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The Crystal Structure of Cr_5O_{12}

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Cr_5O_{12}, synthesized at high pressure, crystallizes in the orthorhombic system, space group *Pbcn* (No. 60), with the unit-cell dimensions $a = 12.044$ Å, $b = 8.212$ Å and $c = 8.177$ Å and four formula units in the unit cell. The structure contains pairs of CrO_6 octahedra joined by sharing edges. By sharing corners the pairs of octahedra are linked with CrO_4 tetrahedra to form a threedimensional framework.

The Cr_5O_{12} structure can alternatively be described as a distorted cubic close-packed array of oxygen atoms with all the metal atoms in the interstices. There are 48 oxygen atoms in the unit cell with 12 chromium atoms in tetrahedral and 8 chromium atoms in octahedral holes. The coordination numbers as well as the interatomic distances indicate that the former chromium atoms are hexavalent and that the latter are trivalent.

The bond distances are briefly compared with those found in some other chromium compounds.

The system Cr—O has been the subject of many investigations. A large number of oxides have been claimed to exist with compositions between CrO_3 and CrO_2, often with only slightly different formulae. In recent years the thermal decomposition of CrO_3 at low oxygen pressures have been studied carefully by means of X-ray methods by Schwartz, Fankuchen and Ward,[1] Glemser, Hauschild and Trüpel [2] and Kubota.[3] Their results are not consistent throughout, but it can be concluded that at least four oxides are formed when CrO_3 is decomposed: Cr_3O_8 (= $CrO_{2.67}$), Cr_2O_5 (= $CrO_{2.50}$), CrO_2 and Cr_2O_3. So far no crystal structure determinations of Cr_3O_8 and Cr_2O_5 have been published and the formulae of these two oxides must be regarded as rather uncertain. Pure ferromagnetic CrO_2 with the rutile-type crystal structure has been obtained from thermal decomposition of CrO_3 by various authors.[4,5] By properly controlling the syntheses, single crystals of sufficient size for physical studies have been prepared.[6] The Cr_2O_3 phase has the corundum structure.[7]

By using oxygen pressure up to 1 kbar in the temperature range 200—400°C, the existence of each of these oxides has been verified by the present author.

A further examination of the chromium-oxygen system at higher pressures has now been made.[8] This paper gives the results of the determination of the crystal structure of Cr_5O_{12}, one of the decomposition products of CrO_3 at oxygen pressures in the range 1—3 kbar.

EXPERIMENTAL

The starting material in this investigation was chromium trioxide (Baker's analyzed) dried over phosphorus pentoxide.

The samples were prepared by heating CrO_3 in platinum or gold capsules, which had been cleaned with boiling concentrated nitric acid and dried in air at 250°C. To form a capsule the end of a 0.1 mm thick tube (3 × 40 mm) was squeezed shut in a vice and welded with a micro-welder while held in the vice. The charge (*ca.* 100 mg) was then inserted and the tube was welded shut at the top. No decomposition of the CrO_3 during the welding operation occurred because the large heat capacity of the vice effectively reduced the temperature rise of the charge. The welded capsule was then placed within the 5 mm bore of a Stellite 25 vessel, provided with a water cooled cap. The pressure, outside the capsule, was generated by a simple hydraulic water intensifier. The seal was made against a conical seat at the top of the vessel by the pressure induced by the torque applied to the cap on the cone-shaped end of the high-pressure water line. The vessel was then heated while kept at constant pressure, the pressure was controlled with a needle valve and a high-pressure Bourdon gauge.

In these experiments the oxygen needed for stabilization of the new phase was supplied simply by the decomposition of CrO_3. During the heating period (3—7 days) the internal oxygen pressure over the partly decomposed sample in the flexible thin-walled capsules was automatically controlled by the external pressure.

The autoclave was heated in a vertical Kanthal-wound tube furnace, the temperature of which was kept constant by a Hartmann and Braun regulator. The temperature was measured with a calibrated chromel-alumel thermocouple, inserted into a boring at the bottom of the autoclave and a potentiometer bridge (Wheelco Instruments Co.) at the beginning and the end of each heat treatment. The temperature was continuously registered by a recorder.

The short-time variations of the temperature of the samples were negligible but a long-time drift of the temperature was sometimes observed. Tne total variations were, however, always within ±5°C.

The new oxide (CrO_x) was obtained in a pure state in the temperature range 240—260°C and in the pressure range 2—3 kbar. It must be emphasized that the temperature and pressure ranges indicated do not necessarily represent the true stability region of the new oxide. This is difficult to establish because of an observed disposition of precursors to CrO_x to remain in a metastable state together with CrO_x, specially at lower temperatures and pressures.

