The Crystal Structure of KCr_3O_8

KARL-AXEL WILHELMI

Institute of Inorganic and Physical Chemistry, University of Stockholm,
Stockholm, Sweden

KCr_3O_8 crystallizes in the monoclinic system, space group No. 12 $C2/m$, with the unit-cell dimensions $a = 8.593$ Å, $b = 5.466$ Å, $c = 7.641$ Å, $\beta = 96°39'$ and two formula units in the unit cell. The structure is formed by CrO_6 octahedra and CrO_4 tetrahedra arranged in layers by sharing corners. The layers are held together by K ions. The bond distances are briefly compared with those found in some other chromium compounds. KCr_3O_8 is stoichiometric. The structure differs considerably in character from those of the non-stoichiometric vanadium and wolfram bronzes of similar composition.

In connection with work on the thermal decomposition of CrO_3, the compound KCr_3O_8 was obtained by melting CrO_3 with $K_2Cr_2O_7$[1]. The same procedure was described by Suchow et al.[2] for preparing compounds MCr_3O_8 (M = Li, Na, K, Rb). The X-ray study performed by these authors indicated that two of the six chromium atoms in the unit cell occupy positions which are not equivalent to the positions occupied by the other four. This suggested the possibility of the former chromium atoms being trivalent and the latter hexavalent.

EXPERIMENTAL

A complete elucidation of the crystal structure had to be based on single-crystal data. The previous investigators failed in preparing material for such techniques. A satisfactory procedure for obtaining good crystals was, however, to heat a mixture of composition $K_2Cr_2O_7 + 2\ CrO_3$ at 350°C at oxygen pressures up to 55 atm for 2 h.

The reagents used were potassium dichromate (analytical grade, Hopkins and Williams Ltd.) and chromium trioxide (Baker's analyzed, dried over P_2O_5). The materials were powdered, intimately mixed and transferred to a silica crucible. The crucible was then placed in an autoclave consisting of a thickwalled steel tube welded at one end. A lid, containing a small copper tube attached to an oxygen cylinder, was bolted to the open end, a silver gasket being placed between the tube and the lid. A commercial pressure-reducing valve was used to measure the pressure. The autoclave was flushed several

times with oxygen before heating it in an electrical oven. After 2 h the autoclave was allowed to cool slowly.

The excess potassium dichromate was extracted with water, leaving a residue of rod-shaped prisms. After drying in an oven at 120°C, the sample was dissolved in hot concentrated sulphuric acid and the chromium determined using Mohr's salt and standard permanganate solution after oxidation by peroxodisulphate in the presence of silver ions. The potassium was determined gravimetrically as potassium perchlorate in samples dissolved in hot 65 % perchloric acid [3]. The reproducibility of the analyses was found to be good and the results in fair agreement with the values calculated for KCr_3O_8.

Chromium, %		Potassium, %	
Found	Calcd	Found	Calcd
48.30 ± 0.05	48.29	12.0 ± 0.2	12.10

The density of the crystals was determined from the loss of weight in benzene (cf. Table 1).

A single crystal (ca. $0.1 \times 0.05 \times 0.03$ mm^3) was selected. Rotation photographs around [010] and [100] and Weissenberg photographs ($h0l$, $h1l$, $h2l$, $h3l$ and $0kl$) were taken with Cu-K radiation. The crystals proved to be monoclinic with the b-axis along the prism axis and with unit cell dimensions in good agreement with the values given by Suchow et al.[2]. More accurate values for the lattice parameters were calculated from a powder photograph obtained in a Guinier type focusing camera of 80 mm diameter (transmission position) with strictly monochromatized Cu$K\alpha_1$ radiation. Potassium chloride (Analar, British Drug Houses, $a = 6.2919$ Å at 20°C [4]) was added to the specimen as an internal standard (Table 2). The measurement of the reflexions was made on the very sharp high-angle edge of the lines, a procedure introduced by Österlöf [5].

The only reflexions systematically absent were hkl with $h+k$ odd, which is characteristic of the space groups No. 12 $C2/m$, No. 8 Cm and No. 5 $C2$. Since it was found possible to derive a plausible structure assuming the highest symmetry $C2/m$, the space groups Cm and $C2$ were not considered. A test for piezoelectricity accordingly did not show any effect. (Experiment carried out by J. Baecklund, University of Uppsala.) Suchow et al. on prolonged exposure obtained several weak extra powder lines, incompatible with the unit cell and symmetry found here. Such lines were not observed in the present investigation even after ample exposure nor did they show up in the Weissenberg photographs. In this connection it is worth mentioning that the density, 3.15, found by Suchow et al. differs considerably from the calculated value, 3.01, which might indicate that the preparation studied by them is not identical with the one used in the present investigation.

