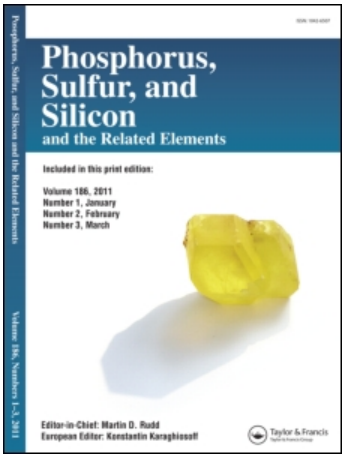

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Crystal Structure of Ordered White Phosphorus(β-P)

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CRYSTAL STRUCTURE OF ORDERED WHITE PHOSPHORUS (ß-P)

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Abstract The low-temperature form of white phosphorus (ß-P, T_{trans}= -76.4°C) is triclinic, $P\bar{1}$. The asymmetric unit contains 3 independent tetrahedral P_4 molecules. Intramolecular angles are 60 ± 0.5° and the P-P distances are $\bar{d}$=220.9(5) pm. The structure of ß-P is related to that of γ-Pu, the Pu atoms being substituted by P_4.

White phosphorus at ambient temperature and pressure has a complicated cubic structure (α-P). Tetrahedral P_4 molecules substitute (58 per unit cell) atomic positions in the α-manganese structure[1-3]. These positions are only partially occupied and all P_4 molecules exhibit (different kinds of) rotational disorder[4,5] which renders a detailed analysis of the molecular geometries impossible.

At -76.4°C (1 atm) α-P transforms into the ß-modification[6]. It has been repeatedly (and unsuccessfully) tried to solve its structure[1,7-9]. In own experiments[4] a single crystal of α-P did not transform even when kept for a day at -140°C. The formation of ß-P and its "in situ" crystal growth on a diffractometer was possible from a solution in CS_2 (mp. -111.5°C) by applying a temperature gradient to the solution enclosed in an X-ray capillary[10].

ß-P crystallizes in the triclinic system ($P\bar{1}$; a=1145.0(2), b=550.3(1), c=1126.1(4) pm, α=71.84(2), ß=90.37(2), γ=71.56(1)° at -115°C; Z=6 P_4 molecules; d_{calc}=1.943 g·cm^{-3}). The structure was solved by direct methods and refined to R = 0.057 (R_w = 0.050) with 3687 independent reflections measured on a Syntex $P2_1$ four circle diffractometer at -115°C (ref. Table 1).

TABLE 1 Positional and Thermal Parameters of ß-P

ATOM	X/A	Y/B	Z/C	U(EQUIV)
P1	.67802(8)	.39370(19)	.00247(09)	.0515(4)
P2	.52922(9)	.88513(19)	.17722(08)	.0520(4)
P3	.18938(9)	.92202(18)	.05123(09)	.0513(4)
P4	.55505(9)	.84909(19)	.37360(09)	.0501(4)
P5	.02641(8)	.34671(20)	.31490(09)	.0496(4)
P6	.87186(9)	.35722(19)	.01126(09)	.0506(4)
P7	.67157(8)	.53535(19)	.30808(10)	.0560(4)
P8	.47750(9)	.58127(19)	.31956(09)	.0516(4)
P9	.13526(9)	.55621(17)	.37416(09)	.0480(4)
P10	.81346(9)	.05347(19)	.14518(08)	.0526(4)
P11	.14244(9)	.15713(18)	.49419(08)	.0480(3)
P12	.22608(8)	.20514(19)	.31893(09)	.0505(4)

ATOM	U11	U22	U33	U23	U13	U12
P1	.0360(4)	.0496(5)	.0587(6)	-.0196(4)	-.0048(4)	.0005(4)
P2	.0639(6)	.0528(5)	.0305(4)	.0003(4)	-.0045(4)	-.0218(4)
P3	.0660(6)	.0445(5)	.0485(5)	-.0294(4)	-.0047(4)	-.0115(4)
P4	.0640(6)	.0472(5)	.0462(5)	-.0289(4)	-.0002(4)	-.0151(4)
P5	.0392(4)	.0627(5)	.0501(5)	-.0222(4)	-.0093(4)	-.0180(4)
P6	.0510(5)	.0486(5)	.0628(6)	-.0191(4)	.0051(4)	-.0303(4)
P7	.0409(5)	.0472(5)	.0709(6)	-.0251(5)	.0006(4)	.0026(4)
P8	.0534(5)	.0467(5)	.0567(5)	-.0076(4)	-.0017(4)	-.0291(4)
P9	.0598(5)	.0353(4)	.0576(5)	-.0216(4)	.0057(4)	-.0216(4)
P10	.0644(6)	.0481(5)	.0323(4)	-.0001(4)	-.0008(4)	-.0148(4)
P11	.0595(5)	.0465(5)	.0305(4)	-.0040(3)	-.0004(4)	-.0163(4)
P12	.0439(5)	.0523(5)	.0515(5)	-.0239(4)	.0135(4)	-.0041(4)

As already suggested[11] by the large entropy change associated with the α-ß transition, the P_4 molecules are ordered in the ß-form. The angles at the P atoms lie all within 60 ± 0.5° and the distances calculated from positional parameters range from 215.7(2) to 217.5(2) pm. A libration analysis reveals significant rigid-body motion of the molecules, the amplitudes for librational (≈ 8°) and translational (≈ 17 pm) molecular displacement are similar for the three independent molecules. The result accounts for the narrow NMR line measured for both α- and ß-P above approx. -150°C[12,13]. The P-P distances, corrected for libration (Table 2)

are near the values determined for gaseous P_4 by electron diffraction (221 ± 2 pm)[14] and Raman spectroscopy (222.28 ± 0.05 pm)[15].