In some experiments water was added to the CrO_3 charge which seemed to favour the formation of larger crystals, the largest of which had dimensions of 0.2 mm.

Table 1. Crystallographic data for Cr_5O_{12}.

Laue symmetry: *mmm*
Unit-cell dimensions: $a = 12.044$ Å
$b = 8.212$ Å
$c = 8.177$ Å
$V = 808.7$ Å^3

Absent reflections: $0kl$ with $k \neq 2n$, $h0l$ with $l \neq 2n$ and $hk0$ with $h+k \neq 2n$
Space group: No. 60 *Pbcn*
Density: 3.68 g cm^{-3} (observed)
3.67 g cm^{-3} (calculated for $Cr_{20}O_{48}$)

Table 2. Powder photograph of Cr_5O_{12}. $CuK\alpha_1$ radiation. Reflections systematically absent in space group *Pbcn* have been omitted. The intensities were calculated from the expression $\frac{P}{1000}(F_c)^2$ where P is the number of equivalent reflections.

h k l	$10^5 \sin^2\Theta$ calc	$10^5 \sin^2\Theta$ obs	I_{calc}	I_{obs}
1 1 0	1 291	—	0	—
2 0 0	1 639	1 645	10	vw
1 1 1	2 180	2 183	29	vw
2 1 1	3 409	—	13	—
0 2 0	3 525	3 533	25	vw
0 0 2	3 555	3 559	19	vw
1 0 2	3 965	3 971	10	vvw
0 2 1	4 414	4 415	53	w
3 1 0	4 568	4 563	132	m
1 2 1	4 824	4 817	156	st
1 1 2	4 846	4 841	113	vw
2 2 0	5 164	—	31	—
2 0 2	5 194	5 193	94	w
3 1 1	5 457	5 472	33	vw
2 2 1	6 053	6 058	40	vvw
2 1 2	6 075	—	3	—
4 0 0	6 555	—	6	—
0 2 2	7 080	—	3	—
3 0 2	7 242	7 249	92	vw
1 2 2	7 490	7 491	52	vw
3 2 1	8 101	—	2	—
3 1 2	8 123	—	18	—
4 1 1	8 325	8 325	238	m
1 3 0	8 342	—	1	—
2 2 2	8 719	—	0	—
1 3 1	9 231	9 231	124	w
1 1 3	9 289	9 282	198	w
4 2 0	10 080	—	11	—
4 0 2	10 110	10 116	53	vw
2 3 1	10 460	10 454	259	w
2 1 3	10 518	10 523	119	vw
3 2 2	10 767	10 762	89	vw
4 2 1	10 969	—	16	—
4 1 2	10 991	—	2	—
5 1 0	11 124	—	0	—
0 2 3	11 523	—	0	—
3 3 0	11 619	—	22	—
1 3 2	11 897	—	13	—
1 2 3	11 933	—	60	—
5 1 1	12 013	12 009	108	vw
3 3 1	12 509	12 516	36	vvw
3 1 3	12 550	—	0	—
2 3 2	13 126	—	2	—
2 2 3	13 162	13 169	44	vvw
4 2 2	13 635	13 606	14	vvw
5 0 2	13 798	—	9	—
0 4 0	14 101	14 110	58	vvw
0 0 4	14 219	14 180	53	vvw
1 0 4	14 629	—	1	—
5 2 1	14 657	—	42	—
5 1 2	14 679	14 677	67	vw
6 0 0	14 749	—	50	—

The CrO_x phase forms black non-ferromagnetic well developed octahedral crystals, readily distinguishable from the other chromium oxides. The crystals are stable in air, insoluble in water but slightly soluble in hot concentrated sulphuric acid.

Rotation photographs around [010] and [001] and integrated Weissenberg photographs (hkl: $k = 0-5$, $l = 0-5$) were taken with Cu—K radiation using the multiple film technique. The crystals proved to be orthorhombic and the crystal data are summarized in Table 1. The unit-cell dimensions were derived from a powder photograph obtained in a Guinier type focusing camera of 80 mm diameter (transmission position) with monochromatized $CuK\alpha_1$ radiation. Potassium chloride (Analar, British Drug Houses, $a = 6.2919$ Å at 20°C, Hambling [9]) was added to the specimen as an internal standard (Table 2).

The intensities of the Weissenberg reflections were estimated visually with a standard scale. The scattering curves for Cr^{6+} and Cr^{3+} were derived from Thomas and Umeda's table,[10] that of O^{2-} from a paper by Suzuki.[11] No corrections for absorption or extinction were made.

The density of the crystals was determined from the loss of weight in benzene. The observed value of 3.68 g cm^{-3} and the cell dimensions correspond to a unit-cell content of $\sim$1800 atomic weight units.