The crystallographic data obtained in this investigation are summarized in Table 1.

The Weissenberg reflexions were recorded photographically using multiple film techniques and their intensities were estimated visually. The F^2 values were then calculated using nomograms given by Lu [6]. No correction was applied for absorption. The maxima in the Fourier syntheses were located by an interpolation table given by Booth [7]. The analytical representation of atomic scattering factors given by Vand, Eiland and Pepinsky [8] for chromium, potassium and oxygen atoms were used when calculating the F values.

Table 1. Crystallographic data for KCr$_3$O$_8$.

Laue symmetry: 2/m.
Unit-cell dimensions: a = 8.593 ± 0.001 Å
                       b = 5.466 ± 0.001 Å
                       c = 7.641 ± 0.001 Å
                       β = 96°39′ ± 20′.

Absent spectra: hkl with $h+k \neq 2\,n$
Space group: No. 12 $C2/m$
Density: 3.02 (observed)
Density: 3.01 (calculated for K$_2$Cr$_6$O$_{16}$)

DERIVATION OF THE STRUCTURE

In $C2/m$ the following point positions exist:

$(0,0,0; \frac{1}{2},\frac{1}{2},0)+$
2(a): $(0,0,0)$; 2(b): $(0,\frac{1}{2},0)$; 2(c): $(0,0,\frac{1}{2})$; 2(d): $(0,\frac{1}{2},\frac{1}{2})$
4(e): $(\frac{1}{4},\frac{1}{4},0; \frac{1}{4},\frac{3}{4},0)$; 4($f$): $(\frac{1}{4},\frac{1}{4},\frac{1}{2}; \frac{1}{4},\frac{3}{4},\frac{1}{2})$
4(g): $(0,y,0; 0,\bar{y},0)$; 4(h): $(0,y,\frac{1}{2}; 0,\bar{y},\frac{1}{2})$; 4($i$): $(x,0,z; \bar{x},0,\bar{z})$
8(j): $(x,y,z; x,\bar{y},z; \bar{x},y,\bar{z}; \bar{x},\bar{y},\bar{z})$

The two potassium atoms may be assumed arbitrarily to occupy the twofold position 2(a).

In order to determine the positions of the six chromium atoms, the projection $P(upw)$ of the Patterson function was calculated (Fig. 1). All the chromium atoms cannot occupy two-fold positions as this would require maxima in this function only at $u = 0$ or $\frac{1}{2}$ and $w = 0$ or $\frac{1}{2}$. Actually $P(upw)$ in addition to such maxima (A and B of Fig. 1) also shows three further high maxima (C, D and E). Of the six chromium atoms, two must thus be accomodated in a two-fold position and four in a four-fold position. The position 2(b) is not probable since it would give the far too short K-Cr distance of $b/2 = 2.733$ Å. The positions 4(e)—4(h) would only require maxima at $u = 0$ or $\frac{1}{4}$ and $w = 0$ or $\frac{1}{2}$. Thus it is concluded that the six chromium atoms occupy 2(c) or 2(d) and 4(i). To decide between 2(c) and 2(d), the linear Harker section $P(0v\frac{1}{2})$

Table 2. Powder photograph of KCr$_3$O$_8$. CuKa_1 radiation. Reflexions systematically absent in space group $C2/m$ have been omitted. The intensities were calculated from the expression $\frac{p}{100}$ $(F_{\text{calc}})^2$ where p is the number of equivalent reflexions.

hkl	$10^5\sin^2\Theta$ calc	$10^5\sin^2\Theta$ obs	I_{calc}	I_{obs}	hkl	$10^5\sin^2\Theta$ calc	$10^5\sin^2\Theta$ obs	I_{calc}	I_{obs}
001	01 030	01 033	65	st	22$\bar{4}$	26 340	26 333	361	m
110	02 800	—	2	—	422	26 438	26 444	484	m
200	03 258	03 258	115	st	331	26 737	—	17	—
11$\bar{1}$	03 663	03 664	228	vvst	40$\bar{4}$	26 827	—	15	—
20$\bar{1}$	03 952	03 951	123	st	20$\bar{5}$	27 330	—	7	—

