Notes on some Structures of the Ilmenite Type.

By

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(With 2 figures.)

Introduction.

In connection with the study of ilmenite recorded in the preceding article the formation and properties of mixed crystals in the system, $Fe_2O_3\text{-}Ti_2O_3$, of which ilmenite is a member, as well as several other compounds of this general type were examined. The latter included $CdTiO_3$, $MgTiO_3$, $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$. Except for $CdTiO_3$ and $CoTiO_3$, the similarity of the powder photographs obtained from these compounds to that of ilmenite had been shown previously by other investigators[1]. $CdTiO_3$ was recorded by Zachariasen (op. cit.) to have a perovskite-like structure while the preparation we had made of this compound was found to possess the ilmenite type structure. This apparent disagreement made it necessary to investigate whether $CdTiO_3$ existed in more than one modification. The confirmative results we obtained gave the study of $CdTiO_3$ especial interest, as it thus furnished in accordance with Goldschmidt's theory a case that defines the limiting ratio value for the atomic dimensions that is required for the crystallization of titanates in one or the other structural arrangement.

Solid Solutions in the System, $Fe_2O_3\text{-}Ti_2O_3$.

In the system, $Fe\text{-}Ti\text{-}O$, the composition $FeTiO_3$ corresponding to the mineral ilmenite lies at the intersection of the binary systems, $FeO\text{-}TiO_2$, and $Fe_2O_3\text{-}Ti_2O_3$. The question whether in ilmenite the iron is di- or trivalent, and correspondingly the titanium quadri- or trivalent has often been the subject of discussion. Only very recently, however, has a satisfactory solution been presented by Hámos and Stscherbina[2]), who measured the X-ray absorption edge of the titanium in ilmenite, and compared it with that in titanium compounds of known valency.

1) V. M. Goldschmidt, Geochemische Verteilungsgesetze VII, Oslo 1926. W. H. Zachariasen, Vid. Akad. Skr. Oslo, 1928, No. 4. N. W. Taylor, Z. physik. Ch. (B) 9, 241. 1930.

2) L. V. Hámos and W. Stscherbina, Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. 232. 1933.

The conclusion they arrived at was that in ilmenite at ordinary temperature the iron was divalent and titanium quadrivalent.

The view that iron was trivalent in ilmenite was partly based on the apparent isomorphism — between hematite and ilmenite there was a continuous series of solid solutions. It was shown, however, by Warren[1]) that iron-rich ilmenites were often inhomogeneous, containing hematite as inclusions. Ramdohr[2]) made some experiments which showed that at higher temperatures such inhomogeneous ilmenites could be homogenized. While therefore no complete solubility may exist at ordinary temperature, at elevated temperatures such miscibility does take place, and, by quenching, the solid solution may be preserved at ordinary temperature.

In connection with other work we had made some experiments relating to the question of solid solutions in the system, Fe_2O_3-TiO_2, and it seems useful to report here some of the results and give a few determinations of the properties of pertinent preparations. These preparations were made by heating appropriate mixtures sealed in evacuated silica glass tubes in an electric furnace at about $1200°$ for a number of hours, and then quenching them. The resulting products were examined microscopically in reflected light by Dr. J. W. Greig, and if found inhomogeneous were reground and heated as before. No difficulties in preparing homogeneous material of the composition of ilmenite, and of a solid solution midway between hematite and ilmenite were encountered. Beyond this, that is, between ilmenite and titanium sesquioxide, repeated grinding and heating did not result in the formation of a single homogeneous phase. However, as we have made up to the present only a very limited number of experiments, these negative results do not permit us as yet to exclude the possibility that some solid solutions may exist between ilmenite and titanium sesquioxide. Considering the crystallographic data of titanium sesquioxide, the absence of solid solutions in this portion of the system, Fe_2O_3-Ti_2O_3, would be rather unexpected.

In Table I, and graphically in Fig. 1, are given the values showing the changes in the dimension of the unit cell, the axial angle, and the volume from hematite to ilmenite. From this it will be seen that the approximately linear relation of the volume change between them is due to the compensating effects of the changes in the size of the unit cell and the axial angle, the curve of the latter having a distinct minimum[3]).

1) C. H. Warren, Econ. Geol. 8, 419. 1918.

