Ba is twelve-coordinated, and this implies that every O atom is linked to three Ba atoms and one T atom, giving it fourfold coordination. In Table 2 the twelve Ba—O distances, which range from 2·73 to 3·31 Å, are reported, in keeping with the statement of Hill (1977) that all of them are significant in the electrostatic valence balance. In a previous refinement of baryte Colville & Staudhammer (1967) set a somewhat arbitrary limit between nearest and next-nearest neighbouring O atoms.

As regards the (Cr,S) tetrahedron, the resulting site occupancy (Cr 84%, S 16%) is intermediate between the compositions given by Hauff *et al.* (1983) for a dark and a zoned crystal of hashemite (93 and 77% Cr, respectively); our composition seems quite reasonable, if one considers the dark appearance of the crystal, which indicates a Cr-rich variety of hashemite. The Cr/S ratio was calculated from the refined average T—O bond length of 1·651 Å (as obtained from the first least-squares cycles, in which the occupancy of the T site was allowed to vary) through linear interpolation of the theoretical Cr—O and S—O distances, 1·68 and 1·50 Å respectively, assuming 1·38 Å as the ionic radius of the four-coordinate O^{2-} species (Shannon & Prewitt, 1969). In the last cycles of refinement the occupancy of the T site was held fixed.

The O(1) and O(2) atoms display large U_{22} thermal parameters, *i.e.* major vibration in the direction perpendicular to the mirror plane on which O(1) and O(2) lie; Hill (1977) noticed the same phenomenon during his refinement of baryte, and ascribed this behaviour to the weaker bonding of O(1) and O(2) by Ba cations. In hashemite a further cause of the anomalous thermal vibration may be found in the statistical occupancy of the tetrahedral site by different cations, with consequent variations in the O positions.

We wish to thank P. Orlandi for supplying the hashemite crystal and providing information about its paragenesis; S. Merlino is thanked for a thoughtful reading of the manuscript and for many useful suggestions.

Note added in proof: After this paper had been sent to the press we discovered that an independent refinement had been carried out by Duesler & Foord [*Am. Mineral.* (1986), **71**, 1217–1220]. The structural results are in close agreement.

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Aluminophosphate Number 5: Time-of-Flight Neutron Powder Diffraction Study of Calcined Powder at 295 K

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Abstract. Aluminium phosphate, $AlPO_4$, $M_r = 121·95$, hexagonal, $P6cc$ for ordered Al and P but refined in $P6/mcc$ for disordered Al, P, $a = 13·7707$ (3), $c = 8·3789$ (6) Å, $V = 1376·0$ (2) Å^3, $Z = 12$, $D_x = 1·76$ g cm^{-3}, range of wavelengths from time-of-flight pulsed neutron technique, $T \sim 295$ K, $R_p = 1·9\%$ for $d = 0·865$–$3·308$ Å and 396 allowed Bragg reflections. Significant non-crystalline scattering was observed and successfully removed. Refinement in space group $P6/mcc$ resulted in T—O distances ranging from 1·56 to 1·64 Å and T—O—T angles from 143 to 176°. Attempts to refine the ordered structure in $P6cc$ were not entirely successful. The sample was obtained by calcination of as-synthesized $(AlPO_4)_{12}$–tetrapropylammonium hydroxide (1/2). Removal of tetrapropylammonium hydroxide from the as-synthesized material results in 0·3% expansion of a, 1·2% contraction of c,

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal displacements* ($Å^2 \times 10^3$) *of calcined and as-synthesized* $AlPO_4$-5

	Calcined*				As-synthesized†			
	x	y	z	U_{eq}‡	x	y	z	U_{eq}‡
T	4574 (4)	3367 (7)	8095 (6)	46 (4)	4551 (3)	3330 (2)	8140 (30)	40 (2)
O(1)	2098 (3)	4196 (5)	2500	61 (5)	2105 (2)	4210 (5)	2500	64 (6)
O(2)	4530 (13)	3336 (11)	0	159 (11)	4555 (8)	3312 (10)	0	104 (9)
O(3)	3639 (6)	0	2500	104 (6)	3627 (7)	0	2500	70 (6)
O(4)	5778 (3)	1556 (6)	2500	89 (5)	5779 (8)	1559 (8)	2500	70 (5)

* This refinement in *P*6/*mcc*.

† Conversion of coordinates from refinement in *P*6*cc* as explained in text. T is $Al_{0.5}P_{0.5}$.

