

## Crystallographic Shear Structures Derived from $\text{CrO}_2$ : An Electron Microscopic Study

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We have established by electron microscopy and electron diffraction the existence of several crystallographic shear phases in the family of chromium oxides  $\text{Cr}_n\text{O}_{2n-1}$ , where  $n = 4$  and  $6$ . As in the systems  $\text{Ti}_n\text{O}_{2n-1}$  and  $\text{V}_n\text{O}_{2n-1}$ , the phases are based on crystallographic shear on the planes  $\{1\bar{1}1\}$ . A further series of phases found in this study show a superlattice along  $\bar{g}_{210}$  and bear similarities to the  $\text{M}_m\text{O}_{2m-2}$  phases found by Gibb and Anderson in the  $\text{Ga}_2\text{O}_3\text{-TiO}_2$  system.

### Introduction

Chromium is exceptional amongst the first-row transition metals because of the many distinct oxides that it forms:  $\text{CrO}_3$ ,  $(\text{CrO}_3)_n$ ,  $\text{Cr}_3\text{O}_8$ ,  $\text{Cr}_6\text{O}_{15}$ ,  $\text{Cr}_5\text{O}_{12}$ ,  $\text{CrO}_2$ , and  $\text{Cr}_2\text{O}_3$  (1, 2). These oxides display a rich range of solid state phenomena encompassing unusual magnetic, electrical, and catalytic properties.  $\text{CrO}_2$ , the subject of this paper, has remarkable properties in that it is both metallic and ferromagnetic, which make it important technologically in view of its utilization in the manufacture of magnetic tapes (3-5). Its special merit for our purpose, however, is that upon thermal decomposition, it ultimately yields  $\text{Cr}_2\text{O}_3$  (6-9), so that we have, in effect, the conversion of a metallic undeformed rutile-type structure into an insulating corundum-type structure.

It is first instructive to recall briefly the reasons for the currently accepted structural and stoichiometric identity of  $\text{CrO}_2$ . Some authors, e.g., Cotton and Wilkinson (10), have designated this material as nonstoichiometric. There were even some early claims that the true composition

lay between  $\text{CrO}_{1.8}$  and  $\text{CrO}_{1.9}$ , but it is now realized (11) that solids of that composition were mixtures of  $\text{CrO}_2$  and  $\text{Cr}_2\text{O}_3$ . Other workers, having measured lattice parameters and/or bulk and X-ray densities, suggested the presence of chromium interstitials (6) or oxygen vacancies (12). When  $\text{CrO}_2$  is heated beyond about 700 K, there is loss of oxygen, the ferromagnetism disappears, and the color changes from metallic black to pale brown (8). In addition, differential thermal analysis demonstrates the existence of two distinct thermal effects (9); yet, despite these changes, the X-ray powder diagram after the first of the thermal effects does not significantly alter, and there is certainly little evidence for the appearance of the  $\text{Cr}_2\text{O}_3$  pattern before the decomposition is almost complete.

We were prompted to study  $\text{CrO}_2$  and its partially decomposed analogues, using electron microscopy, partly because we felt it should be possible to observe directly, and to identify, by electron diffraction analysis, intermediate phases and partly because we felt it sensible to examine a system possessing a rutile-type structure but with a transition metal other than Ti and V. We expected that these phases would be analogous to the homologous series of intermediate oxides

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first identified by Andersson et al. (13) and Andersson (14) and later characterized and interpreted in terms of crystallographic shear [as proposed by Wadsley (15)] by a number of investigators, notably S. Andersson (14, 16), J. S. Anderson (17), and Bursill and Hyde (18).

We have indeed found a series of crystal structures in the family of chromium oxides based upon crystallographic shear (CS) and bearing close resemblance to those found in the homologous series  $Ti_nO_{2n-1}$  with CS recurring on  $\{121\}$ .

