \text{ \AA}^3 \end{aligned}$$

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

In accordance with the experimental density (*cf.* above), there are twelve formula units in the unit cell.

INTENSITY DATA

Rotation photographs, taken about the a and b axes with comparatively long exposure times, show very weak continuous streaks between the layer lines. Consequently, the structure is a so-called OD-structure⁵ which may be considered to consist of ordered layers whose stacking is disordered in the c direction. The reflexions for which $h = 2H$, $k = 2K$ and $l = L$, where H , K and L are integers, are all sharp and correspond to axes of $A = B = 6.87 \text{ \AA}$ and $C = 29.03 \text{ \AA}$ in direct space. Reflexions with reciprocal coordinates HKL give rise to a superposition structure whereas the true structure emanates from sharp reflexions HKL as well as from the continuous streaks with reciprocal coordinates $hk\zeta$. The coordinate ζ can assume any value, which implies a true structure with axes $a = b = 13.74 \text{ \AA}$ extending infinitely in the ζ direction, due to the disorder. The unit length in the ζ direction is defined as the distance between adjacent layers, which, in accordance with the nomenclature of Dornberger-Schiff,⁵ is denoted c_0 .

* The use of capital letters will be explained later.

Table I. Guinier powder data for $\text{Zr}(\text{OH})_2\text{CrO}_4$. $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$.

$h k l$	$10^6 \sin^2 \theta$ obs	$10^6 \sin^2 \theta$ calc	F calc	I obs
0 0 4	1123	1127	141	vw
1 0 3	1889	1892	238	st
1 0 5	3019	3018	59	vvw
0 0 8	4506	4507	118	vvw
1 0 7	4705	4709	387	st
2 0 0	5024	5032	*	vst
2 0 4	6152	6158	94	vw
2 1 1	6360	6360	33	vvw
2 1 3	6924	6923	159	m
1 0 9	6959	6962	56	vvw
1 1 10	9564	9558	332	w
2 1 7	9739	9740	189	w
2 2 0	10062	10063	288	w
2 2 4	11188	11190	63	vvw
3 0 3	11960	11955	271	w
2 0 10	12080	12074	171	vw
3 0 5	13087	13082	87	vvw
1 0 13	13167	13159	127	vvw
3 1 4	13703	13706	50	vvw
3 0 7	14779	14772	363	m
2 1 11	14797	14810	143	vw
1 1 14	16328	16318	330	w
3 2 3	16988	16986	206	w
1 0 15	17096	17103	149	vvw
3 1 10	19625	19621	372	m
3 2 7	19809	19803	219	vw
3 0 11	19854	19842	84	vvw
4 0 0	20132	20126	549	m
4 0 4	21252	21253	119	vvw
1 0 17	21615	21610	280	vw
4 1 3	22015	22018	183	vw
4 1 5	23138	23145	87	vw
4 1 7	24844	24835	164	vw
4 2 0	25159	25158	299	vw
3 1 14	26378	26381	237	vw
2 1 17	26635	26641	158	vvw
{ 3 0 15	27160	{ 27166	{ 154	vvw
{ 4 0 10		{ 27168	{ 99	
3 3 10	29692	29684	378	vw
3 0 17	31675	31673	238	vvw
4 3 3	32089	32081	201	vw
3 2 15	32188	32197	92	vvw
4 3 5	33210	33208	99	vvw
{ 4 3 7	34895	{ 34898	{ 176	vw
{ 5 0 7		{ 34898	{ 160	
3 3 14	36436	36445	173	vvw
3 2 17	36701	36704	144	vvw
2 1 21	37351	37345	207	vvw
5 1 10	39739	39747	164	vvw

* Too strong to be estimated.

The crystal used in this investigation had a cross-section of 0.065×0.065 mm² (x and y directions) and a thickness of 0.01 mm. Using multiple film Weissenberg techniques and $\text{CuK}\alpha$ radiation, intensities from layer lines $h0\zeta - h10\zeta$ were registered with the exception of $h7\zeta$ and $h9\zeta$. The times of exposure required to obtain visible intensities for $hk\zeta$ with h or k odd varied between six and seventeen days. Layer lines with $k = 2K$ show sharp reflexions for $h = 2H$ and more or less continuous streaks, without any pronounced maxima, parallel to \vec{c}^* for $h = 2H + 1$. For layer lines with $k = 2K + 1$ no sharp reflexions appear and weak continuous streaks appear only for $h = 2H$. The conditions of reflection are:

- (i) $hk\zeta$ with $h = 2H$, $k = 2K$ if $\zeta = L$
or $h + k = 2n + 1$ with $\zeta = \text{any value}$
- (ii) HKL » $H + K + L = 2n$
- (iii) $HK0$ » $H, (K) = 2n$
- (iv) HHL » $2H + L = 4n$
- (v) $hk0$ » $h + 2k = 4n$ if $k = 2n + 1$
 $2h + k = 4n$ if $h = 2n + 1$

From the conditions of reflection (ii), (iii), and (iv) it is evident that the superposition structure is I -centered with the symmetry of space group No. 141, $I4_1/amd$.⁶ The superposition structure, denoted by $\hat{\rho}(xyz)$, is related to the true structure, $\rho(xyz)$, by the relation $\hat{\rho}(xyz) = \frac{1}{4}[\rho(xyz) + \rho(\frac{1}{2} + xyz) + \rho(x\frac{1}{2} + yz) + \rho(\frac{1}{2} + x\frac{1}{2} + yz)]$.

DETERMINATION OF THE SUPERPOSITION STRUCTURE

The intensities of the sharp reflexions from layer lines $H0L - H5L$ were estimated visually by comparison with an intensity scale made from the actual crystal. The linear absorption coefficient for $\text{Zr}(\text{OH})_2\text{CrO}_4$ is 395 cm^{-1} and hence the intensities were corrected for absorption, as well as for Lorentz and polarization effects, with the program DATAP2.⁷ At the same time, preliminary calculations for extinction correction were performed.

