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LV. Results of crystal analysis.—III.

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LV. *Results of Crystal Analysis.*—III.
By L. VEGARD, *Dr. phil.*, University of Christiania *.

[Plate XII.]

§ 1. **A**S an addition to the results of Crystal Analysis given in two previous papers †, I shall give an account of the determination of the structure of the following crystals:

Xenotime (YPO_4),

Anatase (TiO_2).

Both crystals belong to the ditetragonal bipyramidal class of the tetragonal system.

Xenotime.

§ 2. This mineral has a chemical formula analogous to that of zircon (ZrSiO_4); but although the formula may have a similar appearance, there are probably considerable differences with regard to chemical constitution. Thus the two elements associated with oxygen in the case of zircon have both a valency of four, while in the case of xenotime the one element (Y) has a valency of three, the other one (P) a valency of five.

Now, in spite of their chemical differences, the two substances have crystals which, both as regards form and physical properties, are very similar. Both belong to the ditetragonal bipyramidal class, and the ratios of the axes are very nearly the same.

For Zircon $a : c = 1 : 0.6391$,

„ Xenotime $a : c = 1 : 0.6177$.

In a previous communication it was found that in zircon the Zr and Si atoms took up a similar position in the lattice as regards their relation to the oxygen atoms. The arrangement corresponds to a formula ZrO_2SiO_2 and not $\text{Zr}(\text{SiO}_4)$. In view of the crystallographic similarity, the question arises whether also the atoms in xenotime might be arranged in a zircon lattice, which would mean that Y and P—in spite of their difference of valency—would have the same relation to

* Communicated by the Author.

† L. Vegard, *Phil. Mag.* January 1916, Paper I.; *ibid.* July 1916, Paper II.

the oxygen atoms. Thus the determination of the structure of xenotime is of considerable importance for the question of the part played by the valency in the constitution of solids.

The experimental determination of the X-ray spectra of the different faces is somewhat difficult on account of the fact, that most crystals are more or less transformed into amorphous mass, are partly "metamict," and as a consequence, it was impossible to get reflexion from a number of specimens tested.

At last I got from the Geological Laboratory some fresh and pure samples which gave fairly good reflexion for some of the faces.

The spectra of the faces (100) and (110) were obtained from a sample from the Langesundsfjord, Norway; those of the faces (111) and (101) from a crystal from Raade, Norway.

Several attempts to get reflexion from the base (001) were not successful.

The glancing-angles (θ_n) and intensities (I_n) of the observed spectra for the four faces are given in Table I. and in fig. 1.

TABLE I.

n.	(100).		(110).		(101).		(111).	
	θ_n .	I_n .	θ_n .	I_n .	θ_n .	I_n .	θ_n .	I_n .
1.....	7° 16'	1.4	5° 9'	6.0	6° 58'	3.5	...	0
2.....	14 39	1.0	10 21	3.5	14 2	0.6	...	0
3.....	...	...	15 37	1.5	...	0	...	0
4.....	...	...	...	...	...	...	15° 42'	1.5

In the elementary cell $d_{100}^2 d_{001} = d_{100}^2 \frac{c}{a}$, we find from observations a number of molecules equal to 0.127 or $\frac{1}{8}$, which is the same as was found for zircon.

In a similar way, as in the case of zircon, we are led to a similar space-lattice for the Y and P atoms, as found for the Zr and Si atoms in zircon. If so, both the P and Y atoms are arranged in a lattice of the diamond type.

The lattice of P can be made to cover that of Y by a translation along the tetragonal axis a distance $c/2$.

The spacings of the four faces are in the relation :

$$d_{100} : d_{110} : d_{101} : d_{111} = 1 : 1.409 : 1.043 : 0.468,$$

Fig. 1.