The density of the anion packing may be expressed in terms of the quotient V/n_o (V = unit cell volume in Å^3 and n_o = the number of oxygen atoms in the unit cell). This quantity has the value of 19.6 for CrO_3 and 14.5 for CrO_2. It thus seemed likely that the number of oxygen atoms per unit cell in this case lies in the range $40 > n_o > 56$.

It seemed reasonable to assume that the oxygen-chromium ratio was between the limits $3 > O/Cr > 2$ as the decomposition of CrO_3 to CrO_2 takes place at a temperature just about 50°C higher than the one used in the present experiments. Thus the number of the chromium atoms should be in the range 14—28 with a most probable value of 20, as in the space group No. 60 only fourfold and eightfold point positions exist (see below).

The calculated density for a cell content of $Cr_{20}O_{48}$ is in excellent agreement with the observed value (*cf.* Table 1) and the structure determination was started with the assumption that the unit cell contains four formula units Cr_5O_{12}.

DETERMINATION OF THE STRUCTURE

In *Pbcn* the following point positions exist:

$4(a)$: $(0,0,0;\ 0,0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$
$4(b)$: $(0,\tfrac{1}{2},0;\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,0;\ \tfrac{1}{2},0,\tfrac{1}{2})$
$4(c)$: $\pm(0,y,\tfrac{1}{4};\ \tfrac{1}{2},\tfrac{1}{2}+y,\tfrac{1}{4})$
$8(d)$: $\pm(x,y,z;\ \tfrac{1}{2}-x,\tfrac{1}{2}-y,\tfrac{1}{2}+z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\bar{z};\ \bar{x},y,\tfrac{1}{2}-z)$

In order to find the positions of the chromium atoms the Patterson projections $P(upw)$ and $P(uvp)$, were calculated. As the projections suffered heavily from overlap of peaks, the Harker sections $P(\tfrac{1}{2}vw)$, $P(u0w)$, $P(uv\tfrac{1}{2})$, and $P(u\tfrac{1}{2}0)$ were calculated.

The Patterson projections and the Harker sections are included in a document,[12] copies of which may be obtained by request from the Secretary of the Institute of Inorganic Chemistry.

Good agreement between calculated and observed vectors was obtained with the following positions for the chromium atoms in the unit cell:

4 Cr(1) in 4(*c*)	$x \approx 0$	$y \approx 0.39$	$z \approx 1/4$
8 Cr(2) in 8(*d*)	$x \approx 0.17$	$y \approx 0.89$	$z \approx 0.48$
8 Cr(3) in 8(*d*)	$x \approx 0.09$	$y \approx 0.75$	$z \approx 0.11$

The lengths of the Cr—Cr vectors were calculated and the following distances were found:

Cr(1) — Cr(1)	~ 4.4 Å	Cr(3) — Cr(3)	$\sim 3.0_5$ Å
Cr(1) — Cr(3)	~ 3.3 Å	Cr(2) — Cr(3)	~ 3.3 Å
Cr(1) — Cr(2)	$\geqslant 3.7$ Å	Cr(2) — Cr(2)	~ 4.4 Å

At this stage of the structure determination it seemed better to try to get the positions of the 48 oxygen atoms from consideration of the interatomic distances than from Fourier summations. A Cr—Cr distance of $\sim$3.3 Å usually corresponds to tetrahedra or octahedra sharing corners, while a Cr—Cr distance of $\sim$3.0 Å usually corresponds to octahedra sharing edges.[13] Three assumptions were thus made:

(1) The coordination figure around Cr(3) was assumed to be a regular octahedron with the bond lengths Cr—O $\approx$ 2.0 Å.

(2) The short Cr(3)—Cr(3) distance is formed when two octahedra are joined by sharing one edge forming a double-octahedron with the composition Cr_2O_{10}.

(3) The remaining Cr(1) and Cr(2) atoms are situated in holes formed by the pairs of CrO_6 octahedra.

With these assumptions, trial coordinates for all the oxygen atoms could be obtained including those which are not in contact with the Cr(3) atoms.

8 O(1) in 8(*d*)	with $x \approx 0.24$	$y \approx 0.75$	$z \approx 0.13$
8 O(2) in 8(*d*)	with $x \approx 0.08$	$y \approx 0.75$	$z \approx 0.37$
8 O(3) in 8(*d*)	with $x \approx 0.08$	$y \approx 0$	$z \approx 0.13$
8 O(4) in 8(*d*)	with $x \approx 0.08$	$y \approx 0.50$	$z \approx 0.13$
8 O(5) in 8(*d*)	with $x \approx 0.08$	$y \approx 0.25$	$z \approx 0.37$
8 O(6) in 8(*d*)	with $x \approx 0.25$	$y \approx 0.50$	$z \approx 0.37$

To refine the parameters of the atoms use was made of a least-squares program on the computer FACIT EDB [14] and the refinement was started with the set of atomic positions given above. There are 900 possible independent reflections for Cr_5O_{12} using Cu$K\alpha$ radiation. About 850 of these were within the range of the data recorded but only 430 reflections were detectable. The coordinates and the isotropic temperature factor of each atom were refined together with the scale factors between the different Weissenberg photographs. The residuals $S = w(|F_o| - |F_c|)^2$ were minimized with all the observed and independent reflections included in the calculations (Table 3). For the weight w, the weight function given by Hughes [15] was used.

