



Norman F.H. Bright

DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*THE POLYMORPHISM OF  
THE OXIDE  $Ti_3O_5$*

H. IWASAKI, N. F. H. BRIGHT AND J. F. ROWLAND

MINERAL SCIENCES DIVISION

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## THE POLYMORPHISM OF THE OXIDE $Ti_3O_5$ \*

H. IWASAKI\*\*, N. F. H. BRIGHT AND J. F. ROWLAND

*Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa (Canada).*

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### SUMMARY

The oxide  $Ti_3O_5$  has been prepared by reduction of  $TiO_2$  (as anatase and as rutile) using Ti metal as reductant and vacuum sintering, or by using CO or  $H_2$  as reductant. The oxides produced, and also their oxidation products at  $650^\circ C$ , were examined by X-ray diffraction. Three forms of  $Ti_3O_5$  were characterized:

(a) a form designated as D-type, produced by the hydrogen reduction of anatase, which yielded rutile only on oxidation;

(b) a form designated as D'-type, produced by the hydrogen reduction of rutile, which had an apparently similar X-ray diffraction pattern to that of the D-type, but which yielded a mixture of anatase and rutile on oxidation;

(c) a form designated as M-type, produced by the vacuum-sintering of  $TiO_2$  with Ti metal, which had a different X-ray diffraction pattern but which also yielded a mixture of anatase and rutile on oxidation.

Forms (a) and (b) are similar to the previously-claimed high-temperature form of MAGNÉLI; form (c) is similar to his low-temperature form; the transition temperature is slightly in excess of  $100^\circ C$ .

The D'-type could be derived from the M-type. The D-type could easily be changed into the M-type by cooling from  $1350^\circ C$  under vacuum. By annealing experiments, the D-type was shown to be a meta-stable form. Some crystallographic considerations concerning the oxidation behaviour of the various polymorphs of  $Ti_3O_5$  are proposed, also a possible correlation with the various types of compounds having the pseudobrookite structure.

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### INTRODUCTION

It is well known that titanium forms many compounds with oxygen having various Ti:O atomic ratios. The Ti-O system has been extensively investigated and many partial phase diagrams have been proposed<sup>1-5</sup>. Nevertheless, the system has not yet been fully elucidated. MAGNÉLI and his co-workers<sup>6</sup> investigated to oxide  $Ti_3O_5$  by the X-ray diffraction method and showed the existence of a solid-state transition

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\*\* Present address: The Nippon Telegraph and Telephone Public Corporation, Tokyo, Japan.

temperature at about 120°C. They also investigated the crystal structures of the low- and high-temperature forms of  $Ti_3O_5$ <sup>7</sup>. Prior to the work of MAGNÉLI, a transition temperature had been proposed by NAYLOR<sup>8</sup> as a result of his investigation of the heat content of  $Ti_3O_5$ . More recently, the magnetic susceptibility of  $Ti_3O_5$  has been measured precisely and some anomalous behaviour of the magnetic susceptibility at the transition point was observed<sup>9</sup>. Thus,  $Ti_3O_5$  is considered to have at least two crystalline forms, a low- and a high-temperature form. The possibility of the existence of other forms is not to be discounted.

One of the authors of this present paper, in an earlier investigation<sup>10</sup>, studied the oxidation of  $Ti_3O_5$  that had been prepared by the hydrogen reduction of anatase and also by the vacuum sintering of a stoichiometric mixture of anatase and titanium metal powder, and found a remarkable difference between the oxidation products yielded by the  $Ti_3O_5$  made by the two different methods.

In order to investigate the cause of this difference of oxidation behaviour of the two forms of  $Ti_3O_5$  and, if possible, to correlate the behaviour with the crystalline forms, the studies described in the present paper were conducted.

#### PREPARATION OF $Ti_3O_5$

The oxide  $Ti_3O_5$  was made by reducing  $TiO_2$ ; its presence was confirmed by X-ray diffraction. Its composition was verified by a determination of the oxygen content; using an oxidation method to yield stoichiometric  $TiO_2$ .

Two forms of  $TiO_2$  were used as source materials: anatase (Baker's Analyzed Grade), and rutile prepared from this anatase by partial reduction and subsequent re-oxidation at a temperature high enough to ensure that all the  $TiO_2$  produced was present in the rutile form. The impurities present in the anatase are listed in Table I;

TABLE I  
ANALYSIS OF ANATASE

Impurity	wt. %
Water-soluble salts	0.04
As	0.00001
Fe	0.001
Pb	0.001
Zn	0.001

The above figures are the manufacturer's batch analysis.

TABLE II  
ANALYSIS OF Ti METAL

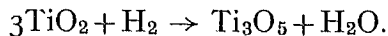
Impurity	wt. %		
Si	0.26	Dissolved O <sub>2</sub>	1.33%
Al	0.05		
Mn	0.05	Dissolved N <sub>2</sub>	0.17%
Mg	0.13		
Cr	0.17	The oxygen was determined by	
Fe	0.30	neutron-activation analysis and	
Cu	0.03	the nitrogen by chemical means.	