Xenotime

or approximately

$$= 1 : \sqrt{2} : \frac{2}{\sqrt{1 + \left(\frac{a}{c}\right)^2}} : \frac{1}{\sqrt{2 + \left(\frac{a}{c}\right)^2}} \dots (1a)$$

If for a moment we do not take into consideration the oxygen atoms, but only the Y and P atoms, the lattice would give the following relation :

$$d_{100} : d_{110} : d_{101} : d_{111} = 1 : \sqrt{2} : \frac{2}{\sqrt{1 + \left(\frac{a}{c}\right)^2}} : \frac{4}{\sqrt{2 + \left(\frac{a}{c}\right)^2}}. (1b)$$

We see that the relations (1a) and (1b) are the same except for the face (111), where the spacing observed is only $\frac{1}{4}$ of the value to be expected from the lattice.

The question is now, whether the oxygen atoms might be arranged in such a way as to make the three first maxima of the (111) face disappear or become vanishingly small.

Arrangement of Oxygen Atoms.

§ 3. As far as the Y and P atoms are concerned, we have assumed a lattice of the Zircon type. The first question we shall put is: Can such an arrangement of the oxygen atoms as that found for zircon explain the spectra of xenotime?

The spectra of the faces (100), (110), (101), might be accounted for by a proper choice of the parameters, and the test will be whether the zircon lattice can explain the peculiar spectrum of the face (111), in other words, explain the fact that the first three spectra are too weak to be detected. With regard to the determination of the intensities I shall only refer to my previous paper (II. p. 84).

The functions $f_1(n)$ and $f_2(n)$, which determine the strength of the spectrum of order n , are for the (111) face of an arbitrary lattice of the Zircon type given by the expressions (II. eq. 12)

$$f_1(n) = N_1 + (-1)N_2 + (N_1 + N_2 + 4N_3) \cos n \frac{\pi}{2} \\ + 2N_3 (\cos n\alpha_1 + (-1)^n \cos n\alpha_2), \\ f_2(n) = (N_1 - N_2) \sin n \frac{\pi}{2}.$$

N_3 is the atomic number of oxygen; N_1, N_2 those of the two other elements. In our case we have to put $N_1=39$, $N_2=15$, $N_3=8$.

We can, however, prove that there is no value of the parameters which can give a distribution of intensities in accordance with observations. Thus it is impossible to make the first order spectrum sufficiently small as compared with the fourth.

Remembering that the amplitude $A_n = \sqrt{f_1(n)^2 + f_2(n)^2}$, we shall find that the smallest value of A_1 is 24, and the largest value of A_4 is 172. This would mean that the first order spectrum should be at last half as strong as that of the fourth order, and the spectra of the second and third orders would not be sufficiently weak at the same time.

Now the maximum observed was not very strong, but we should easily have detected a peak equal to $\frac{1}{8}$ of that observed for the fourth order spectrum. *We can then safely conclude that the oxygen atoms in xenotime cannot be arranged in a lattice of the Zircon type.*

If in the lattice proposed for the Y and P atoms of xenotime, both sorts of atoms were replaced by atoms of the same reflecting power, the first three orders of the face (111) would vanish. Then we must arrange the oxygen atoms so

as to increase the weight of the P planes so that the group of P and O atoms can balance the heavier Y atoms, and we are led to try to arrange the oxygen atoms tetragonally round the P atoms.

There are mainly two different arrangements possible :—

(1) The oxygen atoms are arranged on a line through the P atoms parallel to the tetragonal axis. This would make the spectra of the faces (110) and (100) normal; but in the case of the face (100) the second order spectrum is nearly as strong as that of the first order, consequently such an arrangement is excluded.

(2) Four oxygen atoms are arranged in a plane through the P atoms perpendicular to the tetragonal axis.

In order to keep up the highest symmetry class there will only be two arrangements of this description possible :

(a) The oxygen atoms are placed on lines through the P atoms which are parallel to the sides of the base ; (b) they are placed on lines through the P atoms which are parallel to the diagonals of the square base of the lattice.

