Rutile-Type Compounds.
V. Refinement of MnO₂ and MgF₂

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Single-crystal X-ray diffraction data (computer-controlled four-circle diffractometer) on rutile-type MnO₂ have been refined with anisotropic temperature factors to $R = 0.014$ (295 F_o). Result: $x = 0.30515$ (11), $(Mn-O)_1 = 1.8795$ Å and $(Mn-O)_2 = 1.8981$ Å [with $a = 4.3983$ (3) and $c = 2.8730$ (3) Å]. Single-crystal data of Niederauer & Göttlicher [*Z. angew. Phys.* (1970), **29**, 16] have been refined with anisotropic temperature factors to $R = 0.016$ (190 F_o). Result: $x = 0.30293$ (6), $(Mg-F)_1 = 1.9968$ and $(Mg-F)_2 = 1.9798$ Å [with $a = 4.6213$ (1) and $c = 3.0519$ (1) Å]. Rutile-type fluorides of the first transition-metal series conform to a simple ionic model and have within the coordination octahedra apical bonds which are shorter than the equatorial bonds (apically *compressed* octahedra). Deviations of individual compounds from the normal geometry are consistent with static Jahn–Teller distortions due to degeneracies in e_g orbitals (CrF₂ and CuF₂) and in t_{2g} orbitals (FeF₂ and CoF₂). The main Group IV rutile-type oxides (SiO₂, GeO₂, SnO₂ and PbO₂) have apically *elongated* octahedra which are not compatible with an ionic model. VO₂ and CrO₂ deviate from the oxide rutile-type geometry in a manner not consistent with Jahn–Teller distortions of ions with unfilled t_{2g} orbitals.

Introduction

When I refined the crystal structures of rutile-type TiO₂, SnO₂, GeO₂ and MgF₂ (Baur, 1956) I also attempted to study rutile-type MnO₂ (pyrolusite). However, the samples of pyrolusite then available to me were either other modifications of MnO₂ or else they were polycrystalline or finely twinned or very poorly crystallized. Attempts to grow single crystals of MnO₂ failed. A precise evaluation of the powder diffraction data was unsuccessful because of the diffuse background in the patterns taken with Cu *K*α or Fe *K*α radiation or because of the poor resolution achieved with Mo *K*α radiation. Therefore Brenet's (1950) semiquantitative determination of the O atom position in rutile-type MnO₂ is still the most precise work on pyrolusite. Brenet found a positional parameter x of the O atom of 0·303, which would mean that all the Mn–O distances within the coordination octahedron of O atoms around Mn should be of equal length. However, he also mentions that for $x = 0.310$ the agreement between F_o and F_c would be even better. In this case the two apical Mn–O bonds would be longer than the four equatorial bonds (apically elongated) thus resulting in the same type of distortion as is observed in TiO₂, SiO₂, GeO₂, SnO₂, and PbO₂, while in rutile-type fluorides and in CrO₂, RuO₂, and OsO₂ the four equatorial bonds are longer than the two apical bonds (Baur, 1956; Baur & Khan, 1971). Abrahams & Bernstein (1971) pointed out that the compounds with apically elongated bonds contained all Group IV oxides crystallizing in the rutile-type. If this observation indicates a general rule we would expect the coordination octahedron in MnO₂ to be distorted in the opposite sense compared with the dis-

tortion found in Group IV rutile-type oxides, that is the O atom in MnO₂ should have an x smaller than 0·303 (in contradiction to Brenet's observation). Since Rogers, Shannon, Sleight & Gillson (1969) have grown hydrothermally single crystals of rutile-type MnO₂ this question can now be settled by an accurate X-ray study of these crystals.

The crystal structure of rutile-type MgF₂ was refined from two-dimensional single-crystal X-ray data by difference syntheses (Baur, 1956) and the same data were subsequently re-refined by least-squares techniques (Baur & Khan, 1971). The positional parameters for the F atom were found to be $x = 0.303$ (1) and $x = 0.3028$ (6), respectively. Recently Niederauer & Göttlicher (1970) determined the electron-density distribution in MgF₂. They measured and evaluated a precise set of structure factors but did not attempt to refine the positional parameter of the F atom. Instead they used the value of $x = 0.303$ (1) determined by Baur (1956) for their calculations. Their set of X-ray data has been refined here to yield a precise definition of the structural geometry of MgF₂.

