The Crystal Structure of Chromium Trioxide

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Two suggestions have been made previously concerning the structure of chromium trioxide, CrO_3. Wooster and Wooster[1] gave the dimensions of the unit cell as $a = 8.50$ Å, $b = 4.73$ Å, and $c = 5.72$ Å, and showed that the observed density corresponded to a cell content of four formula units. The space group was assumed to be D_{2h}^{17}-$Ccmm$ with the chromium atoms in the positions $u, 0,1/4; \bar{u}, 0,1/4; \frac{1}{2}+u, \frac{1}{2},1/4; \frac{1}{2}-u, \frac{1}{2},1/4$. Because of the twinning of the crystals, u was difficult to determine but was assumed to be about 1/9. They also stated that the observed halvings appeared to require a structure consisting of tetrahedra of CrO_4 linked together in chains parallell to the c-axis. Further work on the structure was announced but has not yet been published. Bräkken[2] obtained a unit cell with approximately the same dimensions ($a = 8.46$, $b = 4.77$, and $c = 5.70$ Å) and suggested a structure, in which the chromium atoms are octahedrally surrounded by oxygen atoms. A structure which follows Bräkkens suggestions, is given in Strukturbericht (II), and in Wyckoff[3], and is also described by Wells[4,5] as a deformation of the simple ReO_3 structure. Bräkken also promised further work on the structure but no account of this work has been published.

DETERMINATION OF THE STRUCTURE

A determination of the cell dimensions from powder photographs (Table 1), taken with a 19 cm Bradley camera with Cr-K radiation ($\lambda = 2.2909$ Å) gave the following values:

$$a = 4.789 \pm 0.005 \text{ Å}, \qquad b = 8.557 \pm 0.005 \text{ Å}, \quad c = 5.743 \pm 0.005.$$

Weissenberg photographs were taken with the crystals sealed up in thin tubes of lithiumborate glass, using $Cr-K$, $Cu-K$, and $Mo-K$ radiation. Due to an abnormally rapid decrease with increasing glancing angle in the intensity of the reflexions, the
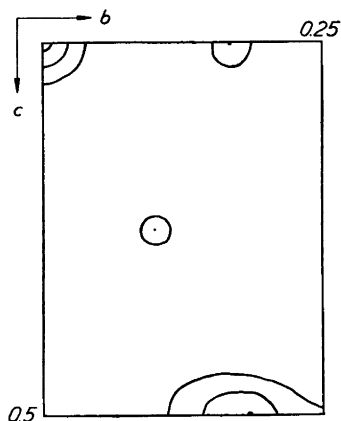
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Fig. 1. CrO_3. Patterson projection in (100).

photographs taken with Mo-K radiation showed only a few reflexions that were not registered in the Cu-K photographs.

Photographs registering $0kl$, $1kl$, $hk0$, $hk1$ were made. The following reflexions appeared:

hkl for $h + k = 2n$
$0kl$ for $k = 2n$
$hk0$ for $h + k = 2n$
$h0l$ for $h = 2n$ and $l = 2n$ (less certain than the other halvings)

Thus the following space groups must be taken into account:

D_{2h}^{17}, C_{2v}^{12}, C_{2v}^{16}

and also (if the last criterion is in reality $h0l$ for $h = 2n$):

D_2^5, D_{2h}^{19}, D_2^6, C_{2v}^{11}, C_{2v}^{14}.

A Patterson projection in the yz-plane (Fig. 1) can only be interpreted in one way, if the space group is D_{2h}^{17}, with the atoms in the following positions:

4 Cr in $4(c)$: 0_1 y_1 $1/4$ with $2\pi y \sim 150°$
4 O_1 in $4(b)$: 0_1 $\frac{1}{2}_1$ 0
8 O_2 in $8(g)$: x_1 y_1 $1/4$ with $2\pi y \sim 90°$

The values of $|F_{obs}|$ were calculated from the estimated values of I according to the formula: $|F_{obs}| = \sqrt{\dfrac{I}{PL}}$. The scattering factors of O^{2-} and Cr^{6+} have been used in the calculations of F_{calc}.

