

## Disorder in a Crystalline Condensed Phosphate

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$\text{Na}_2\text{P}_4\text{O}_{11}$  crystallizes in two distinct forms. Form I is monoclinic with  $a = 30.7$ ,  $b = 6.77$ ,  $c = 7.12$  Å,  $\beta = 94^\circ 6'$ ; space group  $P2_1/a$ . Form II is also monoclinic but markedly pseudo-orthorhombic with  $a = 18.74$ ,  $b = 14.79$ ,  $c = 7.03$  Å,  $\beta = 90^\circ 0'$ ; space group  $B2/a$  or  $Ba$ . Reflections from form II with  $l$  odd consist of diffuse circular discs oriented normal to the  $c^*$  axis. In the structure postulated for form II, rings of four phosphate tetrahedra are linked into chains by the sharing of an oxygen between adjacent rings.

### Introduction

Griffith (1956) reported the preparation of a series of crystalline sodium acid phosphates, one of which he described as  $\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$ . He pointed out that the compound for a tetrametaphosphate is surprisingly insoluble in water and shows an equally surprising fibrous crystal habit. To explain these properties he mentioned the possibility of a molecular rearrangement on dissolving but considered this conjecture to be unlikely. Intrigued by these observations we started a crystallographic investigation of this compound.

Griffith's procedure for synthesizing  $\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$  was followed, and the identity of our sample was checked by comparing its powder pattern with that of material kindly furnished by Dr Griffith. The transparent, colorless, crystalline product is found to consist of *two* distinct crystalline forms intimately intergrown. Single crystals were studied using rotation, Weissenberg, and precession cameras with  $\text{Cu } K\alpha$  ( $\lambda = 1.5418$  Å) and  $\text{Mo } K\alpha$  ( $\lambda = 0.7107$  Å) radiations.

### Crystal data

Form I comprises approximately 10% by weight, as estimated from the relative intensities of powder lines. It consists of crystals of thick tabular habit and average dimensions  $0.3 \times 0.05 \times 0.02$  mm. They are monoclinic, elongated [010], with cell dimensions

$$\begin{aligned} a &= 30.7, \quad b = 6.77, \quad c = 7.12 \text{ \AA}, \quad \text{all } \pm 0.5\%, \\ \beta &= 94^\circ 6' \pm 10', \\ V &= 1476 \text{ \AA}^3. \end{aligned}$$

A pronounced pseudo-repeat  $a' = \frac{1}{2}a$  is evident. Because it proved impossible to separate a sufficient

amount of phase I for accurate density determination, we can report only that its density is  $2.62 \text{ g.cm.}^{-3}$  or greater, as determined by the flotation method using a mixture of bromoform and toluene as the inert liquid. For the same reason a chemical analysis of this phase was not possible. The space group is uniquely determined as  $P2_1/a$  by the systematic absences  $h0l$  with  $h$  odd and  $0k0$  with  $k$  odd. Only the forms  $\{100\}$  and  $\{001\}$  are observed, the larger faces being those of  $\{100\}$ . Cleavage is extremely fibrous along  $b$  and for this reason good single crystals are difficult to obtain. No further work on this form is contemplated.

Form II, the bulk of the material, consists of thin to thick rectangular plates which grow up to 5 mm. in length. Only cleavage fragments can be removed from the matrix of the melt and therefore morphology gives no clue concerning the point-group symmetry. Cell dimensions were determined on precession films taken with  $\text{Mo } K\alpha$ :

$$\begin{aligned} a &= 18.74, \quad b = 14.79, \quad c = 7.03 \text{ \AA}, \quad \text{all } \pm 0.3\%, \\ \beta &= 90^\circ 0' \pm 5', \\ V &= 1948 \text{ \AA}^3. \end{aligned}$$

Parallel to  $\{100\}$  the cleavage is very easy and very good, parallel to  $\{010\}$  it is easy and fairly good, and parallel to  $\{110\}$  it is fairly easy and good. The four cleavage directions result in platy to fibrous fragments.