Experimental

Vegard (1916) has shown that rutile-type compounds crystallize in space group $P4_2/m2_1/n2/m$ (systematic absences $0kl$ if $k + l = 2n + 1$, and the symmetrically related $h0l$ if $h + l = 2n + 1$). The metal atoms occupy equipoints 2(*a*) with site symmetry *mmm*, the anions are in equiponts 4(*f*) at $\pm (x,x,0; \frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2})$ (site symmetry *mm*). The structure has three free parameters: two cell constants and the parameter x.

Crystals of MnO₂ were prepared hydrothermally at 700°C and 3000 atm by Rogers *et al.* (1969). An

almost perfect sphere of diameter 0.015 ± 0.001 cm was ground from the material made available by Dr R. D. Shannon. Three-dimensional X-ray intensities within a complete sphere of reflection were collected on a computer-controlled four-circle diffractometer using monochromatic Ag $K\alpha$ radiation (graphite crystal monochromator). For details of data-measuring procedures and for a list of computer programs used in the course of the work see Table 1 and Baur & Khan (1970). The structure amplitudes were corrected for absorption. The data were only slightly affected by extinction since the refinement of the extinction parameter (Zachariasen, 1963) reduced R only by 0.003 ($C = 0.45 \times 10^{-6}$) to 0.0144. The scattering factors of Mn^{2+} and O^- used for the calculation of structure factors (see Table 2* for F_o and F_c) were taken from International Tables for X-ray Crystallography (1962).

Niederauer & Göttlicher's (1970) structure factors for MgF_2 were processed in the same way as the structure factors for MnO_2 resulting in a final R of 0.0155. Scattering factors of Mg^{2+} and F by Doyle & Turner (1968) were used in the structure-factor calculations (see Table 3* for F_o and F_c).

The positional parameter x_{exp} of the O atom in MnO_2 is greater than the value of x_m (Table 4). Therefore, the distortion of the coordination octahedron around Mn is of the same type as in SiO_2, TiO_2 and GeO_2. The equatorial bonds are about 0.02 Å shorter than the apical bonds. Thus MnO_2 shows the same type of distortion as the Group IV oxides. The geometry of the coordination polyhedron in MgF_2 has not been changed by the new refinement compared with the old work (Baur, 1956; Baur & Khan, 1971). The thermal ellipsoids in MgF_2 are almost spherical (Table 5). The only other rutile-type structure where this is true is SiO_2 (Baur & Khan, 1971), which however has not been determined with the same degree of accuracy as MgF_2.
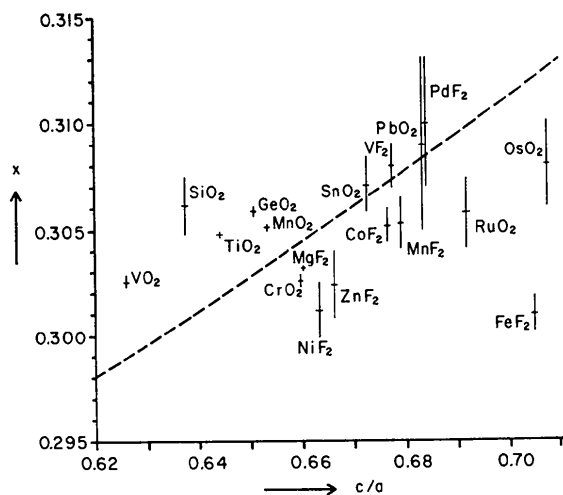
Discussion

In the rutile-type structure the anions form coordination octahedra around the cations. These octahedra join into chains parallel to [001] by sharing edges. The chains are connected sideways to four neighboring chains by sharing corners. Every anion is coordinated by three cations. The site symmetry of the cation (mmm) allows deviations from the maximum symmetry ($4/m\bar{3}2/m$) of an octahedron. In well determined rutile-type structures two types of distortion have been

Fig. 1. Axial ratio c/a versus positional parameter x for all rutile-type compounds for which they have been determined so far (Table 6). The lengths of the vertical bars of the crosses indicate the estimated standard deviations of x. The dashed line corresponds to those x, c/a values for which $(A-B)_1 = (A-B)_2$. If a compound is located above the line the coordination octahedron is axially compressed.