Table 1. Weissenberg photographs of chromium trioxide, CrO_3.

Comparison between $|F_{obs}|$ and $|F_{calc}|$. Cu$-K$ radiation and Cr$-K$ radiation. Intensities taken from Weissenbergh photographs with Cr$-K$ are marked with an asterisk.

hkl	$|F_{obs}|$	$|F_{calc}|$	hkl	$|F_{obs}|$	$|F_{calc}|$
002	90	89	110	45	74
004	96	84	130	25	38
006	45	44	150	53	49
008	44	54	170	22	27
			190	32	26
020	13	3			
021	40	63	200	68	56
022	21*	39	220	21	36
023	53	50	240	36	64
024	15	4	260	53	30
025	57	37	280	28	10
026	—	4	2 10 0	40	32
027	38	33			
			310	45	30
040	13	9	330	32	23
041	30	36	350	61	38
042	44	32	370	33	35
043	38	30	390	31	33
044	25	5			
045	35	24	400	31	42
046	38	23	420	—	15
			440	50	38
060	28	50	460	37	23
061	28	23			
062	77	61	510	18	25
063	30	20	530	—	10
064	35	33	550	39	48
065	25	16	600	30	46
066	44	45			
080	15	25	111	32	38
081	25	38	131	50	57
082	—	2	151	26	4
083	33	36	171	71	36
084	13	18	191	39	24
085	21	35			
			221	35	51
0 10 0	21	36	241	33	32
0 10 1	—	5	261	23	27
0 10 2	18	29	281	47	35

hkl	$\lvert F_{\text{obs}}\rvert$	$\lvert F_{\text{calc}}\rvert$	hkl	$\lvert F_{\text{obs}}\rvert$	$\lvert F_{\text{calc}}\rvert$
311	26	27	111	42*	38
331	55	43			
			112	47*	40
351	—	3	113	46*	30
371	42	33	114	70*	43
391	32	24	130	26*	38
			131	33*	57
421	45	34	132	25*	20
441	14	23	133	41*	46
461	12	17	134	24*	18
511	—	20			
531	26	34	150	36*	49
551	—	3	151	26*	4
			152	42*	66
110	50*	74	153	21*	4

The agreement between observed and calculated F-values was rather good, but some discrepancies appeared which could not be removed by a variation of the two y-parameters. However, in most cases the sign of the structure factor could be evaluated. A Fourier synthesis using all the observed $0kl$ reflexions except those very few ones with doubtful signs, showed the expected maxima for the Cr and O_1 atoms. However, the maximum corresponding to the two O_2 atoms, superimposed in the a-direction, was elongated and besides, a ghost-maximum of the same height as an oxygen peak appeared. It seemed that the suggested structure was in some way distorted, and that the symmetry must in fact be lower than D_{2h}^{17}. This was confirmed by the intensities of the reflexions $h00$, which did not correspond to an arrangement with only one parameter in the a-direction.

Then the symmetry of the space group D_2^5 was considered, but the same difficulties were met with as in D_{2h}^{17}. A survey of the other possible space groups showed that only in C_{2v}^{16} a suitable modification of the arrangement in D_{2h}^{17} could be obtained with the atoms in the following positions:

$(000; \tfrac{1}{2}\tfrac{1}{2}0)\ +$

4 Cr in $4(b) : x_1\ y_1,\ 1/4;\ x_1,\ \bar{z}_1,\ 3/4;$ $2\pi y_1 \sim 150°$

4 O_1 in $4(a) : x_2,\ 0,\ 0;\ x_2,\ 0,\ 0;$

4 O_2 in $4(b) : x_3,\ y_3,\ 1/4;\ x_3,\ \bar{y}_3,\ 3/4;$ $2\pi y_3 \sim 90°$

4 O_3 in $4(b) : x_4,\ y_4,\ 1/4;\ x_4,\ \bar{y}_4,\ 3/4;$ $2\pi y_4 \sim 90°$

Fig. 2. CrO_3. Projection of the electron density in (100).
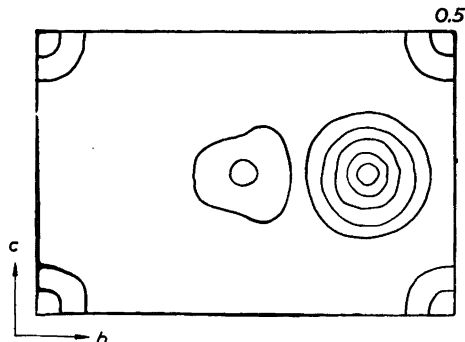
A variation of the y-parameters indicated that the agreement between observed and calculated F-values is satisfying for the following values:

$$2\pi y_1 = 145° \pm 1° \quad y_1 = 0.403 \pm 0.003$$
$$2\pi y_3 = 80° \pm 5° \quad y_3 = 0.222 \pm 0.013$$
$$2\pi y_4 = 100° \pm 5° \quad y_4 = 0.278 \pm 0.013$$

As will be seen from Table 1, there are still some discrepancies between observed and calculated F-values. As it was expected, that for this comparetively simple structure a better agreement between observed and calculated F-values should be possible to obtain, parameter values were also tried, which differed much more from the values obtained with Patterson and Fourier synthesis, than the probable errors in these values. However, this variation did not show improved agreement for any other values of the y-parameters, and indicated that the values we have chosen are in fact the best ones. As will be seen, the agreement is generally better for reflexions with high k-values ($k = 6$, 8, and 10) and therefor it seems reasonable to assume, that these discrepancies are at least partly due to some other factor than parameter errors.

A recalculation of the electron density projection showed that the ghost-maximum mentioned above was very much depressed, and the projection gave a parameter value for Cr agreeing with the value obtained through the trial and error process. Because of the partial super position of the O_2 and O_3 oxygen atoms, their parameters are difficult to determine from the projection. However, a comparison with the oxygen maximum, corresponding to the O_1-atom, and an estimation of the effect of the superposition shows, that the form of this elongated oxygen maximum agrees with that of a maximum composed of two partially superimposed maxima from oxygen atoms with the assumed parameters (Fig. 2).

The Weissenberg photographs, taken with [001] as rotation axis, were not as good as those with [100] as rotation axis. A lot of crystals have been

tried but the only really good one was the crystal that was used for the $0kl$ and $1kl$ photographs. In all the other cases, the crystals actually consisted of bundles of single individuals with slightly different orientation.

The Patterson projection in (001) showed only the Cr—Cr and the Cr—O_1 vectors clearly. The Cr—Cr vector agreed with the assumed Cr-position and further it could be deduced that $2\pi x_1 - 2\pi x_2 = 130°$. However, in that part of the projection where the Cr—O_2 and Cr—O_3 peaks were expected, only a very large region of about equal height was obtained. Obviously the x_3 and x_4 parameters must be deduced in another way.

With the symmetry of the space group C_{2v}^{16}—$C2cm$ one of the x-parameters can be arbitrarily chosen as 0. Therefor the x_3 parameter was taken as 0 and, to obtain reasonable O_2—O_3 distances, x_4 must be $\frac{1}{2}$. These values of x_3 and x_4 correspond to an O_2—O_3 distance of 2.44 Å. A study of previous works shows, that the shortest O—O distances in oxygen compounds of adjacent elements in the periodic system with tetrahedral or octahedral networks of oxygen atoms are 2.4—2.5 Å. (A surprisingly short value of 2.13 Å is reported [6] for O—O in V_2O_5 but as will be shown in another paper, this distance must be increased considerably [7].) As both the O_2 and O_3 atoms are linked to only one Cr-atom, it is reasonable to assume that the distances Cr—O_2 and Cr—O_3 are equal. Then the following values of the x-parameters are obtained.

$$2\pi x_1 = 70° \qquad x_1 = 0.194 \qquad 2\pi x_3 = 0 \qquad x_3 = 0$$
$$2\pi x_2 = 200° \qquad x_2 = 0.556 \qquad 2\pi x_4 = 180° \qquad x_4 = 0.5$$