By means of a three-dimensional Patterson synthesis, computed with the program DRF,⁷ the positions of the twelve zirconium atoms in the unit cell were located. A three-dimensional Fourier synthesis based on the signs obtained from the zirconium parameters revealed the positions of four structurally different oxygen atoms ($\text{O}_1, \text{O}_2, \text{O}_3, \text{O}_4$). Subsequent Fourier syntheses yielded the positions of the chromium atoms and the remaining oxygen atoms and also showed that the occupation numbers for $\text{Cr}_1, \text{Cr}_2, \text{O}_5$, and O_6 were 0.5. The following preliminary positions were thus obtained from electron density calculations, x and z referring to the unit cell $A = B = 6.87 \text{ \AA}$ and $C = 29.03 \text{ \AA}$.

4	Zr ₁	in $I4_1/amd$:	4(a)	
8	Zr ₂	»	8(e)	with $z = 0.166$
4	Cr ₁	»	8(e)	» $z = 0.774$
8	Cr ₂	»	16(h)	» $x = 0.190$ $z = 0.294$
16	O ₁	»	16(h)	» $x = 0.043$ $z = 0.425$
16	O ₂	»	16(h)	» $x = 0.548$ $z = 0.184$
8	O ₃	»	8(e)	» $z = 0.241$
16	O ₄	»	16(h)	» $x = 0.450$ $z = 0.111$
8	O ₅	»	16(h)	» $x = 0.563$ $z = 0.289$
8	O ₆	»	16(h)	» $x = 0.444$ $z = 0.009$

The structural parameters, including atomic coordinates, isotropic temperature coefficients, scale factors and the isotropic extinction coefficient, were refined with the least squares full matrix programme LINUS.⁷ To ensure that the atoms Cr₁, Cr₃, O₅, and O₆ had been given the correct occupation numbers, a few cycles of refinement were performed in which these parameters were refined together with the above-mentioned parameters. During the refinement correction was made for anomalous dispersion and primary extinction, the finally adopted value of the extinction parameter being 4.7×10^{-4} . After completed refinement based on 574 structure factors which rendered an *R* value of 0.10, mean values of those structure factors not independent according to the Laue symmetry 4/*mmm* were calculated. A few cycles of refinement

Table 2. Observed and calculated structure factors. Non-observed reflexions are denoted by a dash. (The columns are *L*, *F*_o, and *F*_c, respectively.)

