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Structural Chemistry of Magnéli Phases Ti_nO_{2n-1} ($4 \leq n \leq 9$). I. Cell and Structure Comparisons

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A body-centered triclinic cell based on the mesh in the shear plane and the period along the pseudo rutile chains is proposed for comparisons of the members of the title series. This cell permits a simple and systematic formulation of the S. Andersson and L. Jahnberg (1961, *Ark. Kemi* **21**, 413) model both for the cell parameters with $c = (2n - 1)\, c_{\text{rutile}}$ as the only variable cell parameter and for the atomic positions. The parameters b, β, and γ are found experimentally to obey the model closely, while a and α show a deviation from the model which is proportional to the oxygen deficiency with respect to rutile. The experimental c parameter is shorter by 0.26 ± 3 Å than its value from the model. This shortening is due to the approximate mutual compensation of three structural deviations from the model: the repulsion of the face-sharing Ti atoms, the shortening of the Ti–Ti distances in the chain, and the inclination of the chains toward the interior of the cell.

Introduction

The oxides Ti_nO_{2n-1} with $4 \leq n \leq 9$ form a series of "Magnéli phases" which contain rutile-like chains of edge-sharing TiO_6 octahedra interrupted every nth octahedron at a shear plane {121}, where the octahedra share faces in addition to edges and corners. The model structures of these oxides have been derived by Andersson *et al.* (*1*, *2*) from the known structure of Ti_5O_9. The cells derived by these authors, however, are not very convenient for comparisons because the pseudo rutile chains extend in different directions for various members of the series and because two families of cell parameters correspond to the even-n and to the odd-n members. The structural discussion by Bursill and Hyde (*3*) shows that the increase of n by 1 corresponds to the insertion of one TiO_2 unit in each pseudo rutile chain with no other structural modification of the model. The only basic crystallographic change corresponding to this insertion is that centrosymmetry occurs at the Ti atom in the middle of each chain for n odd while it occurs midway between the two central Ti in the chain for n even. Such a subtle difference should not reflect dramatically on the cell parameters.

Proposed Model

We propose here to use a cell based on the mesh in the "crystallographic shear plane" (*4*) and the period along the row parallel to the pseudo rutile chain direction (Fig. 1). Using the indices R, A, or P to mean rutile, Andersson and Jahnberg (*2*), or the present proposed system of axes, this system would be

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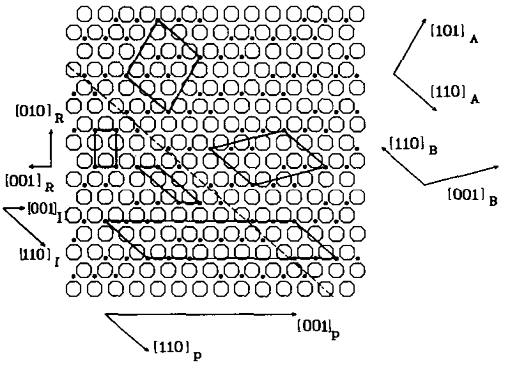

FIG. 1. The various systems of axes in use shown in the pseudo rutile *bc* section of the Ti_5O_9 structure (large open circles: oxygen atoms; black dots: titanium atoms). Systems of axes are as follows. A: Andersson and Jahnberg (*2*); B: Bursill and Hyde (*3*); I: transformed rutile; P: present proposed cell; R: rutile. The rutile unit vectors shown correspond to the A, I, and P systems of axes. The B system of axes corresponds to opposite sense for a_R and c_R. The dotted line is the race of the shear plane.