A comparison of observed and calculated F-values for the $hk0$ reflexions (Table 2) showed that these x-values must be approximately correct, but it was also found that the intensities of these reflexions are almost entirely due to the Cr and O_1 atoms, and are thus determined by the difference $x_1 - x_2$, which is fixed from the Patterson projection (see above). The intensities of the reflexions permitted a variation of $x_3 - x_1$ with about $\pm 30°$. To prove the chosen x-parameters the projection of the electron density in the xy-plane was calculated. Because of the lack of a centre of symmetry in this projection, the formula for the electron density will be:

$$\sigma(xy) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hk)| \cdot \cos\{2\pi hx + 2\pi ky - a(hk)\},$$ which can be transformed into

$$\sigma(xy) = \sum_{0}^{\infty} \sum_{0}^{\infty} C(hk) \cdot \cos 2\pi hx \cos 2\pi ky + \sum_{0}^{\infty} \sum_{0}^{\infty} S(hk) \sin 2\pi hx \cos 2\pi ky \text{ with}$$

$$C(hk) = |F(hk)|_{obs} \frac{A}{|F(hk)|_{calc}} \text{ and } S(hk) = |F(hk)|_{obs} \frac{B}{|F(hk)|_{calc}}$$

Fig. 3. CrO_3. *Projection of the electron density in (001).*
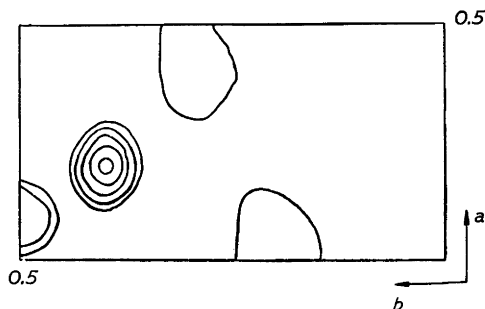
As will be seen from the projection, the suggested x-parameters are confirmed (Fig. 3). In Table 2, the intensities from the powder photographs are compared with those calculated. It is obvious, that the reflexions $0kl$ are enhanced compared with the reflexions with $h \neq 0$. However, if due consideration is given to this enhancement, the agreement between observed and calculated intensities is satisfying.

THE INTERATOMIC DISTANCES

The following interatomic distances are obtained.

$$Cr—2O_1 = 1.79 \pm 0.05 \text{ Å}$$
$$Cr—\ O_2 = 1.81 \pm 0.1 \ \ \text{Å}$$
$$Cr—\ O_3 = 1.81 \pm 0.1 \ \ \text{Å}$$

$$Cr—Cr = 3.32 \text{ Å}$$
$$O_1—O_1 = 2.87 \text{ Å}$$
$$O_1—O_2 = 2.79 \text{ Å}$$
$$O_1—O_3 = 3.20 \text{ Å}$$
$$O_2—O_3 = 2.44 \text{ Å}$$

The four bond angles O—Cr—O are:

$$O_1—Cr—O_1 = 107°$$
$$O_1—Cr—O_2 = 104°$$
$$O_1—Cr—O_3 = 126°$$
and $$O_2—Cr—O_3 = \ \ 85°$$

The angle $Cr—O_1—Cr$ is 136°.

The accuracy of the $Cr—O_1$ distance depends on the accuracy of the difference between the x_1 and x_2 parameters, all other errors ($\triangle y_1$ and the errors in the cell dimensions) being comparatively small. The maximal error in $x_1—x_2$ does not exceed 0.015 and thus the maximal error in $Cr—O_1$ is about $\pm$ 0.05 Å. As was mentioned above, the x_3 and x_4 parameters are determined with the assumption that the corresponding distances $Cr—O_2$ and $Cr—O_3$ are of equal length. If this assumption is accepted, then the maximal error in the $Cr—O_2$ and $Cr—O_3$ distances is about $\pm$ 0.1 Å, chiefly due to the inaccuracy of the y_3 and y_4 parameters ($= \pm$ 0.015).