4	0	0	L	4	0	0	L	8	-	2	5	1	L	19	43	41	0	8	2	L	10	162	-176		
8	137	-118		2	524	549		12	40	47	2	4	29	-37	21	132	130	0	8	91	-91	12	89	-79	
12	46	34		4	115	-119		14	16	22	4	50	-59	25	34	28	2	33	29	14	28	-27			
16	61	70		6	-	-		16	-	-	6	-	-1	27	96	90	4	58	50	18	24	-29			
20	119	-147		8	29	-24		18	29	30	8	49	-51	29	45	-36	6	-	-7						
24	191	219		10	95	6		20	10	12	10	158	164	31	77	-81	8	22	-20	8	3	L	-12		
28	59	-70		12	68	68		22	341	332	14	172	-167	33	22	21	10	33	-54	1	17	-42			
32	70	-75		14	35	31		24	339	16	41	38	0	4	257	-299	3	3	L	3	70	-92			
36	31	-36		16	21	18		26	22	44	30	18	91	76	2	33	35	2	48	55	7	48	62		
	1	0	L	18	24	-16		28	22	44	45	20	57	45	4	95	94	6	88	91					
	3	17		20	150	-145		30	26	35	-27	22	40	32	6	20	-22	10	340	-378	4	4	L	275	
	5	287	-238	24	160	153		32	61	-63	24	20	-19	10	8	26	-22	10	183	173	0	0	222	-106	
	7	61	59	26	-	-68		34	63	88	26	60	-57	10	-	10	-	18	-	-48	3	5	41	-99	
	9	472	387	28	73	-6		36	-	-	28	37	-38	12	62	-68	22	64	-57	8	17	16			
	11	60	56	30	12	12		38	1	L	1	L	14	19	-20	26	47	33	12	88	87				
	13	73	-65	32	33	-33		40	1	L	2	1	L	16	29	28	30	39	16	20	137	-137			
	15	144	-149	5	0	L		42	3	33	1	31	19	18	18	18	15		4	101	-106				
	17	260	280	5	63	71		44	5	21	28	3	144	147	20	146	150		3	3	L	24	111	107	
	19	29	-27	7	45	-47		46	7	180	-189	5	91	94	22	14	13	1	28	-26	28	47	-62		
	21	135	-147	9	34	36		48	9	24	-18	7	120	-101	24	161	-156	3	170	-201					
	23	51	-46	11	157	160		50	11	144	143	9	47	48	26	32	28	5	86	-99	5	4	L	50	
	25	71	-69	13	38	-36		52	15	75	12	13	70	-63	28	94	98	7	163	176	1	53	50		
	27	57	-67	15	113	-109		54	17	163	158	15	-	12	30	21	-23	9	20	-18	5	60	61		
	29	-	-11	17	124	-116		56	19	29	29	17	107	83	5	2	L	13	70	71	7	83	74		
	31	123	151	19	101	-101		58	21	200	-207	19	30	-27	1	48	-50	15	66	-63	9	22	-22		
	33	11	10	21	178	184		60	23	15	11	21	111	-110	3	35	27	17	136	-117	11	102	-96		
	35	17	-20	23	42	37		62	25	38	-35	23	34	31	5	26	-28	19	-	-2	13	84	-84		
	2	0	L	25	83	-68		64	27	94	98	2	7	1	L	7	48	-87	21	105	-89	15	47	-42	
	4	104	-94	27	22	-18		66	29	31	29	2	1	L	9	48	60	23	-	8	9	115	99		
	6	41	-28	29	44	-43		68	31	123	-139	2	4	7	11	120	137	25	18	16	19	50	48		
	8	30	-23	31	33	18		70	33	18	24	8	6	54	-41	13	55	46	27	82	-87	21	75	-74	
	10	182	171	33	0	L		72	35	1	L	10	182	168	15	68	61	29	38	-35	6	4	L	186	
	12	40	35	35	342	337		74	37	2	28	-31	12	-	19	129	-121	31	5	3	L	0	175	186	
	14	21	17	4	115	-98		76	39	4	49	-50	14	121	-106	21	105	104	2	43	53	2	19	-19	
	16	-	-11	6	-	-		78	41	6	35	-23	16	61	-60	23	20	-19	4	25	22	4	104	-88	
	18	-	2	8	-	-		80	43	8	14	-17	18	35	33	25	-	5	6	53	32	6	-	-2	
	20	115	-129	10	64	76		82	45	10	363	372	10	182	168	27	58	65	8	35	32	8	27	24	
	22	43	-45	12	67	73		84	47	12	15	-12	1	8	1	L	10	195	-190	10	15	11			
	24	210	221	14	31	38		86	49	14	15	-12	1	85	87	0	199	-200	14	137	124	14	-	13	
	26	40	44	16	25	17		88	51	16	63	62	5	51	56	2	45	48	16	-	9	16	-	4	
	28	100	-114	18	28	-23		90	53	18	15	13	7	58	-54	4	87	82	18	74	-62	18	-	-9	
	30	22	-18	20	131	-119		92	55	20	43	-44	9	16	14	6	-	-12	20	71	-62	20	95	-115	
	32	52	-51	22	49	-53		94	57	22	26	-24	11	44	42	8	24	-27	22	43	-36				
	34	16	-17	24	95	100		96	59	24	42	-30	12	68	-73	10	20	-16	24	-	4	7	4	L	
	1	38	39	1	60	51		98	61	26	42	-30	12	68	-73	12	68	-73	26	54	57	1	46	42	
	3	251	-271	3	106	-84		100	63	28	13	-12	0	2	L	14	34	-31	14	34	-31	3	83	-80	
	5	79	87	5	44	44		102	65	30	47	-51	0	236	-288	16	18	14	18	25	21	5	54	59	
	7	382	363	7	157	145		104	67	32	4	L	8	50	-45	18	25	21	6	3	L	1	40	-74	
	9	29	27	9	35	-31		106	69	34	147	183	2	12	29	20	109	110	3	151	-155	5	5	L	-35
	11	80	-84	11	83	-75		108	71	36	17	154	-164	16	69	22	32	28	5	87	-98	2	51	-51	
	13	98	-109	13	82	-78		110	73	38	20	106	114	24	82	82	-103	7	114	110	6	48	-35		
	15	145	-154	15	90	-84		112	75	40	24	212	-222	28	82	82	-103	9	29	-26	10	100	90		
	17	244	238	17	150	130		114	77	42	26	142	147	32	38	29	7	2	L	11	65	-53	14	102	-90
	19	39	-40	19	10	15		116	79	44	30	32	38	32	38	29	1	45	-40	13	76	18	85	92	
	21	84	-77	21	32	-26		118	81	46	34	36	32	38	29	1	45	-40	13	76	18	85	92		
	23	-	10	23	0	L		120	83	48	38	40	40	40	40	1	45	-40	13	76	18	85	92		
	25	61	-58	25	135	166		122	85	50	42	42	42	42	42	1	45	-40	13	76	18	85	92		
	27	62	-63	27	135	166		124	87	52	44	44	44	44	44	1	45	-40	13	76	18	85	92		
	29	-	6	29	135	166		126	89	54	46	46	46	46	46	1	45	-40	13	76	18	85	92		
	31	82	89	31	135	166		128	91	56	48	48	48	48	48	1	45	-40	13	76	18	85	92		
	33	21	-16	33	135	166		130	93	58	50	50	50	50	50	1	45	-40	13	76	18	85	92		
								132	95	60	52	52	52	52	52	1	45	-40	13	76	18	85	92		
								134	97	62	54	54	54	54	54	1	45	-40	13	76	18	85	92		
								136	99	64	56	56	56	56	56	1	45	-40	13	76	18	85	92		
								138	101	66	58	58	58	58	58	1	45	-40	13	76	18	85	92		
								140	103	68	60	60	60	60	60	1	45	-40	13	76	18	85	92		
								142	105	70	62	62	62	62	62	1	45	-40	13	76	18	85	92		
								144	107	72	64	64	64	64	64	1	45	-40	13	76	18	85	92		
								146	109	74	66	66	66	66	66	1	45	-40	13	76	18	85	92		
								148	111	76	68	68	68	68	68	1	45	-40	13	76	18	85	92		
								150	113	78	70	70	70	70	70	1	45	-40	13	76	18	85	92		
								152	115	80	72	72	72	72	72	1	45	-40	13	76	18	85			

with the program LALS⁷ based on the final data set, which consisted of 375 independent structure factors, yielded an R value of 0.093. When non-observed reflexions were included by assigning them a structure factor value of $F_{\text{obs}(\text{min})}/2$, an R value of 0.096 (*cf.* Table 2) was obtained.

Table 3. Final atomic parameters for the superposition structure of $\text{Zr}(\text{OH})_2\text{CrO}_4$. Atomic coordinates are expressed as fractions of the cell edges ($A=B=6.87$ Å, $C=29.03$ Å) and standard deviations are given within parentheses.

