

On the Chemical Bond Type in AlPO_4

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The z parameter of oxygen in AlPO_4 has been determined, using a Fourier projection on the c axis. The intensity of 0003 is shown to be almost exclusively due to the contributions of the oxygen atoms, and hence the contributions of the Al and P atoms cancel each other; this proves that ions Al^{n+} and $\text{P}^{(n+2)+}$ (probably $n = 3$) are present. It is also shown how the Banerjee method can be used for the calculation of the z parameters directly from the F values.

Introduction

The close crystallographic relation between AlPO_4 and SiO_2 might easily be understood as implying that AlPO_4 can be derived from SiO_2 by replacing one half of the silicon atoms by Al and the other half by P. Since the essential properties are very nearly the same in both substances (crystal structure, polymorphism, melting point and mechanical behavior) one could expect that in the structure of AlPO_4 the aluminum and phosphorus atoms are randomly distributed over the Si positions in SiO_2 . But this, certainly, is not the case. The fact that in the quartz modification of AlPO_4 the c axis is twice as long as the c axis in quartz indicates that we have an alternating sequence of planes, perpendicular to the c axis, occupied by Al and P atoms respectively.

If the z coordinates of the oxygen atoms were given by one parameter only (z and $z + \frac{1}{2}$), oxygen would not contribute to the intensity of 0003; i.e. this reflection should only be generated by the difference between the scattering power of Al and P. Hence, an absolute measurement of the intensity of the 0003 reflection would directly indicate the state of charge of Al and P. This consideration led us to measure the absolute intensity of 0003 (Brill & deBretteville, 1948). The corresponding F value came out to be $F_{0003} = 12.8$. This value is much too high. Assuming that the two atoms are as different as possible, i.e. that P has three negative charges and Al three positive ones, the difference in scattering power of these two ions is only of the order of 2, so that the maximum intensity scattered by the three molecules of one cell could be only 3×2 , i.e. about half the observed value. One has to assume, therefore, that the distances between O and Al differ from those between P and O. In the following, the z parameters of the oxygen atoms are determined and the values are used for a discussion of the structure factor of 0003. Our experiments show that the intensity of 0003 is almost completely caused

by the oxygen atoms. Hence the contributions of Al and P practically cancel each other. This is in agreement with the assumption that the ionic bond type prevails in AlPO_4 .

Experimental procedure

The absolute intensities of the AlPO_4 basal plane reflections of Mo $K\alpha$ radiation were measured, using a combination two-circle goniometer and X-ray spectrometer (Baron & deBretteville, 1950), and a rectified d.c. power supply for the X-ray tube.

Monochromatic X-radiation was obtained from the 002 reflection of a pentaerythritol crystal grown by the Harshaw Chemical Company.

Before each measurement, the AlPO_4 crystal was adjusted so that the output intensity remained constant to $\pm 10\%$ as the crystal was rotated 360° in the plane of reflection. This can be achieved only if the reflecting atomic planes are oriented correctly within 1 min. of arc.

In order to measure the intensity of reflection, the Geiger counter was set at the calculated Bragg angle 2θ , and the intensity was taken point by point by moving the crystal through the maximum. At each setting the time for 10,000 counts was recorded. For the region where the intensity changes slowly and is near the background, the points were taken at 0.5° intervals, while near the Bragg angle measurements were taken at 0.05° intervals. The measured values of each order of reflection were then plotted and the area above the background was integrated by means of a planimeter. Recordings were also made of the primary beam after diminishing its intensity by absorption on nickel foils in a defined way. Absolute values of $Q/2\mu$ were then calculated in the usual way; the results are shown in Table 1. The Geiger counter was a No. 62019 mica-window (3.5 mg.cm.^{-2}) N. A. Philips type. Precautions were taken not to exceed 500 counts/sec. so as

to keep the counting rate below the saturation point of the Geiger counter. This was accomplished by the use of a count-rate meter for which full-scale reading was approximately 500 counts/sec. A plot was also made of the number of foils (approximately 0.0003 in. nickel foil) against counts/sec. on semi-log paper. The absorption constant of the foils was calculated from the slope of the straight line of this plot.

No correction was made for secondary extinction of AlPO_4 because of the weak intensity of reflection. In fact, no reflections (00*l*) appear on an ordinary Debye powder film because of their low intensity.

The crystals were grown by Mr Joseph M. Stanley of the Frequency Control Branch, Squier Signal Laboratory, by means of the hydrothermal method with aluminum phosphate in phosphoric acid solution. The crystals are electrically twinned (Dauphiné twinning), but are not optically twinned (Brazil twinning).