Let us first consider the first possibility (a), and calculate the intensities for the faces (111) and (110).

After some reduction we find for the amplitudes,

$$\left. \begin{aligned} (111) \quad A_n &= (0.47 + (-1)^n 1.22 + \cos n\alpha) \cos \frac{\pi n}{4}, \\ (110) \quad A_n &= 1.69 + \cos 2n\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned} \right\} \quad (2)$$

where α is a parameter determining the distance between P and O.

In order to explain the disappearance of the three first spectra of (111) we should have to choose a value of α smaller than 25° , because a greater value would make the third order spectrum too strong not to be detected ; and even for $\alpha < 25^\circ$ the first order spectrum would probably be too strong to escape detection. Further, we cannot assume a very small value of α , because it would bring the centres of the P and O atoms of the group too close together.

Finally, a value of $\alpha < 25^\circ$ would produce a distribution of intensities of the face (110) which is not in accordance with observations. The observations give for the intensities of the first three orders the relative intensities 100, 58, 25, showing that the intensities of the second and third orders are larger than in the normal spectrum. In other words, the oxygen atoms must be arranged in such a way that

$$A_1 < A_2 < A_3,$$

while for $\alpha < 25^\circ$ the arrangement considered would give

$$A_1 > A_2 > A_3.$$

Hence we conclude that the arrangement (a) must be excluded.

We shall then consider the second possibility (b), which gives the spacings represented in fig. 2 for the four faces

Fig. 2.
Xenotime

examined. The amplitudes are determined by the following expressions :

$$\left. \begin{aligned} (111) \quad A_n &= [2.44 + (-1)^n(1.94 + \cos n\alpha)] \cos \frac{n\pi}{4}, \\ (110) \quad A_n &= 4.37 + \cos 2n\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \\ (100) \quad A_n &= 1.69 + \cos 2n\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \\ (101) \quad A_n &= 1.69 + \cos n\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned} \right\} \quad (3)$$

If l is the distance from an oxygen atom to the central P atom :

$$\alpha = \frac{4\pi}{\sqrt{2}} \frac{l}{a}.$$

The equation for the amplitude of (111) shows that the second order spectrum will disappear for all values of α . The first order spectrum will vanish for $\alpha = 60^\circ$, and for this value the ratio of the intensity of the third to that of the fourth order spectrum will be 1:7 and the third order spectrum might well be so weak as not to be detected.

In order to get the best possible agreement between

calculated and observed values for the other three faces, we put $\alpha = 65^\circ$.

In the following Table II. are given the calculated intensities corresponding to this value of α , as also the observed intensities.

TABLE II.

$$\alpha = 65^\circ.$$

(111).		(110).		(100).		(101).	
I _{cal.}	I _{obs.}	I _{cal.}	I _{obs.}	I _{cal.}	I _{obs.}	I _{cal.}	I _{obs.}
0.4	<20	100	100	100	100	100	100
0	<20	45	58	74	70	9	17
12	<20	20	25	...	...	1	0
100	100	...	...	...	...	...	...

The agreement between calculated and observed values is quite satisfactory.

§ 4. Comparing the lattices found for the xenotime with that of zircon, we see that the lattice at the same time accounts for the crystallographic similarity and the difference in chemical constitution.

Both lattices have the symmetry properties which are necessary to give a crystal of the ditetragonal bipyramidal class.

If we would imagine the oxygen atoms removed the two lattices would be exactly of the same type.

In both lattices the same relative number of oxygen atoms are arranged with tetragonal symmetry in a plane perpendicular to the tetragonal axis, which accounts for the fact that the ratio c/a is almost the same for both minerals.

The difference found for the arrangement of the oxygen atoms accounts for the different chemical constitution to be expected for the two minerals. In zircon both Zr and Si take up essentially the same position towards the oxygen atoms; in xenotime, however, the oxygen atoms are attached in a singular way to the P atoms and we get groups (radicles) of the composition PO_4 . Thus the Röntgen-ray analysis of the space-lattice gives as the constitution formulæ:

Anatase (TiO₂).