* Tables 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31650 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Crystal data, details of data collection and R values*

	MnO_2	MgF_2
Space group	$P4_2/m2_1/n2/m$	$P4_2/m2_1/n2/m$
a (Å)	$4.3983 (3)^a$	$4.6213 (1)^b$
c (Å)	$2.8730 (3)^a$	$3.0519 (1)^b$
V (Å^3)	55.58	65.18
Z	2	2
F.W.	86.94	62.31
λ (Å)	Ag $K\alpha$, 0.56083	Mo $K\alpha$, 0.71069
μ (cm^{-1})	59.5	7.46^c
D_x (g cm^{-3})	5.193	3.174
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	1.37	1.00
Number of I_{hkl} measured	4267	190^c
Number of unique I_{hkl}	352	190^c
Number of unobserved reflections	57	0
$R_1 = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0144^d	0.0155^d
$R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$	0.0243^d	0.0440^d
R_1 (including $F_{hkl} = 0$)	0.0277	

(a) Shannon, private communication. (b) Naidu (1966). (c) Niederauer & Göttlicher (1970). (d) Excluding $F_{hkl} = 0$.

Table 4. Refinement results, bond lengths and bond angles for MnO_2 and MgF_2

The value of x_{exp} is the experimentally determined positional parameter of the anion B, while x_m is the calculated value assuming that the six cation–anion distances (A–B) are of equal length, that is $x = \frac{1}{4} + (c^2/8a^2)$. Listed are the β_{ij} ($\times 10^4$) where the temperature factor is exp $[-(\beta_{11}(h^2 + k^2) + \beta_{33}l^2 + 2\beta_{12}hk)]$. The multiplicities refer to one coordination octahedron. The mean cation–anion distance $(A–B)_m$ is calculated with x_m as parameter.

	MnO_2	MgF_2
c/a	0·65321	0·66040
x_m	0·3033	0·3045
x_{exp}	0·30515 (11)	0·30293 (6)
β_{11}, anion	63 (1)	96 (2)
β_{33}, anion	98 (3)	215 (4)
β_{12}, anion	−24 (2)	0 (1)
β_{11}, cation	38 (1)	71 (1)
β_{33}, cation	76 (1)	158 (4)
β_{12}, cation	1 (1)	0 (1)
$(A–B)_1$, equatorial $(4\times)$	1·8795 (2) Å	1·9968 (1) Å
$(A–B)_2$, apical $(2\times)$	1·8981 (3)	1·9798 (2)
$(A–B)_m$	1·8868	1·9902
$(B–B)_1$ $(8\times)$	2·6712 (2)	2·8819 (1)
$(B–B)_2$ $(2\times)$	2·4240 (7)	2·5759 (4)
$(A–A)_1 = (B–B)_3 = c$ $(2\times)$	2·8730 (3)	3·0519 (1)
$(A–A)_2$ $(8\times)$	3·4258 (2)	3·6065 (1)
$(B–A–B)_1$ $(2\times)$	80·31 (2)°	80·33 (1)°

observed: (a) The angle anion–cation–anion towards the shared anion–anion edge varies from 75·0 to 84·2° (see Table 6). (b) The apical distances cation–anion can be different and usually are different in length from the four equatorial distances cation–anion within the plane (110) normal to the apical distances. The distortion of the coordination octahedra is a function of two parameters: the ratio c/a of the cell constants, and the free parameter x of the anion. In Fig. 1 all data for rutile-type oxides and fluorides are entered for which both x and c/a have been experimentally determined.

