

basal layers resulting in an infinite columnar unit along the *c* axis. In the 4C type structure, the clustering is the complicated three-dimensional chain (Tokonami, Nishiguchi & Morimoto, 1972). Thus the 3C and 4C Fe₇S₈ structures differ not only in the arrangement of vacancies but also in the shape of the Fe clusterings (Fig. 2).

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Refinement of the Crystal Structure of Silicon Diphosphate, SiP₂O₇ AIV – A Phase with Six-Coordinated Silicon

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Abstract. Synthetic SiP₂O₇ AIV, monoclinic, *P*2₁/*n*, *a*₀ = 4.713 (1), *b*₀ = 11.987 (2), *c*₀ = 7.628 (2) Å, β = 91.20 (2)°, *Z* = 4; *R* (unweighted) = 0.050, *R* (weighted) = 0.035. [PO₄] tetrahedra are linked in pairs to form [P₂O₇] groups. Si is octahedrally coordinated, with a mean Si–O distance of 1.766 Å.

Introduction. SiP₂O₇ was prepared by Liebau, Bissert & Köppen (1968). A SiO₂·*m*P₂O₅·H₂O mixture was held for 64 h at 1223 K in a silica-glass ampoule.

The structure was solved by Liebau & Hesse (1971) by means of multiple-film methods using *hk0* and *0kl* reflections only; *R* (*hk0*) was 8.7% and *R* (*0kl*) was 9.9%. The aim of the present work was to refine the structure from general *hkl* reflections.

A crystal measuring 0.1 × 0.06 × 0.03 mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo *K*α radiation (λ = 0.7107 Å) and a θ–2θ scan (θ_{max} = 30°). The intensities of 2804 crystallographically independent reflections were measured; 608 of these had |*F*_o| > 3σ(|*F*_o|) and were used in the subsequent refinement. The standard deviation, σ(*F*_o), was estimated from the formalism presented by Stout & Jensen (1968).

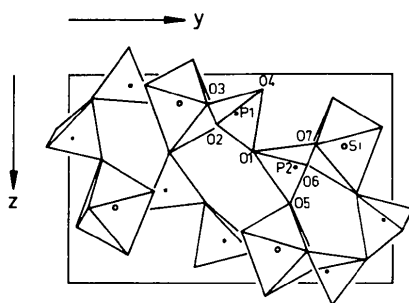
Lorentz and polarization corrections were applied, but no correction was made for absorption [μ(Mo *K*α) = 1.251 mm⁻¹]. The structure as determined by Liebau & Hesse (1971) was proven using Fourier techniques and was refined by full-matrix least-squares analysis with the program *ORFLS* of Busing, Martin & Levy (1962), starting with the atomic coordinates given by Liebau & Hesse (1971). (The *x* coordinates of their Table 1 are incorrect and have to be replaced by 0.5 – *x*.) Isotropic refinement of the crystal structure

Table 1. *Positional* (×10⁴) *and thermal parameters with standard deviations*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Si	2195 (4)	8505 (2)	3474 (3)	0.48 (3)
P(1)	7991 (4)	5182 (2)	1962 (2)	0.35 (3)
P(2)	7203 (4)	6970 (2)	4483 (3)	0.34 (3)
O(1)	7073 (10)	5725 (4)	3743 (6)	0.44 (8)
O(2)	805 (10)	4645 (4)	2364 (6)	0.60 (9)
O(3)	5788 (10)	4350 (4)	1412 (6)	0.45 (9)
O(4)	8249 (10)	6109 (4)	651 (6)	0.57 (8)
O(5)	6224 (9)	6873 (4)	6315 (6)	0.34 (8)
O(6)	215 (10)	7364 (4)	4303 (6)	0.53 (9)
O(7)	5153 (9)	7624 (4)	3379 (6)	0.51 (9)