Table 3. Weight analysis used in the last cycle of the refinement of Cr_5O_{12}. w = weighting factor, $\Delta = |F_o| - |F_c|$.

sin Θ interval	$\overline{w\,\Delta^2}$ (normalized)	Number of independent reflections	$\lvert F_o \rvert$ interval	$\overline{w\,\Delta^2}$ (normalized)	Number of independent reflections
0.00−9.45	0.97	69	0− 13	0.99	2
0.45−0.57	0.81	57	13− 26	1.67	21
0.57−0.66	0.90	54	26− 39	1.71	66
0.66−0.72	0.83	37	39− 52	1.22	84
0.72−0.78	0.98	44	52− 65	0.93	70
0.78−0.83	0.98	35	65− 78	0.85	52
0.83−0.87	1.31	33	78− 91	0.50	34
0.87−0.91	1.53	30	91−104	0.42	34
0.91−0.95	1.00	24	104−117	0.61	15
0.95−0.98	0.85	34	117−130	0.53	51

Table 4. Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement of Cr_5O_{12}. Space group: *Pbcn* (No. 60).

$4(c)\ \pm(0,y,\frac{1}{4};\ \frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$

$8(d)\ \pm(x,y,z;\ \frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\ \bar{x},y,\frac{1}{2}-z)$

	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Cr(1) in 4(*c*)	0	0.3939 ± 0.0006	1/4	0.52 ± 0.07
Cr(2) in 8(*d*)	0.1719 ± 0.0003	0.8878 ± 0.0004	0.4768 ± 0.0004	0.47 ± 0.05
Cr(3) in 8(*d*)	0.0857 ± 0.0003	0.7517 ± 0.0006	0.1119 ± 0.0003	0.32 ± 0.05
O(1) in 8(*d*)	0.2454 ± 0.0014	0.7314 ± 0.0019	0.0906 ± 0.0014	0.26 ± 0.20
O(2) in 8(*d*)	0.0750 ± 0.0011	0.7736 ± 0.0020	0.3535 ± 0.0016	0.36 ± 0.22
O(3) in 8(*d*)	0.1003 ± 0.0011	0.9899 ± 0.0023	0.1032 ± 0.0017	0.70 ± 0.25
O(4) in 8(*d*)	0.0806 ± 0.0013	0.5080 ± 0.0024	0.1356 ± 0.0017	0.81 ± 0.30
O(5) in 8(*d*)	0.0707 ± 0.0012	0.2700 ± 0.0023	0.3741 ± 0.0016	0.79 ± 0.25
O(6) in 8(*d*)	0.2538 ± 0.0015	0.4894 ± 0.0020	0.3625 ± 0.0014	0.65 ± 0.21

$$w = 1/16|F_{o,\min}|^2 \text{ for } |F_o| \leq 4|F_{o,\min}| \text{ and } w = |F_o|^{-2} \text{ for } |F_o| \geq 4|F_{o,\min}|$$

During twelve cycles of refinement the disagreement index R, dropped from 0.403 (the R value of the trial structure) to 0.098.

Finally the non-observed reflections were also introduced in the least-squares refinement. Their F_o values were then taken as the treshold value of the photographs that they should have appeared in. After six additional cycles a final R value of 0.099 was obtained. At this stage, the average coordinate shifts for the oxygen atoms were 2 % of their standard deviations.

The final fractional atomic parameters obtained and their standard deviations σ are shown in Table 4 as well as the refined thermal parameters.* A three-dimensional full-difference synthesis was computed at points spaced 0.2 Å along the *a*, *b*, and *c* axes. This function shows maxima and minima, the largest

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* Since no absorption correction was applied, the latter values have no real physical meaning.

of which has a magnitude of less than 20 % of the mean peak height of the oxygen atoms in the electron density function. The obseved and calculated structure factors as well as the F_o- and $(F_o - F_c)$-syntheses are given in Ref. 12.

DESCRIPTION OF THE STRUCTURE OF Cr_5O_{12}

The interatomic distances and bond angles are given in Table 5. The arrangement of the atoms in the structure of Cr_5O_{12} is shown in Figs. 1—2.

