

CHROMIUM DIOXIDE:
HIGH PRESSURE SYNTHESIS AND BOND LENGTHS

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ABSTRACT

Single crystals of CrO_2 with the rutile structure have been grown from a KOH flux at a pressure of 36 kbar and a temperature of 900°C . The lattice parameters are $a = 4.4190 \pm 0.0003$ and $c = 2.9154 \pm 0.0001$ Å. The crystal structure has been refined from x-ray data. The least-squares refinement was carried out on 85 independent reflections which gave an R index of 0.017. The four equatorial Cr-O distances are 1.910 Å and the two apical ones 1.891 Å. The CrO_6 octahedra are therefore apically compressed.

As a continuing program of study of transition metal oxides in this laboratory, we have synthesized single crystals of CrO_2 under high pressure and refined its structure from x-ray data. Accurate bond lengths in CrO_2 are of importance to us for comparative purposes. The latest available data are not accurate enough as the standard deviations of the Cr-O distances are greater than 2%. (1) Chromium dioxide which is known to be a ferromagnetic metal (2) has the tetragonal rutile structure. The space group is $P4_2/mnm$ with 2 molecules per unit cell. The two chromium atoms are in the 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ positions whereas the four oxygen atoms are in the special positions $4f(x,x,0)$ with $x \sim 0.3$. The oxygen array is hexagonal close-packed and the chromium atoms

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occupy the octahedral sites. The octahedra share edges along the *c* axis so as to form infinite chains, while each one shares a corner with the eight octahedra along the body diagonals of the unit cell. In the rutile structure the MO_6 octahedra consist of four planar equatorial M-O distances and two linear apical ones. The ratio M-O apical/M-O equatorial varies from 0.98 to 1.03 among the dioxides. In the recently well refined TiO_2 structure this ratio was found to be 1.016.(3) From the data of reference (1) this ratio for CrO_2 is calculated to be 0.98, but because of the large standard deviation this value cannot be differentiated from the one found for TiO_2 .

The single crystals of CrO_2 were prepared by mixing equimolar proportions of CrO_3 and Cr_2O_3 to which was added approximately 5% by weight of KOH serving as flux. This mixture was packed into a platinum container of 5.5 cc volume. A pressure of 36 kbar was attained by a piston and cylinder apparatus. A temperature of 900°C was maintained at pressure for two hours. After this time, power to the heater was discontinued. No attempt was made at slow cooling. After the pressure was released the platinum container was opened and placed in distilled water whereupon the KOH was rapidly dissolved and small single crystals were freed. Several rinses with distilled water and the final rinse with acetone completed the cleaning procedure. The crystals were strongly magnetic at room temperature.

A Debye-Scherrer photograph of the crushed crystals was taken with $\text{CrK}\alpha$ radiation ($\lambda_{\text{K}\alpha_1} = 2.28962 \text{ \AA}$, $\lambda_{\text{K}\alpha_2} = 2.29352 \text{ \AA}$). The pattern was fully indexed on a tetragonal cell with $a = 4.4190(3)$ and $c = 2.9154(1) \text{ \AA}$. A single crystal with the shape of a parallelepiped was mounted on a goniometer head and oriented with the *c* axis vertical. Precession photographs revealed that the crystal was untwinned. All reflections in the upper hemisphere having $2\theta \leq 80^\circ$ were collected with a GE-XRD-5 automatic diffractometer using Zr-filtered $\text{MoK}\alpha$ radiation. The systematic absences corresponding to space group $\text{P4}_2/\text{mm}$ are: $Ok\ell$ for $k + \ell = 2n + 1$. The data collection was done with the stationary crystal-stationary counter technique described in detail elsewhere.(4) The total number of observed independent reflections was 85. The intensities were converted into structure

factors by applying the Lorentz-polarization corrections. No absorption correction was applied. The dimensions of the parallelepipedal crystal were: 0.049×0.073 mm in the xy plane and 0.122 mm along the z axis. The linear absorption coefficient for CrO_2 and $\text{MoK}\alpha$ radiation is 96.5 cm^{-1} , which gives an average $\mu_R = 0.29 \pm .05$ in the xy plane and 0.59 along the z axis. Therefore, the absorption correction is negligible in the xy plane, but varies significantly with the intercept on the vertical axis. The positional and thermal parameters for $\text{VO}_2 + 2.4\% \text{ Cr}$ at 360 K were taken as the initial values for the least squares refinement of CrO_2 . (5) The atomic scattering factors for neutral Cr and O given by Cromer and Waber (6) and the dispersion corrections given by Cromer (7) were used with the ORFLS least squares program. Four scale factors were used as a first approximation to correct for absorption. The $\cos X$ (X = angle of the intercept on the c axis) was divided into four equal intervals. Each hkl reflection was given a scale factor according to its X angle. After four cycles of refinement convergence was attained with isotropic temperature parameters. The conventional R and wR indices were 0.019 and 0.027 respectively. After the introduction of anisotropic temperature parameters these indices decreased to 0.017 and 0.022. The final positional and thermal parameters are shown in Table 1. A list of observed and calculated structure F-values is omitted, but it is available on request.