Table 2. *Powder photograph of chromium trioxide, CrO₃. Comparison between observed and calculated sin² Θ values and intensities. Cr—K radiation, β-reflexions omitted.*

hkl	$\sin^2\Theta_{calc} \cdot 10^4$	$\sin^2\Theta_{obs} \cdot 10^4$	I_{calc}	I_{obs}
020	0716	0725	0.3	w
110	0751	0757	320	v.st.
021	1114	1117	155	v.st.
111	1149	1158	105	v.st.
002	1591	1593	100	st.
130	2183	2195	25	v.v.w.
200	2288 ⎫	2288	24 ⎫	st.
022	2307 ⎭		26 ⎭	
112	2342	2346	50	st.
131	2581	2594	86	st.
201	2685	—	0.0	—
040	2864	—	0.5	—
220	3004	—	15	—
041	3262	3272	14	m +
221	3402	3394	52	st.
132	3774	—	7	—
202	3879	3880	18	v.v.w.
023 ⎫	4296 ⎫	4303	20 ⎫	m(diff.)
113 ⎭	4331 ⎭		14 ⎭	
042	4455	4464	8	w.
222	4595	4595	43	w +
150	5047	5067	17	v.w.
240	5152	5162	39	v.w.
310	5327	5332	6	v.w.
151	5445	—	0.2	—
241	5550	5554	14	v.w.
311	5725 ⎫	5741	10 ⎫	w(diff.)
133	5763 ⎭		29 ⎭	
203	5868	—	0.0	—
004	6365	6356	25	m.
043	6444 ⎫	6447	6 ⎫	m.
060	6444 ⎭		9 ⎭	
223	6584	6551	26	w.
152	6638	6641	61	m.
242	6743 ⎫	6740	34 ⎫	w.
330	6759 ⎭		4 ⎭	
061	6842	6867	4	v.v.w.
312	6918	6911	40	m.
024	7081	7103	0.0	v.w.
114 ⎫	7116 ⎫	7146	27 ⎫	m(diff.)
331 ⎭	7157 ⎭		27 ⎭	
062	8035	8044	35	w.
134	8548	—	2	—

hkl	$\sin^2\Theta_{calc} \cdot 10^4$	$\sin^2\Theta_{obs} \cdot 10^4$	I_{calc}	I_{obs}
153⎫ 204⎭	8627⎫ 8653⎭	8636	0.4⎫ 18⎭	v.w.
243	8732	8743	19	v.v.w.

v.w. = very weak, w. = weak, m. = medium, st. = strong,
v.v.w. = very very weak, v.st. = very strong, diff. = diffuse

I_{calc} is calculated according to the formula $I_{calc} = F^2 \cdot m \cdot \dfrac{1 + \cos^2 2\Theta}{\sin^2\Theta\cos\Theta}$ where

m = multiplicity.

DISCUSSION OF THE STRUCTURE

As will be seen from Fig. 4, the oxygen atoms form distorted tetrahedra around the Cr-atoms. These tetrahedra are linked together to chains by sharing corners in the c-direction in agreement with Wooster and Wooster's previous suggestion [1]. This chain direction is often marked on the crystals by a heavy striation and the crystals break up very easily into small needles parallel to the streaks. This agrees very well with the fact that the bonds between the chains both in the a- and b-direction must be rather weak. It seems that no secondary Cr—O bonds can operate in these directions between atoms in different chains,

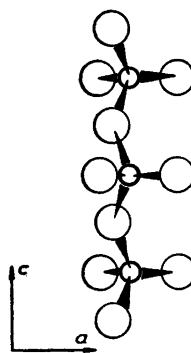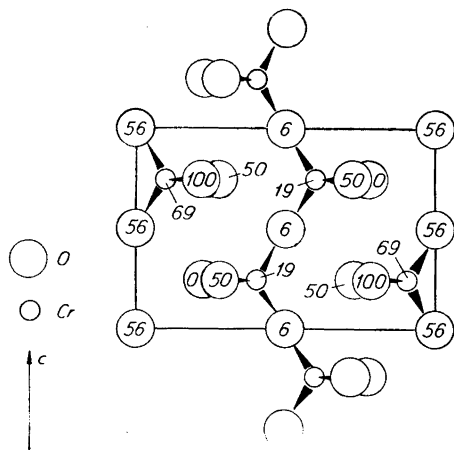

Fig. 4. CrO₃. Projection of the structure in (100). Small circles denote chromium atoms, large circles oxygen atoms. The figures denote the height of the atoms in percentages of a.