The cell is monoclinic but markedly pseudo-orthorhombic. Although the zero-level net (010)\* shows symmetry  $U2$ , parallel upper levels show that  $a^*$  and  $c^*$  are not symmetry directions. The pseudo-orthorhombic character is emphasized by the optical orientation—the principal axes of the index ellipsoid lie along the crystallographic axes within experimental error. The optical character is biaxial positive with the

plane of the optic axes parallel to (100) and the acute bisectrix along [001]. The indices are

$$n_{\alpha}=1.485\pm 0.005, \quad n_{\beta}=1.510\pm 0.005, \quad n_{\gamma}=1.545\pm 0.001$$

(determined by J. D. H. Donnay). Since the systematic absences are  $hkl$  with  $h+l$  odd and  $h0l$  with  $h$  and  $l$  both odd, the space group is  $B2/a$  or  $Ba$ . The  $B$ -centered lattice is used to bring out the pronounced pseudo-symmetry with pseudo space group  $Bmam$ ,  $Bma2$ , or  $B2am$ . The test for pyroelectricity with liquid nitrogen gave negative results.

As shown by the precession patterns containing reflections  $hk0$  (Fig. 1(a)),  $hk1$  (Fig. 1(b)),  $hk2$ , and  $hk3$ , the reflections with  $l$  odd appear as diffuse circles. The  $c$ -axis rotation pattern consists of odd layer lines which are diffuse streaks and of even layer lines which contain sharp spots, the width of the two types of layer lines being the same. It follows that the reflections with  $l$  odd are diffuse circular discs oriented normal to the  $c^*$  axis. This conclusion is confirmed by Weissenberg photographs. The intensity distribution within the streaky layer lines varies from crystal to crystal (Figs. 1(c) and (d)). The radius of the disc was measured for one of the specimens (Fig. 1(d)) and was found to be  $0.021\pm 0.001 \text{ \AA}^{-1}$ . It follows that the crystal structure shows disorder which consists of displacements of random portions of the structure through a distance of  $\frac{1}{2}c$  in the  $z$  direction.

Because form II is present in much larger amounts than form I, its density could be determined more accurately. The lowest density obtained by the pycnometric method, using toluene as the inert liquid, is  $2.34\pm 0.02 \text{ g.cm.}^{-3}$ . The flotation method, using a mixture of bromoform and toluene, indicated that the density varied from 2.34 to  $2.62 \text{ g.cm.}^{-3}$ , obviously according to the proportion of form I.

Using  $2.34 \text{ g.cm.}^{-3}$  as the density, and Griffith's formula, we calculate  $7.54\pm 0.08$  formula units per cell. The space groups  $B2/a$  and  $Ba$  permit only an even number of  $\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$  units per cell; consequently the observed density must be compared to the calculated densities of  $1.86 \text{ g.cm.}^{-3}$  for 6 and  $2.48 \text{ g.cm.}^{-3}$  for 8 units per cell. These values are well outside the limits of our experimental error. If one molecule of water is subtracted from the empirical formula, the result is  $\text{Na}_2\text{P}_4\text{O}_{11}$ . For eight such formula units per cell the calculated density is  $2.36 \text{ g.cm.}^{-3}$ , within the limits of error of the experimental value. In  $\text{Na}_2\text{P}_4\text{O}_{11}$  the  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$  formula ratio is  $< 1$ , so that some of the  $\text{PO}_4$  tetrahedra have more than two shared corners. Following van Wazer's terminology (1955), the material is therefore an ultraphosphate. It is the first crystalline ultraphosphate to be described in the literature.

### Structural hypothesis

In the structure of  $\text{Na}_2\text{P}_4\text{O}_{11}$  which we consider most likely, rings of four phosphate tetrahedra are linked

into chains by the sharing of an oxygen between adjacent rings. Our structural hypothesis is supported by the following observations and reasoning:

1. The four cleavage directions observed in the zone of the  $c$  axis indicate a chain structure with the chain parallel to  $c$ .

2. The optical character suggests a chain structure with chains parallel to  $c$ .

3. The observed very slow rate of solution is explained by the fact that hydrolysis is a necessary first step in the dissolution of chains.

4. The principal product of hydrolysis at approximately neutral pH is tetrametaphosphate, as is to be expected if hydrolysis occurs between rings. It is indeed the only ring phosphate that is obtained.

5. When the compound is treated with 3 N NaOH a viscous, plastic mass is formed. Such behavior is again predicted from the proposed structure because *in base* ring phosphates hydrolyze much more rapidly than chain phosphates. In strong base, therefore, the probability of opening the rings is enhanced and becomes comparable to the probability of breaking the chains between rings. The result will be the formation of polyphosphate chains of various lengths, which are known to form plastic aggregates.

