Table 4. *Unit cells of phosphorus*(III,V) *oxides*

In the case of $P_4O_9$ the unit cell according to crystallographic symmetry has been transformed for better comparison.

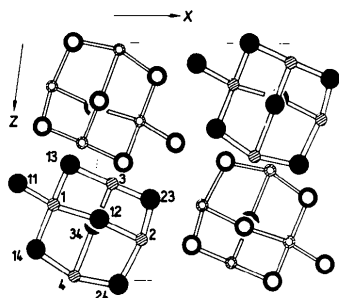| | $a$ (Å) | $b$ (Å) | $c$ (Å) | Monoclinic angle (°) | Space group |
|---|---|---|---|---|---|
| $P_4O_7$ | 9·808 (2) | 9·966 (1) | 6·852 (1) | 96·81 (1) | $P2_1/n$ |
| $P_4O_8$ | 9·66 (4) | 10·10 (4) | 6·93 (3) | 96·8 (3) | $C2/c$ |
| $P_4O_9$ | 9·66 (3) | 10·05 (3) | 2 × 6·95 (3) | 93·0 (4) | $R3c$ |



Fig. 2. Structure of $P_4O_7$ projected along |010|. Hatched circles: P, black circles: O; filled circles: upper layer of molecules, open circles: lower layer. The numbering of the atoms is according to Table 1.

For $P_4O_6$ and $P_4O_{10}$ the data given are for the free molecules determined by gas electron diffraction; for the other oxides the data were determined by crystal structure analysis and then averaged according to the pseudosymmetry of the molecules in the crystal.

The pseudosymmetry for the $P_4O_7$ molecule is accurately fulfilled. Distances and angles, of which average values are given in Table 3, are equal within the $3\sigma$ limit. Only the temperature factors of P(4) and its O

neighbours deviate markedly from the pseudosymmetry, probably due to intermolecular forces.

A striking feature of the crystal structures of the phosphorus(III,V) oxides is the similarity of their lattice parameters, which becomes obvious when a unit cell suitable for this comparison is chosen (Table 4). The structures (that of $P_4O_7$ is shown in Fig. 2) are similar, but they become more open in the row from $P_4O_9$ over $P_4O_8$ to $P_4O_7$. This may be responsible for the very high hygroscopicity of $P_4O_7$, which exceeds that of molecular $P_4O_{10}$.

The shortest intermolecular contacts in the $P_4O_7$ structure are between trivalent P and O. P(2)···O(13) and P(2)···O(11) are 3·21 and 3·25 Å respectively and O(34)···O(11) is 3·24 Å.

For data processing and structure analysis the programs of the CPA system, *SHELX* (Sheldrick, 1976) and *XANADU* were used. We thank Mrs H. Schrauber and Mrs Ch. Krause of the Computing Center of the Academy in Berlin-Adlershof for their assistance.

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# The Structure of TiZn₁₆

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**Abstract.** $TiZn_{16}$, $Cmcm$, $Z = 4$, $a = 7·720$ (7), $b = 11·449$ (7), $c = 11·755$ (9) Å. $R = 0·11$ for 407 reflexions. The structure is compared to the $TMZn_{13}$ (TM = Mn, Fe, Co) structure.

**Introduction.** In the course of a study of the intermediate phases formed between transition metals, single crystals of a phase in the Ti–Zn system were obtained. According to a phase-diagram study (Heine

& Zwicker, 1962), the composition would be TiZn$_{15}$. We describe in this paper the determination of the unknown structure of this compound whose composition has been found to be TiZn$_{16}$.