Simple Born-model type calculations, which took into account the electrostatic part of the lattice energy as well as non-electrostatic repulsion terms showed that according to this electrostatic model we should expect, in rutile-type crystals, the four equatorial $(A–B)_1$ bonds to be always longer than the two apical

$(A–B)_2$ bonds (Baur, 1961). We see in Fig. 1 that most fluorides conform with this, while most oxides do not. This is reasonable since fluorine is the most electronegative of the elements. However, we cannot accept this agreement as proof of the ionic character of these fluorides since it could be fortuitous. But the disagreement for the oxides in which the equatorial cation–oxygen bonds are shorter than the apical bonds must be taken as a strong indication that they are, at least partly, covalent: a simple ionic model cannot account for this observation.

The x values for the different rutile-type compounds tend to increase as c/a increases (Fig. 1). By and large both x and c/a increase with increasing mean distance A–B (Fig. 2); this is true for the fluorides (except for FeF_2) and for the main elements of the fourth group. These trends have been interpreted using the ionic model, by the smaller influence of the non-electrostatic terms on the total lattice energy with increasing A–B distance (Baur, 1961). The transiton-metal oxides
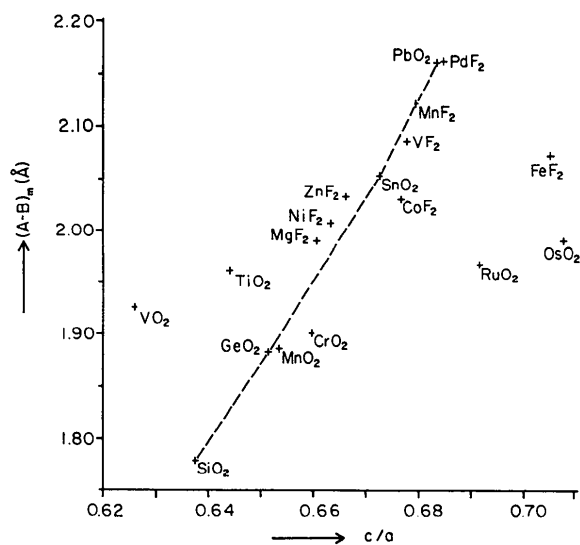

Fig. 2. Axial ratio c/a versus mean cation–anion distance $(A–B)_m$ for 18 rutile-type compounds (Table 6). The dashed line connects the main Group IV oxides.

Table 5. Dimensions and orientations of the ellipsoids of thermal vibration of the atoms in MnO_2 and MgF_2

| Compound | Atom | Principal axis | R.m.s. component (Å) | Angle (°) between principal axes and vectors a,b,c, $(A–B)_1$ and $(A–B)_2$ | | | | |
				a	b	c	$(A–B)_1$	$(A–B)_2$
MnO_2	Mn	1	0·056 (1)	90	90	0		
		2	0·060 (1)	135	45	90		
		3	0·062 (1)	45	45	90		
	O	1	0·062 (1)	45	45	90	130·15	0
		2	0·064 (1)	90	90	180	40·15	90
		3	0·092 (1)	45	135	90	90·00	90
MgF_2	Mg	1	0·086 (1)	90	90	0		
		2	0·087 (1)	135	135	90		
		3	0·088 (1)	45	135	90		
	F	1	0·101 (1)	90	90	0	139·83	90
		2	0·102 (1)	135	135	90	49·83	180
		3	0·102 (1)	45	135	90	90·00	90

(except for MnO_2) do not follow these trends. It is possible that the asymmetries of the distribution of the d electrons over their orbitals are causing these slightly irregular geometries of the transition-metal rutile-type oxides. The apically compressed octahedron around Mn(1) in $DyMn_2O_5$ (Abrahams & Bernstein, 1967) is compressed because O(3) is underbonded compared with the other ligands of Mn(1). The distortions of the
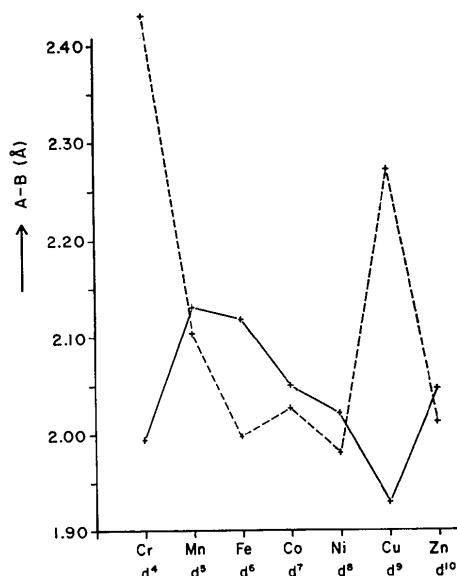