The lattice constants of these crystals were measured with Cu $K\alpha$ radiation on a Weissenberg camera. The constants were found to be in substantial agreement with those of Huttenlocher (1935). We found

$$a = 4.97, c = 10.84 \text{ \AA}$$

with three molecules per unit cell. The crystal used for the spectrometer measurement was a flat hexagonal plate, cut perpendicular to the *c* axis, about 3.4 in. across the greatest diameter.

Results

The experimentally determined structure factors are given in Table 1.

Determination of oxygen parameters by Fourier methods

For the determination of the oxygen parameters a projection on the *c* axis was made. Some of the signs of the Fourier coefficients can be determined by the following considerations: According to the space group the *z* coordinates of Al are $0, \frac{1}{3}, \frac{2}{3}$ and for phosphorus $\frac{1}{6}, \frac{1}{2}, \frac{5}{6}$. Thus, the 6th order certainly will have a

Table 1. Experimentally determined structure amplitudes

00 <i>l</i>	$Q/2\mu \times 10^5$	F_{00l}
0003	2.03	12.8
0006	2.09	19.5
0009	0.009	1.6
0,0,0,12	1.65	19.7
0,0,0,15	0.071	4.2
0,0,0,18	1.14	18.9
0,0,0,21	0.150	7.3
0,0,0,24	0.121	6.3

positive sign. The 3rd order could be taken either positive or negative. But, if Al is supposed to be at $z = 0$ the negative sign should be chosen so that the electron density at $z = 0$ is a little lower than at $z = \frac{1}{6}$. The 12th order also should be positive because it will roughly determine the position of the oxygen layers with their center of gravity in the middle between the phosphorus and aluminum layers. The 18th order then obviously splits the accumulation of electrons caused by the 12th order in two. Therefore, it also has to be positive. As far as the 24th order is concerned it can be shown from the numerical calculation of its *F* value that, if a negative sign has to be assigned to it, $|F_{0,0,0,24}|$ cannot be larger than 1.3. The observed value is 6.3. Hence, also the 24th order has to be positive. With these signs, and using exclusively the orders for which the signs could be fixed by these considerations, a Fourier summation was carried out leading to the parameters $z = 0.059$ and $z' = 0.052$. The *z* parameters of the oxygen atoms are given by the space group as follows:

z	$z + \frac{1}{3}$	$z + \frac{2}{3}$
\bar{z}	$\bar{z} + \frac{2}{3}$	$\bar{z} + \frac{1}{3}$
$z' + \frac{1}{6}$	$z' + \frac{1}{2}$	$z' + \frac{5}{6}$
$\bar{z}' + \frac{1}{6}$	$\bar{z}' + \frac{5}{6}$	$\bar{z}' + \frac{1}{2}$

The *F* values calculated with the preliminary values for *z* and *z'* are given in column (2) of Table 2.

From the table it can be seen that the agreement between calculated and observed values is fair. The calculation uniquely assigns to the 21st order the negative sign. As far as the 9th and 15th orders are

Table 2. Calculated and observed *F* values

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
<i>z</i>		0.059	0.069	0.069	0.068	0.067	0.068	0.068	0.066	0.066	
<i>z'</i>		0.052	0.049	0.049	0.051	0.051	0.050	0.048	0.048	0.050	
<i>l</i> = 3	—	5.5	—14.9	—14.9	—12.6	—11.9	—13.3	—14.5	—13.0	—11.8	12.8
6		25.8	22.1	20.1	18.9	19.4	19.8	21.5	22.5	20.8	19.5
9	—	0.9	0.2	0.1	0	—0.2	—0.2	—0.7	—1.7	—1.1	1.6
12		21.9	28.6	23.9	24.1	23.5	24.2	23.0	21.0	22.5	19.7
15		0.7	7.0	3.1	2.1	2.1	2.7	3.7	3.7	2.7	4.2
18		37.3	27.8	16.5	17.4	17.9	17.2	16.6	17.5	18.1	18.9
21	—	8.5	—18.3	—7.0	—6.6	—6.4	—6.7	—6.9	—6.4	—6.3	7.3
24		6.5	11.8	5.6	4.8	4.7	5.1	5.6	5.3	4.8	6.3
<i>R</i>	—	—	—	0.143	0.140	0.131	0.130	0.131	0.093	0.115	—

Individual temperature correction has been applied to columns (4)–(10).

concerned the calculated F values are so small that a unique assignment of the sign cannot be achieved. In the next approximation another Fourier summation was performed using the signs of the F values in column (2) of Table 2. This summation gives the parameter $z = 0.069$ and $z' = 0.049$. A calculation of the structure factor with these parameters gives the values in column (3) of Table 2. Considering the fact that the temperature factor will lower the higher orders, the agreement between observed and calculated values is improved. The F values show that the sign of the 15th order is probably positive and that also the sign of the 9th order could be positive.