#### Previously Identified CS Structures in Rutile

To date, two series of ordered structures related by CS have been found in rutile-like compounds: both may be described by the general formula  $M_nO_{2n-1}$ , but, in one case,  $n = 4-10$  ( $M = Ti$  or  $V$ ), with a displacement vector  $\frac{1}{2} [0\bar{1}1]$  and CS occurring in the  $(1\bar{2}1)$  oxygen-only family of planes (16). In the other,  $n = 16-25$  and the operation of crystallographic shear takes place on the  $(1\bar{3}2)$  family of planes (again, oxygen only) and with the same displacement vector. The known examples are for  $M = Ti$  and  $Ti + Cr$  (ternary system) 18, 19). It has recently been found that, between these two series, there exists an indeterminate number of intermediate compounds (20) in which the CS plane swings from  $(1\bar{3}2)$  to  $(1\bar{2}1)$  by an amount characteristic of the precise composition. The essence of the situation throughout is that CS is a means by which oxygen deficiency in a solid can be eliminated by insertion of planar faults across which the normal M/O ratio is modified. In rutile, at  $(1\bar{2}1)$  CS planes, for example, the normal edge-sharing of  $[MO_6]$  octahedra is replaced by face-sharing of octahedra with a consequent retention of the cation coordination number and a diminution in the M-M separation.

By suitable substitutions in  $TiO_2$ , Gibb and Andersson (21) demonstrated that another homologous series of oxides may be generated: i.e.,  $Ga_4 Ti_{n-4} O_{2n-2}$  (15 and 23,  $n$  odd). In this case the planes removed are (210) oxygen only planes.

#### Experimental

Single crystals of  $CrO_2$  were produced at 65 kbar and 1473 K as described in Ref. 12. The spectrographic analysis given there indicated the presence of 200–1000 ppm of Fe and 100–500 ppm of Ni. The results reported in this paper



FIG. 1. Diffraction pattern of  $Cr_6O_{11}$ , a member of the  $(1\bar{2}1)$  family of CS structures in  $CrO_2$ . Zone axis  $[1\bar{1}\bar{3}]_r$ . The indices to the right of any vertical row—subindexed  $r$ —belong to the basic rutile-like cell, the indices to the left belong to the  $Cr_6O_{11}$  cell.

refer to a sample subsequently heated to 693 K in air and then quenched to room temperature. The crystals were fractured between glass slides and the fractured flakes mounted on copper grids.

The electron microscopic observations were carried out in a Phillips EM300 fitted with goniometer and high resolution stages and an image intensifier.

#### Results and Discussion

For the series based on  $(1\bar{2}1)$ , we found  $Cr_4O_7$  and  $Cr_6O_{11}$ . In Fig. 1 is shown an electron diffraction pattern corresponding to  $Cr_6O_{11}$

TABLE I

UNIT CELL PARAMETERS,<sup>a</sup> AND OBSERVED AND CALCULATED  $d$ -SPACINGS FOR  $Cr_6O_{11}$ <sup>b</sup>

$hkl$	$d_{calc}$ (Å)	$d_{obsd}$ (Å)
002	8.99	8.96
121	3.12	3.18
123	2.74	2.84
$1\bar{2}, 11$	1.63	1.59
244	1.47	1.48
246	1.37	1.42

<sup>a</sup> The unit cell parameters were calculated from the  $CrO_2$  parameters given in Ref. 12 on the assumption that the relations between basic cell and supercell are in this case the same as those deduced by Andersson and Jahnberg (16) for  $Ti_nO_{2n-1}$  ( $4 < n < 9$ ).

<sup>b</sup>  $a_0 = 3.30 \pm 0.05 \text{ Å}$ ,  $b_0 = 6.90 \pm 0.05 \text{ Å}$ ,  $c_0 = 22.09 \pm 0.05 \text{ Å}$ ,  $\alpha = 97.3^\circ$ ,  $\beta = 120.0^\circ$ ,  $\gamma = 107.5^\circ$ .