$$\begin{aligned} \mathbf{a}_P &= \mathbf{a}_A = \mathbf{a}_R - \mathbf{c}_R, \\ \mathbf{b}_P &= \mathbf{b}_A = -\mathbf{a}_R - \mathbf{b}_R - \mathbf{c}_R, \\ \mathbf{c}_P &= (2n-5)\,\mathbf{a}_A + (n-2)\,\mathbf{b}_A + p\,\mathbf{c}_A \\ &= -(2n-1)\,\mathbf{c}_R, \qquad (1) \end{aligned}$$

where p is 1 for n even and 2 for n odd. The above formulation takes into account the fact that the transformation actually used by (*2*) has all the signs reversed with respect to the transformation they quote which alters the hand of the system of axes. The above proposed cell is nonconventional because it is I centered in all the cases. This is due to the fact that the odd-n cells of (*2*) are primitive while the even ones are A face centered, as was shown experimentally by Marezio *et al.* (*5*) for Ti_4O_7 and as can be seen on the theoretical coordinates of (*2*) for Ti_6O_{11} and Ti_8O_{15}. This cell cannot be made conventional because its shape is mostly imposed by the building principle of the series of structures. Its advantages are that (i) the theoretical parameters a_P, b_P, α_P, β_P, and γ_P are constants that can be calculated from the rutile cell data, while the theoretical value of c_P is $(2n-1)\ c_R$, and (ii) the description of the atomic coordinates is much simplified. The content of the rutile cell with the system of axes $[10\bar{1}]_R$, $[\bar{1}\bar{1}\bar{1}]_R$, $[00\bar{1}]_R$, designated below by the index I, is made of two Ti and four O atoms whose coordinates are explicitly given in Table I. These atoms can be translated along $\mathbf{c}_P$ by amounts equal to $c_R = c_P/(2n-1)$ to produce the pseudo rutile chains, the origin being selected on Ti(1) for n odd, $\mathbf{c}_R/2$ away from it for n even. A given atom, e.g., O(1), will produce several atoms O(1,0), O(1,1), . . . , O(1,m) whose coordinates are

$$\begin{aligned} x_P[O(1,k)] &= x_I[O(1)], \\ y_P[O(1,k)] &= y_I[O(1)], \qquad (2) \\ z_P[O(1,k)] &= \{z_I[O(1)] + k + q\}/(2n-1), \end{aligned}$$

where k is an integer while q is 0 for n odd and $-\frac{1}{2}$ for n even to fix the origin appropriately. If the resulting value of z_P is in the range 0 to $\frac{1}{4}$, the corresponding atom belongs to the asymmetric unit of the proposed cell with space group $I\bar{1}$. The corresponding values of k that can produce such values of z_P range from 0 to $n/2$.

We checked that the calculated cell parameters and atomic coordinates given in (*2*) transform into the same numbers as those of the present proposed model using the transformation (1) given above. It is to be noted that the results in (*5*) require an

TABLE I

REPRESENTATION OF THE RUTILE STRUCTURE (TiO_2) IN THE TRANSFORMED CELL

Conventional representation [*data from* (*6*)]
S.G. $P4_2/mnm$, $a_R = 4.59366(2)$, $c_R = 2.95868(1)$ Å, $Z = 2$
Ti 0, 0, 0; O 0.3048(1), 0.3048, 0.
Representation in transformed cell
Cell axes: $\mathbf{a}_I, \mathbf{b}_I, \mathbf{c}_I = [10\bar{1}]_R, [\bar{1}\bar{1}\bar{1}]_R, [00\bar{1}]_R$
Cell parameters: $a_I = 5.4640$, $b_I = 7.1384$, $c_I = 2.9587$ Å
$\alpha_I = 65.514$, $\beta_I = 57.215$, $\gamma_I = 108.456°$
Cell content:

	x_I	y_I	z_I
Ti(1)	0	0	0
Ti(2)	0	0.5	0
O(1)	0	0.6952	0.3048
O(2)	0	0.3048	0.6952
O(3)	0.6096	0.8048	0.0856
O(4)	0.3904	0.1952	0.9144