TiZn$_{16}$ was prepared by diffusion of liquid Zn in solid Ti. Samples containing stoichiometric amounts of Zn and Ti were placed in Ta containers sealed under an argon atmosphere and then heat-treated at 1273 K for 48 h. Metallographic examination showed the presence of pure Zn, TiZn$_{16}$ and the eutectic TiZn$_{16}$–Zn. These observations are consistent with the phase diagram published by Heine & Zwicker (1962). One plate-like single crystal (0·15 × 0·10 × 0·04 mm) suitable for X-ray analysis was isolated. Weissenberg and precession photographs showed the crystal to have space group *Cmcm* (systematic absences, *hkl*: *h + k = 2n*; *h0l*: *l = 2n*). Intensities were measured with Zr-filtered Mo *Kα* ($\lambda = 0.71069$ Å) radiation on a computer-controlled three-circle goniometer in the $\theta/2\theta$ scan mode. Intensities of 587 independent reflexions to a limit of sin $\theta/\lambda = 0.60$ Å$^{-1}$ were measured and corrected for background, Lorentz and polarization factors. All computer programs were those of the XRAY system (1972). The structure was solved by direct methods in the space group *Cmcm*. The phases of the 73 largest normalized structure factors ($E > 1.2$) were determined with *SINGEN* and *PHASE*. Evaluation of $E$ maps gave the whole structure. Positioning of Ti atoms as compared to Zn atoms was easy due to the large difference in the scattering factors (Cromer & Mann, 1968). Positional and isotropic thermal parameters refined satisfactorily with *CRYLSQ*. Anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). $R (= \sum|\Delta F|/\sum|F_o|)$ was 0·11 for 407 independent reflexions* with $|F_o| > 3\sigma_F$. The final positional and thermal parameters are listed in Table 1. Lattice parameters (see *Abstract*) were refined by least

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35649 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters for* TiZn$_{16}$

The e.s.d.'s are given in parentheses. The Debye–Waller factor is defined as exp $[2\pi^2 \times 10^{-2}U(2 \sin \theta/\lambda)^2]$.

|       | Equipoint | $x$ | $y$ | $z$ | $U$ (Å$^2$) |
|-------|-----------|-----|-----|-----|-------------|
| Ti    | 4(*c*)    | 0        | 0·953 (1)  | $\frac{1}{4}$   | 0·4 (2) |
| Zn(1) | 4(*a*)    | 0        | 0          | 0               | 1·2 (2) |
| Zn(2) | 4(*c*)    | 0        | 0·7114 (9) | $\frac{1}{4}$   | 1·4 (2) |
| Zn(3) | 8(*f*)    | 0        | 0·3807 (6) | 0·0306 (6)      | 0·9 (2) |
| Zn(4) | 8(*f*)    | 0        | 0·1763 (6) | 0·1399 (6)      | 1·4 (2) |
| Zn(5) | 8(*g*)    | 0·166 (1)| 0·3553 (6) | $\frac{1}{4}$   | 1·2 (2) |
| Zn(6) | 16(*h*)   | 0·3316 (7)| 0·3135 (4)| 0·0702 (4)      | 1·2 (2) |
| Zn(7) | 16(*h*)   | 0·2942 (7)| 0·0529 (4)| 0·1352 (4)      | 1·3 (1) |

squares with *PARAM* to fit values for 30 independent reflexions.

**Discussion.** The structure can be described by an interpenetrating packing of coordination polyhedra. The coordination number for each atom was evaluated with the gap criterion for the distribution of the distances (Bruzzone, Fornasini & Merlo, 1970). The atomic distribution around one atom was calculated and represented by plotting the number of surrounding atoms at a distance $d$ against the ratio $d/\sum r$, where $\sum r$ = radius of the central atom + radius of the adjacent atom. The radii used for this calculation were 1·47 for Ti and 1·38 Å for Zn. For each atom the gap limit occurs at $d/\sum r \leq 1.15$. According to this limit, the interatomic distances corresponding to the coordination polyhedra are given in Table 2. The coordination numbers are 11 for Zn(2) and Zn(5), 12 for Zn(1), Zn(3), Zn(4), Zn(7) and 13 for Zn(6). The schematic drawings in Fig. 1 show the connexions between the corners of the polyhedra only when these are parallel or nearly parallel to the plane of projection. The surfaces of the Zn coordination polyhedra consist of triangles and deformed squares. Thus, the analysis and classification of Frank & Kasper (1958),

Table 2. *Interatomic distances* (Å) *in* TiZn$_{16}$

All e.s.d.'s are 0·01 Å.