The structure of Cr_5O_{12} can be visualized by regarding it as composed of polyhedra connected by sharing corners and edges. There are three crystallographically non-equivalent chromium and six non-equivalent oxygen atoms in the structure. Each Cr(1) is surrounded by a tetrahedron of four oxygen atoms (2 O(4) + 2 O(5)), the Cr—O distances within this CrO_4-tetrahedron are all of the same magnitude, the range being 1.64 — 1.67 Å with a mean of 1.65 Å. Each Cr(2) atom is surrounded by a more distorted tetrahedron of oxygen atoms (O(1) + O(2) + O(3) + O(6)), the distance range being 1.54—1.81. Each Cr(3) atom is surrounded by a somewhat distorted octahedron of six oxygen atoms: (O(1) + 2 O(2) + O(3) + O(4) + O(5)), the distance range being 1.94 — 2.01 Å (average 1.97_2 Å).

Pairs of octahedra are formed by sharing one edge, the shared edge is O(2) — O(2) of length 2.48 Å, the shortest O—O distance in the structure. This is in agreement with the observation that in ionic structures, the mutual

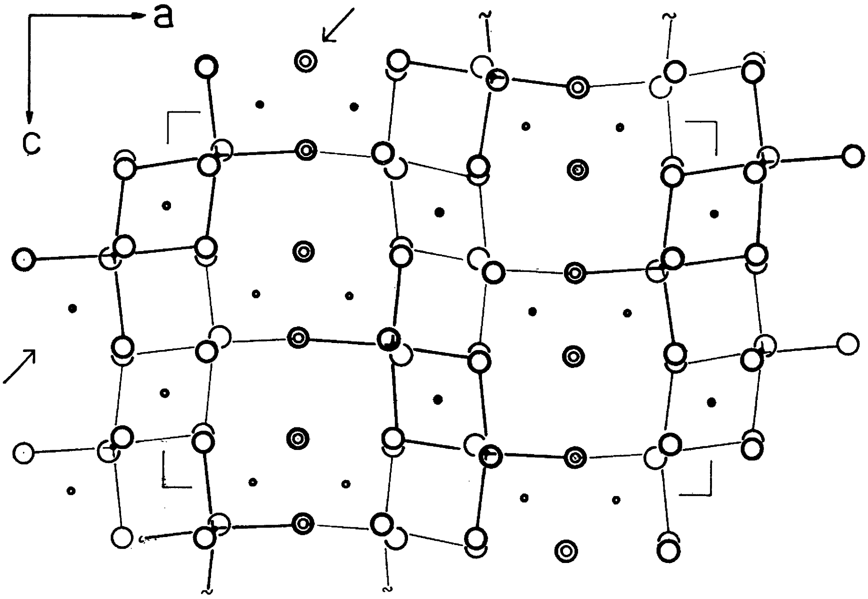

Fig. 1. Plan view of the Cr_5O_{12} structure viewed along [010]. Lines connecting atoms indicate the manner in which the CrO_6 octahedra are joined by the oxygen atoms. A Cr_5O_{18}-unit is indicated between the arrows (*cf.* Fig. 2).

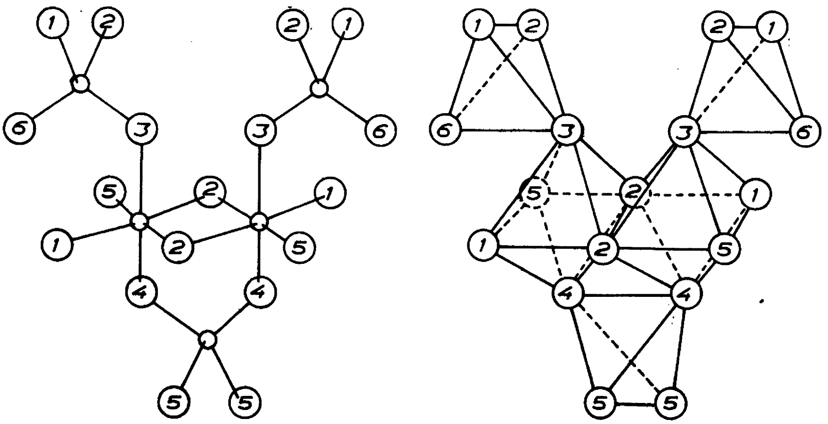

Fig. 2. Perspective view of the arrangement of the CrO_6 octahedra and CrO_6 tetrahedra in a Cr_5O_{18}-unit. The Cr—O and the O—O bonds are indicated. The bond distances and angles are given in Table 5.

repulsion of the positive ions tends to reduce the length of the shared edges of the anion polyhedra.[16]

The pairs of octahedra are joined together by the $Cr(1)O_4$ and $Cr(2)O_4$ tetrahedra. Each O(1), O(3), O(4) and O(5) atom forms a common corner of one octahedron and one tetrahedron, each O(2) atom forms the corner of two octahedra and one tetrahedron. The distance Cr(2)—O(2) is 1.81 Å which is considerably longer than the observed distances in the $Cr(1)O_4$-tetrahedron; *vide infra*. The O(6) atom belongs only to one Cr(2) tetrahedron and is thus in closer contact with the Cr(2) atoms, the distance being 1.54 Å compared with 1.65 Å, mean value of six distances (*cf.* Table 5).