2) P. Ramdohr, N. Jb. Min. Geol. 54, Beilage B., 320. 1926.

3) The straight line relation previously given by G. Doby and G. Melczer (Z. Krist. 39, 526. 1904) between the axial ratio and the composition is doubtful on account of the probably inhomogeneity of the material. Cf. Warren, op. cit.

Table I. Unit cell dimensions of various members of the system, Ti_2O_3-Fe_2O_3. (Composition in mol per cent.)

Ti_2O_3	Fe_2O_3	a	r_0	volume
100[1])	0	56° 50'	5.42	104.6
50	50	54° 50'	5.52	104.8
Ilmenite[2])		54° 40'	—	—
25	75	54° 30'	5.50	102.7
0[1])	100	55° 14'	5.42	100.1
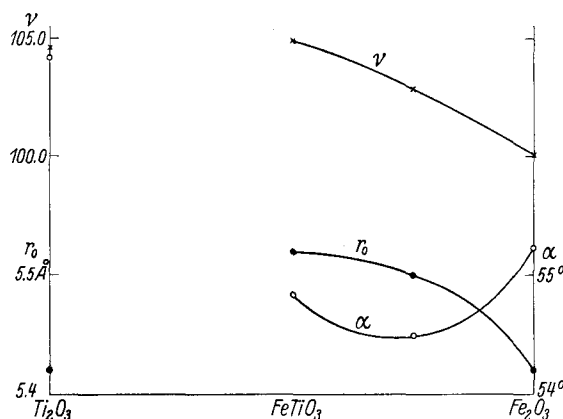
Fig. 1. Changes in the unit cell dimensions, the axial angle and the volume in the system, Fe_2O_3-Ti_2O_3.

Since hematite and ilmenite form a continuous series of solid solutions it becomes of some interest to compare the interatomic distances of these compounds. In hematite the Fe-atoms are not equally spaced along the trigonal axes but show alternate spacings of 2.89 Å and 3.98 Å. Ilmenite can be regarded as hematite in which pairs of Fe-atoms have been replaced by pairs of Ti-atoms. By this replacement the distance Fe-Fe as well as the distance Ti-Ti remains 3.98 Å, whereas the distance Fe-Ti becomes 3.03 Å, as graphically shown in Fig. 2.
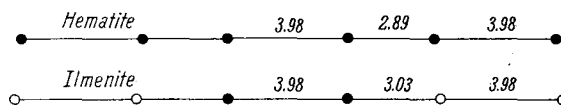

Fig. 2. The distribution of the metal atoms along the trigonal axis in hematite and ilmenite. Solid circles represent iron and open circles titanium.

1) Zachariasen, op. cit.
2) Calculated from the crystallographic measurements of Kokscharov.

Six oxygen atoms in an irregular octahedral arrangement surround each metal atom, the minimum distance O-O being 2.40 Å in ilmenite.

In Table II the distances metal-oxygen encountered in $FeTiO_3$, Fe_2O_3, and Ti_2O_3 are all given.

Table II. Interatomic distances in $FeTiO_3$, Fe_2O_3, and Ti_2O_3.

	FeO		TiO	
	I	II	I	II
Ilmenite	2.00	2.05	2.05	2.05
Fe_2O_3[1]) and Ti_2O_3[1])	1.99	2.06	2.03	2.06

In the ilmenite structure there are 5 variable parameters the values of which cannot possibly be determined with great accuracy; the limit of error in the interatomic distances given is about $\pm$ 0.1 Å.

Dimorphism of $CdTiO_3$.

As was mentioned above, $CdTiO_3$ was found by Zachariasen[2]) to have a perovskite-like structure. The preparation, he stated, was made by Professor Goldschmidt by melting a compressed tablet of the mixed oxides in an acetylene-oxygen flame. Our first preparation was made by heating a mixture of titanium oxide and cadmium carbonate below 1000°. It was found that combination took place readily even at lower temperatures, and that by repeated heating after regrinding a microscopically homogeneous preparation of $CdTiO_3$ was obtained in this way. The powder photographs of this preparation, however, showed not a structure like that of perovskite but one similar to ilmenite. This raised the question whether Zachariasen's material was really $CdTiO_3$. An experiment we made by heating some of the material of our original mixture in an oxygen flame showed that at these high temperatures considerable volatilization took place: cadmium was apparently driven off. To prevent this as much as possible by not heating to unnecessarily high temperatures, and to be able to control the temperature, further work was done in an electric furnace. It was soon found that the material melts in the neighborhood of 1400°, and that the powder spectrogram of preparations made at the higher temperature resembled that of perovskite. The latter thus confirms Zachariasen's earlier statement of the existence of a $CdTiO_3$ that crystallizes with a perovskite type structure.