§ 5. This mineral is isomeric with rutile, but although both crystals belong to the ditetragonal bipyramidal class of the tetragonal system they are not isomorphous. For rutile the ratio $c:a$ is equal to 0·644, for anatase it is equal to 1·777.

Also, in the case of anatase, we had some difficulty in obtaining reflexion from a sufficient number of faces; but finally we succeeded in finding a number of maxima for the following five: (100), (001), (110), (111), and (112).

The positions and intensities of the observed maxima are given in Table III. and in fig. 3.

TABLE III.

n.	(001).		(100).		(110).		(111).		(112).	
	θ.	I.	θ.	I.	θ.	I.	θ.	I.	θ.	I.
1.....	7° 30'	10	13° 19'	5·8	9° 21'	3·2	5° 0'	4·6	11° 48'	1·5
2.....	15 8	0·6	27 26	1·4	18 58	0·8	10 2	0	...	0
3.....	23 3	0·15	...	...	...	...	15 9	0·3		
4.....	32 50	0·14	...	...	...	...	20 24	0·5		

If we would write the formula $(\text{TiO}_2)_2$ as in the case of rutile, we should find that only $\frac{1}{16}$ of a molecule is associated with the elementary cell $d_{100}^2 d_{001}$, or just half the number found for the rutile cell.

For the ratios of the spacings we get:

$$d_{100} : d_{110} : d_{111} : d_{001} : d_{112} = 1 : 1·418 : 2·643 : 1·765 : 1·126,$$

or approximately

$$= 1 : \sqrt{2} : \frac{4}{\sqrt{2 + \left(\frac{a}{c}\right)^2}} : \frac{c}{a} : \frac{1}{\sqrt{\left(\frac{a}{c}\right)^2 + \frac{1}{2}}}.$$

These are exactly the ratios which correspond to a lattice of the diamond type which is drawn out in the direction of the tetragonal axis. For the sake of comparison we remember that in the case of the isomeric substance, rutile, the lattice of the Ti atoms is composed of two lattices of the diamond type put inside one another in such a way that the elementary cell is not altered. The lattices give the

right number of atoms in the elementary cell and explain the fact that the numbers in anatase are just half the number found for rutile. We should probably state this fact in the

Fig. 3.

Anatase

best way by writing the molecular formula of anatase TiO_2 , and that of rutile $(\text{TiO}_2)_2$, then we should have in both crystals $\frac{1}{2}$ molecule associated with the elementary cell.

The Position of the Oxygen Atoms.

§ 6. A fact of the first importance for the determination of the positions of the oxygen atoms is, that the faces (100) and (001) give spectra with very different relative intensities. This fact excludes any pseudocubic arrangement, or the tetragonal structure is also in the present case to be ascribed to a tetragonal arrangement of the oxygen atoms.

The oxygen atoms cannot be arranged with tetragonal symmetry in a plane perpendicular to the c -axis, as in the case of zircon and xenotime. Such an arrangement would

make the (001) spectrum normal, contrary to the observations, which give an abnormally weak second order spectrum.

We are then naturally led to assume the following arrangement :

Two oxygen atoms are associated with each Ti atom with the latter in a central position forming a kind of molecular element. In the case of anatase all the molecular axes are parallel to the c -axis.

The spacings corresponding to this arrangement are shown in fig. 4.

Fig. 4.

Anatase

We see that the faces (100) and (110) should give a normal spectrum, and that the relative intensities of the faces (001) and (112) should be equal. Both consequences are in agreement with observations; it is only to be remarked that in the case of the face (112) the reflexion is so weak that the very weak spectra of second and third order could not be detected at all.

The arrangement has one parameter (the length of the molecular axis), and it remains to be seen whether a proper

choice of the parameter can give the right intensities for the spectra (001) and (111).