There is significant difference between the Cr—O distances within the CrO_4 tetrahedra and the CrO_6 octahedra. The average of the former 1.65 Å agrees well with corresponding values for the tetrahedra sharing corners in KCr_3O_8 [13] (1.65, 1.64 and 1.64 Å). In KCr_3O_8 there are also unshared oxygen atoms which are in significantly closer contact with the tetrahedral chromium atoms (1.55 Å in KCr_3O_8). The Cr—O distances in the octahedra of Cr_5O_{12} (average 1.97 Å) also agree well with those found in KCr_3O_8 (average 1.97 Å). Thus the coordination numbers as well as the interatomic distances indicate that the Cr_5O_{12} structure, as well as the KCr_3O_8 structure, is built up of trivalent and hexavalent chromium atoms.

Thus the oxide can be formulated as $Cr_2^{III}\ Cr_3^{VI}\ O_{12}$ or $Cr_2(CrO_4)_3$. A similar formulation can be used for the structurally related compounds KCr_3O_8 and $KAl(SO_4)_2$.

A HYPOTHETICAL CLOSE-PACKED STRUCTURE M_5O_{12}

It is possible to describe the structure of Cr_5O_{12} as a slightly distorted cubic close-packed array of oxygen atoms with chromium atoms occupying certain

Table 5. Interatomic distances (in Å) and angles (°) in the structure of Cr_6O_{12}.

Distances Cr—O within the chromate tetrahedra ($\sigma \approx \pm$ 0.017 Å).

Cr(1) — O(4)	1.642	Cr(2) — O(1)	1.678
Cr(1) — O(4)	1.642	Cr(2) — O(2)	1.805
Cr(1) — O(5)	1.670	Cr(2) — O(3)	1.679
Cr(1) — O(5)	1.670	Cr(2) — O(6)	1.540

Distances Cr—O within the chromate octahedron ($\sigma \approx \pm$ 0.017 Å).

Cr(3) — O(1)	1.938	Cr(3) — O(3)	1.965
Cr(3) — O(2)	1.964	Cr(3) — O(4)	2.011
Cr(3) — O(2)	1.989	Cr(3) — O(5)	1.962

Distances Cr—Cr < 4.0 Å

Cr(1) — Cr(2)	3.824	Cr(2) — Cr(3)	3.324
Cr(1) — Cr(3)	3.355	Cr(2) — Cr(3)	3.376
Cr(1) — Cr(3)	3.312	Cr(2) — Cr(3)	3.325
Cr(2) — Cr(3)	3.352	Cr(3) — Cr(3)	3.060

Bond angles O—Cr—O within the chromate tetrahedra

O(4) — Cr(1) — O(4)	110.4	O(1) — Cr(2) — O(2)	113.0
O(4) — Cr(1) — O(5)	113.1	O(1) — Cr(2) — O(3)	108.2
O(4) — Cr(1) — O(5)	107.6	O(1) — Cr(2) — O(6)	107.9
O(4) — Cr(1) — O(5)	107.6	O(2) — Cr(2) — O(3)	108.8
O(4) — Cr(1) — O(5)	113.1	O(2) — Cr(2) — O(6)	108.5
O(5) — Cr(1) — O(5)	105.0	O(3) — Cr(2) — O(6)	110.4

Bond angles O—Cr—O within the chromate octahedron

O(1) — Cr(3) — O(2)	176.9	O(2) — Cr(3) — O(5)	93.5
O(1) — Cr(3) — O(2)	99.3	O(2) — Cr(3) — O(3)	87.2
O(1) — Cr(3) — O(3)	89.6	O(2) — Cr(3) — O(4)	89.6
O(1) — Cr(3) — O(4)	87.3	O(2) — Cr(3) — O(5)	171.0
O(1) — Cr(3) — O(5)	89.7	O(3) — Cr(3) — O(4)	175.2
O(2) — Cr(3) — O(2)	77.6	O(3) — Cr(3) — O(5)	93.6
O(2) — Cr(3) — O(3)	90.1	O(4) — Cr(3) — O(5)	90.1
O(2) — Cr(3) — O(4)	92.7		