Atom	Special position	Occupation number	x	y	z	B Å ²
Zr ₁	4(<i>a</i>)	1	0	3/4	1/8	1.85(7)
Zr ₂	8(<i>e</i>)	1	0	1/4	0.16718(5)	1.44(7)
Cr ₁	8(<i>e</i>)	$\frac{1}{2}$	0	1/4	0.7736(2)	1.71(13)
Cr ₂	16(<i>h</i>)	$\frac{1}{2}$	0	0.1789(7)	0.2958(1)	1.22(8)
O ₁	16(<i>h</i>)	1	0	0.0500(15)	0.4258(3)	1.63(17)
O ₂	16(<i>h</i>)	1	0	0.5548(15)	0.1871(3)	1.58(16)
O ₃	8(<i>e</i>)	1	0	1/4	0.2452(6)	2.58(31)
O ₄	16(<i>h</i>)	1	0	0.4454(15)	0.1105(3)	1.52(17)
O ₅	16(<i>h</i>)	$\frac{1}{2}$	0	0.5469(39)	0.2880(8)	2.84(43)
O ₆	16(<i>h</i>)	$\frac{1}{2}$	0	0.4352(34)	0.0089(7)	2.36(40)

Atomic parameters for the superposition structure are given, together with their standard deviations, in Table 3. In Fig. 1 a fourth of the unit cell ($0 < x < 1$, $0 < y < 1$, $-0.125 < z < 0.125$), corresponding to the cell dimensions 6.87 Å and 29.03 Å, is shown projected on the xy plane. Atoms which have occupation numbers equal to one do not contribute to the disorder in the true structure and have therefore been omitted from this figure (*cf.* Table 3).

DETERMINATION OF THE TRUE STRUCTURE

The true structure is periodic in the a and b directions but has no periodicity in the c direction. Hence, the true structure consists of ordered layers stacked upon each other with a separation c_0 . Since the superposition structure has a fourfold screw axis, the distance between two successive layers is $c_0 = c/4$. Alternate layers are linked by the translation $\pm \vec{a}/4 \pm \vec{b}/4 \pm 2\vec{c}_0$ in consequence of the space group $I4_1/amd$ of the superposition structure.

To determine the symmetry of the true structure, condition of reflection (*i*) is first taken into consideration, *i.e.* for reflections hkc , h and k cannot both be odd integers. This implies two pairs of atomic positions with coordinates x, y, z ; $\frac{1}{2} + x, y, z$ and x', y', z' ; $x', \frac{1}{2} + y', z'$, respectively, where the fractional coordinates refer to the unit cell $a = b = 13.74$ Å and $c = 29.03$ Å. Due to the fourfold screw axis, these two pairs of equivalent positions belong to different layers in such a way that alternate layers have the equipoints x, y, z ; $\frac{1}{2} + x, y, z$ while those in between have the equipoints x', y', z' ; $x', \frac{1}{2} + y', z'$. Consequently, layers which have atoms in positions x, y, z ; $\frac{1}{2} + x, y, z$ give no contributions to

structure factors F_{hkc} with h odd and layers with atoms in x', y', z' ; $x', \frac{1}{2} + y', z'$ do not contribute to structure factors with k odd.

Since reflexions $hk0$ are independent of the disorder, any systematic absence for $hk0$ must originate from symmetry related atoms belonging to the same layer. The reflection condition (v) can therefore be explained as follows: There exist partial glide planes in the structure in such a way that every layer in the true structure has an n glide plane perpendicular to the c axis with translational components $\vec{a}/4 + \vec{b}/2$ for every other layer and $\vec{a}/2 + \vec{b}/4$ for the intermediate layers. Performing each of these symmetry operations twice gives rise to the equivalent positions x, y, z ; $\frac{1}{2} + x, y, z$ and x', y', z' ; $x', \frac{1}{2} + y', z'$ and, accordingly, condition of reflection (i) for $hk\zeta$ is a consequence of these partial glide planes.

The space group $I4_1/amd$ implies that the four layers that constitute one unit cell in the true structure are situated in $z=0$ (L0), $z=\frac{1}{4}$ (L1), $z=\frac{3}{4}$ (L2) and $z=1$ (L3), those in $z=0$ and $z=\frac{1}{2}$ having glide planes with the translation component $\vec{a}/2 + \vec{b}/4$.

The plane group of *e.g.* layer L0 is derived from the above-stated symmetry relations of the layers and the fact that all atoms of interest for the disorder, that is Cr_1 , Cr_2 , O_5 , and O_6 , are situated in special positions of space group $I4_1/amd$ (*cf.* Fig. 1). The plane group of layers L0 and L2 can therefore unam-

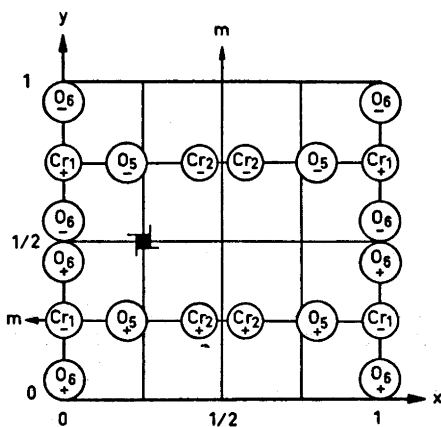


Fig. 1. Projection on the xy plane at $z=0$ of the atoms in the superposition structure which contribute to the disorder in $Zr(OH)_2CrO_4$. The z coordinates of the atoms are indicated by a + sign ($0 < z < 0.125$) or a - sign ($-0.125 < z < 0$). The remaining part of the unit cell ($A=B=6.87$ Å, $C=29.03$ Å) is derived by means of the fourfold screw axis at $x=\frac{1}{2}$, $y=\frac{1}{2}$.