The amplitudes are determined by the following expressions:

$$\left. \begin{aligned} (001) \quad A_n &= 1.375 + \cos n\alpha, \quad . \quad . \quad . \\ (111) \quad A_n &= (1.375 + \cos n\beta) \cos \frac{n\pi}{4}, \\ \beta &= \frac{\alpha}{4} = 2\pi \frac{l}{c}. \quad . \quad . \quad . \quad . \end{aligned} \right\} \quad . \quad . \quad (4)$$

where l is the distance from the Ti atom to one of its oxygen atoms.

It follows from the lattice that $l/c < \frac{1}{2}$ or $\beta < \pi$, and $\alpha < 4\pi$. Let the smallest value of α which gives the right intensities of (001) be α_0 , then the amplitudes of (001) will be unaltered if we interchange α_0 by the values:

$$2\pi - \alpha_0, \quad 2\pi + \alpha_0, \quad 4\pi - \alpha_0.$$

Which of these is the right one must be determined from the (111) spectrum.

The right value of α_0 is very nearly equal to 60° , and from (111) we find $\alpha = 2\pi - \alpha_0 = 300^\circ$ and $\beta = 75^\circ$.

Table IV. gives the calculated and observed intensities for the two faces.

TABLE IV.

$$\beta = 75^\circ.$$

(001).		(111).	
I _{cal.}	I _{obs.}	I _{cal.}	I _{obs.}
100	100	100	100
7.6	6	0	0
0.5	1.5	2.3	6.6
0.8	1.4	9	11

The calculated and observed values agree as well as can be expected, and we have no doubt found the right lattice for anatase with the right symmetry properties.

Also in the case of anatase the tetragonal structure is produced by the oxygen atoms.

The molecular element must require much more space in the direction of its axis than in a direction perpendicular to it. As all molecular axes are parallel to the tetragonal axis,

the lattice must be drawn out in this direction, and also in this case the position of the oxygen atoms accounts for the value of c/a , which in this case is greater than unity.

To make clear the relation between the lattices of anatase and rutile, we imagine that in the latter substance we remove one of its two Ti lattices of the diamond type and the oxygen atoms associated with the Ti atom. The lattice left with the molecular axes in tetragonal arrangement in planes perpendicular to the tetragonal axis does not seem to be stable. If, however, all molecular elements are turned through an angle of 90° , so as to have their axes all parallel with the tetragonal axis, the configuration becomes stable and forms the mineral anatase.

Photographs of models of the lattices of xenotime and anatase are shown on Plate XII.

§ 7. The absolute dimensions of the lattices are given in Table V. For the sake of comparison I have also given the dimensions of the Zircon group.

TABLE V.

Substance.	a .	c .	c/a .	V .	l .
ZrO_2SiO_2	10^{-8} cm. 9.20	10^{-8} cm. 5.87	0.639	10^{-22} cm. ³ 4.97	10^{-8} cm. (Zr) 2.71 (Si) 1.08
$(SnO_2)_2$	9.35	6.29	0.673	5.50	2.08
$(TiO_2)_2$ (Rutile)	9.05	5.83	0.644	4.77	1.99
TiO_2 (Anatase).	5.27	9.37	1.777	2.60	1.95
YPO_4 ..	9.60	5.94	0.618	5.49	1.23

V is the volume of the elementary lattice, l is the distance from an oxygen atom to the central atom to which it belongs.

We see that also with regard to the absolute dimensions of the lattice xenotime comes very close to the Zircon group.

The minerals of the Zircon group show a small, but regular increase of dimensions with increase of atomic number of the central atom of the molecular group. Comparing the dimensions of rutile and anatase, we notice that in the direction which is perpendicular to all molecular axes the linear dimensions are nearly equal, and the value of a of rutile is nearly equal to the value of c of anatase. This may be due to the fact that in both cases there is the same number of molecular elements inside the lattice which have their molecular axis directed along the axis considered.