Fig. 3. Equatorial (solid line) and apical (dashed line) bond lengths of the rutile-type fluorides of the first transition-metal series as a function of the number of d electrons. Data for CrF_2 are from Jack & Maitland (1957), for CuF_2 from Billy & Haendler (1957).

coordination octahedra in rutile-type crystals are not a consequence of unequal bond-strength distributions (Baur, 1970) as they are found in more complicated structures and this is precisely the reason why they are of interest.

Static Jahn–Teller effects are pronounced when partially filled e_g orbitals are involved. In the series of fluorides of the first transition series $CrF_2(d^4)$ and $CuF_2(d^9)$ display strong distortions (and are monoclinic rather than tetragonal). According to Dunitz & Orgel (1960) partially filled t_{2g} orbitals should result in slight distortions compared with the high-spin d^4 and d^9 arrangements. Specifically they are predicting that in high-spin d^1 and d^6 configurations the coordination octahedron should be axially compressed, while in d^2 and d^7 configurations it should be elongated. As a possible example of the former they cite the case of FeF_2 (d^6) where the equatorial Fe–F bond lengths are 2·118 Å and the apical bonds measure 1·998 Å. However, they also remark that 'the opposite distortion which would be expected in CoF_2 does not seem to occur'. In fact there is a slight indication that this opposite distortion is occurring in CoF_2 (d^7). In MnF_2, NiF_2 and ZnF_2, which have no degeneracies in their electron configurations, the mean difference in equatorial and apical bond lengths (the bond-delta) is $-0·034$ Å (Fig. 3). The difference between $-0·034$ and $-0·022$ Å (for CoF_2) is possibly significant and shows that in CoF_2 there is a tendency to a distortion opposite to the one observed in FeF_2, since the bond-delta is *smaller* than for the 'spherical' ions Mn, Ni and Zn, while in FeF_2 the bond-delta is *larger* than in MnF_2, NiF_2 and ZnF_2. Vanadium difluoride (Table 6) has not been considered here because the determina-

Table 6. *Rutile-type compounds*: c/a, x, *bond lengths, bond angle*

The mean distance $(A-B)_m$ has been calculated using $x_m = \frac{1}{4} + (c^2/8a^2)$.

Compound AB$_2$	c/a	x_{exp}	$(A-B)_1$ equatorial (Å)	$(A-B)_2$ apical (Å)	$(A-B)_m$ (Å)	B–A–B (°)	Reference
SiO_2	0·63769	0·3062 (13)	1·757 (5)	1·810 (8)	1·778	81·4 (4)	a, b
TiO_2	0·64408	0·30479 (10)	1·9485 (5)	1·9800 (9)	1·9610	81·21 (4)	c
VO_2	0·62605	0·3026 (3)	1·921 (1)	1·933 (1)	1·926	84·17 (6)	d
CrO_2	0·65974	0·3026 (3)	1·9096 (7)	1·8910 (10)	1·902	80·48 (5)	e
MnO_2	0·65321	0·30515 (11)	1·8795 (2)	1·8981 (3)	1·8868	80·31 (2)	f, g
GeO_2	0·65094	0·3059 (2)	1·872 (1)	1·902 (1)	1·884	80·3 (1)	a, h
RuO_2	0·69160	0·3058 (16)	1·984 (6)	1·942 (10)	1·968	76·9 (4)	i
SnO_2	0·67254	0·3071 (13)	2·052 (5)	2·057 (9)	2·054	78·1 (4)	a, h
OsO_2	0·70749	0·3081 (20)	2·006 (8)	1·962 (13)	1·990	75·0 (5)	j
PbO_2	0·68322	0·309 (4)	2·16 (3)	2·17 (4)	2·161	76·4 (20)	k, h
MgF_2	0·66040	0·30293 (6)	1·9968 (1)	1·9798 (2)	1·9902	80·33 (1)	f, h
VF_2	0·67772	0·308 (1)	2·083 (3)	2·090 (4)	2·085	77·4 (2)	l, m
MnF_2	0·67929	0·3053 (12)	2·131 (6)	2·104 (9)	2·121	78·1 (4)	a, h
FeF_2	0·70502	0·3010 (8)	2·118 (4)	1·998 (6)	2·072	77·2 (2)	a, h
CoF_2	0·67670	0·3052 (8)	2·049 (3)	2·027 (5)	2·040	78·3 (2)	a, h
NiF_2	0·66321	0·3012 (13)	2·022 (6)	1·981 (9)	2·006	80·6 (4)	a, h
ZnF_2	0·66609	0·3024 (16)	2·046 (7)	2·012 (10)	2·033	80·0 (5)	a, h
PdF_2	0·68382	0·310 (3)	2·16 (2)	2·17 (3)	2·162	76·3 (15)	n