The other determinations were spectrographic and are semiquantitative only.

these are as quoted by the manufacturer's batch analysis. The same impurities will thus apply to the rutile made therefrom. Metallic impurities in the Ti metal used as a reducing agent were analyzed spectrographically. The dissolved oxygen was determined by neutron-activation analysis; dissolved nitrogen was determined chemically. Table II shows the results of these analyses.

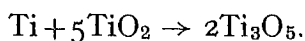
The following three methods were employed to reduce the  $\text{TiO}_2$ :

(a) *Hydrogen reduction*, according to the equation:



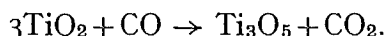
One gram of  $\text{TiO}_2$  (in either the rutile or anatase form) was placed in a molybdenum boat and reduced, usually at  $1250^\circ\text{C}$  for 3 h, in a hydrogen gas stream; the product was cooled to room temperature in the furnace, in the hydrogen gas stream. In addition, a few reduction experiments were done at  $900^\circ$ ,  $1000^\circ$ ,  $1150^\circ$ ,  $1200^\circ$  and  $1350^\circ\text{C}$  for appropriate times.

(b) *Reduction by Ti metal powder*, according to the equation:



The stoichiometric amounts of fine Ti metal powder ( $< 230$  mesh) and  $\text{TiO}_2$  powder in the appropriate form were mixed well and pressed into disks. The disks were placed in a vacuum furnace and sintered for about 3 h at  $1250^\circ$ – $1280^\circ\text{C}$  at a pressure of  $< 10^{-5}$  mm Hg, and then cooled under vacuum to room temperature. The resulting sintered black disks were again crushed to powder, re-pressed, and sintered for a second time at  $1250^\circ$ – $1300^\circ\text{C}$  for a further 3 h.

(c) *Reduction by CO*, according to the equation:



The method of reduction was the same as that used in the case of hydrogen.

All reduction products were examined by X-ray diffraction and, if desired, the oxygen content of the product was determined from the weight increase on re-oxidation to stoichiometric  $\text{TiO}_2$ .

#### EXPERIMENTAL RESULTS

In the following description and discussion the terminology D-type and M-type  $\text{Ti}_3\text{O}_5$  will be used. The D-type form is that modification of  $\text{Ti}_3\text{O}_5$  which gives an X-ray diffraction pattern very similar to that of the dititanates of the type  $\text{AO} \cdot 2\text{TiO}_2$ , where A can be  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , etc., or that of the isomorphous pseudobrookite,  $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ . This structure, with the metallic ions quoted, is, in fact, orthorhombic, whereas, with the  $\text{Ti}_3\text{O}_5$  oxide, the unit cell is slightly distorted to a monoclinic symmetry. The cell edges, however, are closely similar to those of the other dititanates. The M-form of the  $\text{Ti}_3\text{O}_5$  is slightly more monoclinic, with  $a:c$  and  $b:c$  ratios being somewhat different from those of the D-form. These forms have been discussed in some detail in the earlier paper<sup>10</sup> by one of the present authors, and will be further commented upon in the present paper.

*Reduction of anatase*

The oxide  $Ti_3O_5$  was prepared by the hydrogen reduction of anatase at  $1250^\circ C$  for 3 h. The product was demonstrated by X-ray diffraction to be the D-type  $Ti_3O_5$ . On the other hand,  $Ti_3O_5$  prepared from the vacuum sintering of the mixture of  $Ti + 5TiO_2$  (in either the anatase or rutile form) was the M-type  $Ti_3O_5$ , which corresponded to the low-temperature form  $Ti_3O_5$  claimed by MAGNÉLI<sup>5,6</sup>. The X-ray diffraction data for both the D- and M-Types of  $Ti_3O_5$  are listed in Tables III and IV, respectively.