At this stage Fourier difference analyses were carried out for the oxygen atoms alone.* The combinations of signs used are given in Table 3.

Table 3. Signs used in difference synthesis

l	(1)	(2)	(3)	(4)	(5)	(6)
3	-	-	-	-	-	-
6	+	+	+	+	+	+
9	+	-	-	-	+	+
12	+	+	+	+	+	+
15	+	+	-	-	-	+
18	+	+	+	+	+	+
21	-	-	-	+	+	+
24	+	+	+	+	+	+
z	0.067	0.066	0.066	0.055	0.055	0.059
z'	0.053	0.053	0.054	0.067	0.066	0.067

The difference analyses showed that the two oxygen maxima have the same or almost the same height only for the combination (1) and (3) and equal values at $z = 0$ and $z = \frac{1}{8}$ only for combination (1). Since also the F values, calculated by combination (3), agreed slightly less well with the experimental values, combination (1) was taken to be the right one. A Fourier calculation with these signs gave the result drawn in Fig. 1. The positions of the oxygen maxima are at $z = 0.070$ and $\frac{1}{8} - z' = 0.118$, which corresponds to $z' = 0.049$. The shift of the maximum with respect to the difference analysis (Table 3) is obviously caused by overlapping. It just indicates that overlapping is a serious source of error in one-dimensional syntheses. Hence the only criterion for the right choice of z and z' is the agreement between calculated and experimental F values. Results of these calculations are given in Table 2.

The calculations were carried out with the atomic scattering factors of the *International Tables* for Al^{3+} and P^{5+} , whereas for O^{2-} the experimental values were used which were determined by Brill, Hermann & Peters (1948) on MgO . The temperature correction was carried out in the following way. By trial

* Since only F_{0003} is influenced by the amount of charge of Al and P, it is irrelevant whether theoretical atomic scattering factors for charged or uncharged atoms are used for the difference synthesis.

it was found that a mean temperature factor $\exp[-\bar{M}(\sin\theta/\lambda)^2]$, with $\bar{M} = 0.91$ ($\Theta = 440^\circ$), corrected the calculated values in a reasonable way. A further improvement was obtained by attributing individual temperature factors to the different atomic species. These individual temperature factors were

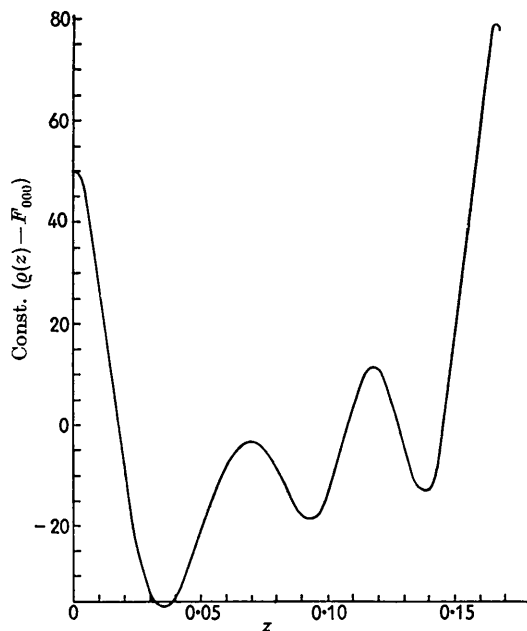


Fig. 1. Variation of the electron density projected on the c axis.

obtained by replacing, in the expression for M , the average atomic mass by the masses of the individual atoms, i.e. the following relation was used: $M_x = \bar{M}(\bar{m}/m_x)$, where M_x means the temperature factor for the species x , \bar{m} the mean mass of one atom (= mass of the molecule/number of atoms) and m_x the mass of atom x . (Hence $M_{\text{Al}} = 0.685$, $M_{\text{P}} = 0.597$, $M_{\text{O}} = 1.157$.)

From Table 2 it can be seen that the best agreement between observed and calculated F values is obtained for $z = 0.066$, $z' = 0.048$. Other combinations than those given in the table were tried also, but without success. The still-present deviations from the experimental values are ascribed to errors in the measurements, inaccuracy of the scattering factors used for the calculations, and to the method of temperature correction.