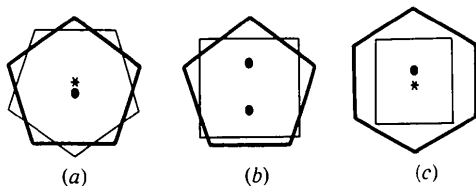| | | | |
|---|---|---|---|
| Ti–Zn(2)     | 2·77 | Zn(5)–2Zn(6) | 2·52 |
| –2Zn(5)      | 2·81 | –Zn(5)       | 2·56 |
| –2Zn(4)      | 2·86 | –2Zn(7)      | 2·65 |
| –4Zn(7)      | 2·88 | –2Zn(4)      | 2·74 |
| –4Zn(6)      | 2·95 | –Ti          | 2·81 |
| –2Zn(1)      | 2·99 | –2Zn(3)      | 2·89 |
|              |      | –Zn(2)       | 3·06 |
| Zn(1)–2Zn(4) | 2·60 |              |      |
| –4Zn(6)      | 2·63 | Zn(6)–Zn(5)  | 2·52 |
| –4Zn(7)      | 2·84 | –Zn(6)       | 2·54 |
| –2Ti         | 2·99 | –Zn(6)       | 2·60 |
|              |      | –Zn(1)       | 2·63 |
| Zn(2)–4Zn(6) | 2·74 | –Zn(3)       | 2·71 |
| –4Zn(7)      | 2·76 | –Zn(2)       | 2·74 |
| –Ti          | 2·77 | –Zn(4)       | 2·79 |
| –2Zn(5)      | 3·06 | –Zn(3)       | 2·84 |
|              |      | –Ti          | 2·95 |
| Zn(3)–2Zn(7) | 2·63 | –Zn(7)       | 3·01 |
| –Zn(4)       | 2·67 | –Zn(7)       | 3·02 |
| –2Zn(6)      | 2·71 | –Zn(7)       | 3·09 |
| –2Zn(7)      | 2·81 | –Zn(4)       | 3·11 |
| –Zn(3)       | 2·82 |              |      |
| –2Zn(6)      | 2·84 | Zn(7)–Zn(3)  | 2·63 |
| –2Zn(5)      | 2·89 | –Zn(5)       | 2·65 |
|              |      | –Zn(4)       | 2·68 |
| Zn(4)–Zn(4)  | 2·59 | –Zn(7)       | 2·70 |
| –Zn(1)       | 2·60 | –Zn(2)       | 2·76 |
| –Zn(3)       | 2·67 | –Zn(3)       | 2·81 |
| –2Zn(7)      | 2·68 | –Zn(1)       | 2·84 |
| –2Zn(5)      | 2·74 | –Ti          | 2·88 |
| –2Zn(6)      | 2·79 | –Zn(6)       | 3·01 |
| –Ti          | 2·86 | –Zn(6)       | 3·02 |
| –2Zn(6)      | 3·11 | –Zn(6)       | 3·09 |
|              |      | –Zn(7)       | 3·18 |