TABLE III

X-RAY DIFFRACTION DATA FOR D-TYPE  $Ti_3O_5$ 

Line no.	Present work		Earlier work <sup>10</sup>		hkl	$d_{calc.} (\text{Å})$
	Int.	$d_{obs.} (\text{Å})$	Int.	$d_{obs.} (\text{Å})$		
1	s	4.92	2+ (br)	4.874	002	4.949
2	vs	3.52	10	3.507	200	4.914
					$\bar{2}02$	3.526
3	vw	3.33	0.5	3.300	110	3.524
					$\bar{1}11$	3.330
					111	3.312
4	vvw	2.86	< 0.5	2.839	003	3.299
					112	2.860
5	m	2.771	2-	2.770	$\bar{2}03$	2.768
6	m	2.715	2	2.708	203	2.710
7	w	2.472	1	2.461	400	2.457
8	w	2.410	1-	2.406	$\bar{3}11$	2.410
					113	2.399
9	wbr.	2.203	2br 0.5	2.186 2.097	$\bar{4}01$	2.396
					204	2.190
					402	2.180
10	w	1.992	1	1.992	$\bar{3}13$	1.996
11	vw	1.953	< 0.5	1.949	$\bar{4}03$	1.992
					403	1.949
12	s	1.889 <sub>1</sub>	7	1.888	020	1.888
13	vvw	1.862 <sub>0</sub>	0.5	1.857	$\bar{0}21$	1.855
					$\bar{2}05$	1.851
14	vw	1.832 <sub>8</sub>	0.5	1.828	205	1.821
					$\bar{3}14$	1.765
15	vw	1.764 <sub>4</sub>	1	1.762	022	1.764
					$\bar{4}04$	1.763
					220	1.762
16	vw	1.734 <sub>9</sub>	> 0.5	1.740	$\bar{5}10$	1.743
					$\bar{2}21$	1.735
					222	1.656
17	w	1.655 <sub>2</sub>	2	1.654	$\bar{5}12$	1.655
					006	1.650
18	w	1.633 <sub>1</sub>	1	1.636	023	1.639
					600	1.638
19	w	1.561 <sub>0</sub>		etc.		etc.
20	w	1.551 <sub>3</sub>				
21	vvwbr.	1.535 <sub>2</sub>				
22	vvwbr.	1.496 <sub>3</sub>				
23	vwbr.	1.434 <sub>2</sub>				
24	vw	1.372 <sub>8</sub>				
25	vw	1.358 <sub>3</sub>				
26	w	1.249 <sub>0</sub>				
	etc.					

Both sets of results were obtained using  $CoK\alpha$  radiation.

vs = very strong      w = weak  
s = strong      vw = very weak  
m = medium      vvw = extremely weak  
br. = broad, diffuse

The calculated figures given in these tables are based upon the following unit-cell dimensions:

	<i>D-Form</i>	<i>M-Form</i>
<i>a</i>	9.828 Å	9.76 Å
<i>b</i>	3.776 Å	3.80 Å
<i>c</i>	9.898 Å	9.43 Å
$\beta$	91°19'	91°35'
<i>Z</i>	4	4
Probable space group	<i>C2/m</i>	<i>C2/m</i>
Density	4.11 g/ml	4.16 g/ml

TABLE IV  
X-RAY DIFFRACTION DATA FOR M-TYPE Ti<sub>2</sub>O<sub>5</sub>

Line no.	Present work			<i>hkl</i>	ANDERSSON <i>et al.</i> <sup>5</sup>		
	<i>d</i> <sub>meas.</sub> (Å)	<i>Int.</i>	<i>d</i> <sub>calc.</sub> (Å)		<i>d</i> <sub>meas.</sub> (Å)	<i>Int.</i>	<i>d</i> <sub>calc.</sub> (Å)
1	9.4	0.5	9.43	001	9.417	vw	9.438
2	4.9	0.5	4.88	200			
3	4.7	0.5	4.72	002	4.721	vvw	4.719
4	4.27	2	4.29	201	4.280	m	4.282
5	3.53	10	3.54	110	3.539	vs	3.542
				202	3.436	vw	3.436
6	3.30	1 br.	{ 3.34 3.33 3.30	202	3.345	w	3.344
				111	3.327	w	3.327
				111	3.307	w	3.305
7	3.13	3	3.14	003	3.146	m	3.146
				112	2.846	vw	2.846
8	2.674	0.5	2.676	203	2.676	m	2.676
9	2.616	0.5	2.610	203	2.610	w	2.611
				311	2.377	w	2.377
				113	2.364	w	2.364
10	2.35	3 br.	{ 2.363 2.346 2.339	401	2.345	w	2.345
				113			
11	2.189	7	2.192	402	2.190	s	2.189
12	2.101	7	2.100	204	2.102	s	2.101
13	1.899	9	1.900	020	1.901	s	1.901
14	1.746	0.5	{ 1.744 1.743	221			
				205			
15	1.689	2	1.688	314	1.689	m	1.689
16	1.665	1	1.663	222	etc.		
17	1.644	3	1.643	512			
18	1.623	1	{ 1.627 1.626	600			
				023			
19	1.550	0.5	1.549	223			
20	1.525	0.5	1.525	602			
21	1.508	2	{ 1.513 1.508	405			
				206			
22	1.476	0.5	1.477	421			
				116			
23	1.434	3	{ 1.442 1.436	422			
				514			
24	1.409	4	{ 1.415 1.409	224			
	etc.						

The results in the present work were obtained using CoK $\alpha$  radiation.

vs = very strong      w = weak  
s = strong            vw = very weak  
m = medium          vvw = extremely weak  
br. = broad, diffuse

A comparison of these figures with those quoted in our earlier work<sup>10</sup> will show that the data for the D-form have been re-arranged so that the cell orientation results in the standard nomenclature for the space group. The actual figures are unchanged. Some modifications have, however, been made to the values for the M-form. The main difference is the halving of the *b*-value, with the consequent halving of the *Z*-value. This change has come about because of a more critical examination of the precession camera films involved; the cell edges were recalculated from the powder data after indexing, using the single-crystal photographs as a guide to the relative intensities. The figures observed and calculated by ANDERSSON *et al.*<sup>5</sup> for the monoclinic M-form are given for comparison in Table IV. The powder patterns involved in the present work have also been re-measured, resulting in slight changes from some of the *d*-spacing values quoted in our earlier work<sup>10</sup>. It will, in addition, be observed that certain faint lines were observed in our work that were not recorded by ANDERSSON *et al.* and also *vice-versa*; however, in all cases, these lines could be satisfactorily indexed on the chosen unit-cell values. Further, a few faint lines were observed in our patterns for the M-form that were attributable to the presence of a very small amount of the MAGNÉLI phase,  $Ti_4O_7$ ; these have been omitted from Table IV.