‡ U_{eq} is defined as $\frac{1}{3}\sum_{i=1}^{i=3}\sum_{j=1}^{j=3} U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$.

and minor change of framework geometry so that the 12-ring of O atoms is circular within experimental error (diameter 10·0 Å).

Introduction. A new group of materials was synthesized from aluminophosphate gels using organic amines and quaternary ammonium cations as templates (Wilson, Lok, Messina, Cannan & Flanigen, 1982, 1983). Calcination removes the encapsulated organic material to produce microporous products whose tetrahedral frameworks contain alternating Al and P, including an analog of the aluminosilicate zeolite erionite ($AlPO_4$-17). The novel framework of $AlPO_4$-5 encloses non-connecting parallel channels bounded by 12-rings, and the as-synthesized material (Wilson, Lok & Flanigen, 1982) contains tetrapropylammonium hydroxide (TPAOH) in a tripod configuration (Bennett, Cohen, Flanigen, Pluth & Smith, 1983).

We report a structure refinement of the calcined variety of $AlPO_4$-5 by Rietveld analysis of a time-of-flight powder spectrum of pulsed neutrons from a spallation source. The aims were (*a*) to find out how the framework geometry of the as-synthesized material changed upon removal of TPAOH during calcination, and (*b*) to investigate the value of the Rietveld technique for a complex structure with strong pseudosymmetry associated with Al, P ordering.

Experimental. About 8 g of as-synthesized material were packed into a cylindrical vanadium can (1·1 cm diameter, 15 cm long, wall thickness 0·5 mm), whose end was epoxied to a glass tube attached to a vacuum system. The sample was heated to 573 K for 4 h under diffusion-pump vacuum and the glass tube sealed at temperature. Data were collected on the General-Purpose-Powder Diffractometer of the Intense Pulsed Neutron Source of Argonne National Laboratory for 20 h at 295 and 7 K. The low-temperature pattern has not yet been interpreted. The room-temperature data from the ±90° banks of detectors were analyzed with the Rietveld refinement technique (Rietveld, 1969), modified for use with time-of-flight data from a pulsed neutron source (Jorgensen & Rotella, 1982; Von Dreele, Jorgensen & Windsor, 1982). The coherent neutron scattering lengths (fm) are: Al, 3·45; P, 5·13; O, 5·80; T (disordered Al, P), 4·29. Backgrounds were fitted with a refinable six-parameter analytical function (Rotella, 1986). The range of reciprocal space used was $d = 0{\cdot}865$–$3{\cdot}308$ Å, 2345 consecutive 8μs-wide channels were used, and 396 Bragg reflections were allowed.

Satisfactory refinement was ultimately obtained for an averaged structure with (Al, P) in *P*6/*mcc*. The first refinements were unsatisfactory, and it became obvious that the conventional Rietveld background function was not accounting fully for the non-crystalline features in the diffraction pattern indicated by a slowly oscillating component superimposed on the Bragg peaks. This non-crystalline component was accounted for by a Fourier-filtering technique relatable to a radial distribution function (Richardson & Faber, 1985); details are given below. Further refinement of the crystalline component then proceeded routinely (Table 1). Attempted refinement with alternating Al and P over the tetrahedral nodes did not reach a convincing answer, at least in part because of strong correlations associated with the non-centrosymmetry of space group *P*6*cc*. In general, six out of the eight T—O distances were plausible [*e.g.* P—O(2) 1·48 (3), —O(3) 1·43 (2), —O(4) 1·45 (2); Al—O(2) 1·75 (3), —O(3) 1·70 (2), —O(4) 1·69 (2) Å] and two were reversed [P—O(1) 1·70 (2); Al—O(1) 1·59 (2) Å]. Attempts to direct the refinement by deliberate choice of input parameters failed, and the product invariably contained two reversed distances. Fourier maps based on (F_o) and on (F_o—F_c) revealed no scattering density attributable to residual organic material. Max. $\Delta/\sigma = 0{\cdot}10$.