Bond angles Cr—O—Cr

Cr(3) — O(1) — Cr(2)	133.5	Cr(3) — O(3) — Cr(2)	131.6
Cr(3) — O(2) — Cr(3)	101.5	Cr(1) — O(4) — Cr(3)	129.8
Cr(3) — O(2) — Cr(2)	127.2	Cr(1) — O(5) — Cr(3)	128.2
Cr(3) — O(2) — Cr(2)	124.1		

(Estimated standard deviations in the angles are ± 1.2°.)

of the octahedral and tetrahedral interstices in an ordered way. The unit-cell dimensions of the perfect close-packed structure were averaged from the real structure by means of the expressions:

$$a_0 = \tfrac{3}{7}(a + b + c) = 12.19 \text{ Å} \qquad b_0 = c_0 = \tfrac{2}{7}(a + b + c) = 8.12 \text{ Å}$$

The cell content is maintained at 48 oxygen atoms with 12 M atoms in tetrahedral and 8 M atoms in octahedral holes as illustrated in Figs. 3 and 4. The ideal coordinates of the atoms and the corresponding shifts are given in Table 6.

It can be seen that the displacements of the atoms are comparatively small and are in the range 0.11—0.32 Å. The calculated M—O distances within

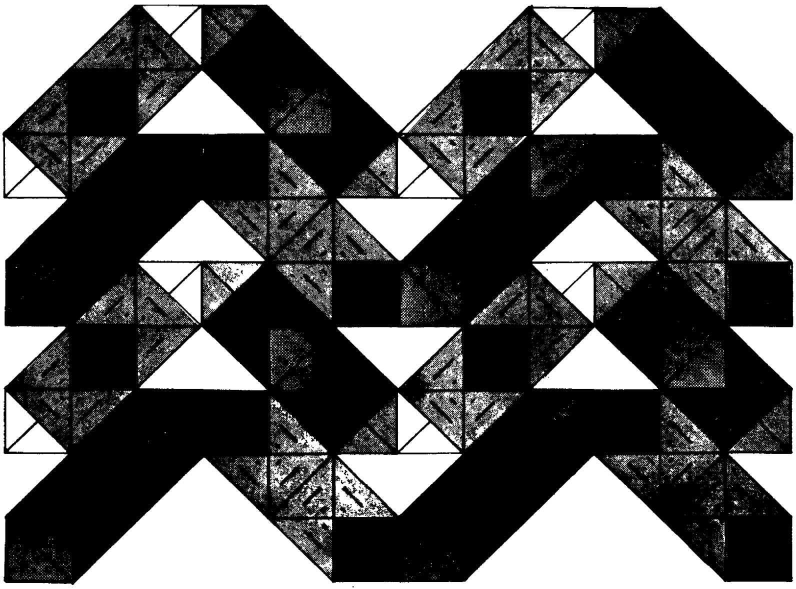

Fig. 3. Plan view of the idealized close-packed Cr_5O_{12} structure showing the arrangement of the CrO_6 octahedra and CrO_4 tetrahedra.

the tetrahedra are 1.76 Å and within the octahedra 2.03 Å. The Cr—O distances actually found are 0.1 Å shorter for the tetrahedral bonds, but are close to the ideal value for the octahedral bonds. The calculated $M(3)-M(3)$ distances of octahedra sharing edges are short, 2.87 Å, and below those found in the real structure (3.06 Å). As no intermetallic bonds are expected, the repulsion between highly charged metal atoms would lead to metal-metal distances of octahedra sharing edges considerably longer than the ideal geometrical value. The calculated $M-M$ distances, 3.52 Å, between unshared tetrahedra are also shorter than the observed value of 3.82 Å. However, the observed chromium-chromium distances in the bridges $Cr^{3+}-O-Cr^{6+}$ are 3.34 Å (mean value of six distances, *cf.* Table 5), which is very close to the ideal value, 3.37 Å, for the close-packed structure.

According to Pauling[16] the electroneutrality in a structure ought to be locally approximately fulfilled if the structure is to be considered reasonable. In the hypothetical M_5O_{12} structure the octahedra and tetrahedra are perfectly regular and therefore it would be doubtful that such a structure could exist. The oxygen atoms O(1), O(3), O(4) and O(5) are all equivalent to each other and are attached to one sixcoordinated M^{3+} -atom and one fourcoordinated M^{6+}-atom. Thus the bond numbers at these oxygen atoms are equal to $3/6 + 6/4 = 2$. However, the O(2) and the O(6) atoms are not equivalent, the bond numbers are $2\frac{1}{2}$ and $1\frac{1}{2}$, respectively. In conformity with this the Cr(2)—O(2) and Cr(2)—O(6) distances observed in the Cr_5O_{12} structure are 1.81 Å and 1.54 Å, *i.e.* quite different from the normal value for the $Cr^{6+}-O$ distances (1.65 Å) observed in the $Cr^{6+}-O-Cr^{3+}$ bridges.

