

## The Crystal Structure of Ilmenite.

By

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(With 2 figures.)

Although no determination of the crystal structure of ilmenite  $FeTiO_3$ , has been published, several authors have expressed the opinion that its atomic arrangement is closely related to that of various structurally isomorphous sesquioxides such as  $Al_2O_3$ ,  $Ti_2O_3$ ,  $Fe_2O_3$ , which are all known to crystallize in the so-called corundum type.

The reason for this supposition is that the X-ray diffraction patterns of ilmenite and of the said sesquioxides are very similar, e. g., the similarity between a Laue photograph of ilmenite and one of hematite ( $Fe_2O_3$ ) is so pronounced that the two can be differentiated only by very accurate spacing measurements.

In the present paper a complete determination of the atomic arrangement of ilmenite, based on an evaluation of new experimental data, will be given. The result thus obtained verifies the assumption that the crystal structure of ilmenite is intimately related to the corundum type.

The writers are indebted to Dr. W. F. Foshag of the U. S. National Museum for the loan of various crystals of ilmenite, and also to Prof. C. Palache, Harvard University, for specimens of small crystals of ilmenite from Quincy, Massachusetts, representing original material crystallographically described by Warren and Palache<sup>1</sup>).

Crystals of the corundum type have been shown to be isomorphous with the space group  $D_{3d}^6$ ; and yet important crystallographic data place ilmenite in the point group  $C_{3i}$ . In this point group there are only two space groups, one with hexagonal and one with rhombohedral axes, and since it can be shown that the unit cell of ilmenite is a rhombohedron, only the second space group,  $C_{3i}^2$ , can be isomorphous with crystals of ilmenite.

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1) Proc. Amer. Acad. Arts Sci. **47**, 165. 1911.

However, a space-group determination from purely röntgenographic data of the usual kind would very likely give a different result. As just stated, Laue photographs of ilmenite are practically identical with those of hematite and exhibit a holohedral trigonal symmetry. Moreover, analyses of Laue photographs and powder spectrograms using space-group criteria in combination with chemical considerations seem definitely to indicate that ilmenite is isomorphous with  $D_3^7$ . But since the crystallographic evidence of external face development is so very definite in favor of the point group  $C_{3i}$  one must assume that this is the true symmetry of ilmenite, and that the Laue and powder reflections in this case record only an apparent symmetry produced by special numerical values of the parameters of the constituent atoms.

In the unit rhombohedron of ilmenite there are two molecules of  $FeTiO_3$ , and the positions of the atoms in the cell must be as follows:

$$\begin{array}{l} 2 \text{ Fe and } 2 \text{ Ti in } u u u, \bar{u} \bar{u} \bar{u}. \\ 6 \text{ oxygens in } \quad x y z, y z x, z x y \\ \quad \quad \quad \bar{x} \bar{y} \bar{z}, \bar{y} \bar{z} \bar{x}, \bar{z} \bar{x} \bar{y}. \end{array}$$

It is a point of great interest that for a certain set of numerical values of these 5 parameters a structure which is very similar to that of hematite is produced. The ideal case arises, as already pointed out by Ewald and Hermann<sup>1)</sup>, if  $x$ ,  $y$ , and  $z$  for oxygen be taken equal to  $\frac{7}{12}$ ,  $-\frac{1}{12}$ , and  $\frac{3}{12}$ , respectively, and if  $u$  for  $Fe$  and  $Ti$  be taken equal to  $\frac{1}{6}$  and  $\frac{1}{6}$ , respectively. Such a structure would be identical with that of hematite except that every other  $Fe$ -atom in the hematite structure is replaced by a  $Ti$ -atom.

A region around these positions was therefore investigated, and excellent agreement between calculated intensities and those estimated from powder spectrograms was obtained. Through these calculations the holohedral symmetry of the Laue photographs could also easily be explained, for it can be shown that among all the possible X-ray reflections from ilmenite, except some very faint ones the calculated relative intensities of which are less than 1, only the reflections from the rhombohedrons, (210), can disclose the hemihedral symmetry of the mineral.