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1) According to W. H. Zachariasen, op. cit.
2) Zachariasen, op. cit., p. 111.

Next it was of interest to ascertain the relation of the two forms of $CdTiO_3$. Without going into detailed description of the experiments that were made, we may summarize the results of these experiments by stating that slow cooling of the modification formed at the higher temperature down to room temperature does not cause it to invert to the modification obtained at the lower temperature. Neither does the higher temperature modification appear to invert when held for several days just below $1000°$. It was found that from about $1050°$ on, the perovskite type modification was always formed, while up to about $1000°$ only the ilmenite type modification could be obtained; the latter when heated at temperatures above about $1050°$ was readily converted into the perovskite type. These results indicate that the relation of the two modifications of $CdTiO_3$ is monotropic.

The interest attached to the existence of the two modifications of $CdTiO_3$, the ilmenite and the perovskite type, lies in that it gives us in accordance with Goldschmidt's theory a definite limiting value of the ratio of the atomic dimensions that is required in compounds of this type for the formation of one or the other structural arrangements. For the discussion of the theory the reader must be referred to Goldschmidt's original work (op. cit.), where also will be found the values for the atomic ratios of several compounds of this type crystallizing either in the ilmenite or the perovskite arrangement. The existence of the two modifications of $CdTiO_3$ determines and limits Goldschmidt's "Toleranzfaktor" to the value 0.85 (using his own atomic distances). This, however, may be taken as the limiting value only for titanates, and in other compounds of the ABX_3-type it may be apparently somewhat different. Thus in $NaNbO_3$ that has the perovskite structure the ratio (Toleranzfaktor) has the value of 0.81 according to Goldschmidt. His assumption that 0.80 was the general lower limiting value for the formation of the perovskite structure would seem therefore not to be tenable, and very likely the value may differ somewhat for each series of compounds.

The Structures of $MgTiO_3$, $MnTiO_3$, $NiTiO_3$, $CoTiO_3$ and $CdTiO_3$.

From crystallographic data we know that $MnTiO_3$, pyrophanate, is isomorphous with ilmenite, i. e. isomorphous with the space group C_{3i}^2. X-ray spectrograms of $MnTiO_3$ are very similar to those of ilmenite, and consequently the parameter values of the atoms in the unit cell of $MnTiO_3$ must be similar to those in ilmenite, and thus the apparent holohedral symmetry of Laue photographs of $MnTiO_3$ is explained.

$MgTiO_3$, $NiTiO_3$, $CoTiO_3$, and $CdTiO_3$ have been obtained only as fine powders. The powder spectrograms of these substances are very similar to the ilmenite powder spectrogram, and this in combination with the close chemical analogy suggests that all these substances crystallize in the corundum-ilmenite type. An intensity calculation for $NiTiO_3$ showed this assumption to be correct and the data for all are given in Tables III and IV.

Table III. Observed spacings.

	$NiTiO_3$	$CoTiO_3$	$MnTiO_3$	$MgTiO_3$	$CdTiO_3$
111	4.58	—	—	4.70	4.95
100	4.20	4.16	—	4.22	4.36
110	3.695	3.71	3.75	3.73	3.88
211	2.70	2.725	2.78	2.74	2.87
1̄10	2.51	2.53	2.57	2.55	2.62
221 } 222	2.30	—	—	—	2.48
210	2.21	2.22	2.25	2.23	2.32
11̄1̄	2.14	—	—	—	2.24
200	2.07	2.125	2.18	2.07	2.17
220	1.84	1.849	1.89	1.860	1.935
322	1.795	—	—	1.815	—
311	1.740	—	—	—	—
321	1.694	1.707	1.745	1.715	1.799
1̄20	1.627	—	—	—	1.713
332 } 2̄11	1.601	1.610	1.655	1.647 / 1.620	—
333	1.522	—	—	1.545	—
310	1.483	1.491	1.518	1.501	1.556
2̄11	1.449	1.455	1.480	1.465	1.511
320	—	1.422	—	1.433	1.484
422	1.352	1.354	—	—	1.440
300 } 22̄1̄	—	—	1.388	1.400	—
432 } 433	1.311	1.320	1.357	1.328	—
421	—	1.280	—	—	1.334
2̄20	1.255	1.261	1.280	1.269	1.311
411 } 330	1.227	1.229	—	—	1.290
431	—	—	—	—	1.260
2̄21	—	—	—	1.221	—
3̄10	1.188	1.192	—	1.200	1.241
442	1.462	1.470	1.200	—	—
32̄1̄	1.137	1.083	—	1.175	1.191
420	1.100	1.105	1.129	1.111	1.157