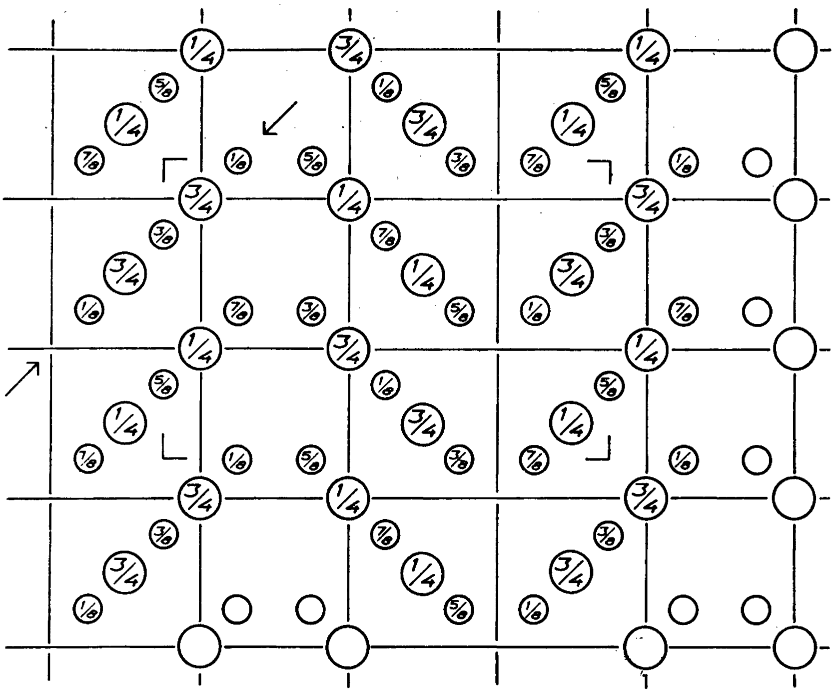

Fig. 4. The idealized Cr_5O_{12} structure viewed along [010]. The figures denote the heights of the chromium atoms in fractions of *b*. The cubic close-packed oxygen atoms are indicated with a plane net. A Cr_5O_{18}-unit is indicated between the arrows (*cf.* Fig. 2).

In pressure induced structure changes there is always an increase in density. This is brought about by a more developed close-packing of the atoms in which some or all of the atoms increase their numbers of near neighbours. In Cr_5O_{12} there is no increase of the coordination number of the chromium atoms, but the oxygen atoms have a rather high coordination number around them-

Table 6. The idealized structure of Cr_5O_{12} represented as cubic close-packing of the oxygen atoms. Space group: *Pbcn* (No. 60). Unit-cell dimensions: a_0 = 12.19 Å, b_0 = = c_0 = 8.12 Å The shifts from the real structure are also given.

	x_0	y_0	y_0	Δx	Δy	Δz	Δd Å
Cr(1) in 4(*c*)	0	3/8	1/4	0	0.0189	0	0.15
Cr(2) in 8(*d*)	1/6	7/8	1/2	0.0052	0.0128	−0.0232	0.22
Cr(3) in 8(*d*)	1/12	3/4	1/8	0.0024	0.0017	−0.0131	0.11
O(1) in 8(*d*)	1/4	3/4	1/8	−0.0046	−0.0186	−0.0344	0.32
O(2) in 8(*d*)	1/12	3/4	3/8	−0.0083	0.0236	−0.0115	0.24
O(3) in 8(*d*)	1/12	0	1/8	0.0131	−0.0101	−0.0218	0.25
O(4) in 8(*d*)	1/12	1/2	1/8	−0.0027	0.0080	0.0106	0.11
O(5) in 8(*d*)	1/12	1/4	3/8	−0.0126	0.0200	−0.0009	0.23
O(6) in 8(*d*)	1/4	1/2	3/8	0.0038	−0.0106	−0.0125	0.14

selves as a consequence of the cubic close-packing of the lattice. Furthermore, some oxygen atoms O(2) have three chromium atoms as next neighbours. The density of Cr_5O_{12} (3.68 g cm^{-3}) is considerably higher than that of the phase known as Cr_2O_5 (3.24 g cm^{-3}), which is formed in the range 0—1 kbar and according to Kubota[3] with an oxygen-chromium ratio close to 2.40. Thus the high density of Cr_5O_{12} is mainly caused by the remarkably good close-packing of the oxygen atoms and the compound can be regarded as a high-pressure phase, probably metastable at atmospheric pressure.

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