In this symmetry class there is for each rhombohedron a corresponding rhombohedron with interchanged indices; for example, the right rhombohedron, (210), and the left rhombohedron, (120). These two rhombohedrons are identical as to spacing and angles, but are different

1) P. P. Ewald and C. Hermann, »Strukturbericht« 1934, S. 300.

physically, and the calculated intensity of the X-ray reflection from the right rhombohedron, (210), is 3 times as strong as that from the left rhombohedron, (120).

Similar in principle are the conditions for all other rhombohedrons in ilmenite; the physical difference between two such rhombohedrons is strongly evinced in the habit of the crystals and was thus easily recognized by crystallographers, who have therefore placed the mineral in the rhombohedral class. But it is a peculiar fact that in ilmenite the special  $F$ -values and the special form of the structure factor make the difference of the X-ray scattering power of two such rhombohedrons almost negligible in the great majority of cases; the hemihedral symmetry is therefore not readily evinced in the X-ray spectrum, and since the rhombohedron, (210), having a spacing of 2.3 Å, cannot be brought into positions for reflection on an ordinary Laue photograph, the only criterion of the hemihedral symmetry will be missing in such photographs, and the result of the most careful analysis of the Laue data must necessarily be misleading. Ilmenite thus clearly illustrates the danger of reliance on Laue and powder data alone in the determination of an atomic arrangement.

In order to demonstrate the difference in scattering power of (210) and (120) oscillation and X-ray goniometer spectrograms were prepared. On the oscillation spectrogram the reflections from 110 and 220 could

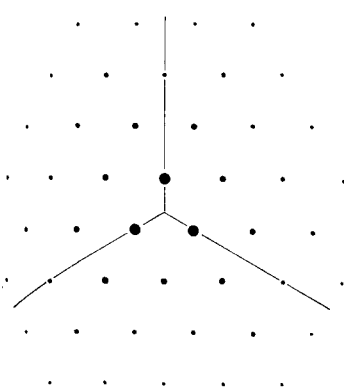


Fig. 1.

Fig. 1. Reciprocal lattice of the fourth layer-line of ilmenite. The perfect apparent holohedral symmetry with the rhombohedral axes in the pseudosymmetry plane is easily noted.

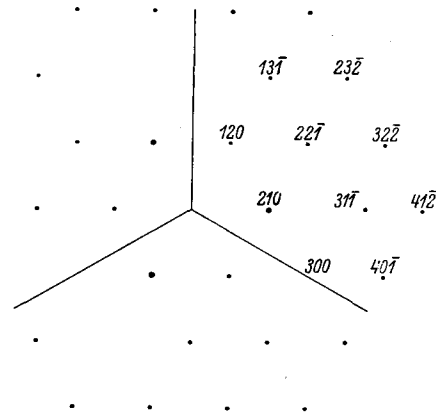


Fig. 2.

Fig. 2. Reciprocal lattice of the third layer-line of ilmenite. The hemihedral symmetry is evinced by a few reflections only.

be used as comparison standards, and, in good agreement with the powder spectrograms, the relative intensities of 110 and 220 could be taken as 4 and 6 respectively. Between these two spots a very weak reflection from the left rhombohedron, 120, occurs, the observed intensity of which is not more than 1. Since the sum of the intensities from the right and from the left rhombohedron makes 4, as demonstrated by the powder spectrogram, the reflected intensity from the right rhombohedron, (210), alone must be about 3. This is also shown directly by a Weissenberg photograph of the third layer-line. On it the spot, 210, is seen to be 2 or 3 times as strong as 120 (see Fig. 2).

The same photograph also shows that  $31\bar{1}$  is absent, whereas  $13\bar{1}$  is present. This whole layer-line is extremely weak, however; indeed, none of the reflections belonging here except (210) is visible in the powder spectra, and thus the faintness of  $13\bar{1}$  makes the absence of  $31\bar{1}$  very inconspicuous. However, it is in agreement with the calculations (see Table I) and furnishes another indication of the correctness of the space-group determination.