hkl				
111	03 998	04 000	189	st
002	04 120	—	0.2	—
201	04 624	04 628	220	vst
11$\bar{2}$	06 585	06 591	553	vvst
20$\bar{2}$	06 707	—	4	—
112	07 256	07 255	184	st
020	07 944	07 941	302	vst
202	08 049	08 057	18	vvw
021	08 974	08 990	1	vvw
003	09 270 ⎫	09 312	71 ⎫	vvst
310	09 316 ⎭		265 ⎭	
31$\bar{1}$	09 843	09 853	20	vw
311	10 850	10 864	65	vw
220	11 202	11 193	6	vvw
20$\bar{3}$	11 521 ⎫	11 567	7 ⎫	vw
11$\bar{3}$	11 567 ⎭		56 ⎭	
22$\bar{1}$	11 896	11 905	225	st
022	12 064	12 072	54	vw
31$\bar{2}$	12 429	12 433	42	vvw
221	12 567 ⎫	12 569	55 ⎫	w
113	12 574 ⎭		32 ⎭	
400	13 032	13 050	34	vvw
40$\bar{1}$	13 390	—	1	—
203	13 535	13 544	128	vw
312	14 443	—	4	—
22$\bar{2}$	14 651	14 651	120	vw
401	14 733	—	18	—
40$\bar{2}$	15 809	15 819	51	vw
222	15 993	15 998	169	w
004	16 480	16 488	77	vw
31$\bar{3}$	17 076	17 073	164	vw
023	17 214	—	4	—
20$\bar{4}$	18 395	18 430	286	m
402	18 493	18 508	300	w
11$\bar{4}$	18 609	—	8	—
130	18 688	—	1	—
22$\bar{3}$	19 465	19 481	87	vw
13$\bar{1}$	19 550	19 555	110	vw
131	19 886	19 873	93	vw
114	19 952	19 953	203	vw
313	20 096	—	18	—
40$\bar{3}$	20 288	—	27	—
420	20 975	20 979	7	vvw
204	21 080	—	4	—
42$\bar{1}$	21 334	—	10	—
223	21 479	—	1	—
13$\bar{2}$	22 472	22 465	347	m
51$\bar{1}$	22 539	—	1	—
421	22 677	—	38	—
132	23 144	23 153	163	vw
42$\bar{2}$	23 753	23 747	129	m
511	24 217	24 223	62	vw
403	24 315	—	3	—
024	24 424	24 421	76	vw
51$\bar{2}$	24 790	—	10	—
330	25 204	25 194	174	m
33$\bar{1}$	25 730 ⎫	25 740	27 ⎫	vw
005	25 750 ⎭		158 ⎭	

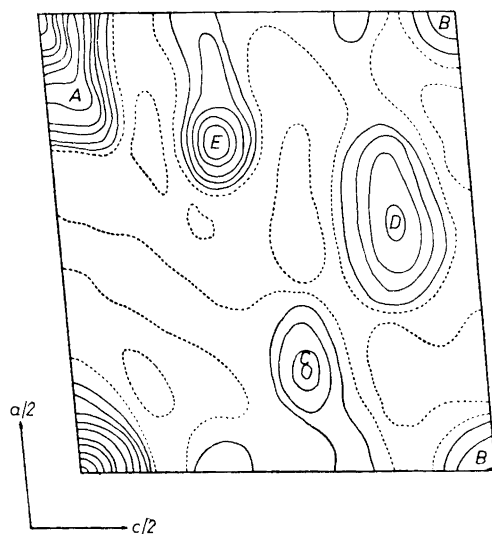| hkl				
13$\bar{3}$	27 455	—	28	—
11$\bar{5}$	27 711	—	16	—
314	27 810	27 824	297	vw
512	28 146	—	23	—
42$\bar{3}$	28 214	28 240	1	vw
33$\bar{2}$	28 317	—	7	—
133	28 461	—	37	—
224	29 024	—	2	—
51$\bar{3}$	29 101	—	7	—
600	29 321	—	74	—
60$\bar{1}$	29 344 ⎫	29 392	8 ⎫	vw
115	29 389 ⎭		100 ⎭	
332	30 331	—	1	—
205	30 686	—	6	—
601	31 358	—	18	—
60$\bar{2}$	31 428	31 430	50	vvw
040	31 775	31 762	366	w
404	32 196	—	8	—
423	32 259	32 259	148	vvw
31$\bar{5}$	32 550	32 563	73	vvw
041	32 805	32 810	15	vvw
33$\bar{3}$	32 964	32 968	103	vvw
025	33 694	33 676	27	vvw
513	34 135	34 121	69	vvw
13$\bar{4}$	34 497	—	1	—
42$\bar{4}$	34 771	—	—	—
240	35 033	35 032	39	vvw
22$\bar{5}$	35 274	—	31	—
40$\bar{5}$	35 426	—	15	—
602	35 455	—	1	—
51$\bar{4}$	35 472	35 481	421	vw
60$\bar{3}$	35 571	—	18	—
24$\bar{1}$	35 727	—	80	—
134	35 839	35 863	107	vw
042	35 895	—	1	—
333	35 984	35 977	10	vvw
241	36 399	36 412	148	vw
006	37 080	—	47	—
620	37 265	—	16	—
62$\bar{1}$	37 288	37 305	71	vvw
315	37 583	37 578	75	vvw
20$\bar{6}$	38 324	—	7	—
24$\bar{2}$	38 482	—	—	—
225	38 630	—	8	—
11$\bar{6}$	38 874	38 855	296	vw
621	39 302 ⎫	39 364	61 ⎫	w
62$\bar{2}$	39 371 ⎭		93 ⎭	
33$\bar{4}$	39 670	—	2	—
242	39 824	—	43	—
424	40 140	40 116	82	vvw
116	40 887	—	3	—
043	41 045	41 006	26	vvw
603	41 612	—	3	—
60$\bar{4}$	41 774	—	6	—
405	42 138	—	15	—
206	42 352	42 359	231	vw
24$\bar{3}$	43 296	—	1	—