Fig. 1 shows the agreement between observed and calculated profiles for the disordered structure. Several minor peaks apparently result from impurities (2·34 Å, Al; 1·84 Å, unidentified; shoulder at 1·90 Å, unidentified). Discrepancy indices R_{F^2}, R_p and R_{wp} (Lager, Jorgensen & Rotella, 1982) are 8·56, 1·91 and 2·83% respectively; there are 40 variable parameters. The lack of significant anisotropy in the (Al, P) atomic displacements (available as supplementary material) indicates that any preferred orientation was small.*

Discussion. The coordinates of the ordered $AlPO_4$ framework of the as-synthesized material in space group *P6cc*, obtained from single-crystal X-ray diffraction (Bennett *et al.*, 1983), were converted to those of a mathematically disordered $(Al_{0.5}P_{0.5})O_4$ framework in *P6/mcc* (Table 1) as follows: (*a*) addition of 0·75 to all *z* coordinates so that O(2) lies at an *xy*0 position, (*b*) simple averaging of the *xyz* coordinates of Al and P, (*c*) movement of O(1) from *xyz* with $x \sim 2y$ to *x*,2*x*,0·25, (*d*) movement of O(3) from *xyz* with $x \sim y$ to *x*,*x*,0·75 and then to its equivalent *x*,0,0·25, and (*e*) movement of O(4) from *x*,*y*,*z* with $x \sim -y$ to *x*,2*x*,0·25. Because the transformed coordinates are similar to those found for the calcined material, it can be concluded that removal of the TPAOH had little effect on the framework. This is consistent with the rather rigid set of connections between the tetrahedral nodes of the $AlPO_4$ framework (see Fig. 2). Each cylindrical channel is bounded by a 6.6.6 net, and each channel is separated from the next one by a double wall. This kind of rigid structure is quite different from that of chabazite, for instance, whose four-ring hinges allow a 'concertina' movement between the hexagonal prisms when the extraframework species are changed (Smith, 1964).

In detail, there are small changes upon calcination of $AlPO_4$-5. The cylindrical channel of as-synthesized material is slightly scalloped [O(3)–O(3′) = 9·96; O(1)–O(1′) = 10·08 Å] whereas that of the calcined material is circular within experimental error [10·02 (1) and 10·01 (1) Å]. This minor change is associated with the small increase in *a* from 13·73 to 13·77 Å upon calcination. A corresponding reduction in *c* from 8·48 to 8·38 Å is associated particularly with reduction of the apparent *T*—O(2)—*T* angle from 178 to 176° (see later). In spite of the increase of *a*, the larger proportional decrease in *c* results in a small reduction of volume upon calcination. Although the changes are within experimental errors (2σ), all four *T*—O—*T* angles decrease as the TPAOH is removed (Table 2).

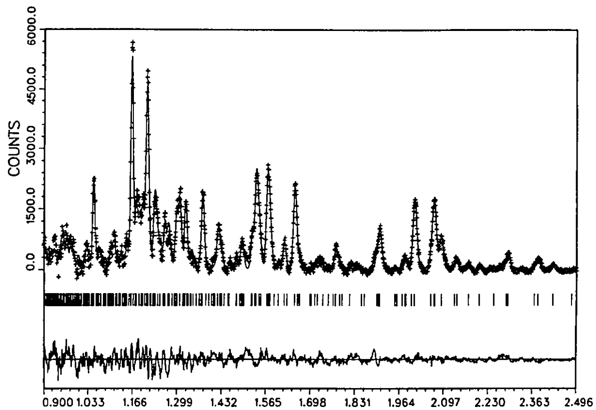

Fig. 1. Time-of-flight pulsed neutron profile of calcined $AlPO_4$-5 powder at 295 K in the range $d = 0·9–2·5$ Å. Plus marks indicate observed data, the solid line is the calculated profile and the vertical bars indicate the positions of allowed diffractions. A difference profile is given at the bottom of the figure.

Detailed interpretation of the interatomic distances and angles requires recognition of two factors. First, conversion from *P6cc* to *P6/mcc* requires mathematical averaging for the positions of all four O atoms. The centroid is actually the mean for two general positions which are forced onto a special position. This explains the high values of U_{33} for O(1), O(3) and O(4).* Second, O(2) in $AlPO_4$.TPAOH is statistically distributed over three positions related by a vertical triad axis, and this is apparently carried over to the calcined structure because of the high values of U_{11} and U_{22}. The combination of these two effects means that the *T*—O distances between the centroids are too low, and the *T*—O—*T* angles are too high, especially for O(2). The distances calculated for riding motion (Table 2) provide the best comparison between the calcined and uncalcined structures, even though there is a mathematical difference between an average of individual Al—O and P—O distances and a distance for the disordered model. Within experimental error (2σ) the *T*—O distances and *T*—O—*T* angles agree for the calcined and uncalcined structures. By analogy with the data for the as-synthesized structure, it is likely that the true *T*—O—*T* angles are near 150° for the calcined material.