Fig. 5. CrO₃. Projection of a CrO₃-chain on (010).

because of the fact that these distances are all very long, the shortest being 3.10 Å. Thus only van der Waal's attraction between the CrO_3-chains holds the structure together in the a- and b-directions. In agreement with this assumption it was observed that the orientation in the a- and b-direction is often disturbed. (See above.) The low melting-point of the substance ($\sim 197°$ C) is also explained by this structure.

It would be expected that the O_2 and O_3 atoms which are bonded only to one chromium atom would lie closer to the Cr-atom than the O_1 atom which is bonded to two Cr-atoms. However, such a difference has not been observed, but as will be seen from the errors in the interatomic distances, it may exist but is probably < 0.15 Å.

COMPARISON WITH THE INTERATOMIC DISTANCES IN OTHER COMPOUNDS OF HEXAVALENT CHROMIUM

As will be seen from the table below, the Cr—O (resp. Cr—O,F) distances in the chromates, fluorochromates, and in CrO_2Cl_2 are shorter than in CrO_3.

Reference	Compound	Cr − O (Cr − O,F resp.)
Zachariasen and Ziegler [8]	K_2CrO_4	1.60
Clouse [9]	$CaCrO_4$	1.64
Miller [10]	Na_2CrO_4	1.60
Palmer [11]	CrO_2Cl_2	1.57
Ketelaar [12]	$KCrO_3F$	1.58
Brandt [13]	$CuCrO_4$	1.67

With the exception of the distances in $CuCrO_4$, the Cr—O distances are all very close to 1.60 Å.

These distances are thus 0.2 Å shorter than the Cr—O distances for the oxygen atoms which form one Cr-bond in CrO_3. As will be seen, this difference in length is somewhat bigger than the biggest possible difference between the Cr—O_2 and the Cr—O_3 distances (one Cr-bond) and the Cr—O_1 (two Cr-bonds) distances in CrO_3.

Pauling [14] has assigned a crystal radius of 0.52 Å to the Cr^{VI} ion and thus 1.92 Å would be expected for a six-coordinated Cr^{VI} ion, and $0.922 \cdot 1.92 = 1.77$ Å (Pauling [14] p. 346 and 368) for a four-coordinated hexavalent chromium ion. As will be seen, this value agrees very well with the observed distances in CrO_3. However, the bright colour of the substance indicates that there is probably an appreciable and maybe dominating amount of covalent character in the bonds.

SUMMARY

The crystal structure of CrO_3 has been determined. The atomic positions are:

Space group C_{2v}^{16}—$C2cm$

$(000; \frac{1}{2}\frac{1}{2}0) +$

4 Cr in $4(b)$: x_1, y_1, $1/4$; x_1, $\bar{z}_1$, $3/4$; $x_1 = 0.194$	$y_1 = 0.403 \pm 0.003$
4 O_1 in $4(a)$: x_2, 0, 0; x_2, 0, $\frac{1}{2}$; $x_2 = 0.556$	
4 O_3 in $4(b)$: x_3, y_3, $1/4$; x_3, $\bar{y}_3$, $3/4$; $x_3 = 0$	$y_3 = 0.222 \pm 0.013$
4 O_4 in $4(b)$: x_4, y_4, $1/4$; x_4, $\bar{y}_4$, $3/4$; $x_4 = 0.5$	$y_4 = 0.278 \pm 0.013$

The oxygen atoms form distorted tetrahedra around the chromium atoms and the Cr—O distances are 1.79—1.81 Å. The tetrahedra are linked together to chains in the c-direction by sharing corners. Between the CrO_3 chains probably only weak van der Waal's bonds are operating.

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