TABLE II

CELL PARAMETERS FOR THE SERIES Ti_nO_{2n-1}, $4 \leq n \leq 9$

Compound	Source	a_P	b_P	c_P	α_P	β_P	γ_P	Space group
Ti_4O_7	Model[a]	5.464	7.138	20.711	65.514	57.215	108.456	$I\bar{1}$
	(*2*)[b]	5.604(2)	7.137(3)	20.456(8)	67.706(4)	57.145(5)	108.773(4)	
	(*5*)[c]	5.593	7.125	20.43	67.63	57.17	108.73	
Ti_5O_9	Model	5.464	7.138	26.628	65.514	57.215	108.456	$I\bar{1}$
	(*2*)	5.577(4)	7.127(5)	26.35(2)	67.260(8)	57.028(10)	108.524(7)	
	(*7*)[c]	5.569	7.117	26.32	67.24	57.04	108.51	
Ti_6O_{11}	Model	5.464	7.138	32.546	65.514	57.215	108.456	$I\bar{1}$
	(*2*)	5.566(3)	7.144(4)	32.30(2)	66.941(5)	57.066(6)	108.520	
	(*8*)[c]	5.552(1)	7.126(1)	32.233(6)	66.94(1)	57.08(1)	108.51(2)	
Ti_7O_{13}	Model	5.464	7.138	38.463	65.514	57.215	108.456	$I\bar{1}$
	(*2*)	5.547(4)	7.140(5)	38.20(3)	66.742(7)	57.093(8)	108.517(6)	
	(*8*)	5.537(1)	7.132(1)	38.151(8)	66.70(1)	57.12(1)	108.50(2)	
Ti_8O_{15}	Model	5.464	7.138	44.381	65.514	57.215	108.456	$I\bar{1}$
	(*2*)	5.534(3)	7.144(4)	44.13(2)	66.515(5)	57.143(6)	108.470(5)	
	(*8*)	5.526(1)	7.133(1)	44.059(6)	66.54(1)	57.18(1)	108.51(1)	
Ti_9O_{17}	Model	5.464	7.138	50.298	65.514	57.215	108.456	$I\bar{1}$
	(*2*)	5.527(3)	7.141(4)	50.06(3)	66.428(5)	57.157(7)	108.499(5)	
	(*8*)	5.524(1)	7.142(1)	50.03(1)	66.41(1)	57.20(1)	108.53(1)	

[a] Model from Ref. (*2*) in the setting defined by the cell transformation (1).

[b] Cell parameters obtained by least-squares refinement of the Guinier patterns from Ref. (*2*) with indices transformed with use of (1).

[c] Cell parameters obtained on single crystals at room temperature. The cell parameters from Refs. (*5*, *7*) were transformed from the cell parameters quoted. They are likely to be accurate to the last digit quoted.

origin shift of $\mathbf{b}_A/2$ before the transformation.

No comparison was attempted with the primitive cell proposed by Horiuchi *et al.* (9) for the V_nO_{2n-1} series because the pseudo rutile chain direction has different indices in the various compounds and because this cell has not been used in the T_i series.

Comparison with Experimental Cell Parameters

Table II summarizes the experimental cell parameters in the series from Refs.

TABLE III

CELL PARAMETERS IN THE ANDERSSON AND JAHNBERG (*2*) SYSTEM OF COORDINATES

Compound	Source	a_A	b_A	c_A	α_A	β_A	γ_A	Space group
Ti_4O_7	(*2*)	5.604(1)	7.137(1)	12.478(2)	95.072(4)	95.157(4)	108.773(5)	$A\bar{1}$
Ti_5O_9	(*2*)	5.577(2)	7.127(2)	8.872(3)	97.561(7)	112.356(9)	108.524(7)	$P\bar{1}$
Ti_6O_{11}	(*2*)	5.566(2)	7.144(2)	24.066(7)	98.473(4)	120.802(8)	108.520(6)	$A\bar{1}$
Ti_7O_{13}	(*2*)	5.547(2)	7.140(3)	15.370(7)	98.905(6)	125.457(9)	108.517(6)	$P\bar{1}$
Ti_8O_{15}	(*2*)	5.534(2)	7.144(2)	37.613(12)	99.167(3)	128.384(6)	108.470(4)	$A\bar{1}$
Ti_9O_{17}	(*2*)	5.527(2)	7.141(3)	22.278(8)	99.264(4)	130.338(7)	108.499(4)	$P\bar{1}$