(a) Baur & Khan (1971). (b) Chao, Fahey, Littler & Milton (1962). (c) Abrahams & Bernstein (1971). (d) McWhan, Marezio, Remeika & Dernier (1974). (e) Porta, Marezio, Remeika & Dernier (1972). (f) This work. (g) Shannon, private communication. (h) Naidu (1966). (i) Boman (1970a). (j) Boman (1970b). (k) Leciejewicz & Padlo (1962). (l) Lau *et al.* (1969). (m) Shafer (1969). (n) Bartlett & Maitland (1958).

tion is reported only in an abstract (Lau, Stout, Koehler & Child, 1969).

The bond-deltas for the main group oxides diminish with increasing bond length and atomic number (Fig. 4). However, in this case the apical distances are longer than the equatorial distances. No theory is available which could help to interpret the detailed geometry of the main group oxides. If we accept the bond-deltas of the main group oxides with completely filled d shells and the smooth curve SiO_2-GeO_2-SnO_2-PbO_2 in Fig. 1 as the normal geometry of rutile-type oxides then TiO_2 and MnO_2 are close to this normal behaviour, while VO_2, CrO_2, RuO_2 and OsO_2 deviate from it. The more 'normal' behaviour of TiO_2 and MnO_2 can be rationalized because they do not have degeneracies in their d-electron distribution. However both VO_2 and CrO_2 are showing the 'wrong' type of distortion. According to Dunitz & Orgel (1960) the octahedron in VO_2 (d^1) should be compressed while in CrO_2 (d^2) it should be elongated. Actually, however, the reverse is true (Fig. 5). This may be possibly connected with the observation of metallic conductivity in some of the rutile-type oxides, namely VO_2, CrO_2, MnO_2, RuO_2 and OsO_2 among those mentioned here (Rogers et al., 1969).

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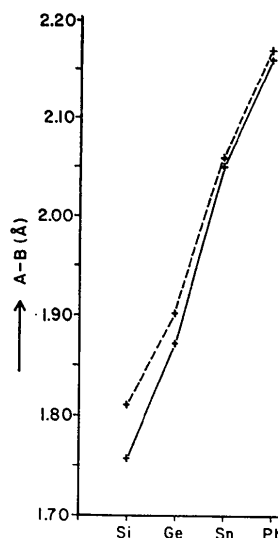

Fig. 4. Equatorial (solid line) and apical (dashed line) bond lengths of rutile-type oxides of Group IV with increasing atomic number.
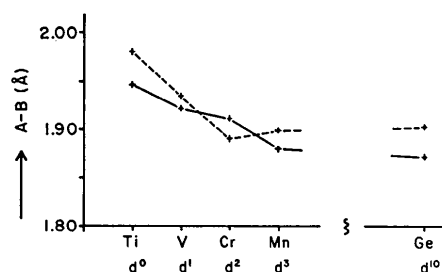

Fig. 5. Equatorial (solid line) and apical (dashed line) bond lengths of rutile-type oxides of the first transition-metal series as a function of the number of d electrons.

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