As far as the question of bond type is concerned, its influence on 0003 should be greatest because the Al and P atoms contribute with opposite phases. We have

$$F_{0003} = 3\{f_{\text{Al}} - f_{\text{P}} + 2f_{\text{O}}(\cos 2\pi(3z) + \cos 2\pi(3z' + \frac{1}{2}))\}.$$

With $f_{\text{O}} = 7.1$, $z = 0.066$, $z' = 0.048$ one obtains

$$F_{0003} = 3\{f_{\text{Al}} - f_{\text{P}}\} + 12.63.$$

Since the observed value is $F_{0003} = 12.8$, the difference $f_{\text{Al}} - f_{\text{O}}$ is practically zero. This indicates that both

atoms have almost the same scattering factor for 0003, which is the case only if the phosphorus atom has two more positive charges than the aluminum. It is therefore most probable that Al^{3+} and P^{5+} ions are present.

Determination of oxygen parameters by the Banerjee relation

It might be of interest to show, also, how in this case the Banerjee relation can be used for a direct calculation of the parameters z and z' from the observed intensities. According to Banerjee there exists a linear relation between the unitary structure factors

$$U = F / \sum_1^N f_n:$$

$$U_{h,k,l+N} + a_1 U_{h,k,l+N-1} + \dots + a_N U_{h,k,l} = 0. \quad (1)$$

The coefficients a_N are defined by the basic relation

$$\sum_{n=1}^N \left(\gamma_n^l \prod_{j=1}^N (\gamma_n - \gamma_j) \right) = \sum_1^N \gamma_n^{l+N} + a_1 \sum_1^N \gamma_n^{l+N-1} + \dots + a_N \sum_1^N \gamma_n^l = 0; \quad (2)$$

N is the number of atoms per cell and $\gamma_n = \exp[-2\pi iz_n]$, with z_n the z coordinate of the n th atom.

For simplification in this case a cell with $c' = \frac{1}{3}c$ can be used with $l' = l/3$. With respect to this cell, which contains 1 molecule, the z coordinates of the atoms and the corresponding γ -values are listed in Table 4.

Table 4. *Parameters and phase factors in new cell*

Atom	z parameter	γ
Al	0	$\gamma_1 = 1$
P	$\frac{1}{3}$	$\gamma_2 = -1$
O	z	$\gamma_3 = \exp[-2\pi iz]$
O	\bar{z}	$\gamma_4 = \exp[2\pi iz]$
O	$z' + \frac{1}{3}$	$\gamma_5 = -\exp[-2\pi iz']$
O	$\bar{z}' + \frac{1}{3}$	$\gamma_6 = -\exp[2\pi iz']$

$\gamma_3\gamma_4 = 1$
 $\gamma_5\gamma_6 = 1$

With $N = 6$ and the above γ values we have, from (1),

$$U_{l'+6} - U_{l'} + a_1(U_{l'+5} - U_{l'+1}) + a_2(U_{l'+4} - U_{l'+2}) = 0. \quad (3)$$

Equation (2) gives:

$$\left. \begin{aligned} a_1 &= -\gamma_3 - \gamma_4 - \gamma_5 - \gamma_6 = \\ & \quad 2(\cos 2\pi z' - \cos 2\pi z) = -a_5, \\ a_2 &= 1 + \gamma_3\gamma_5 + \gamma_3\gamma_6 + \gamma_4\gamma_5 + \gamma_4\gamma_6 = \\ & \quad 1 - 2(\cos 2\pi(z+z') + \cos 2\pi(z-z')) = -a_4, \\ a_3 &= 0. \end{aligned} \right\} \quad (4)$$

From the observed F values the values for U_l shown in Table 5 were calculated.

Table 5. *Values of the unitary structure amplitude U_l*

l	3	6	9	12	15	18	21	24
l'	1	2	3	4	5	6	7	8
U_l	0.091	0.194	0.022	0.353	0.094	0.488	0.219	0.233
Sign	-	+	-	+	+	+	-	+

The signs chosen are those of the calculated intensities for the best agreement between calculated and observed values. Applying (3) to the orders with $l' = 1$ and $l' = 2$ one obtains:

$$a_1 = 0.349, \quad a_2 = 0.220.$$

Two convenient values for z and z' calculated from (4) are, referred to the large elementary cell, 0.064 and 0.053, in good agreement with the values derived above.

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