(*2, 5, 7, 8*). The observed Guinier patterns from (*2*) were refined by least-squares using the published indices transformed according to the cell transformation (1) above. This procedure disclosed considerable calculation errors in the observed parameters reported by (*2*) for Ti_8O_{15} and Ti_9O_{17}. Calculated cell parameters in the A system of axes are quoted in Table III. The new values are in excellent agreement with single-crystal data, confirming the quality of the observed patterns reported in (*2*).

The parameters b_P, β_P, and γ_P are more or less constant for the series and equal to the values b_I, β_I, and γ_I in Table I, as expected from the model, with the exception of γ_P for Ti_4O_7, which differs by approximately 0.2° from the corresponding angles of the other members of the series. This is indicated by both powder and single-crystal data and is a small but genuine effect.

The parameters a_P and α_P show a linear variation when plotted versus $x = 1/n$, where x is the oxygen deficiency in the Magneli phase TiO_{2-x} (Fig. 2). The intercepts of the lines with the y axis at $x = 0$ corresponding to the rutile composition are virtually equal to the values a_I and α_I from

TABLE IV

CALCULATED AND EXPERIMENTAL ATOMIC POSITIONS IN THE PROPOSED SYSTEM OF AXES FOR Ti_4O_7, Ti_5O_9, AND Ti_9O_{17}

	Calculated from rutile using formula (2)				Experimental transformed to present system of axes		
	x	y	z	Ti_4O_7[a]	x	y	z
Ti(1,1)	0.	0.	0.07413	Ti(2)	0.01998	0.02022	0.06618
Ti(1,2)	0.	0.	0.21429	Ti(4)	0.08450	0.03959	0.20136
Ti(2,1)	0.	0.5	0.07143	Ti(1)	0.02771	0.52718	0.06282
Ti(2,2)	0.	0.5	0.21429	Ti(3)	0.07995	0.53772	0.20115
O(1,1)	0.	0.6952	0.11497	O(4)	0.9120	0.6611	0.1387
O(2,0)	0.	0.3048	0.02789	O(1)	0.0620	0.3325	0.0151
O(2,1)	0.	0.3048	0.17074	O(5)	0.0348	0.3171	0.1639
O(3,1)	0.6096	0.8048	0.08366	O(3)	0.6125	0.8342	0.0811
O(3,2)	0.6096	0.8048	0.22651	O(7)	0.6232	0.8429	0.2238
O(4,0)	0.3904	0.1952	0.05920	O(2)	0.4139	0.1768	0.0577
O(4,1)	0.3904	0.1952	0.20206	O(6)	0.4434	0.1738	0.1981
				Ti_5O_9[b]			
Ti(1,0)	0	0	0	Ti(2)	0	0	0
Ti(1,1)	0.	0.	0.11111	Ti(4)	0.03934	0.03655	0.10257
Ti(1,2)	0.	0.	0.22222	Ti(6)	0.08826	0.03938	0.21193
Ti(2,0)	0	$\frac{1}{2}$	0	Ti(1)	0	$\frac{1}{2}$	0
Ti(2,1)	0.	0.5	0.11111	Ti(3)	0.03766	0.53439	0.10318
Ti(2,2)	0.	0.5	0.22222	Ti(5)	0.08704	0.54152	0.21066
O(1,0)	0.	0.6952	0.03387	O(2)	0.9615	0.6814	0.04025
O(1,1)	0.	0.6952	0.14498	O(6)	0.9214	0.6674	0.16200
O(2,0)	0.	0.3048	0.07724	O(3)	0.0575	0.3356	0.06755
O(2,1)	0.	0.3048	0.18836	O(7)	0.0340	0.3162	0.18370
O(3,0)	0.6096	0.8048	0.00951	O(1)	0.5946	0.8209	0.01035
O(3,1)	0.6096	0.8048	0.12062	O(5)	0.6224	0.8347	0.11905
O(3,2)	0.6096	0.8048	0.23173	O(9)	0.6247	0.8436	0.22900
O(4,0)	0.3904	0.1952	0.10160	O(4)	0.4133	0.1837	0.10170
O(4,1)	0.3904	0.1952	0.21271	O(8)	0.4419	0.1759	0.20975