biguously be written $Pmm(n)_{1, \frac{1}{2}}11$, in accordance with the nomenclature of Dornberger-Schiff⁵ (*cf.* Fig. 2). Two different groupings of atoms in the true structure are possible due to the mirror plane perpendicular to the x axis being situated either in $x=0$ or $x=\frac{1}{2}$ in layer L0. Because the atom Cr_1 is situated in the special position $8(e)$ of space group $I4_1/amd$ with $z=0.9764$, the mirror plane perpendicular to the x axis in layer L0 has to be situated in $x=0$. Although the symmetry $Pmm(n)_{1, \frac{1}{2}}11$ generates sixteen general equivalent positions in each layer, there are only four Cr_1 atoms, eight Cr_2 atoms, eight O_5 atoms and eight O_6 atoms. Atoms Zr_1 , Zr_2 , O_1 , O_2 , O_3 , and O_4 have,

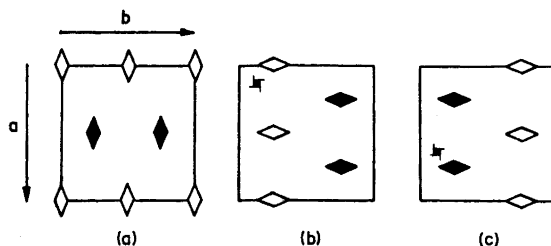


Fig. 2. Diagrams showing the symmetry elements in layer L0 (a), layer L1 (b) and the alternative layer L1 (c). The z coordinates of the asymmetric triangles are denoted: L0: $\blacktriangle z$, $\blacktriangle \bar{z}$; L1: $\blacktriangle \frac{1}{4} + z$, $\blacktriangle \frac{1}{4} - z$. The unit cell dimensions are $a = b = 13.74 \text{ \AA}$, $c = 29.03 \text{ \AA}$ and the origin is at $0, \frac{1}{8}, 0$ with reference to the true unit cell consisting of four centred superposition unit cells.

of course, the symmetry of the space group $I4_1/amd$ in each quarter of the layer and are not taken into consideration. The OD-groupoids can then be formulated,⁵ starting from layer L0 or L2 as:

$$P m m (n)_{1,1/2} \quad \left\{ \begin{array}{cc} 1 & 1 \\ 1 & 1 \end{array} \left(\begin{array}{c} \bar{4} \\ 4_4 \end{array} \right) \quad \begin{array}{c} 2_{1/2} \\ n_{1/4,2} \end{array} \quad \begin{array}{c} 2 \\ n_{1/4,2} \end{array} \right\}$$

and from layer L1 or L3 as:

$$P m m (n)_{1/2,1} \quad \left\{ \begin{array}{cc} 1 & 1^* \\ 1 & 1 \end{array} \left(\begin{array}{c} \bar{4} \\ 4_4 \end{array} \right) \quad \begin{array}{c} 2 \\ n_{1/4,2} \end{array} \quad \begin{array}{c} 2_{1/2} \\ n_{1/4,2} \end{array} \right\}$$

The symmetry elements of layers L0 and L1 can be described diagrammatically as in Fig. 2, where the origin is at $0, 1/8, 0$ with reference to the true unit cell originating from four centred superposition unit cells. Layer L1 is derived from layer L0 (Fig. 2a) by a fourfold screw axis either through $x = 1/8$, $y = 1/8$ (Fig. 2b) or through $x = 5/8$, $y = 1/8$ (Fig. 2c). Superimposing the two possible layers L1 explains how a quarter of the superposition structure arises.

Since the intensities for $hk\zeta$ with h or k odd are extremely weak, the real positions of Cr_1 , Cr_2 , O_5 and O_6 cannot be evaluated from a Patterson calculation. Kutschabsky⁸ has described a method for determining atomic coordinates in one direction of a centrosymmetric structure when the coordinates in the other two directions are known, a system of linear equations being set up with the aid of non-observed structure factors. In a similar way, it was possible to determine the positions of Cr_1 , Cr_2 , O_5 and O_6 in the true structure. The atomic parameters of these atoms in layer L0 are x, y, z or $\frac{1}{2} + x, y, z$, the coordinates being referred to the unit cell dimensions $a = b = 13.74 \text{ \AA}$, $c = 29.03 \text{ \AA}$ and given in Table 4a (cf. Table 3).

* General equivalent positions of the different layers (origin as in Fig. 2, unit cell parameters a , b and c):

$$\begin{aligned} [L0] &= [\pm x, \pm y, z; 1/2 \pm x, 1/4 \pm y, \bar{z}] + (0, 0, 0; 0, 1/2, 0) \\ [L1] &= (0, \pm 1/4, 1/4) + [\pm y, \pm x, z; 1/4 \pm y, 1/2 \pm x, \bar{z}] + (0, 0, 0; 1/2, 0, 0) \\ [L2] &= (\pm 1/4, 1/4, 1/2) + [L0] \\ [L3] &= (1/4, \pm 1/4, 1/2) + [L1] \end{aligned}$$

Although L0, L2 and L1+L3 have centres of symmetry, the combination L0+L2, which gives rise to F_{hkc} with h odd, lacks a centre of symmetry. In spite of this, the contributions to F_{hkc} (h odd) from Cr₁, Cr₂, O₅, and O₆ are additive, since they all have the same phases, regardless of where the origin is placed.

The non-observed structure factors, F_{hkc} , for h odd can be written: $F(hkc) = \sum_j [F_{calj}(hkc) G_j] \approx 0$, where G_j is either +1 or -1 and j corresponds to the specific atoms included in the structure factor.