Table 2. *Interatomic distances (Å) and angles (°)*

[PO ₄] tetrahedra			[SiO ₆] octahedra				
P—O distances			Si—O distances				
P(1)—O(1)	1.575 (5)	P(2)—O(1)	1.596 (5)	Si—O(2)	1.786 (5)	Si—O(5)	1.759 (5)
P(1)—O(2)	1.500 (5)	P(2)—O(5)	1.485 (5)	Si—O(3)	1.736 (5)	Si—O(6)	1.779 (5)
P(1)—O(3)	1.494 (5)	P(2)—O(6)	1.505 (5)	Si—O(4)	1.784 (5)	Si—O(7)	1.752 (5)
P(1)—O(4)	1.502 (5)	P(2)—O(7)	1.491 (5)	Average		Average	1.766
Average	1.518	Average	1.519				
O—O distances			O—O distances				
O(1)—O(2)	2.440 (7)	O(1)—O(5)	2.436 (7)	O(2)—O(3)	2.498 (7)	O(3)—O(6)	2.486 (7)
O(1)—O(3)	2.490 (7)	O(1)—O(6)	2.492 (7)	O(2)—O(4)	2.520 (7)	O(4)—O(6)	2.528 (7)
O(1)—O(4)	2.477 (7)	O(1)—O(7)	2.463 (7)	O(2)—O(5)	2.496 (7)	O(4)—O(7)	2.486 (7)
O(2)—O(3)	2.484 (7)	O(5)—O(6)	2.522 (7)	O(2)—O(7)	2.527 (7)	O(5)—O(6)	2.511 (7)
O(2)—O(4)	2.484 (7)	O(5)—O(7)	2.456 (7)	O(3)—O(4)	2.505 (7)	O(5)—O(7)	2.480 (6)
O(3)—O(4)	2.481 (7)	O(6)—O(7)	2.466 (6)	O(3)—O(5)	2.475 (7)	O(6)—O(7)	2.466 (6)
Average	2.476	Average	2.473	Average		Average	2.498
O—P—O angles		T—O—T angles		O—Si—O angles			
105.0 (3)	104.4 (3)	P(1)—O(1)—P(2)	133.0 (3)	90.3 (2)	O(3)—Si—O(7)	178.5 (3)	
108.4 (3)	106.9 (3)	Si—O(2)—P(1)	136.6 (3)	89.8 (2)	O(4)—Si—O(5)	178.9 (2)	
107.2 (3)	105.8 (3)	Si—O(3)—P(1)	159.1 (3)	89.5 (2)	O(2)—Si—O(6)	179.7 (3)	
112.2 (3)	115.0 (3)	Si—O(4)—P(1)	141.9 (3)	91.1 (2)	Average	179.0	
111.7 (3)	111.2 (3)	Si—O(5)—P(2)	145.2 (3)	90.7 (2)			
111.9 (3)	112.6 (3)	Si—O(6)—P(2)	140.9 (3)	90.1 (2)			
Average 109.4	Average 109.3	Si—O(7)—P(2)	143.2 (3)	90.0 (2)			
		Average	144.5	90.4 (2)			
				89.3 (2)			
				90.4 (2)			
				89.9 (2)			
				88.6 (2)			
				Average 90.0			

Fig. 1. The projection on *yz* of SiP₂O₇, AIV.

converged at R (unweighted) = 0.05 and R (weighted) = 0.035 $\{R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / (\sum wF_o^2)^{1/2}, w = 1/\sigma^2\}$.*

A list of positional and thermal parameters with estimated standard deviations is given in Table 1. Atomic distances and valence angles are shown in Table 2.

Discussion. The structure as described in detail by Liebau & Hesse (1971) has been confirmed but the precision of the atomic coordinates has been improved. The [SiO₆] coordination polyhedron deviates only

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34104 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

slightly from a regular octahedron. The distances and angles within the [SiO₆] octahedron agree with those found in other structures containing [SiO₆] octahedra. The [PO₄] tetrahedra are corner-linked in pairs to form [P₂O₇] diphosphate groups. In addition, each [PO₄] tetrahedron shares three corners with three different [SiO₆] octahedra forming a three-dimensional framework of [P₂O₇] groups and [SiO₆] octahedra, as shown in Fig. 1. As in other phosphates, the P—O bonds to the bridging oxygen, O(1), are notably longer than those to the terminal O atoms. The value of 133.0° for the P—O—P valence angle is very close to the mean value (131°) reported by Liebau (1966) for other phosphates.

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