Table 2 shows the interatomic distances of CrO_2 together with the corresponding ones of TiO_2 and $\text{VO}_2 + 2.4\% \text{ Cr}$. The average Cr-O distance is $1.903 \text{ \AA}$, the expected distance being $1.91 \text{ \AA}$. (8) The four equatorial and the two apical Cr-O distances are 1.910 and $1.891 \text{ \AA}$ respectively, whereas the values reported by Cloud et al. (1) were 1.92 ± 0.03 and $1.88 \pm 0.04 \text{ \AA}$. The ratio apical/equatorial is 0.990. This distortion is different from the one found in TiO_2 and $\text{VO}_2 + 2.4\% \text{ Cr}$ where this ratio is 1.016 and 1.007 respectively. Other dioxides in which this ratio is less than unity are RuO_2 and OsO_2 . (9,10) Of interest are the cation-cation distances across the shared edge, i.e. the c-parameter. If these distances are normalized with respect to the ionic radii for each of the three compounds, then the largest separation of cations occurs in CrO_2 . Also, the oxygen

TABLE 1

Positional and Thermal Parameters

	Cr	O
x	0	0.3048(1)
y	0	0.3048
z	0	0
β_{11}	0.0060(1)	0.0047(2)
β_{22}	0.0060	0.0047
β_{33}	0.0091(4)	0.0081(5)
β_{12}	-0.00016(4)	0.0020(1)
β_{13}	0	0
β_{23}	0	0

Scale Factor 1 = 1.000(7)

Scale Factor 2 = 1.021(8)

Scale Factor 3 = 1.02(1)

Scale Factor 4 = 1.05(1)

The thermal parameters are the coefficients in the expression:

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

By symmetry $\beta_{11} = \beta_{22}$ and $\beta_{13} = \beta_{23} = 0$

TABLE 2

Interatomic Distances (Å) and Angles (°)

	CrO ₂ ¹	VO ₂ + 2.4% Cr ²	TiO ₂ ³
a	4.4190(3)	4.5508(6)	4.59366(2)
c	2.9154(1)	2.8535(8)	2.958689(5)
c/a	0.6597	0.6271	0.64408
V	56.930	59.11	62.434
M-O apical	1.891(1)	1.933(1)	1.9800(4)
M-O equatorial	1.9096(7)	1.920(1)	1.9485(3)
M-O ap./M-O eq.	0.990	1.007	1.016
M-O average	1.903	1.924	1.959
reported ionic radius	0.55	0.59	0.605
O-O × 2 = c	2.9154(1)	2.854(1)	2.9587(2)
O-O × 2	2.4670(1)	2.569(1)	2.5364(2)
O-O × 8	2.6876(1)	2.725(1)	2.7780(1)
O-M-O × 2	80.48(5)	83.99(6)	81.21(2)
O-M-O × 2	99.52(5)	96.01(6)	98.79(2)
O-M-O × 8	90	90	90
M-M across edge = c	2.9154(1)	2.854(1)	2.9587(2)
M-M across corner	3.4480(2)	3.520(1)	3.5692(3)

1 present work

2 Reference 5. These data correspond to 360K

3 Reference 3

ERRATUM

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Table 1, which appeared on page 160 of Volume 7, Number 2, should have been as shown below.

TABLE 1
Positional and Thermal Parameters

	Cr	O
x	0	0.3026(3)
y	0	0.3026
z	0	0
β_{11}	0.0056(2)	0.0069(4)
β_{22}	0.0056	0.0069
β_{33}	0.0098(6)	0.0128(15)
β_{12}	0.0003(2)	-0.0011(6)
β_{13}	0	0
β_{23}	0	0

Scale Factor 1 = 1.000(7)

Scale Factor 2 = 1.021(8)

Scale Factor 3 = 1.02(1)

Scale Factor 4 = 1.05(1)

The thermal parameters are the coefficients in the expression:

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

By symmetry $\beta_{11} = \beta_{22}$ and $\beta_{13} = \beta_{23} = 0$

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octahedron about Cr^{4+} is the most distorted among the three compounds as can be seen by comparing O-M-O angles.

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