The results reported in Table III for the D-type  $Ti_3O_5$  do not call for any special comment. There is good agreement between the results of the present work and those reported in our earlier paper<sup>10</sup> in almost every case; all the observed lines could be satisfactorily indexed on the basis of the space-group and unit-cell dimensions quoted, when allowance is made for the change of orientation as mentioned above. It will be seen that there is no risk of confusion between the patterns of the D- and M-types of  $Ti_3O_5$ .

High-temperature X-ray photographs were also taken of both D- and M-types of  $Ti_3O_5$  at temperatures up to 300°C. No evidence of any transition temperature was observed with the D-type  $Ti_3O_5$  within the temperature and time ranges employed, whereas the M-type  $Ti_3O_5$  was transformed to the high-temperature form of MAGNÉLI at about 100+ °C. The X-ray diffraction pattern of this high-temperature form of the M-type, observed at temperatures above the transition point, was very similar to that of the D-type  $Ti_3O_5$ , but the details were not well defined because of the poor resolution of the high-temperature X-ray photographs. Some effort was expended in an attempt to quench this high-temperature form of the M-type to room temperature in order to clarify the details of the X-ray diffraction pattern, but this proved fruitless.

One of the authors noticed<sup>10</sup> that the D-type  $Ti_3O_5$  was changed into the M-type  $Ti_3O_5$  on melting in an argon gas atmosphere and subsequent quenching. Hence, in order to discover more concerning the relative stability of the D- and M-types of  $Ti_3O_5$ , the D-type  $Ti_3O_5$  was vacuum-sealed in a Vycor glass tube and annealed at various temperatures for a range of times. On annealing at 370°C for 6 h and subsequent cooling to room temperature, the presence of a trace of the M-type  $Ti_3O_5$  was observed by X-ray diffraction. A complete change into the M-type  $Ti_3O_5$  occurred on annealing at 1350°C for 1 h and subsequent cooling to room temperature.

A critical observation concerning these polymorphs of  $Ti_3O_5$  was that the D-type and the M-type  $Ti_3O_5$  showed quite different behaviours on oxidation at about 650°C or higher. The D-type  $Ti_3O_5$  produced only rutile at *any* oxidation temperature, whereas the M-type  $Ti_3O_5$  produced a mixture of anatase and rutile, the ratio of rutile to anatase increasing with increasing oxidation temperature.



A schematic diagram of the reduction and the oxidation experiments is shown in Fig. 1.

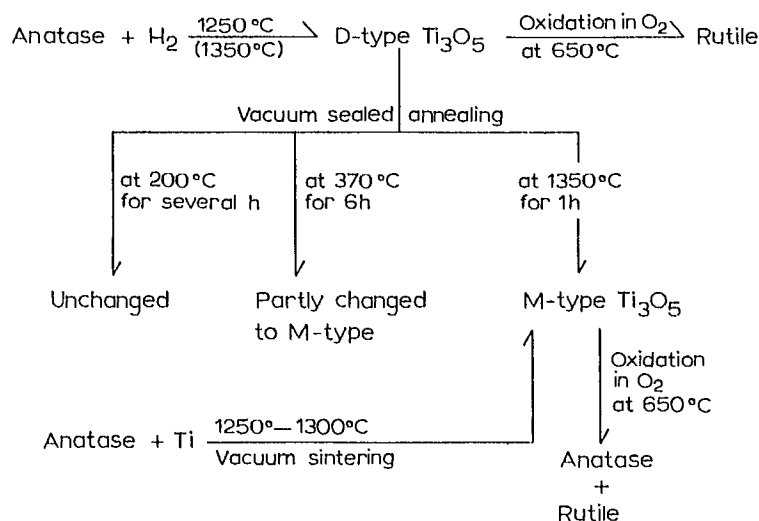


Fig. 1. Oxidation/reduction scheme for anatase/ $Ti_3O_5$ .

### Reduction of rutile

The rutile powder used as the starting material was made by reducing anatase with hydrogen at  $900^\circ C$  for 2 h and then re-oxidizing it in an oxygen stream at  $850^\circ - 900^\circ C$ . This procedure prevented any grain growth and the particle size of the rutile powder was as fine as that of the original anatase. The product was examined by X-ray diffraction; only rutile was detectable.