Table III (continuation).

	$NiTiO_3$	$CoTiO_3$	$MnTiO_3$	$MgTiO_3$	$CdTiO_3$
144 225 2̄22	—	—	—	—	1.120
522 532	1.053	1.060	1.086	1.066	—
400 430	1.037	1.040	1.058	—	1.082
3̄21 521 531	0.985	0.992	1.010	0.997	—
41̄1 3̄21 511	0.955	0.961	0.970	0.970	1.004

	a	r_0
$NiTiO_3$	55° 8′	5.45
$CoTiO_3$	54° 42′	5.49
$MnTiO_3$	54° 16′	5.62
$MgTiO_3$	54° 39′	5.54
$CdTiO_3$	53° 36′	5.82

Table IV. Calculated and observed intensities.

	$NiTiO_3$ Calc.[1]	$NiTiO_3$ Obs.	$CoTiO_3$ Obs.	$FeTiO_3$ Calc.[1]	$FeTiO_3$ Obs.	$MnTiO_3$ Obs.	$MgTiO_3$ Obs.	$CdTiO_3$ Obs.
111	0.5	0.5	—	0.3	—	—	4	2
100	0.4	0.5	—	0.2	—	—	4	4
110	2.3	5	5	1.7	4	3	5	3
211	10.0	10	10	10.0	10	10	10	10
11̄0	8.0	9	9	7.1	9	9	7	9
221	0.2	0.5	—	0.1	—	—	—	1
222	0.2			0.0	—	—	—	
210	3.4	5	4	3.0	3	5	8	4
120	0.7			1.0	1			
1̄1̄1̄	0.1	0.5	2	0.0	—	—	--	2
200	0.2			0.1	—	—	1	0.5
220	6.7	7	6	6.7	6	7	6	8
322	0.1	0.5	—	0.0	—	—	0.5	—
311	0.0	0.5	—	0.0	—	—	0.5	—
321	10.0	9	8	7.7	8	8	9	7
2̄10	0.0	0.5	—	—	—	—	—	3
1̄20	0.2			—	—	—	—	
2̄1̄1	0.6	2	2	0.5	3	1	2	—
332	2.0			2.6			0.5	

Table IV (continuation).

	$NiTiO_3$		$CoTiO_3$	$FeTiO_3$		$MnTiO_3$	$MgTiO_3$	$CdTiO_3$
	Calc.[1])	Obs.	Obs.	Calc.[1])	Obs.	Obs.	Obs.	Obs.
333	0.1	0.5	—	0.1	—	—	0.5	—
310	7.6	6	7	7.8	7	7	5	7
$\bar{2}$11	8.3	6	6	7.7	7	6	6	5
320	—	—	0.5	—	—	—	0.5	0.5
422	0.9	1	1 +	1.7	2	1	—	1
300 } 22$\bar{1}$	—	—	—	—	—	—	1	—
432 } 342 } 433	0.0 / 0.9 / 3.2	3	3	0.0 / 0.3 / 0.2	— ? / — ?	4	3	—
421	—	—	1	—	—	—	—	0.5
2$\bar{2}$0	2.3	2	2	2.2	3	2	2	2
411 } 330	0.8	0.5	1	0.5 / 0.4	1	—	—	1
431	—	—	—	—	—	—	—	2
3$\bar{1}$0	0.5	1 —	2	—	2	1	2	1
442	1.8	1 +	2 +	1.4	2	1	—	—
32$\bar{1}$	2.9	2	3	3.1	2	2	2	3 +
420	3.0	3	3	2.3	2	1 +	3	2
144 } 225 } 22$\bar{2}$	0.3	—	—	0.2	—	—	—	3
522 } 532	0.1 / 3.0	3	3	0.0 / 2.4	3	2	3 —	—
400 } 430	0.9 / 0.1	0.5	0.5	1.0	1	1 —	—	2 —
3$\bar{2}$1 } 521 } 531	0.1 / 1.2 / 0.3	0.5	1	0.1 / 1.6 / 0.1	2	1	0.5	—
41$\bar{1}$ } 3$\bar{2}$1 } 511	1.3 / 2.2 / 0.0	3	2	1.3 / 2.1 / 0.0	1	1	1	1