Fig. 1. Projection of the Patterson function $P(upw)$. Dashed lines indicate negative values.

was calculated and found to have only one high maximum, *viz.* at $v = 0$. This locates these two chromium atoms at the point position 2(c) and thus we conclude the following arrangement of the metal atoms: 2 K in 2(a), 2 Cr$_I$ in 2(c) and 4 Cr$_{II}$ in 4(i).

The projections in $P(upw)$ of the interatomic vectors corresponding to the metal atoms are given in Table 3 (*cf.* Fig. 1). Reasonable Cr$_I$—Cr$_{II}$ distances are only obtained if it is assumed that the maximum C is caused by a K—Cr$_{II}$ vector $(\frac{1}{2}+x,z)$ and thus the x and z parameters for the Cr$_{II}$ atoms are 0.62 and 0.29, respectively. These values require further peaks in $P(upw)$ in perfect agreement with the observed data (*cf.* Table 3 and Fig. 1).

Table 3. Observed and calculated metal-metal peaks in $P(upw)$.

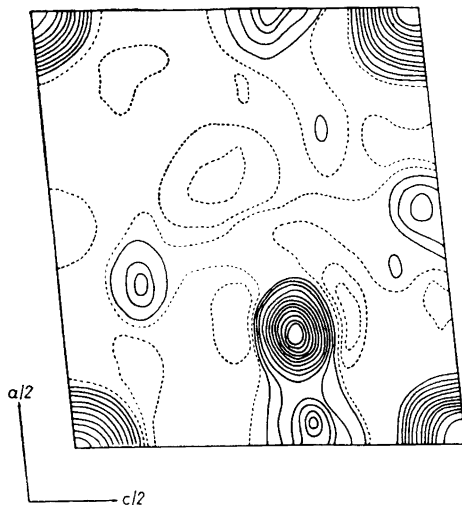| Vector groups		Weight	Maximum calc		Maximum obs		Max. in $(Pupw)$
			u	w	u	w	
K—K	$\frac{1}{2}$, 0	1	$\frac{1}{2}$	0	0.50	0.00	A
K—Cr₁	0, $\frac{1}{2}$	1	0	$\frac{1}{2}$	0.00	0.50	B
	$\frac{1}{2}$, $\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	0.50	0.50	B
K—Cr₂	$\pm(x,z)$; $\pm(\frac{1}{2}+x,z)$	1	0.12	0.28	0.12	0.28	C
Cr₁—Cr₁	$\frac{1}{2}$, 0	1	$\frac{1}{2}$	0	0.50	0.00	A
Cr₂—Cr₂	$\pm(2x,2z)$; $\pm(\frac{1}{2}+2x,2z)$	1	0.26	0.42	0.28	0.42	D
	$\frac{1}{2}$, 0	2	$\frac{1}{2}$	0	0.50	0	A
Cr₁—Cr₂	$\pm(\frac{1}{2}+x, \frac{1}{2}+z)$; $\pm(x,\frac{1}{2}+z)$	1	0.38	0.21	0.38	0.20	E

Fig. 2a. Electron density projection $\varrho_2(xpz)$. Dashed lines indicate negative values.

Since the b axis is rather short, the xz projection of the electron density should show little or no overlapping. At first this projection was calculated using only those F values whose signs could be derived from the potassium and chromium contributions. Three pronounced maxima were found giving the positions of the potassium (height 1 165) and chromium atoms (height
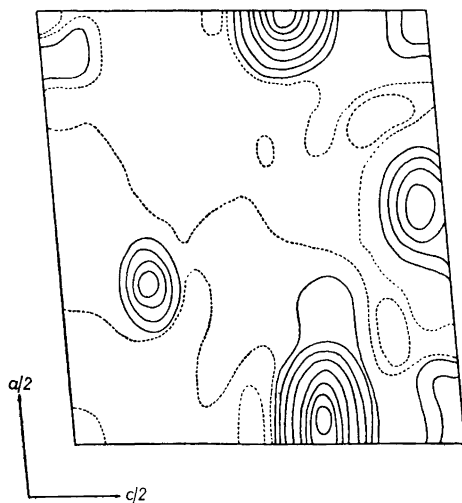

Fig. 2b. Electron density projection $\varrho_3(xpz)$ with the potassium and chromium atoms (Cr$_1$ and Cr$_2$) subtracted. Dashed lines indicate negative values.