TABLE IV—*Continued*

	Calculated from rutile using formula (2)				Experimental transformed to present system of axes		
	x	*y*	*z*	Ti_4O_7[a]	*x*	*y*	*z*
				Ti_9O_{17}[c]		Experimental	
Ti(1,0)	0	0	0	Ti(9)	0	0	0
Ti(1,1)	0.	0.	0.05882	Ti(1)	0.01284(8)	0.01106(6)	0.057343(9)
Ti(1,2)	0.	0.	0.11765	Ti(4)	0.03725(8)	0.02811(6)	0.113554(9)
Ti(1,3)	0.	0.	0.17647	Ti(5)	0.06027(8)	0.05701(6)	0.170154(9)
Ti(1,4)	0.	0.	0.23529	Ti(8)	0.09266(8)	0.04166(6)	0.229844(9)
Ti(2,0)	0	½	0	Ti(10)	0	½	0
Ti(2,1)	0.	0.5	0.05882	Ti(2)	0.02191(8)	0.51380(6)	0.057078(9)
Ti(2,2)	0.	0.5	0.11765	Ti(3)	0.03915(8)	0.52960(6)	0.114287(9)
Ti(2,3)	0.	0.5	0.17647	Ti(6)	0.05638(8)	0.54882(6)	0.171596(9)
Ti(2,4)	0.	0.5	0.23529	Ti(7)	0.09580(8)	0.54775(6)	0.228114(9)
O(1,0)	0.	0.6952	0.01793	O(2)	0.9956(3)	0.69378(24)	0.01865(3)
O(1,1)	0.	0.6952	0.07675	O(6)	0.9996(3)	0.70035(24)	0.07726(4)
O(1,2)	0.	0.6952	0.13558	O(9)	0.0026(3)	0.70937(25)	0.13528(4)
O(1,3)	0.	0.6952	0.19440	O(14)	0.9292(3)	0.67779(25)	0.20287(4)
O(2,0)	0.	0.3048	0.04089	O(3)	0.0144(3)	0.31481(24)	0.03964(3)
O(2,1)	0.	0.3048	0.09972	O(7)	0.0369(3)	0.33014(24)	0.09674(3)
O(2,2)	0.	0.3048	0.15854	O(11)	0.0655(3)	0.34573(24)	0.15317(4)
O(2,3)	0.	0.3048	0.21736	O(15)	0.0366(3)	0.31665(24)	0.21516(3)
O(3,0)	0.6096	0.8048	0.00505	O(1)	0.6069(3)	0.80771(24)	0.00511(3)
O(3,1)	0.6096	0.8048	0.06386	O(5)	0.6180(3)	0.81943(25)	0.06302(3)
O(3,2)	0.6096	0.8048	0.12268	O(10)	0.6283(3)	0.83343(25)	0.12169(4)
O(3,3)	0.6096	0.8048	0.18151	O(13)	0.6456(3)	0.84786(25)	0.17851(4)
O(3,4)	0.6096	0.8048	0.24033	O(17)	0.6226(3)	0.84322(24)	0.23860(3)
O(4,0)	0.3904	0.1952	0.05379	O(4)	0.4057(3)	0.20318(25)	0.05274(3)
O(4,1)	0.3904	0.1952	0.11261	O(8)	0.4148(3)	0.20198(25)	0.11185(3)
O(4,2)	0.3904	0.1952	0.17144	O(12)	0.4225(3)	0.19848(24)	0.17058(3)
O(4,3)	0.3904	0.1952	0.23026	O(16)	0.4479(3)	0.18366(25)	0.22803(3)

[a] Experimental data from Ref. (*5*).