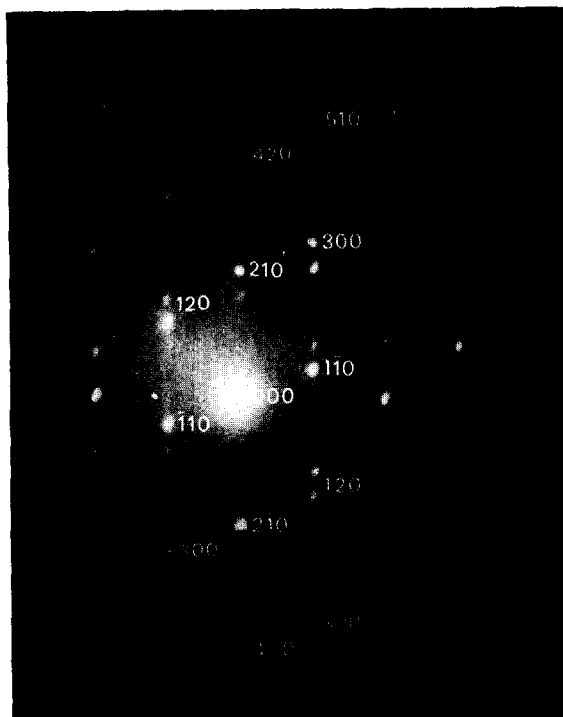


FIG. 2. Diffraction pattern of partly decomposed  $\text{CrO}_2$ , Zone axis  $[001]$  showing a fivefold superlattice along  $\bar{g}_{210}$ .

and Table I gives the unit cell parameters together with some observed and calculated  $d$ -spacings. Diffraction evidence of a sevenfold superlattice along  $\bar{g}_{112}$  has also been found. A series of diffraction patterns has also been found showing a superlattice along  $\bar{g}_{210}$  with two-, three-, four-, and fivefold superlattices, respectively. Figures 2 and 3 are typical diffraction patterns showing fivefold and threefold superlattices, respectively.<sup>1</sup> When these patterns are interpreted in terms of the model hypothesized by Gibb and Anderson (21), one obtains a family of phases with the general formula  $\text{Cr}_m\text{O}_{2m-2}$ , and the patterns found correspond to  $m = 5, 7, 9,$  and  $11$  (according to the model,  $m$  takes only odd values).

Apparently,  $\text{CrO}_2$  is the only undoped binary oxide (neglecting the influence of small amounts of Fe and Ni impurities) to show recurrent

<sup>1</sup> We are grateful to the referee for drawing to our attention that Fig. 3 can also be indexed as  $n = 7(121)$ . However, a  $[1\bar{2}\bar{2}]$  zone axis, with the consequential interpretation of a threefold superlattice along  $\bar{g}_{210}$  of  $\text{CrO}_2$ , seems to us more likely, partly because of the observed intensity distribution of the spots and also because several other diffraction patterns display unmistakable evidence of superlattice spots along  $\bar{g}_{210}$ .

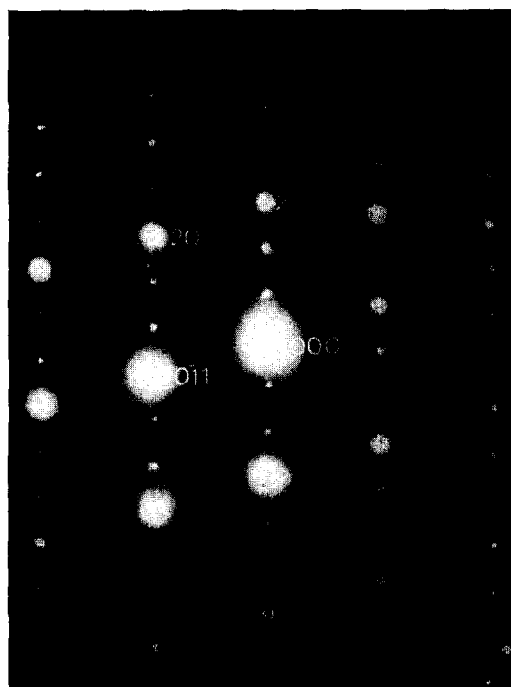


FIG. 3. Diffraction pattern of partly decomposed  $\text{CrO}_2$ —zone axis  $[1\bar{2}\bar{2}]$ —showing a threefold superlattice along  $\bar{g}_{210}$ .