Rutile was found to be somewhat more difficult to reduce than anatase under similar conditions. The  $Ti_3O_5$  that was prepared by reducing rutile with hydrogen had, apparently, a similar X-ray diffraction pattern to that of the D-type  $Ti_3O_5$ , but when this material was oxidized back to  $TiO_2$  it produced a mixture of anatase and rutile. This is characteristic of the behaviour of MAGNÉLI's low-temperature form or the M-type  $Ti_3O_5$ , in contrast to the true D-type material produced by the reduction of

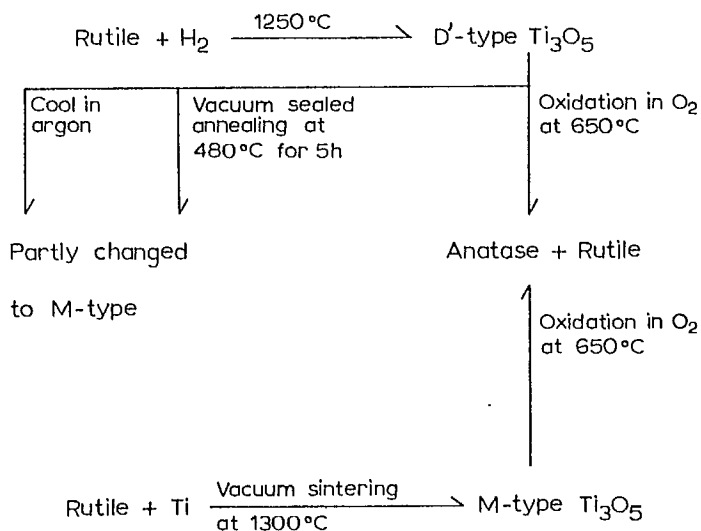


Fig. 2. Oxidation/reduction scheme for rutile/ $Ti_3O_5$ .

anatase which gave only rutile on re-oxidation. Since the anatase and the rutile had substantially the same particle size one would expect that this would also apply to their reduction products; it is not likely, therefore, that the difference in oxidation behaviour is merely a kinetic effect. There must consequently be some difference between this apparent D-type  $Ti_3O_5$ , produced from rutile under similar conditions, and the D-type material produced from anatase. We will, therefore, designate the reduced rutile product as being of the D'-type. A schematic diagram of the reduction and oxidation experiments with rutile is shown as Fig. 2.

When CO was used as the reductant only the D'-type  $Ti_3O_5$  was obtained, irrespective of whether the starting material was rutile or anatase.

## DISCUSSION

### *Chemical and thermodynamic considerations*

One can postulate two possibilities concerning the relative stability of the D- and M-types  $Ti_3O_5$  with varying temperature. One possibility is that the D-type  $Ti_3O_5$  is, in fact, isostructural with MAGNÉLI's high-temperature form of  $Ti_3O_5$ . The other is that there is a third, metastable form of  $Ti_3O_5$  that has not previously been defined but which is entering into the experiments in various ways. We will consider the two possibilities separately.

*D-Type  $Ti_3O_5$  isostructural with the high-temperature form  $Ti_3O_5$ .* In order to explain the observed phenomena, it is necessary to assume that MAGNÉLI's high-temperature form is stabilized in a hydrogen atmosphere for some reason and can be quenched to room temperature without modification. The free energy *vs.* temperature diagram for such a system would then be as shown in Fig. 3. The results of the high-temperature X-ray diffraction experiments support this assumption in that the X-ray diffraction pattern of the high-temperature form cannot be definitely distinguished from that of the D-type  $Ti_3O_5$ . When the M-type  $Ti_3O_5$  was heated to 200°–300°C (*i.e.*, above the transition temperature) in argon or hydrogen gas streams and then cooled rapidly to room temperature in an attempt to "quench in" the high-temperature form, no such quenched high-temperature form could be obtained.

The facts described above are not in disagreement with the assumption of the identity of the D-form with MAGNÉLI's high-temperature form of  $Ti_3O_5$ . The following experiment, however, does *not* support it. When the M-type  $Ti_3O_5$  was kept at 200°C in an argon gas stream for over 1 h (which was enough to transform it into the high-temperature, or presumably D-form) and then the temperature was increased gradually to 650°C in order to start the oxidation when an oxygen stream was passed over the sample, the oxidation product obtained in this case also was a mixture of anatase and rutile. This is in contrast to the oxidation product normally obtained from the D-type  $Ti_3O_5$ , namely, rutile only. This cannot be explained reasonably from the suggested free-energy diagram (Fig. 3). According to this diagram, both the D-type  $Ti_3O_5$  and the high-temperature form  $Ti_3O_5$  derived from the M-form should produce the same oxidation product, namely, rutile only. It should be noted that, in Figs. 3 and 4, both the ordinate and abscissa scales are arbitrary.

*Existence of a metastable phase.* The assumption in this case is that the D-type  $Ti_3O_5$  can exist as a stable phase in a hydrogen atmosphere, and that it is metastable under vacuum at all temperatures. It must also be metastable in air at room tempera-

ture. The free-energy diagram for such a system would then be as shown in Fig. 4.