[b] Experimental data from Ref. (*7*).

[c] Experimental data from Ref. (*8*), using the atom numbering from Ref. (*2*).

Table I. The quantity $(2n - 1)\ c_R - c_P$, which should ideally be equal to 0, is in fact 0.26 ± 3 Å. As the c_P repeat corresponds to two pseudo rutile slabs, it is tempting to interpret this as a contraction by 0.13 Å at each shear plane. The examination of the structural results shows that the reality is quite different.

Comparison with Structural Results

The atomic positions deduced from the model and from single-crystal structure determination at room temperature are listed in Table IV for Ti_4O_7, Ti_5O_9, and Ti_9O_{17}. The differences between theoretical and experimental coordinates, which are quite similar for these three compounds, are considerable and were the source of initial convergence problems in (*8*).

First, the pseudo rutile chains deviate considerably from the $\mathbf{c}_P$ direction. This is obviously related to some strain in the shear plane because the deviation parallel to the $\mathbf{a}_P\mathbf{b}_P$ plane is independent from *n* in a first approximation. This implies that the angle between the chains and the $\mathbf{c}_P$ direction increases with decreasing *n*. The two

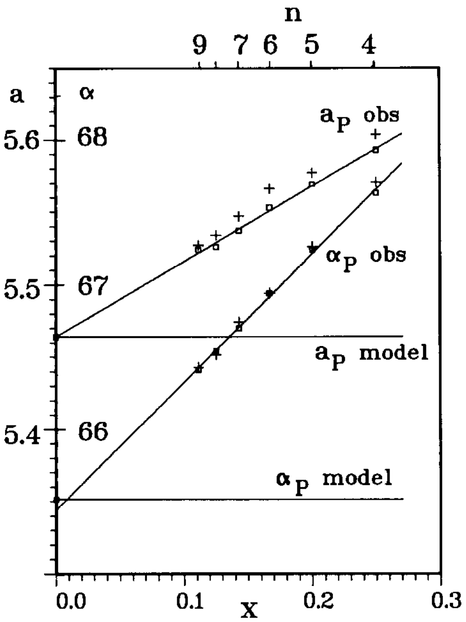

FIG. 2. The variation of the parameters a_P and α_P as a function of x in TiO_{2-x}. (+) Powder data (*2*); (□) single-crystal data (*5*, *7*, *8*).

symmetry-unrelated chains are very nearly parallel and the one which passes through the origin is inclined toward the interior of the cell. This distortion allows a 2.8-Å distance between the face-sharing Ti atoms, while it is 2.3 Å in the model. This could be expected because the reduced screening effect of the oxygens in the case of face sharing increases the repulsion of the strongly charged Ti atoms.

Another observation is the increased separation of the two Ti layers at the shear plane. Their distance measured along c_P is approximately increased by 0.5 Å in the three cases, probably due again to the repulsion of the face-sharing Ti atoms.

A third observation is that the z coordinates of all the Ti layers are less than expected from rutile. The above two factors contribute to this observation, but there is also a shortening of the Ti–Ti distances in the chains attributed to Ti^{3+}–Ti^{3+} pairing as discussed in (*7*).

The observed slight shrinking of c_P with respect to the model now appears to be the approximate mutual compensation of three larger structural effects: the repulsion of the face-sharing Ti atoms which, alone, would increase the length of c_P by approximately 1.1 Å, and the tilting of the pseudo rutile chains and the shortening of the Ti–Ti distances in the chains, resulting in a slight net shortening. The constancy of the shortening appears to be more or less a numerical accident.

Conclusion

The cell proposed here unifies the descriptions of the lattices and the structures in the series. Its close relationship to the structure allows a simple discussion of the large deviations from the model of Andersson and Jahnberg (*2*). These deviations are consistent throughout the series with little distinction between even-*n* and odd-*n* members. The same treatment can be applied to other series containing shear planes.

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