TABLE 2 Interatomic Distances and Angles in ß-P

Distances [pm]		a)	b)	Angles [deg]			a)
P1	- P3	216.6(1)	220.9	P6	- P1 - P3		60.09(5)
	- P6	216.4(1)	221.0	P6	- - P10		59.66(5)
	- P10	218.0(1)	221.0	P3	- - P10		60.02(5)
P2	- P4	216.7(2)	221.6	P8	- P2 - P4		60.15(5)
	- P7	218.0(1)	221.5	P8	- - P7		59.78(5)
	- P8	216.5(2)	220.9	P4	- - P7		59.50(5)
P3	- P1	216.6(1)	220.9	P1	- P3 - P6		59.91(5)
	- P6	216.8(2)	220.5	P1	- - P10		60.31(5)
	- P10	217.3(2)	221.6	P6	- - P10		59.70(5)
P4	- P2	216.7(2)	221.6	P7	- P4 - P2		60.55(5)
	- P7	215.8(2)	220.7	P7	- - P8		60.03(5)
	- P8	217.1(2)	220.8	P2	- - P8		59.86(5)
P5	- P9	216.9(2)	221.1	P12	- P5 - P9		59.95(5)
	- P11	216.9(1)	220.3	P12	- - P11		60.33(5)
	- P12	216.5(1)	220.7	P9	- - P11		59.91(5)
P6	- P1	216.4(1)	221.0	P10	- P6 - P1		60.54(5)
	- P3	216.8(2)	220.5	P10	- - P3		60.28(5)
	- P10	216.0(2)	221.0	P1	- - P3		60.00(5)
P7	- P2	218.0(1)	221.5	P4	- P7 - P8		60.30(5)
	- P4	215.8(2)	220.7	P4	- - P2		59.95(5)
	- P8	216.5(2)	221.1	P8	- - P2		59.75(5)
P8	- P2	216.5(2)	220.9	P2	- P8 - P7		60.45(5)
	- P4	217.1(2)	220.8	P2	- - P4		59.98(5)
	- P7	216.5(2)	221.1	P7	- - P4		59.67(5)
P9	- P5	216.9(2)	221.1	P12	- P9 - P11		60.37(5)
	- P11	216.6(1)	220.8	P12	- - P5		59.93(5)
	- P12	216.5(2)	219.9	P11	- - P5		60.05(5)
P10	- P1	218.0(1)	221.0	P6	- P10 - P3		60.02(5)
	- P3	217.3(2)	221.6	P6	- - P1		59.80(5)
	- P6	216.0(2)	221.0	P3	- - P1		59.67(5)
P11	- P5	216.9(1)	220.3	P9	- P11 - P5		60.04(5)
	- P9	216.6(1)	220.8	P9	- - P12		59.79(5)
	- P12	217.8(1)	221.6	P5	- - P12		59.73(4)
P12	- P5	216.5(1)	220.7	P5	- P12 - P9		60.12(5)
	- P9	216.5(2)	219.9	P5	- - P11		59.94(5)
	- P11	217.8(1)	221.6	P9	- - P11		59.84(5)

a) corrected for thermal motion (ORFFE)
b) corrected for libration (rigid body)

The packing of molecules in ß-P is rather complex. Close-packed layers of P_4 units (6 neighbors) are stacked in a way to coordinate each molecule by 2 times 4 molecules from adjacent layers (cn = 14). As with α-P, the structure of ß-P is closely related to the structure of a metallic element, namely γ-Pu[16], the P_4 substituting the Pu atoms.

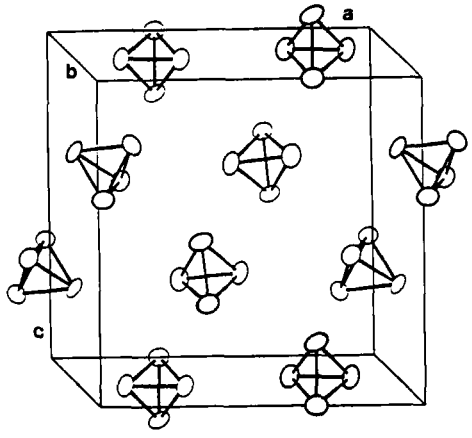

FIGURE 1

Projection of the structure of ß-P on (010). The thermal ellipsoids are drawn at 50% probability.

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