1) Parameter values.

$$u_{Ni} = 127° = 0.353$$
$$u_{Fe} = 129° = 0.358 \qquad \text{Oxygens:} \quad \begin{cases} x = \ \ \ 200° = \ \ \ \ 0.555 \\ y = -20° = -0.055 \\ z = \ \ \ 90° = \ \ \ \ 0.250 \end{cases}$$
$$u_{Ti} = \ \ 51° = 0.142$$

In $CdTiO_3$ the positions of the metal atoms can be approximately determined by using reflections from faces with small spacings since the contribution from the oxygen atoms is negligible for such reflections. The

reflection from $2\bar{2}2$ is independent of the parameter values and can therefore be taken as a standard. The value of the parameters for Cd and Ti must be in the neighborhood of $125°$ and $60°$ respectively, since

$2\bar{2}0 > 3\bar{1}0 = 421 = 320 = 3\bar{2}0 = 511$	corresponding to $123°$ and $54°$		
$2\bar{2}0 < 32\bar{1}$	«	« $126°$ «	$54°$
$2\bar{2}0 \overline{\overline{<}} (2\bar{2}2) + (144) + (255)$	«	« $123°$ «	$58°$
$2\bar{2}0 = 420$	«	« $129°$ «	$54°$
$2\bar{2}0 = 431 = 422$	«	« $128°$ «	$53°$
		or $120°$ «	$60°$

Although the values of the three parameters of the oxygen atoms cannot be determined with any great accuracy from intensity data alone, it is worth noticing that the geometry of the unit rhombohedron of $CdTiO_3$ permits a good determination of the positions of all the atoms. Thus, if it is assumed that all of the oxygen-oxygen distances shall lie between 2.5 Å and 2.6 Å, and that the distance Ti—O shall be 1.89 Å, the largest possible distance Cd—O is 2.24 Å. This distance is appreciably smaller than the distance between cadmium and oxygen found in other compounds. The arrangement giving rise to the above interatomic distances is determined by the following five parameter values:

$$u_{Cd} = 123° = 0.342$$
$$u_{Ti} = 56° = 0.156$$
Oxygens: $x = 195° = 0.54$
$$y = -11° = -0.03$$
$$z = 94° = 0.26$$

Since any deviation from this arrangement would give a still smaller Cd—O distance, it may be assumed that this arrangement represents the most probable structure for the ilmenite type of $CdTiO_3$.

As previously stated, $CdTiO_3$ is dimorphous, with one modification crystallizing in the perovskite type. It is of interest to compare the interatomic distances encountered in the two modifications:

Table V. Distances metal to oxygen in $CdTiO_3$.

	Ti—O	Cd—O	
Ilmenite type	1.89	2.24	•
Perovskite type[1])	1.88	2.66	

1) According to W. H. Zachariasen, op. cit.

Summary.

Some data relating to changes in the properties of solid solutions between hematite and ilmenite are given, and the structure of such solid solutions is discussed.

Cadmium titanate when formed below about 1050° crystallizes with the ilmenite type structure. At higher temperatures it changes to a modification which has a structure of the perovskite type which does not invert on cooling.

The structures of $NiTiO_3$, $CoTiO_3$, $MnTiO_3$, $MgTiO_3$, and low temperature $CdTiO_3$, which are very similar, have been examined. Intensity calculations for $NiTiO_3$ prove it to have the ilmenite type structure.

It is of interest to note that in the low temperature form of $CdTiO_3$ the distance Cd—O appears to be considerably smaller than in previously determined cadmium compounds.

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