The position of Cr₂ was arbitrarily chosen to be 0.2144, $\frac{1}{8}$, 0.0458 and hence G_j for Cr₂ is +1. A set of eleven equations for non-observed structure factors was obtained using the atomic parameters given in Table 4a for Cr₁, Cr₂, O₅, and O₆ and giving Cr₁, O₅, and O₆ the weights G_j , respectively. As the structure factors are only approximately zero, more accurate values of G_j can be calculated by minimizing the sum $\sum_j [F_{calj}(hkc) G_j]^2$ of the squares of the structure factor equations. The solution giving the best fit was: $G_{Cr_1} = -0.9$, $G_{O_5} = 1.0$ and $G_{O_6} = -1.1$. According to the signs obtained for G_j , O₅ has the proposed position, while Cr₁ and O₆ are situated in $\frac{1}{2} + x, y, z$ with reference to the proposed positions. With the exception of atoms not contributing to the disorder, the atomic positions in the true structure are as given in Table 4b.

Table 4. Atomic parameters proposed for the atoms contributing to the disorder, 4a, and resulting atomic parameters for these atoms in the true structure of Zr(OH)₂CrO₄, 4b. The fractional coordinates are related to the cell $a = b = 13.74$ Å, $c = 29.03$ Å.

Atom	x	y	z	Atom	x'	y	z	Number of atoms in each layer
Cr ₁	0	$\frac{1}{8}$	0.9764	Cr ₁	$\frac{1}{2}$	$\frac{1}{8}$	0.9764	4
Cr ₂	0.2144	$\frac{1}{8}$	0.0458	Cr ₂	0.2144	$\frac{1}{8}$	0.0458	8
O ₅	0.1016	$\frac{1}{8}$	0.0380	O ₅	0.1016	$\frac{1}{8}$	0.0380	8
O ₆	0	0.0324	0.0089	O ₆	$\frac{1}{2}$	0.0324	0.0089	8

4a

4b

This result can also be obtained by considering the problem from a chemical point of view. Atoms O₅ and O₆ are coordinated to Cr₂ and Cr₁, respectively, and once the position of Cr₂ is chosen (or any of the other atoms), O₅ must be positioned so as to be at a reasonable distance from Cr₂. One of the two possibilities for O₆ implies an O₅-O₆ distance of 2.07 Å, which is much too short. The most probable positions of Cr₁ and O₆ can thus be deduced.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The most important distances and angles in the structure of Zr(OH)₂CrO₄ are given in Table 5. One unit cell contains 48 zirconium atoms, 16 of which

Table 5. Interatomic distances (in Å) and angles in $Zr(OH)_2CrO_4$.Within the ZrO_8 dodecahedron:

Zr_1-4O_3	2.246 ± 0.009	$O_3-Zr_1-O_3$	$73.3^\circ \pm 0.5$
Zr_1-4O_4	2.134 ± 0.010	$O_2-Zr_1-O_4$	$64.8^\circ \pm 0.3$
O_3-O_3	2.681 ± 0.020		
O_3-O_4	2.347 ± 0.013		
O_3-2O_4'	2.842 ± 0.011		
O_4-2O_4'	3.076 ± 0.015		

Within the ZrO_7 pentagonal bipyramid:

Zr_2-2O_1	2.076 ± 0.011	$O_1-Zr_2-O_1$	$166.2^\circ \pm 0.5$
Zr_2-2O_2	2.172 ± 0.010	$O_1-Zr_2-O_2$	$88.2^\circ \pm 0.1$
Zr_2-O_3	2.264 ± 0.018	$O_1-Zr_2-O_3$	$83.1^\circ \pm 0.3$
Zr_2-2O_4	2.124 ± 0.009	$O_1-Zr_2-O_4$	$95.4^\circ \pm 0.2$
		$O_3-Zr_2-O_3$	$74.6^\circ \pm 0.2$
O_1-2O_2	2.956 ± 0.010	$O_3-Zr_2-O_4$	$66.2^\circ \pm 0.4$
O_1-O_3	2.881 ± 0.016	$O_4-Zr_2-O_4$	$78.4^\circ \pm 0.5$
O_1-2O_4	3.105 ± 0.011		
O_2-O_3	2.688 ± 0.015		
O_3-O_4	2.347 ± 0.013		
O_4-O_4	2.684 ± 0.021		

Within the CrO_4 tetrahedra:

Cr_1-2O_2	1.760 ± 0.010	$O_2-Cr_1-O_2$	$99.2^\circ \pm 0.7$
Cr_1-2O_6	1.583 ± 0.023	$O_3-Cr_1-O_6$	$112.7^\circ \pm 0.5$
O_2-O_3	2.681 ± 0.020	$O_6-Cr_1-O_6$	$106.9^\circ \pm 1.6$
O_3-2O_6	2.785 ± 0.020		
O_6-O_6	2.543 ± 0.047		
Cr_2-2O_1	1.675 ± 0.010	$O_1-Cr_2-O_1$	$110.1^\circ \pm 0.7$
Cr_2-O_3	1.547 ± 0.017	$O_1-Cr_2-O_3$	$112.1^\circ \pm 0.4$
Cr_2-O_5	1.567 ± 0.027	$O_1-Cr_2-O_5$	$111.1^\circ \pm 0.5$
O_1-O_1	2.747 ± 0.021	$O_3-Cr_2-O_5$	$100.1^\circ \pm 0.9$
O_1-O_3	2.673 ± 0.018		
O_1-O_5	2.674 ± 0.024		
O_3-O_5	2.388 ± 0.028		

Other distances:

Zr_1-4Zr_2	3.646 ± 0.001	O_4-2O_5	2.859 ± 0.023
Zr_1-Cr_1	2.943 ± 0.007	O_4-O_6	2.950 ± 0.022
		O_5-2O_6	2.911 ± 0.026

(Zr_1) are eight-coordinated with the coordinated oxygen atoms situated at the vertices of regular dodecahedra. The 32 zirconium atoms denoted Zr_2 are each surrounded by a pentagonal bipyramidal arrangement of seven oxygen atoms. Since the determination of the structure is based on four crystallographically equivalent layers L0, L1, L2, and L3, the structure may be described as being built up from these layers. The atomic arrangement within the layers are as shown in Fig. 3 for layer L0. For the sake of clarity, some of the O_4 oxygen atoms have been omitted and the chromium atoms together with their coordinated oxygen atoms are depicted as tetrahedra.