TABLE II

DIFFERENCES IN IONIC RADII  $(r_{M^{3+}} - r_{M^{4+}})/r_{M^{4+}}$  BETWEEN SOME OF THE CATIONS PRESENT IN CS COMPOUNDS (27, 28)

Cations involved	Electron configuration of the cations		Orientation of planar defects		Effective ionic radii (Å)		Difference (%)
	Tetravalent	Trivalent			$r_{M^{4+}}$	$r_{M^{3+}}$	
Ti <sup>4+</sup> and Ti <sup>3+</sup>	$d^0$	$d^1$	(1 $\bar{2}$ 1)	(1 $\bar{3}$ 2)	0.605	0.67	10.7
Ti <sup>4+</sup> and Cr <sup>3+</sup>	$d^0$	$d^3$	(1 $\bar{2}$ 1)	(1 $\bar{3}$ 2)	0.605	0.615	1.6
Ti <sup>4+</sup> and Fe <sup>3+</sup>	$d^0$	$d^5$	(210)		0.605	0.645	6.6
Ti <sup>4+</sup> and Ga <sup>3+</sup>	$d^0$	$d^{10}$	(210)		0.605	0.62	2.5
V <sup>4+</sup> and V <sup>3+</sup>	$d^1$	$d^2$	(1 $\bar{2}$ 1)		0.580	0.64	10.3
Cr <sup>4+</sup> and Cr <sup>3+</sup>	$d^2$	$d^3$	(1 $\bar{2}$ 1)	(210)	0.550	0.615	11.8

planar faults of the (210) type. In this case, substitution of different trivalent ions does not seem to be necessary to produce {210} structures. Another interesting point is that, in the case of Ga- or (Ga + Fe)-substituted TiO<sub>2</sub>, the only members of the {210} series had values of  $m$  ranging upwards from 15. Now that lower members of the series, i.e., for  $m < 15$ , have been found in CrO<sub>2</sub>, it may be worthwhile to look for lower members in the Ti <sub>$n$</sub> O<sub>2 $n$ -1</sub> and V <sub>$n$</sub> O<sub>2 $n$ -1</sub> systems.

Little is known about the origin of the long-range forces that are undoubtedly involved in the perfect ordering of CS planes, separated by distances which in the case of rutile-like com-

pounds can be of the order of 40 Å. The elimination of oxygen leads to a change in the oxidation number and ionic radius of the cation and to the formation of face-sharing octahedra. Table II shows the relative differences in size between the tetravalent and trivalent ions in all the known rutile-like structures now known to contain planar defects. It should first be noted that, ignoring the effects of removing the oxygen, in all cases the effect of introducing trivalent ions should be to increase the volume of the unit cell. Secondly, the substitution of the foreign ions Cr<sup>3+</sup>, Fe<sup>3+</sup>, or Ga<sup>3+</sup> in TiO<sub>2</sub> leads to smaller volume changes than reduction of the binary oxides TiO<sub>2</sub>, VO<sub>2</sub>, and CrO<sub>2</sub>. This difference

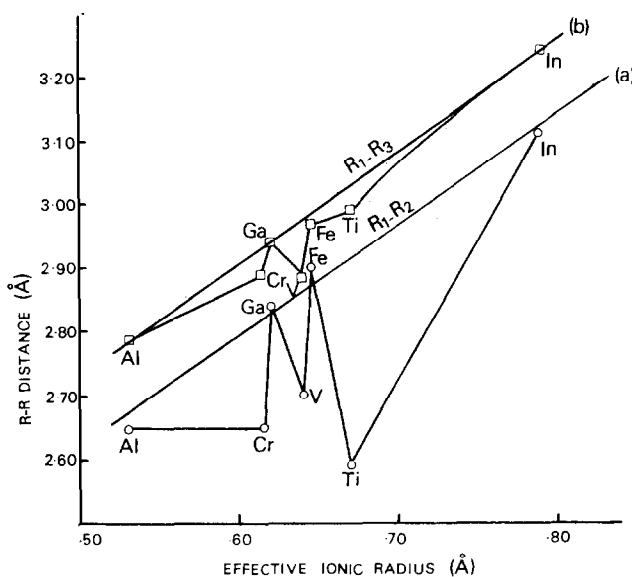


FIG. 4. Correlation between metal-metal distance and effective ionic radius for a series of oxides that crystallize in the corundum structure: distance across (a) shared face and (b) shared edge.