6. The dimensions of one of the two isomeric forms of the tetrametaphosphate ring (Gross, Gryder & Donnay, 1955) were determined in the crystal structure of  $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$  (Romers, Ketelaar & MacGillavry, 1951). Using these values, eight  $\text{P}_4\text{O}_{11}$  chain-links can be readily fitted into the cell. The cell height,  $c = 7.03 \text{ \AA}$ , permits one ring to be placed vertically. The very good  $\{100\}$  cleavage indicates that the plane of the ring is parallel to (100), and the  $b$  dimension,  $14.79 \text{ \AA}$ , just accommodates two of the ribbon-like chains side by side. Finally four ring thicknesses can be placed in the  $a$  length of  $18.74 \text{ \AA}$ .

7. The disorder indicated by the diffuse reflections is easily explained by the chain hypothesis, some chains being displaced by half a chain link in the direction of the  $z$  axis. The circular shape of the diffuse reflections in the  $a^*b^*$  plane shows that the probability of the occurrence of a displacement is the same in the  $x$  and in the  $y$  directions; the sharpness of the same reflections along  $c^*$  indicates that the individual chains are not affected when they suffer displacement.

### APPENDIX

Since this type of displacement has not been encountered previously and is not discussed in Wilson (1949), the intensity distribution in reciprocal space is here derived as a function of the probability of displacement of the chains. For every atom at  $x, y, z$  on an undisplaced chain, disordering, in another cell, places the corresponding atom at  $x, y, z + \frac{1}{2}$ . For reflections with  $l$  even, the structure-factor contributions from the two corresponding atoms are equal in

