as under expt. 2 yielded 1.10 g crystals, m.p. 134°C.

Mixed m.p. of crystals from the three experiments showed no depression, and the spectra (data given in text above) were identical. (Found: C 62.08; H 10.43. Calc. for $C_{12}H_{24}O_4$:C 62.05; H 10.52). Molecular weight was determined with a vapour pressure osmometer. Found: 233, calc. 236. Total active oxygen: Found 13.4 %, calc. 13.5 %.

(Samples of ca. 10 mg were treated with a 10 % solution of sodium iodide in acetonitrile acidified with perchloric acid dihydrate. The mixture was left in a completely filled stoppered flask stored in the dark at ca. 20°C for 15 min and titrated with 0.01 N thiosulphate solution. A blank was run under the same conditions.)

Determination of hydrogen peroxide and ketone after treatment with titanyl reagent: The hydroperoxide was left for 24 h with excess titanyl reagent. The hydrogen peroxide was determined iodometrically as described elsewhere,[10] while the ketone was filtered off, dried and weighed.

IR spectra were taken with a Beckman IR5A spectrophotometer. NMR: A Varian Associate Spectrometer operating at 60 Mc/sec was used with TMS as an internal standard.

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On the Crystal Structure of Sn₄P₃

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The occurrence of several intermediate phases in the tin-phosphorus system has been reported in earlier literature. Depending on the difficulties in determining the phase conditions, however, the data have often been contradictory. The three most recent investigations will be mentioned here. In 1909 Jolibois[1] found a compound Sn_4P_3 by means of electrolytical isolation. A compound SnP_3 was also stated to exist. A more systematic investigation using physico-chemical methods was made by Vivian in 1920.[2] Using thermal, microscopic, and residue analytical methods the three intermediate phases Sn_4P_3, Sn_3P_4, and SnP_3 were found. Later (1957) Katz et al.[3] published X-ray powder data for a phase which they found to be of the composition SnP. This seems to be the only X-ray investigation that has been made of the tin-phosphorus system. All the phases mentioned are in need of further characterization.

An investigation has been started at this institute in order to obtain more information on the tin-phosphorus system. In this paper X-ray powder data will be given for a phase with the ideal crystallographic composition Sn_4P_3, together with preliminary results from a single-crystal structure determination.

The starting materials for the preparations were tin powder (KEBO, purum) or tin rods (Johnson, Matthey & Co., Ltd, spectrographically standardised, containing in ppm: Pb 5, Bi 2, Ca and Cu both < 1) and red phosphorus (purity higher than 99 %). The syntheses were performed by heating weighed amounts in evacuated and sealed silica tubes at temperatures between 400°C and 545°C. The reaction products were examined by X-ray powder methods in Guinier-Hägg-type focussing cameras using $CuK\alpha_1$ or $CrK\alpha_1$ radiation. Silicon ($a = 5.43054$ Å) was used as an internal calibration standard.

Preliminary results of this phase analysis confirm the existence of a phase near the composition Sn_4P_3, and indicate the existence of the phase reported to be SnP.[3] However, there are indications that this phase is a low-temperature phase formed

Table 1. Powder diffraction data up to $\sin^2\theta = 0.50$ for Sn_4P_3. $CrK\alpha_1$ radiation, $\lambda = 2.28962$ Å.

h k l	$\sin^2\theta_o \times 10^5$	$\sin^2\theta_c \times 10^5$	I_o	I_c
0 0 3	—	945	—	0.5
0 0 6	—	3780	—	0.7
0 0 9	—	8504	—	0.4
1 0 1	11210	11205	vw	2.5
0 1 2	11517	11520	w	11.3
1 0 4	12793	12780	vw	2.8
0 1 5	13723	13725	m	25.1
0 0 12	15115	15119	m—	12.8
1 0 7	16235	16245	vst	87.3
0 1 8	17802	17820	vvw	2.2
1 0 10	21585	21599	vvw	1.1
0 0 15	—	23623	—	1.3
0 1 11	23792	23804	vw	2.6
1 0 13	—	28844	—	0.0
0 1 14	31675	31678	st	33.7
1 1 0	33296	33300	st	45.2
0 0 18	—	34017	—	0.8
1 1 3	—	34245	—	0.0
1 1 6	—	37080	—	0.3
1 0 16	—	37978	—	0.5
0 1 17	41451	41443	w	4.7
1 1 9	—	41805	—	0.8
0 2 1	—	44505	—	0.9
2 0 2	44819	44820	vw	4.2
0 2 4	—	46080	—	1.3
0 0 21	46310	46301	w	8.2
2 0 5	47031	47025	w	11.8
1 1 12	48440	48419	st	40.7
1 0 19	49011	49002	m	26.8
0 2 7	49541	49545	st	50.9

somewhat below 500°C. There is at least one more phase with a high phosphorus content.

A more detailed investigation of Sn_4P_3 and the phase equilibria in which it takes part has been started. In Table 1 X-ray powder data for this phase are listed as obtained with $CrK\alpha_1$-radiation. These data were not obtained from a single phase alloy but from the preparation from which the single crystals were picked and corresponds to Sn_4P_3 on the phosphorus rich side. However, variable cell dimensions indicating an extended homogeneity range have not at this stage been observed. The powder pattern could be indexed on the basis of a hexagonal cell with the dimension $a = 3.9677 \pm 0.0003$ Å and $c = 35.331 \pm 0.004$ Å. The errors given are standard deviations as obtained from a least squares refinement. The single-crystal investigation has shown, however, that the

symmetry is trigonal with the space group $R\bar{3}m$. The corresponding rhombohedral cell has the dimensions $a = 11.998 \pm 0.001$ Å and $\alpha = 19.036° \pm 0.003$. The structure was solved from selected Patterson maps, and if described on the basis of the hexagonal cell, the atoms are located as follows:

6 Sn in position 6(c) with $z = 0.134$
6 Sn   »   6(c)   » $z = 0.290$
6 P   »   6(c)   » $z = 0.429$
3 P   »   3(a)   —

The parameters given are preliminary only.

This gives a structure where both the non-equivalent phosphorus atoms are octahedrally surrounded by six tin atoms with a mean value of about 2.78 Å for the Sn—P distances. One of the tin atoms is octahedrally surrounded by six phosphorus atoms while the other tin atom coordinates three phosphorus atoms and three tin atoms octahedrally. The Sn—Sn distances are about 3.25 Å.

Hägg and Hybinette[4] have shown that there exists a phase in the tin-arsenic system which crystallizes with this type of structure. From phase-analytical data they suggested the composition Sn_3As_2 and supposed substitutional solution of tin in Sn_4As_3 to account for the deviation from the stoichiometric composition. The cell dimensions for Sn_3As_2 were given as $a = 4.082$ Å and $c = 35.99$ Å or $a = 12.23$ Å and $\alpha = 19.22°$. No single crystal refinement of this structure seems to have been made.

The Sn_4P_3 structure will be further refined and the final parameters and distances will be published later.

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