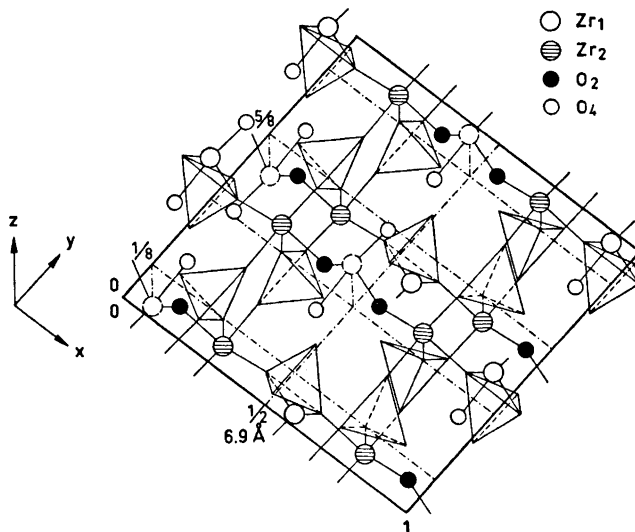


Fig. 3. The atomic arrangement in layer L0 ($z=0$). Tetrahedra with a face at $x=\frac{1}{2}$ and $x=\frac{3}{2}$ represent Cr_2 , 2O_1 , O_3 , O_5 chromate groups and those with an edge at $x=0$ and $x=\frac{1}{2}$ represent the chromate groups Cr_1 , 2O_2 , 2O_6 . The dotted Zr_1 atoms belong to layers L1 and L3.

In every layer, the three oxygen atoms (2O_1 , O_3) in the chromate group Cr_2 , 2O_1 , O_3 , O_5 are coordinated to three zirconium atoms (Zr_2), thus forming chains running parallel to the b axis in layers L0 and L2 and parallel to the a axis in layers L1 and L3. Due to the mirror plane in $x=\frac{1}{2}$ (L0), the chains are mirror images of each other, separated by the distance $a/2$. As can be seen from Fig. 3, in the case where two chromate tetrahedra, belonging to adjacent chains, point away from each other, the space between them is sufficient for a different chromate group, Cr_1 , 2O_2 , 2O_6 , to be positioned above or below a zirconium atom (Zr_1) in the ζ direction.

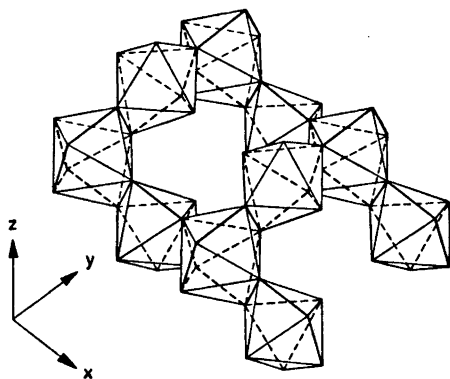


Fig. 4. Part of an infinite net with the composition $[\text{Zr}_3(\text{OH})_6\text{CrO}_4]_n^{4n+}$. Only the zirconium and oxygen atoms are included.

Along the a axis in layers L0, L2 and along the b axis in layers L1, L3, there are zig-zag chains built up of zirconium (Zr_1, Zr_2) and oxygen atoms (O_2). In, e.g., L0, the chains in $y = \frac{1}{8}$ and $y = \frac{5}{8}$ run below the layer while the chains in $y = \frac{3}{8}$ and $y = \frac{7}{8}$ run above the layer. When two layers, e.g. L0 and L1, are considered together, the Zr–O zig-zag chains from above layer L0 and below layer L1 intersect at the Zr_1 atoms and constitute, together with the O_4, Cr_1 and O_6 atoms, an infinite net in the xy plane with the composition $[\text{Zr}_3(\text{OH})_6\text{CrO}_4]^{4n+}$, (cf. Fig. 4). The resulting configuration of oxygen atoms around the two structurally non-equivalent zirconium atoms is thus a dodecahedron ($4\text{O}_2, 4\text{O}_4$) for Zr_1 and a pentagonal bipyramid ($2\text{O}_1, 2\text{O}_2, \text{O}_3, 2\text{O}_4$) for Zr_2 . Each $\text{Zr}-\text{O}_8$ dodecahedron shares edges with four $\text{Zr}-\text{O}_7$ pentagonal bipyramids and each pentagonal bipyramid shares two edges with dodecahedra. The condensed $\text{Zr}-\text{O}_8$ and $\text{Zr}-\text{O}_7$ polyhedra are illustrated and the lengths of their edges are given in Fig. 5, while the Zr–O distances within these polyhedra are given in Fig. 6.

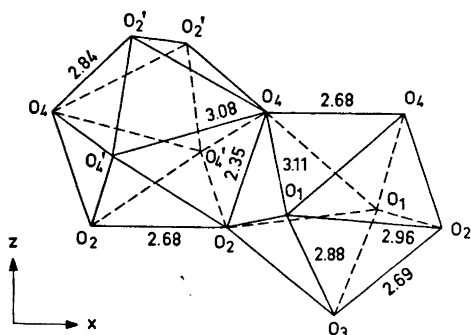


Fig. 5. The condensed $\text{Zr}-\text{O}_7$ and $\text{Zr}-\text{O}_8$ polyhedra.