We may notice that the absolute dimensions are calculated

from the measured glancing-angle and the known wavelength. If V' is the volume of the elementary cell, M and ρ molecular weight and density, n the number of molecules in the cell, N the number of molecules in a gramme-molecule (61.5×10^{22}), we have the relation :

$$V'\rho = n \frac{M}{N}.$$

If we knew ρ and n and had measured V' , we might find M . As the glancing-angle can be found with a very great accuracy, the reflexion of Röntgen rays from crystals might furnish us with a valuable and accurate method of determining the atomic weight of an element which had entered into combination with elements of known atomic weight.

If we only want ordinary relative values of the atomic weight, the accuracy mainly depends on the accuracy of the glancing-angle, and not on the number N . To fix the idea, let us suppose that we have two cubic crystals, one of which we take as a standard. Let the glancing-angle of the cube faces be θ_0 and θ , then

$$\frac{M}{\rho} = \frac{M_0}{\rho_0} \frac{n_0}{n} \left(\frac{\sin \theta_0}{\sin \theta} \right)^3.$$

Summary.

(1) The crystalline structure of xenotime $Y(PO_4)$ and anatase (TiO_2) has been determined.

(2) The lattice of xenotime is not of the zircon type ; the difference, however, is only due to a different arrangement of the oxygen atoms. In xenotime they are arranged in groups of four round each P atom, while in zircon both Zr and Si have essentially the same relation to the oxygen atoms. The lattice gives the constitution formulæ $Y(PO_4)$ and ZrO_2SiO_2 for xenotime and zircon respectively.

(3) In spite of the different arrangement of the oxygen atoms, which accounts for the chemical differences, the lattice also accounts for the crystallographic similarity of the two substances. Both possess the right symmetry, and in both cases the same relative number of oxygen atoms are arranged in planes perpendicular to the tetragonal axis, and will expand the lattice perpendicular to this axis to the same extent and make the ratio c/a smaller than unity and almost equal for both crystals.

(4) We can imagine the lattice of anatase to be derived

from the zircon lattice by removing the Zr atoms and the oxygen atoms associated with them, and substitute the Si with Ti atoms. The oxygen atoms seem no longer to be able to remain in the position they had in zircon, the molecular axes all turn through an angle of 90° so as to become parallel to the tetragonal axis, and so form the stable lattice of anatase.

(5) Also, in the case of anatase, the deformation of the lattice from the cubic form is due to the oxygen atoms. The molecular axes being all parallel, the lattice most expands in the direction of the tetragonal axis to make room for the oxygen atoms, and thus make the ratio c/a greater than unity.

(6) The absolute dimensions of the lattices of zircon and xenotime are very nearly the same. The volume of the lattices of the Zircon group shows a small but regular increase with increasing atomic number.

Also, the distance from a central atom to one of the oxygen atoms associated with it increases with increase of atomic number of elements belonging to the same family. Generally the distance is smaller for a greater affinity to oxygen.

In conclusion, I wish to express my indebtedness to Professor W. C. Brögger, for supplying me with the crystals necessary for the research, and to Mr. H. Schjelderup for valuable assistance in making the observations.

LVI. *A Critical Test of the Crystallographic Law of Valency Volumes; a Note on the Crystalline Structure of the Alkali Sulphates.* By A. OGG, M.A., Professor of Physics, University College, Grahamstown, South Africa, and F. LLOYD HOPWOOD, M.Sc.(Lond.), A.R.C.Sc., Assistant in Physics, University of London, University College*.

THE complete investigation of the structure of crystalline substances involves two distinct inquiries. The first is concerned with the various ways in which the structural units may be arranged to form a homogeneous structure, and the second with the nature of these units.

While it is generally believed that the geometrical theory of crystal structure is now complete, the laws governing the relations between crystalline structure and chemical

* Communicated by Prof. W. H. Bragg, F.R.S.

a

b

a. Xenotime.
b. Anatase.