1 230 and 1 350). (The heights are given on an arbitrary scale.) In addition there were five further maxima:

I. $x = 0$, $z = 0.33$ (Height 470);
II. $x = 0.25$, $z = 0.50$ (»   270);
III. $x = 0.18$, $z = 0.08$ (»   180);
IV. $x = 0.13$, $z = 0.47$ (»   180);
V. $x = 0.22$, $z = 0.25$ (»   130);

Of these maxima, I and II were assumed to correspond to oxygen atoms in the positions $8(j)$ and $4(i)$ in conformity with their relative heights.

The electron density projection obtained after including these twelve oxygen atoms in the calculations (Fig. 2a) showed no displacements of the positions of the potassium and chromium atoms. The oxygen maxima (I) and (II) had moved and were considerably sharpened and their relative heights were in better agreement with the K and Cr maxima. The maxima IV and V had vanished while III now appeared with the same height as II indicating maximum III to correspond to the remaining four oxygen atoms in a fourfold position $4(i)$. Including all the atoms in the calculations improved the agreement between observed and calculated F values but did not change the sign of any structure factor. Fig. 2b shows the appearance of the projection $\varrho(xpz)$ after subtracting the metal atom contributions. The parameter values thus derived are given in Table 4.

There was only one y parameter to be determined, viz. that of the O_{III} atom. In order to find it, the electron density projection $\varrho(pyz)$ was calculated (Fig. 3). Here the potassium and chromium atoms appear very distinctly. The value obtained for $z(Cr_{II})$ is 0.292, in almost perfect agreement with the value found above. The O_I atom is overlapped by Cr_I. The z parameter of the O_{II} atom is somewhat changed from the value obtained from $\varrho(xpz)$. The latter should, however, be more reliable since more F values were used in the calculation of this projection. Also the close vicinity to the high maximum in 0,0 might have contributed to this displacement.

The remaining maximum in $\varrho(pyz)$ is due to two superimposed O_{II} atoms and gives the parameter values $y = 0.250$ and $z = 0.317$, the latter being in fair agreement with the value obtained above.

A careful inspection of the Weissenberg photographs shows a very close agreement between all pairs of structure factors $F(h1l)$ and $F(h3l)$, which supports the reliability of the values for the y parameters.
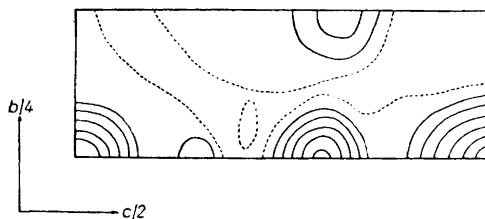

Fig. 3. Electron density projection $\varrho(pyz)$. Dashed lines indicate negative values.

Table 4. Atomic parameters for KCr_3O_8.

(Space-group No. 12 $C2/m$)

Atoms	Point position	x	y	z
2 K	2(a)	0	0	0
2 Cr_I	2(c)	0	0	$\frac{1}{2}$
4 Cr_{II}	4(i)	0.625	0	0.293
4 O_I	4(i)	0.225	0	0.551
4 O_{II}	4(i)	0.682	0	0.108
8 O_{III}	8(j)	0.024	0.250	0.315

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The atomic arrangement thus derived for KCr_3O_8 is summarized in Table 4

Using these parameters, the F values were calculated for the reflexions $h0l$, $h1l$ (identical with $h3l$) and $0kl$ and compared with the observed ones (Table 5). The F_{calc} values were modified by an isotropic temperature factor $B = 0.35$ Å^2 obtained experimentally for $F(h0l)$, $F(h1l)$ and $F(0kl)$. The "reliability" index R calculated according to Booth (1948) was found to be 0.14 for $h0l$, 0.12 for $h1l$ and 0.15 for $0kl$, when the reflexions with vanishingly small amplitudes were taken as having structure amplitudes equal to half the minimum value that it was found possible to observe at the corresponding angle. If only observed reflexions were considered, then the index values for the three groups of reflexions were 0.12, 0.12 and 0.15, respectively. The good agreement between observed and calculated structure factors and the low R values suggest that the coordinates proposed above are essentially correct. The accuracy of the parameters is estimated to be ± 0.002 for Cr_{II} and ± 0.004 for the oxygen atoms.