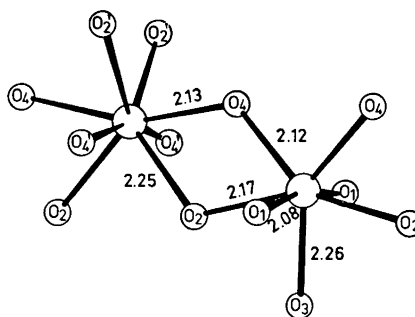


Fig. 6. Distances in Å between the two structurally non-equivalent zirconium atoms and their coordinated oxygen atoms.

The nets are related to each other by glide planes perpendicular to the c axis and are joined in the ζ direction by means of the chromate groups $\text{Cr}_2, 2\text{O}_1, \text{O}_3, \text{O}_5$ in the following manner. The two O_1 atoms are coordinated to two different Zr_2 atoms with the same z coordinate, while the O_3 atom is coordinated to a Zr_2 atom belonging to a net above or below, with the same x and y coordinates as O_3 .

The chromate groups $\text{Cr}_1, 2\text{O}_2, 2\text{O}_6$ are alternately situated above and below the $\text{Zr}-\text{O}_8$ dodecahedra and the two polyhedra share an edge since they have two oxygen atoms (O_2) in common. In the intersecting chains, which constitute the infinite nets, there are double oxygen bridges between the zirconium atoms Zr_1 and Zr_2 , and with respect to this feature, $\text{Zr}(\text{OH})_2\text{CrO}_4$ is structurally similar to $\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2^1$ and $\text{Hf}(\text{OH})_2\text{SO}_4 \cdot \text{H}_2\text{O}^9$.

The $\text{Zr}-\text{O}_8$ dodecahedra have the symmetry $D_{2d}-42m$, whereas the $\text{Zr}-\text{O}_7$ pentagonal bipyramids deviate somewhat from the ideal symmetry D_{5h} . The eight oxygen atoms surrounding Zr_1 form two equivalent trapezoids, $\text{O}_4-\text{O}_2-\text{O}_2-\text{O}_4$, which constitute a regular dodecahedron. Due to the sym-

metry these two trapezoids are mutually perpendicular. At the base of a trapezoid there are O_4 atoms at a distance of 2.13 Å from Zr_1 , whereas the Zr_1-O_2 distance is 2.25 Å. The same condition, *i.e.* that the distances between Zr and the oxygen atoms at the base of the trapezoids are shorter than the other Zr-O distances, is also true for $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ ¹⁰ and $Na_4Zr(C_2O_4)_4(H_2O)_3$.¹¹ In the case of $Zr(OH)_2CrO_4$ this fact is most probably explained by a weakening of the Zr-O₂ bond due to the coordination of O_2 to Cr_1 , as well as to Zr_1 and Zr_2 .

Although the distance between the double-bridged oxygen atoms O_2 and O_4 is comparatively short (2.35 Å), it is in good agreement with those in similar Me-(O)₂-Me arrangements, *e.g.* 2.33 Å in $Hf(OH)_2SO_4 \cdot H_2O$ ⁹ and 2.40 Å in $Al_2(OH)_2(H_2O)_{10}(SO_4)_2(H_2O)_2$.¹² All O_2 and O_4 atoms take part in the double oxygen bridges but the O_2 atoms in one of the two dodecahedral trapezoids constitute an edge which is shared by the tetrahedral chromate group $Cr_1, 2O_2, 2O_6$. Half of the O_2 atoms are therefore hydroxide oxygens and half are chromate oxygens, while all O_4 atoms may be considered to be hydroxide oxygens.

Distances and angles within the Zr-O₇ pentagonal bipyramid (*cf.* Fig. 6) are very nearly the same as the corresponding ones in $Hf(OH)_2SO_4 \cdot H_2O$, with the exception of the distance Zr_2-O_3 and the angle $O_1-Zr_2-O_1$. The distance Zr_2-O_3 is comparatively long (2.26 Å) because of the coordination of O_3 to a chromium atom, while in $Hf(OH)_2SO_4 \cdot H_2O$ the corresponding oxygen atom is not coordinated to a sulfur atom and the Hf-O distance is 2.18 Å. The two O_1 atoms in one bipyramid are coordinated to Cr_2 atoms, thus presumably causing the $O_1-Zr_2-O_1$ angle to be 166° instead of the ideal 180°. As is apparent from Table 5, the Cr-O distances as well as the O-O distances within the chromate groups lie within the normal ranges.

The author thanks Professor Georg Lundgren and Professor K. Boll-Dornberger, Berlin-Adlershof, for valuable discussions. Many thanks are also due to Dr. Susan Jagner for revising the English text of this paper.

The work was supported financially by the Swedish Natural Science Research Council (NFR, Contract No. 2318) and by Chalmers University of Technology, which supplied a grant to cover the costs of the computer work.

REFERENCES

1. Lundgren, G. *Arkiv Kemi* **13** (1958) 59.
2. Briggs, S. H. C. I. *Chem. Soc.* **1929** 242.
3. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., MacMillan, New York 1952, p. 717.
4. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1962, Vol. III.
5. Dornberger-Schiff, K. *Lehrang über OD-Strukturen*, Akademie-Verlag, Berlin 1966.
6. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1965, Vol. I.
7. Lindgren, O. *Computer Programmes in Use at the Department of Inorganic Chemistry, Göteborg. To be published.*
8. Kutschabsky, L. and Höhne, E. *Acta Cryst.* **19** (1965) 747.
9. Hansson, M. *Acta Chem. Scand.* **23** (1969) 3541.
10. McWhan, D. B. and Lundgren, G. *Inorg. Chem.* **5** (1966) 284.
11. Hoard, J. L. and Silvertson, J. V. *Inorg. Chem.* **2** (1963) 250.
12. Johansson, G. *Acta Chem. Scand.* **16** (1962) 403.

Received March 18, 1972.