Curves (1), (2) and (3) show the free energies of the D-type  $Ti_3O_5$ , of the low-temperature form of the M-type, and of the high-temperature form of the M-type, respectively. The stable phase at any given temperature is indicated by a solid line. Metastable or unstable phases are indicated by broken lines. The temperature, A

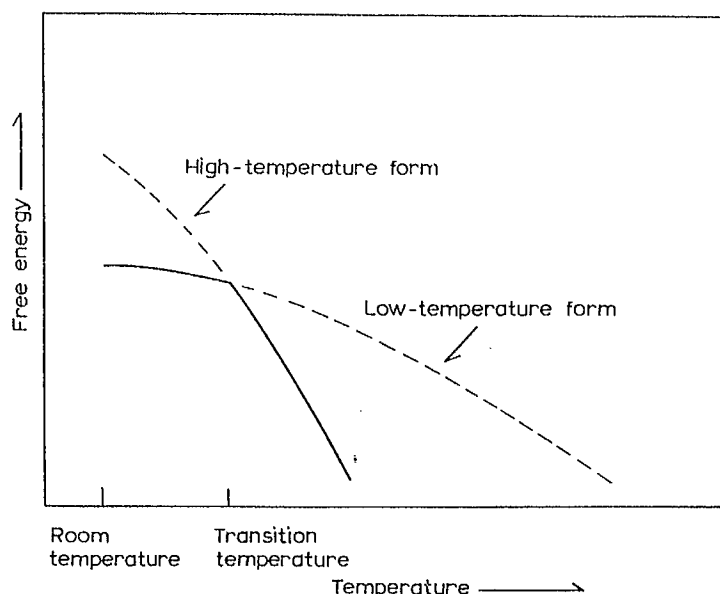


Fig. 3. Possible  $Ti_3O_5$  free-energy diagram.

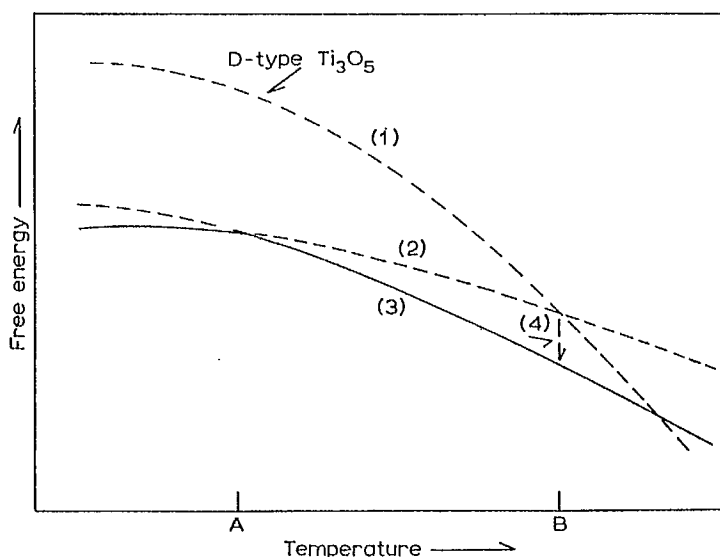


Fig. 4. Alternative possible  $Ti_3O_5$  free-energy diagram.

at the intersection of the lines (2) and (3), is the transition point between the low- and high-temperature form of the M-type  $Ti_3O_5$ . The temperature, B, at the intersection of the lines (1) and (2), may occur between  $1350^{\circ}C$  and  $1450^{\circ}C$ , since the product of reduction of anatase by hydrogen at  $1450^{\circ}C$  is not the D-type  $Ti_3O_5$ , but rather the M-type<sup>10</sup>. When the D-type  $Ti_3O_5$  is heated in vacuum, its free energy changes along the line (1). When it is cooled from above the temperature B, the free energy may change along the line (1) down to B. Since the free energy of the low-temperature M-form is

lower than that of the D-type  $\text{Ti}_3\text{O}_5$  at temperatures below point B, then the D-type  $\text{Ti}_3\text{O}_5$  changes its crystal form at the point B into that of the low-temperature M form. This low-temperature M-form  $\text{Ti}_3\text{O}_5$ , however, does not exist as a stable phase at temperatures above the point A. Therefore, the D-type  $\text{Ti}_3\text{O}_5$  may be changed directly to the high-temperature M-form by following down the line (4) from B. The high-temperature form is easily transformed to the low-temperature form at A, below which temperature the latter is the only stable phase. Thus, the net process of the free-energy change of the D-type  $\text{Ti}_3\text{O}_5$  on cooling from a temperature above the point B, may be as follows: along the line (1) down to B, along the line (4) at B, along the line (3) down to A, and along the line (2) below A. As a result, the D-type  $\text{Ti}_3\text{O}_5$ , when heated up to above the point B and then cooled down to room temperature, is transformed completely to the M-type  $\text{Ti}_3\text{O}_5$  (low-temperature form). On the other hand, when the D-type  $\text{Ti}_3\text{O}_5$  is kept under vacuum below the point B (*i.e.*, at some temperature between A and B), it is changed gradually to the stable form (high-temperature M-type) because the D-type  $\text{Ti}_3\text{O}_5$  is not stable except in the hydrogen atmosphere. Thus, the reduction of anatase by hydrogen at a temperature not significantly above  $1350^\circ\text{C}$  is necessary to obtain the D-type  $\text{Ti}_3\text{O}_5$ . However, no indication of the presence of any OH group in this reduction product, or of that of interstitial hydrogen in the lattice could be obtained, either by infrared spectroscopic examination or by direct chemical analysis, respectively.