The structure of KCr_3O_8 is shown in Fig. 4 in which it can be seen that the chromium coordination is of two kinds. The first type (Cr_I) forms six bonds with oxygen atoms, *viz.* four with O_{III} atoms and two with O_I atoms. The arrangement of these oxygen atoms is very nearly perfectly octahedral. On the other hand, the coordination around the Cr_{II} atoms consists of a tetrahedron of four oxygen atoms, *viz.* one O_I atom, one O_{II} atom and two O_{III} atoms. The octahedra and tetrahedra are linked together by having corners in common forming continuous layers || the ab-plane. All the oxygen atoms except O_{II} belong simultaneously to one CrO_6 octahedron and one CrO_4 tetrahedron. The O_{II} atoms belong only to CrO_4 tetrahedra. The layers are held together by K ions which have ten nearest oxygen neighbours.

Interatomic distances and bond angles are given in Table 6. The accuracy of the Cr-O distance is estimated to be ± 0.04 Å, while the K-O and O-O distances may be in error by ± 0.10 Å and ± 0.10 Å respectively. The distances are of reasonable length throughout.

There is a significant difference between the Cr_I-O and Cr_{II}-O distances. The average of the former (1.97 Å) coincides with that recently found by Douglass[9] in $HCrO_2$ (average value of six Cr^{3+}-O distances 1.97 ± 0.04 Å).

Table 5. Comparison between calulated and observed structure factors from Weissenberg photographs of KCr$_3$O$_8$. CuKα-radiation. Intensities only observed as β-reflexions are marked with an asterisk.

hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
200	81	77	40$\bar5$	24	18	91$\bar2$	57	55
400	38	42	60$\bar5$	− 36	26	913	− 31	34
600	55	56	80$\bar5$	− 26	31	713	2	< 6
800	61	64	806	29	34	513	36	30
1 000	23	22	606	4	< 8	313	− 22	17
1 001	− 26	33	406	36	35	113	− 32	29
801	− 35	28	206	92	98	11$\bar3$	− 40	33
601	26	21	006	41	46	31$\bar3$	60	59
401	− 31	25	20$\bar6$	9	< 5	51$\bar3$	− 6	5
201	−118	115	40$\bar6$	33	25	71$\bar3$	− 38	36
001	− 64	59	60$\bar6$	54	57	91$\bar3$	− 5	< 8
20$\bar1$	83	78	80$\bar6$	15	19	914	13	18
40$\bar1$	− 9	15	607	3	< 9	714	—	< 7
60$\bar1$	− 20	25	407	− 36	41	514	22	16
80$\bar1$	− 6	13	207	− 11	10	314	77	69
1 00$\bar1$	24	20	007	35	31	114	56	59
1 002	35	30	20$\bar7$	3	< 6	11$\bar4$	12	17
802	8	< 7	40$\bar7$	− 10	< 7	31$\bar4$	4	< 4
602	4	< 5	60$\bar7$	− 9	13	51$\bar4$	90	86
402	116	123	80$\bar7$	26	20	71$\bar4$	28	23
202	32	33	408	19	24	91$\bar4$	—	< 9
002	− 7	< 1	208	− 4	< 8	715	6	< 8
20$\bar2$	− 16	9	008	− 5	< 7	515	− 19	15
40$\bar2$	48	53	20$\bar8$	33	35	315	− 42	41
60$\bar2$	44	49	40$\bar8$	25	32	115	44	41
80$\bar2$	− 14	16	60$\bar8$	—	< 9	11$\bar5$	14	14
1 00$\bar2$	—	< 9	209	13	13	31$\bar5$	− 41	36
1 003	19	20	009	− 4	11	51$\bar5$	− 23	23
803	19	11	20$\bar9$	− 25	26	71$\bar5$	23	17
603	− 14	12	40$\bar9$	14	11	91$\bar5$	5	< 10
403	− 13	14	110	8	< 4	716	31	33
203	79	86	310	115	117	516	44	45
003	59	64	510	74	74	316	12	8
20$\bar3$	9	8	710	—	< 5	116	− 8	3
40$\bar3$	− 36	41	910	13	< 7	11$\bar6$	75	72
60$\bar3$	26	27	911	14	12	31$\bar6$	45	41
80$\bar3$	26	28	711	− 10	12	51$\bar6$	10	< 6
1 00$\bar3$	− 27	31	511	− 65	64	71$\bar6$	6	< 8
804	32	30	311	38	34	91$\bar6$	24	23
604	32	31	111	71	72	517	14	< 9
404	18	14	11$\bar1$	− 86	80	317	18	14
204	− 15	14	31$\bar1$	− 28	27	117	− 18	14
004	60	68	51$\bar1$	—	< 4	11$\bar7$	− 30	29
20$\bar4$	114	110	71$\bar1$	31	29	31$\bar7$	11	< 7
40$\bar4$	23	13	91$\bar1$	− 16	19	51$\bar7$	17	12
60$\bar4$	13	< 5	912	27	24	71$\bar7$	− 9	< 9
80$\bar4$	49	43	712	66	64	518	− 6	< 11
1 00$\bar4$	43	36	512	21	18	318	32	33
805	22	27	312	− 3	< 3	118	39	37
605	1	< 7	112	86	80	11$\bar8$	22	25
405	17	15	11$\bar2$	127	127	31$\bar8$	—	< 8
205	− 18	20	31$\bar2$	30	29	51$\bar8$	19	18
005	− 84	92	51$\bar2$	13	< 4	71$\bar8$	39	~ 36*
20$\bar5$	− 19	15	71$\bar2$	24	18	319	− 20	22

hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
119	— 5	6	022	49	58	045	— 50	39
11$\bar{9}$	17	19	042	— 3	< 5	065	— 20	15
31$\bar{9}$	2	< 10	062	14	< 10	026	13	5
51$\bar{9}$	— 22	~ 16*	023	— 17	9	046	27	32
020	128	110	043	29	29	027	25	26
040	121	114	063	1	< 10	047	24	23
060	47	41	024	55	50	028	17	10
021	— 11	17	044	39	32	048	— 2	~ 10*
041	— 26	28	064	28	23	029	— 12	16
061	— 5	< 10	025	— 35	33			

The Cr_{II}-O distances of 1.55—1.65 Å agree well with values around 1.60 Å reported for the $Cr^{6+}O_4$ groups in K_2CrO_4 [10], $CaCrO_4$ [11], Na_2CrO_4 [12] and $CuCrO_4$ [13]. Thus the coordination numbers as well as the interatomic distances indicate that the Cr_I atoms are essentially trivalent and the Cr_{II} atoms hexavalent. While the unsymmetrical Cr_I^{3+}—O—Cr_{II}^{6+} bridges of KCr_3O_8 thus differ completely from the symmetrical bridges Cr^{6+}—O—Cr^{6+} in CrO_3 [14] and $(NH_4)_2Cr_2O_7$ [15] with Cr-O distances of 1.8_0 and 1.9_0 Å, respectively, the
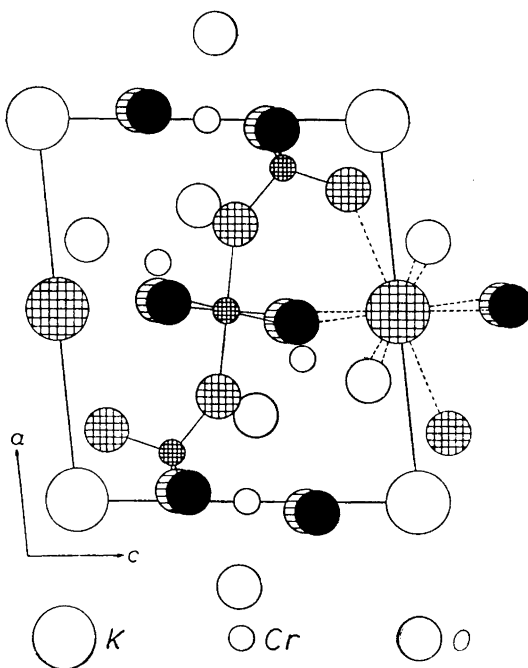
Fig. 4. The unit cell content of KCr_3O_8 projected on (010). Atoms at $y = 0$ open circles, atoms at $y = \frac{1}{4}$ shaded horizontally, atoms at $y = \frac{1}{2}$ shaded horizontally and vertically and atoms at $y = \frac{3}{4}$ black. Bonds between the atoms in a $Cr_3O_8^-$ unit with the chromium atoms at $y = \frac{1}{2}$ are shown with lines. The broken lines represent the K—O bonds.

Table 6. Interatomic distances and bond angles in KCr_3O_8.

Cr_I	$- 2\ O_I$	1.93 Å	K	$- 4\ O_{II}$	3.21 Å
Cr_I	$- 4\ O_{III}$	1.99 Å	O_I	$- 2\ O_{II}$	2.89 Å
Cr_{II}	$- O_I$	1.65 Å	O_I	$- O_{II}$	2.64 Å
Cr_{II}	$- O_{II}$	1.55 Å	O_I	$- 2\ O_{III}$	2.66 Å, 2.72 Å
Cr_{II}	$- 2\ O_{III}$	1.64 Å	O_{II}	$- 2\ O_{III}$	2.59 Å
K	$- 4\ O_{III}$	2.80 Å	O_{III}	$- 2\ O_{III}$	2.73 Å, 2.90 Å
K	$- 2\ O_{II}$	2.94 Å	Cr_I	$- Cr_{II}$	3.39 Å, 3.42 Å