Fig. 1. Schematic drawings of the coordination polyhedra of Zn atoms in TiZn$_{16}$. Thick lines are on top, thin lines underneath. (*a*) 12 coordination around Zn(1): regular icosahedron with central Zn(1) atom equidistant from the two pentagons centered by two single atoms above and below. 11 coordination around Zn(5): central atoms not equidistant from the two pentagons and top centering atom missing. 13 coordination around Zn(6): one vertex of one pentagon replaced by two atoms in a direction perpendicular to the pentagons. 12 coordination around Zn(7): central atom not equidistant from the two pentagons and the larger pentagon centered by two atoms. (*b*) 11 coordination around Zn(2): lower centered pentagon replaced by a square and upper atom replaced by two atoms. (*c*) 12 coordination around Zn(3): the two pentagons replaced by one hexagon and one square. 12 coordination around Zn(4): similar to Zn(3) but square rotated by 30°.
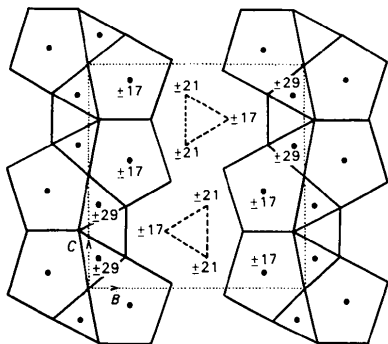


Fig. 2. The arrangement of the chains of pentagons and triangles for a layer at $x = 0$. The dashed lines, between the chains, indicate the trigonal prisms.

which applies to structures with triangulated co-ordination shells only, is not valid for TiZn$_{16}$. A description of the TiZn$_{16}$ model by layers gives a better understanding. In Fig. 2 the major skeleton of the TiZn$_{16}$ structure is given, illustrating the arrangement of pentagons and triangles at $x = 0$. Parallel to $z$ there are independent chains made of pentagons and triangles with common edges. At $x = \pm 0.17$ and $x = \pm 0.29$ there are atoms over the centers of the pentagons and the triangles. Between the parallel chains, up and down the plane at $x = 0$, there are two triangles forming an empty trigonal prism. The other half of the structure can be obtained from this arrangement by translation ($\frac{1}{2},\frac{1}{2},0$).

A comparison of the TMZn$_{13}$ (TM = Mn, Fe, Co) and TiZn$_{16}$ structures shows that in TMZn$_{13}$ the TM atom
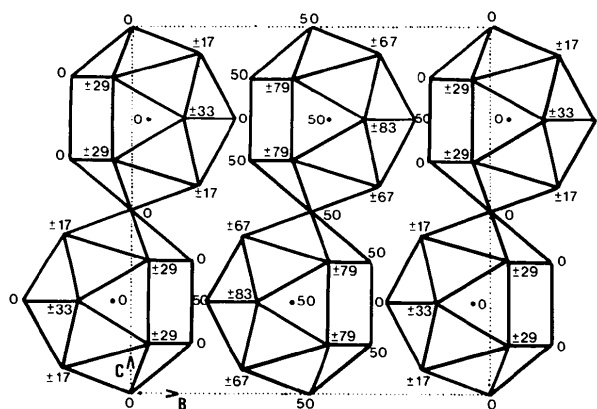


Fig. 3. The arrangement of the coordination polyhedra of Ti in TiZn$_{16}$ viewed down |100|. The Zn(3) atoms, not participating in the polyhedra, are omitted.

is surrounded by an icosahedron of 12 Zn atoms and in TiZn$_{16}$ the Ti atom is surrounded by 15 Zn atoms. This is due to the larger atomic radius of Ti. Moreover, describing the TMZn$_{13}$ structure, Brown (1962) wrote 'The TM atoms are surrounded by twelve Zn atoms at the vertices of a slightly distorted icosahedron; the icosahedra link together sharing one pair of opposite vertices, to form chains parallel to the $c$ axis. These chains pack together in an approximately hexagonal array, and the Zn(1) atoms fit into the interstices between chains'. A similar description of the TiZn$_{16}$ structure, illustrated in Fig. 3, can be made. The Ti atoms are surrounded by fifteen Zn atoms; the coordination polyhedra link together by sharing one pair of opposite vertices to form chains parallel to $c$. These chains pack together in a centered orthorhombic array and the Zn(3) atoms fit into the interstices between chains.

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