The difference of the oxidation products of the D-type  $\text{Ti}_3\text{O}_5$  and the M-type  $\text{Ti}_3\text{O}_5$  can be explained logically; that is, only the metastable  $\text{Ti}_3\text{O}_5$  (D-type) can produce rutile on oxidation, while the M-type  $\text{Ti}_3\text{O}_5$  produces primarily anatase on oxidation. Though the difference between the D-type  $\text{Ti}_3\text{O}_5$  and the high-temperature form of the M-type, which we have designated as the D'-type, could not be definitely detected from the X-ray powder photographs, as described above, these two forms can be differentiated clearly by their oxidation products at low temperature.

In order to investigate the detailed crystalline properties of the D-type  $\text{Ti}_3\text{O}_5$ , a few attempts were made to prepare single crystals by recrystallisation from a borate melt, but no single crystals of the desired oxide were obtained.

When rutile and anatase are gradually reduced in a hydrogen gas stream, many compounds can be produced in succession, such as  $\text{Ti}_n\text{O}_{2n-1}$  (the so-called MAGNÉLI phases) where  $n=10, 9, \dots, 5, 4$ ,  $\text{Ti}_3\text{O}_5$  and, ultimately,  $\text{Ti}_2\text{O}_3$ . According to our experiments, the oxidation product of  $\text{Ti}_n\text{O}_{2n-1}$ , where  $n > 3$ , at  $650^\circ\text{C}$  was rutile only, regardless of whether rutile or anatase was used as the original starting material. On the contrary, in the case of  $\text{Ti}_3\text{O}_5$  made by hydrogen reduction of  $\text{TiO}_2$ , the oxidation product differed, depending on whether the original starting material was in the rutile or anatase form, as has been mentioned above. Thus, one form (D-type) of  $\text{Ti}_3\text{O}_5$  would appear to act as a MAGNÉLI phase whereas the M-type does not, insofar as oxidation behaviour is concerned. Therefore, the D'-type  $\text{Ti}_3\text{O}_5$  must be thought to be different from the D-type  $\text{Ti}_3\text{O}_5$ . In the stability diagram of the various types of  $\text{Ti}_3\text{O}_5$  (Fig. 4) the D'-type is represented by the upper portion of the line (3) and may be considered as being a quenched high-temperature M-form.

Insofar as the X-ray powder patterns are concerned, the D'-type  $\text{Ti}_3\text{O}_5$  (high-temperature form) is not definitely distinguishable from the D-type  $\text{Ti}_3\text{O}_5$ . Therefore, any differences in structure between these two forms of  $\text{Ti}_3\text{O}_5$  must be very small. Compounds of the dititanate or pseudobrookite type all have the formula  $\text{AB}_2\text{O}_5$ .

In the case of the oxide  $Ti_3O_5$ , both A and B positions are occupied by titanium. However, it is possible to conceive of two ways of arranging them:

- (i) As  $TiO \cdot 2TiO_2$ , analogous to ferrous or magnesium dititanate, where the titanium can be regarded as having the equivalent of mixed bi- and tetra-valency, or
- (ii) as  $Ti_2O_3 \cdot TiO_2$ , analogous to pseudobrookite itself or the isomorphous aluminum compound, where the titanium can be regarded as having the equivalent of mixed ter- and tetra-valency.

Members of both types of these arrangements all give extremely similar patterns and indeed are isomorphous, and can produce very extensive solid-solution series between any or all of the compounds mentioned. They all have a structure which, while being orthorhombic is, as has been mentioned earlier, very close to that of the D-type  $Ti_3O_5$ . It is, perhaps, possible that the D-type  $Ti_3O_5$  might be represented by one of the above double-oxide formulae and that the D'-type would be represented by the other. One would, therefore, not expect them to behave significantly differently insofar as X-ray diffraction pattern is concerned. A difference of oxidation behaviour, however, is not impossible. It is, nevertheless, not possible at this stage to substantiate this possibility nor to hazard a guess as to which form corresponds to which formula, or if, indeed, the idea has any validity.

#### *Crystallographic considerations*

The MAGNÉLI phases in the Ti-O system (*i.e.*, oxides having the formula  $Ti_nO_{2n-1}$ ) have been shown<sup>11</sup> to be built up of blocks having essentially the rutile structure, these blocks extending indefinitely in two dimensions but with a finite thickness of  $n$  octahedra, each having the composition  $TiO_6$ . It is, therefore, not surprising that these phases, on oxidation to stoichiometric  $TiO_2$ , should yield the rutile form rather than the anatase form. The D-type  $Ti_3O_5$ , which yields only rutile on oxidation to  $TiO_2$ , may be regarded as the MAGNÉLI phase with  $n = 3$  in respect of oxidation behaviour. However, because no crystal structure work on this oxide is available owing to the inability to prepare single crystals of it up to the present time, it is not yet certain whether it does in fact have the same type of crystal structure as the MAGNÉLI phases or not.