explains perhaps the large difference in solubility of  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$  in  $\text{TiO}_2$  (19). However, differences in ionic radii can not be correlated with the appearance of  $(\bar{1}\bar{2}1)$  and  $(\bar{1}\bar{3}2)$  defects in  $\text{TiO}_2$ - $\text{Cr}_2\text{O}_3$  systems and the lack of their appearance in the  $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ - $\text{Ga}_2\text{O}_3$  systems (21). One empirical observation that can be made from Table II is that all systems showing  $(\bar{1}\bar{2}1)$  and  $(\bar{1}\bar{3}2)$  CS defects contain trivalent ions with a  $d^1$ ,  $d^2$ , or  $d^3$  configuration. For the series of  $\text{M}_2\text{O}_3$  compounds having the corundum-type structure which is characterized by shared-face octahedra, it is known that the metal-metal distance across the faces is anomalously short for  $\text{M} = \text{Ti}, \text{V},$  and  $\text{Cr}$  (see Fig. 4 and Ref. 22). This is a strong indication of metal-metal bonding and it may be that such bonding is a driving force for the long-range ordering or at least reduces the repulsive forces in the shear planes sufficiently to allow their formation. However, this process does not apparently go as far as envisaged by Goodenough (23) who postulated that  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  pairs would be found in the shared-face octahedra. The metal-metal distance across the shared face as determined in  $\text{Ti}_2\text{O}_3$  (24) is 2.59 Å. The results of the structure refinement of  $\text{Ti}_4\text{O}_7$  by Marezio et al. (25) indicate that pairs of  $\text{Ti}^{3+}$ - $\text{Ti}^{4+}$  ions with a distance of 2.838 Å are found in the shared-face octahedra at the CS planes of the ordered semi-conducting phase and  $\text{Ti}^{3.5+}$ - $\text{Ti}^{3.5+}$  pairs with a distance of 2.811 Å are found in the disordered metallic phase.

It is worth mentioning that neither crystallographic shear recurring on  $(\bar{1}\bar{2}1)$  or  $(\bar{1}\bar{3}2)$  oxygen-only planes nor the process recurring on (210) planes can lead to the corundum structure. As recently shown by Andersson and Galy (26), corundum can be derived from rutile by a recurrent crystallographic shear on (101) oxygen-only planes. Because the final product of the thermal decomposition of  $\text{CrO}_2$  is invariably  $\text{Cr}_2\text{O}_3$ , it could be expected that phases belonging to this family should be found in the thermal decompositions of  $\text{CrO}_2$ . So far, however, no such phases have been found in reduced  $\text{CrO}_2$ . We have performed a few preliminary "in situ" decompositions in the electron microscope; these reveal the appearance of quite a number of isolated faults lying on (210), the corresponding diffraction pattern showing that  $\text{Cr}_2\text{O}_3$  is indeed formed in the  $\text{CrO}_2$  matrix such that the (101) planes of the latter are parallel to the (110) planes of  $\text{Cr}_2\text{O}_3$ . Further experiments are in

progress to ascertain the intermediate phases and the particular planes upon which they appear. Decompositions carried out *in vacuo* may well lead to structures different from those produced by decomposition in air.

Another noteworthy point is that, contrary to the case of  $\text{TiO}_2$ , the  $\text{CrO}_2$ -based CS structures cannot be obtained by hydrogen reduction of  $\text{CrO}_2$ , since this procedure yields, as recently demonstrated (9), the orthorhombic  $\text{CrOOH}$ . Considering that between the CS planes present in any of the intermediate oxides the basic structure remains almost undistorted, it seems likely that a series of intermediate oxyhydroxides could also exist in this system. If this is the case, the basic motif between the CS planes will be the orthorhombic unit cell. Experiments are now in progress to test this possibility.

It is perhaps curious that CS structures have not been previously reported in the chromium oxide system. However, recent DTA studies (9) showed that  $\text{CrO}_2$  begins to decompose around 700 K and reaches the composition of  $\text{Cr}_2\text{O}_3$  at around 750 K, and it may be significant that this process shows two distinct thermal effects when followed by DTA performed in an oxidizing atmosphere. Our experience with the thermal decomposition inside the electron microscope indicates that this range may be even narrower. This narrow range of stability is primarily responsible for the difficulty in obtaining the intermediate phases reported in this paper. It is worth stressing at this point that both the  $(\bar{1}\bar{2}1)$  and (210) phases were found in a sample treated in air at a temperature of 693 K.

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