Cr_I	$- O_{III} - Cr_{II}$	138°	$2(O_{III} - Cr_I - O_{III})$	94°
Cr_I	$- O_I - Cr_{II}$	146°	$2(O_I - Cr_{II} - O_{III})$	108°
O_I	$- Cr_I - O_I$	180°	$O_I - Cr_{II} - O_{II}$	111°
$2(O_{III} - Cr_I - O_{III})$		86°	$O_{II} - Cr_{II} - O_{III}$	109°

bond angles Cr—O—Cr have similar values in all three substances, *viz.* 138° and 146° (KCr_3O_8), 136° (CrO_3) and 115° (($NH_4)_2Cr_2O_7$). The O_2 atom which belongs to one Cr atom only (Cr^{6+}) is in slightly closer contact with the latter than are the shared O atoms.

Wadsley recently determined the structures of two vanadium compounds with formulae similar to that of KCr_3O_8, *viz.* the so-called vanadium bronzes $Na_{2-x}V_6O_{15}$ [16] and $Li_{1+x}V_3O_8$ [17]. These phases are intensely coloured, chemically very inert and electric semiconductors as are also the earlier well known wolfram bronzes [18-20]. The present investigation has revealed a fundamental difference in structural character between KCr_3O_8 and these compounds. In the bronzes, all vanadium or wolfram atoms occupy positions which are energetically equivalent or probably nearly so. This is likely to facilitate an electron transfer between the metal atoms which is reflected in the considerable electric conductivity of these compounds. In KCr_3O_8, on the other hand, the chromium atoms of fourfold and sixfold coordination must differ very much in energy and hence electron transport between these atoms must be considerably hindered. This view is supported by the recent observation by Wadsley (private communication) that KCr_3O_8 has a very high electrical resistance. The black colour of KCr_3O_8 might possibly indicate a very slight electron transfer between the Cr^{3+} and Cr^{6+} atoms but it might also be caused by the character of the Cr—O bonds. Accurate determinations of Cr—O distances in other chromates would be of great interest. Determinations of the structures of $Rb_2Cr_2O_7$ ($C2/c$ and $P2_1/n$) are in progress and will be published elsewhere. It is planned to reinvestigate the crystal structure of $(NH_4)_2Cr_3O_{10}$ [21].

A comparison between the structures of KCr_3O_8 and $KAl(SO_4)_2$ [22] reveals a certain structural relationship between these compounds, a fact which was first suggested by Professor J. Zemann (Göttingen).

REFERENCES

1. Wilhelmi, K.-A. *Naturwiss.* **44** (1957) 580.
2. Suchow, L., Fankuchen, I. and Ward, R. *J. Am. Chem. Soc.* **74** (1952) 1678.
3. Charlot, G. and Bézier, D. *Quantitative Inorganic Analysis.* Methuen & Co. Ltd., Frome and London 1957.
4. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
5. Österlöf, J. *To be published. Cf.* also Westman, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1587.
6. Lu, C. S. *Rev. Sci. Instr.* **14** (1943) 331.
7. Booth, A. D. *Fourier Technique in X-ray Organic Structure Analysis.* Cambridge 1948.
8. Vand, V., Eiland, P. E. and Pepinsky, R. *Acta Cryst.* **10** (1957) 303.
9. Douglass, R. M. *Acta Cryst.* **10** (1957) 423.
10. Zachariasen, W. H. and Ziegler, G. E. *Z. Krist.* **80** (1931) 164.
11. Clouse, J. H. *Z. Krist.* **83** (1932) 161.
12. Miller, J. J. *Z. Krist.* **94** (1936) 131.
13. Brandt, K. *Arkiv Kemi, Mineral. Geol.* **A17** (1943) No. 15.
14. Byström, A. and Wilhelmi, K.-A. *Acta Chem. Scand.* **4** (1950) 1131.
15. Byström, A. and Wilhelmi, K.-A. *Acta Chem. Scand.* **5** (1951) 1003.
16. Wadsley, A. D. *Acta Cryst.* **8** (1955) 695.
17. Wadsley, A. D. *Acta Cryst.* **10** (1957) 261.
18. Hägg, G. *Z. physik. Chem.* **B29** (1935) 192.
19. Magnéli, A and Blomberg, B. *Acta Chem. Scand.* **5** (1951) 372.
20. Hägg, G. and Magnéli, A. *Revs Pure and Appl. Chem.* (Australia) **4** (1954) 235.
21. Seiter, E. D. *Diss.* Rutgers Univ., New Brunswick, New Jersey 1956.
22. Vegard, L. and Maurstad, A. *Skrifter Norske Videnskaps-Akad. Oslo. I. Mat. Natur. Klasse* (1928) No. 7.