It has been shown that the M-type  $Ti_3O_5$  yields a mixture of anatase and rutile on oxidation to stoichiometric  $TiO_2$ , the proportion of rutile in the mixture increasing with the temperature of oxidation used. It is considered reasonable to assume that the primary product of oxidation in this case is anatase, and that owing to the instability of anatase at elevated temperatures, the oxidation product then proceeds to invert to rutile at a rate which increases with increasing temperature. If it were kinetically feasible to conduct the oxidation at a low enough temperature, it is considered that the product would be entirely in the anatase form.

One would, therefore, expect that the M-type  $Ti_3O_5$  should have an analogy in crystal structure with that of anatase. In anatase, the structure is again built up from  $TiO_6$  octahedra but, in this instance, the structure is formed by these octahedra sharing edges only and forming zig-zag chains (Fig. 5(a)). According to ÅSBRINK AND MAGNÉLI<sup>6</sup>, the low temperature M-type  $Ti_3O_5$  is also formed from edge-sharing  $TiO_6$  octahedra, in this case forming portions of similar zig-zag chains. These portions link together to form spiral chains (Fig. 5 (b)). It will be seen that there is a common unit of structure (Fig. 5 (c)) occurring in both of these oxides. In the high-temperature M-

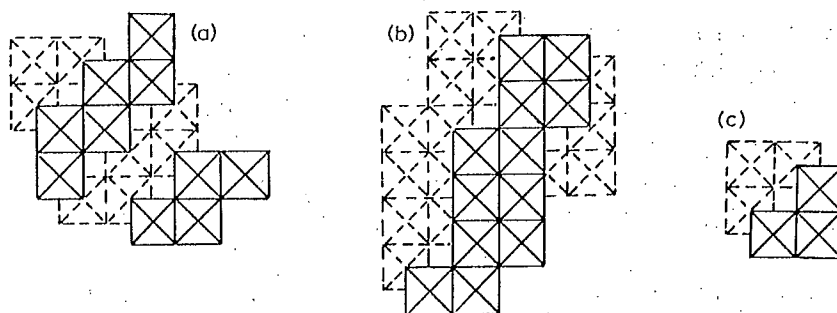


Fig. 5. Arrangement of  $\text{TiO}_6$  Octahedra in (a) anatase, (010) plane; (b) low-temperature M-type  $\text{Ti}_3\text{O}_5$ , (010) plane; (c) common structural unit, present in (a) and (b).

type  $\text{Ti}_3\text{O}_5$ , the structure is essentially similar to that of the low-temperature M-type  $\text{Ti}_3\text{O}_5$ , but with some movement of atoms and distortion of the octahedral arrangement, as indicated by ÅSBRINK AND MAGNÉLI<sup>6</sup>. However, their assignment of the name "anosovite" to this form is not considered to be correct since anosovite yields rutile on oxidation and is thus the D-form, possibly stabilised by the presence of small amounts of other metallic ions. This is supported by the X-ray data of RUSAKOV AND ZHDANOV<sup>12</sup>, who originated the name anosovite.

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#### REFERENCES

- 1 R. C. DE VRIES AND R. ROY, *Am. Ceram. Soc. Bull.*, **33** (1954) 370.
- 2 E. S. BUMPS, H. D. KESSLER AND M. HANSEN, *Trans. Am. Soc. Metals*, **45** (1953) 1008.
- 3 T. H. SCHOFIELD AND A. E. BACON, *J. Inst. Metals*, **84** (1955-56) 47.
- 4 P. G. WAHLBECK AND P. W. GILLES, *J. Am. Ceram. Soc.*, **49** (1966) 180.
- 5 S. ANDERSSON, B. COLLÉN, V. KUYLENSTIERNA AND A. MAGNÉLI, *Acta Chim. Scand.*, **11** (1957) 1641.
- 6 S. ÅSBRINK AND A. MAGNÉLI, *Acta Cryst.*, **12** (1959) 575.
- 7 G. ÅSBRINK AND S. ÅSBRINK, Studies on the crystal chemistry of titanium, vanadium and molybdenum oxides at elevated temperatures, *Final Tech. Rept. No. 1, U.S. Dept. of Army Contract DA-91-591-EUC-935*, by A. MAGNÉLI *et al.*; University of Stockholm, Sweden, October, 1959, p. 18.
- 8 B. F. NAYLOR, *J. Am. Chem. Soc.*, **68** (1946) 1077.
- 9 YA. V. VASILÉV AND S. M. ARIYA, *Inorg. Materials (U.S.S.R.)*, **1** (1965) 322.
- 10 N. F. H. BRIGHT, *Advances in X-Ray Analysis*, Vol. 4, Plenum Press, New York, 1961, p. 175.
- 11 S. ANDERSSON, *Acta Chim. Scand.*, **14** (1960) 1161.
- 12 A. A. RUSAKOV AND G. S. ZHDANOV, *Dokl. Akad. Nauk SSSR*, **77** (1951) 411.