These additional X-ray data bring the internal symmetry of ilmenite into perfect agreement with the external symmetry. The apparent discrepancy was thus due only to the inadequacy of the previous data. The study of the face-development and structure of ilmenite illustrates thus the superiority of the X-ray goniometer method as compared with the Laue method. The best agreement between calculated and observed intensities was found with the following parameter values (see Table I):

$$\begin{aligned} u_{Fe} &= 0.358 \\ u_{Ti} &= 0.142 \\ x &= 0.555 \quad y = -0.055 \quad z = 0.250. \end{aligned}$$

Table I constitutes the proof of the correctness of the proposed structure of ilmenite. As was to be expected, the ilmenite structure is very similar to the corundum structure; indeed, the similarity is so great that it appears appropriate to look upon them as belonging to the same type, the corundum-ilmenite type of structure. The space group of ilmenite is a sub-group of the space group of corundum. This structure type is so well known that a more explicit description of it should be unnecessary here<sup>1</sup>). It may be well to point out, however, that in the

1) Cf. L. Pauling and S. B. Hendricks, *J. Am. chem. Soc.* **47**, 781, 1925.  
— W. H. Zachariasen, *Vid. Akad. Skr. Oslo*, 1928, No. 4, p. 15—25.

present description of the structure the origin has been translated to  $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$  as compared with the descriptions of the corundum structure by previous authors.

Table I: X-ray reflections of ilmenite.

[The spacing measurements and the observed (estimated) intensities have been taken from the powder spectrograms except where otherwise indicated.

*Mo-K $\alpha$* -radiation.]

Indices	Spacing	Intensities		Indices	Spacing	Intensities	
		Calc.	Obs.			Calc.	Obs.
111	4.5	0.3	1	22 $\bar{1}$	—	0.1	present <sup>2)</sup>
100	—	0.2	—	300	—	0.0	absent <sup>2)</sup>
110	3.70	4.7	4	2 $\bar{2}$ 0	1.270	2.2	3
211	2.74	10.0	40	411	1.242	0.5	1
1 $\bar{1}$ 0	2.53	7.1	9	330		0.4	
221	—	0.1	—	3 $\bar{1}$ 0	1.205	1.8	2
222	—	0.0	—	442	1.185	1.4	2
210	2.23	3.0	3 <sup>1)</sup>	32 $\bar{1}$	1.147	3.1	2
120		1.0	1 <sup>1)</sup>	311	—	0.0	absent <sup>2)</sup>
1 $\bar{1}$ $\bar{1}$	—	0.0	—	3 $\bar{1}$ 1	—	0.4	present <sup>2)</sup>
200	—	0.1	—	420	1.111	2.3	2
220	1.865	6.7	6	2 $\bar{2}$ 2	—	0.2	—
322	—	0.0	—	522	1.069	0.0	3
311	—	0.0	—	532		2.4	
321	1.720	7.7	8	400	1.050	1.0	1
2 $\bar{1}$ 1	1.63	0.5	3	430		0.1	
632		2.6					
333	—	0.1	—	3 $\bar{2}$ 1	1.000	0.1	2
310	1.504	7.8	7	521		0.6	
340	1.504	7.8	7	531	0.98	0.1	1
2 $\bar{1}$ 1	1.465	7.7	7	411		1.3	
422	1.375	1.7	2	3 $\bar{2}$ 1	0.1	2.1	1
432	1.347	0.0	1	511			
342		0.3					
433		0.2					

$$a = 54.83^\circ \quad r_0 = 5.52 \text{ \AA}$$

1) In the powder spectrum 210 and 120 are coincident, but they are separated by the X-ray goniometer (see text).

2) These reflections are too weak to be observed in the powder spectrum; "present" or "absent" means presence or absence in the Weissenberg photograph.

**Summary.**

From powder, oscillation, and Weissenberg X-ray photographs of ilmenite its atomic arrangement, which is controlled by five parameter values, has been completely determined. In accordance with the observed external symmetry (face development) of ilmenite it was found that crystals of this mineral are isomorphous with the space group  $C_{3i}^2$ , which is a sub-group of the space group of corundum,  $D_{3d}^6$ . The structure of ilmenite is so closely related to that of corundum that it seems appropriate to regard these two structures as belonging to the same type, the corundum-ilmenite type of structure.

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