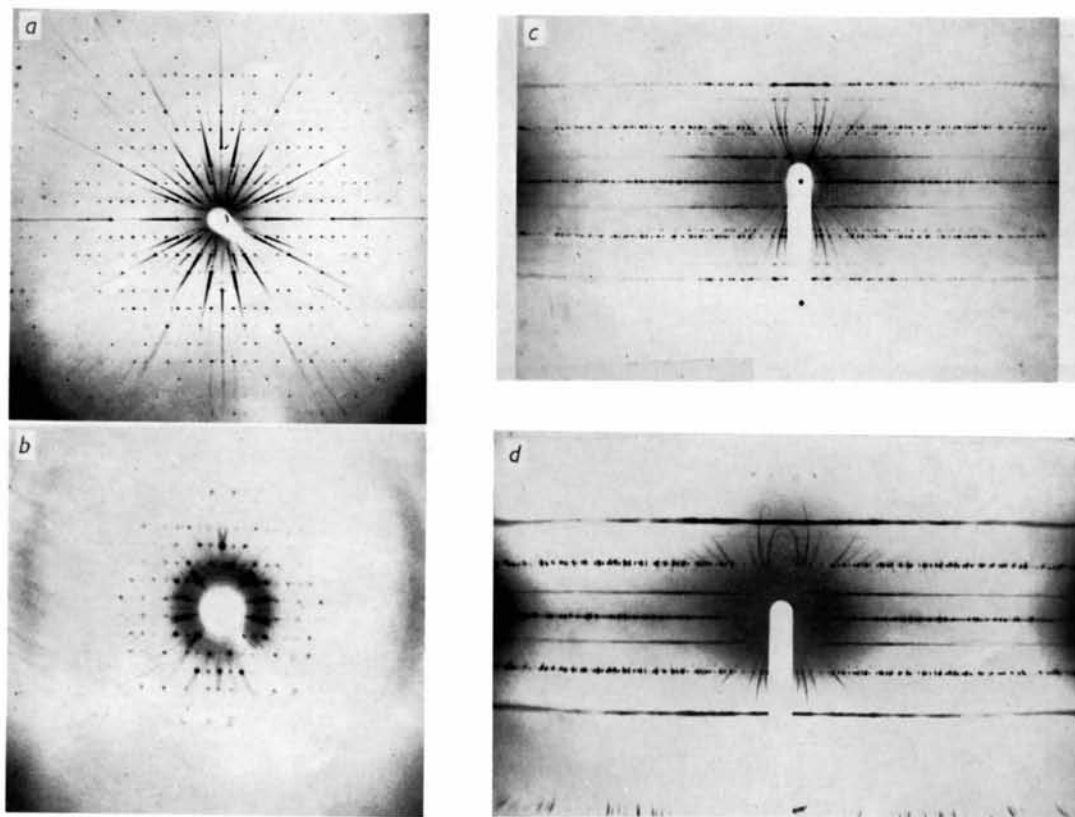


Fig. 1. (a, b)  $\text{Na}_2\text{P}_4\text{O}_{11}$ , form II. Precession, Mo  $K\alpha$  radiation, exposure time: 26 hr. Crystal No. 3. (a) Sharp  $hk0$  reflections. (b) Diffuse  $hkl$  reflections. (c, d)  $\text{Na}_2\text{P}_4\text{O}_{11}$ , form II.  $c$ -axis rotation. (c) Crystal No. 2. Odd layer lines are streaked, but maxima are still visible. Cu  $K$  radiation. Exposure time: 1 hr. 10 min. (d) Crystal No. 3. Odd layer lines are completely smeared into streaks of varying intensity. Cu  $K\alpha$  radiation. Exposure time: 2 hr. 0 min.

magnitude and phase, and sharp reflections result. For reflections with  $l$  odd, the structure-factor contributions of displaced and undisplaced atoms are equal in magnitude but opposite in phase. The cells which result from the disorder can be classified into  $2^8=256$  types on the basis of how many and which of the eight chains per cell are displaced. Let us consider two cells, one of type  $p$ , the other of type  $q$ . Let  $\mathcal{F}_i$  denote the contribution of the  $i$ th chain ( $i=1, 2, \dots, 8$ ) to the structure factor in the cell of type  $p$  and  $\mathcal{F}_{Na}$  the contribution of the sixteen always undisplaced sodium ions. The cell  $q$  will have some chains displaced relative to the analogous chains in cell  $p$ . The structure-factor contribution of these chains will be  $-\mathcal{F}_i$ . The structure factor expressions for cells  $p$  and  $q$  can be written as follows:

$$F^p = \mathcal{F}_{Na} + \sum_{i=1}^n \mathcal{F}_i \text{ same in } p \text{ and } q \\ + \sum_{i=n+1}^8 \mathcal{F}_i \text{ different in } p \text{ and } q, \\ F^q = \mathcal{F}_{Na} + \sum_{i=1}^n \mathcal{F}_i \text{ same in } p \text{ and } q \\ - \sum_{i=n+1}^8 \mathcal{F}_i \text{ different in } p \text{ and } q.$$

Let us denote the first sum on the right-hand side by  $S_s^{pq}$  and the second sum by  $S_d^{pq}$ . Then

$$F^p = S_s^{pq} + S_d^{pq}; \quad F^q = S_s^{pq} - S_d^{pq}.$$

We shall first assume the centrosymmetric space group  $B2/a$ . In a cell in which disorder occurs the center of symmetry may be lost, but for every cell in which only one chain of a centrosymmetric pair is displaced we are able to find another cell in which the other chain of the pair is displaced, so that the structure factor may still be considered to have its  $B$  part equal to zero, or  $F^q = (F^p)^*$ . We may therefore write

$$F^p F^{q*} = (S_s^{pq})^2 - (S_d^{pq})^2.$$

Let  $P_{pq}^{m_1 m_2}$  be the probability of finding a cell type  $q$  at distance  $m_1 a + m_2 b$  from a cell of type  $p$ . The aver-

age value of the product of the structure-factors of two cells can then be written as follows:

$$\overline{F_{m_1 m_2}^2} = \sum_{p=1}^{256} \sum_{q=1}^{256} P_{pq}^{m_1 m_2} [(S_s^{pq})^2 - (S_d^{pq})^2].$$

Wilson (1949) has shown that the intensity distribution in reciprocal space is given by

$$H(u, v, w) = U^{-1} \sum_{m_1} \sum_{m_2} \sum_{m_3} V_{m_1 m_2 m_3} \overline{F_{m_1 m_2 m_3}^2} \\ \times \exp[-2\pi i(m_1 u + m_2 v + m_3 w)],$$

where  $U$  is the volume of one unit cell,  $V_{m_1 m_2 m_3}$  is the volume of the crystal in which two cells can be separated by a distance  $m_1 a + m_2 b + m_3 c$ , and  $u, v$ , and  $w$  are fractional coordinates in reciprocal space.

If we drop the assumption of a centrosymmetric space group, an analogous analysis leads to the conclusion that the reflections are again sharp in the  $c^*$  direction and diffuse in the  $a^*$  and  $b^*$  directions. The intensity maximum would, however, be displaced from the reciprocal-lattice node; the displacement would lie in the  $a^* b^*$  plane. No such displacement is observed.

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