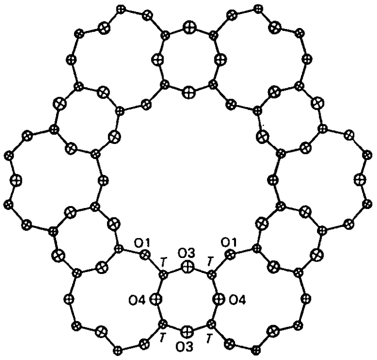

Fig. 2. Projection of $AlPO_4$-5 along the [001] direction. *T* atoms within the layer point alternately up and down. Atom O(2) (not shown) links layers.

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* The numbered intensity of each measured point on the profile and the anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43945 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for calcined and as-synthesized* AlPO$_4$-5

	Centroid	Riding	Centroid*	Centroid†	Riding†
T—O(1)	1·633 (9)	1·654 (8)	1·598	1·601 (18)	1·626 (18)
T—O(2)	1·597 (5)	1·688 (5)	1·578	1·578 (26)	1·645 (26)
T—O(3)	1·590 (5)	1·642 (5)	1·608	1·609 (20)	1·638 (20)
T—O(4)	1·560 (6)	1·589 (6)	1·603	1·604 (16)	1·633 (16)
Mean	1·595	1·643	1·597	1·598	1·636
O(1)—*T*—O(2)	106·8 (6)		109·0	109·0 (16)	
O(1)—*T*—O(3)	107·1 (5)		107·4	107·6 (12)	
O(1)—*T*—O(4)	111·1 (4)		109·3	109·4 (12)	
O(2)—*T*—O(3)	107·2 (6)		110·5	110·4 (16)	
O(2)—*T*—O(4)	110·6 (6)		109·9	109·8 (15)	
O(3)—*T*—O(4)	113·8 (6)		110·7	110·8 (13)	
T—O(1)—*T*	148·0 (5)		150·6	150·2 (7)	
T—O(2)—*T*	176·1 (14)		178·0	178·1 (12)	
T—O(3)—*T*	146·6 (9)		149·0	148·8 (7)	
T—O(4)—*T*	149·0 (8)		151·1	151·0 (9)	
O(3)—O(3′)	10·022 (12)		9·96		
O(1)—O(1′)	10·008 (8)		10·08		

* Using transformed coordinates in Table 1.

† Average of paired data for Al and P in Bennett *et al.* (1983); error is for individual distance.

In order to obtain reliable non-crystalline interatomic-spacing information from the Fourier-filtering technique, diffraction data to $d \simeq 0{\cdot}50$ Å are needed. The quality of our crystalline data does not justify refinement so deep into reciprocal space. We have, however, extended the range of data (without refinement) to $d \simeq 0{\cdot}45$ Å for the purpose of producing this non-crystalline correlation information. The results from Fourier transformation of the residual Rietveld intensity differences include interatomic spacings of 1·56, 2·50, 2·95, broad feature at ~3·80, 4·17 and 5·09 Å, interpretable as *T*—O, O—O, *T*—*T*′, *T*—O′, *T*–*T*″ (in four-rings) and *T*–*T*″ (in six-rings) interactions. These distances, as expected, are rather crude, but consistent with the known topology of AlPO$_4$-5. The short *T*—O distance may be due to atomic displacement effects. The remaining distances are consistent with average angles of O—*T*—O $\simeq$ 107, *T*—O—*T*′ $\simeq$ 142, *T*–*T*′–*T*″ (four-rings) $\simeq$ 90 and *T*–*T*′–*T*″ (six-rings) $\simeq$ 119°; all close to expected values. We can conclude from this that the residual scattering arises from an arrangement of atoms having a topology like that of AlPO$_4$-5, but not the long-range periodicity.

The present structure determination points out the good and bad aspects of neutron powder diffraction. Satisfactory refinement can be obtained of the coarse features of a complex structure with a centrosymmetric space group, but not of a fine feature such as the threefold displacement of an O atom from the averaged position. Strong pseudosymmetry, as exemplified by the present Al, P ordering in a non-centrosymmetric space group, poses severe problems which may be unsolvable.

Finally, the powder pattern of AlPO$_4$-5 at 7 K shows complex features not interpretable on a simple hexagonal cell. Although the pulsed-neutron powder technique is insufficiently sensitive to yield a detailed interpretation, it did provide an easy method for recognition of a phase change deserving of study by other methods.

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