

The Crystal Structure of $Zr_{14}P_9$

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The crystal structure of $Zr_{14}P_9$ has been determined using visually estimated single-crystal X-ray diffraction data and direct methods. The space group is $Pn\bar{m}$. $Z=4$. The cell dimensions are: $a=16.715(2)$ Å, $b=27.572(2)$ Å, $c=3.6742(3)$ Å, $U=1693.3(2)$ Å³. The structure can be described as a complex arrangement of nine non-equivalent PZr_6 trigonal prisms with one to three further zirconium atoms situated outside the quadrilateral faces of the prisms. The structure contains additional zirconium atoms situated in approximately cubic holes between the prisms.

In a previous brief communication in 1966 on the Zr–P system, Lundström reported¹ the occurrence of an orthorhombic phase provisionally denoted ZrP_x with $0.5 < x < 1$. The space group was determined as $Pn\bar{m}$ or $Pnn2$ and the cell dimensions were found to be $a=16.715$ Å, $b=27.572$ Å and $c=3.6742$ Å. X-Ray intensities from a single crystal were recorded photographically, estimated visually and subsequently used to synthesize Patterson maps of the structure. The maps could, however, not be interpreted owing to severe overlaps of the Patterson peaks. The structure investigation was left unfinished for more than a decade.

Encouraged by the power of the direct methods, demonstrated in the solution of the MnP_4 structure² using X-ray powder data solely, we decided to apply these methods to the photographic intensity material of ZrP_x . In the present paper the results of the structure determination and refinement are presented. The structure determination showed that the ideal crystallographic formula is $Zr_{14}P_9$. No indication of any appreciable deviation from this formula was obtained from the refinement of the structure.

EXPERIMENTAL

Preparation. The method of preparation was described in the previous paper.¹ The crystals were invariably needle-shaped with the c axis parallel to the long axis. The crystal used for the collection of the intensity data was selected from an arc-melted alloy containing $Zr_{14}P_9$ and smaller amounts of α -ZrP.

X-Ray investigations. The unit-cell dimensions were determined from powder diffraction films taken with a Guinier-Hägg focussing camera using $CrK\alpha_1$ radiation and silicon as internal calibration standard ($a=5.43054$ Å).

The single-crystal intensity data were recorded in a Weissenberg camera using Zr-filtered $MoK\alpha$ radiation. The multiple film technique with iron foils as absorbers interleaved with the films was used. The intensities were estimated visually by comparison with an intensity scale obtained by known exposures of one of the reflections of the crystal. The crystal used was rotated around the needle (c) axis. The length of the crystal along the rotation axis was approximately 0.13 mm and the average diameter 0.040 mm. The intensities were corrected for Lorentz, polarization and absorption effects. The crystal was relatively irregular and limiting planes were difficult to determine. For this reason an absorption correction was applied assuming a simple cylinder-shaped crystal ($R=0.020$ mm) and using a linear absorption coefficient of 88.3 cm⁻¹ (calculated with mass absorption coefficients from Ref. 3). In total 1891 reflections were measured.

Calculations. The calculations were performed with the computers NORD 100 and IBM 370/158. The programs used have been described by Lundgren.⁴

STRUCTURE DETERMINATION AND REFINEMENT

Attempts to solve the structure using Patterson techniques were unsuccessful. In order to utilize

direct methods, normalized structure factors (E) were calculated. Inspection of the Weissenberg films showed that ($h0l$) reflections with $h+l=2n+1$ and ($0kl$) reflections with $k+l=2n+1$ were not visible. If these extinctions are systematic the space group is either $Pnmm$ or $Pnn2$. The frequency distribution of the normalized structure factors, however, corresponded to an acentric structure and accordingly $Pnn2$ was provisionally adopted as the space group.

415 reflections with $|E| > 1.2$ were selected for the sign determining procedure, which was carried out using the *MULTAN* 71 program.⁵ The sign determination resulted in four structure solutions with the absolute figures of merit 1.72, 1.26, 1.22 and 1.20, respectively. The one with the highest figure of merit was subsequently used to calculate E maps, which yielded the complete structure (15 non-equivalent zirconium positions and 9 phosphorus positions). Signs for 395 of the 415 reflections were obtained. After the refinement of the structure we found that only four of the signs were incorrectly

determined. All phase angles determined by *MULTAN* were 0 or 180° indicating a centrosymmetric structure. Consequently in the subsequent refinements the space group $Pnmm$ was adopted.

The structure refinements were based on F and carried out using a full-matrix, least-squares program. The initial atomic coordinates were those obtained from the E maps. A comparison of observed and calculated structure factors after a few preliminary refinement cycles showed that the strongest observed values were consistently lower than the calculated ones. This can be due to extinction errors, as well as a systematic underestimation of the intensities of low-angle reflections due to small spot size.⁶ Due to this ambiguity we decided to omit the 30 strongest reflections in the final refinement instead of trying to apply an extinction correction. The result was that the conventional R value fell from 10.8% to 9.9% and that the temperature factors increased on the average by approximately 30%.

Table 1. Final structural data for $Zr_{14}P_9$ from refinement based on F . Space group $Pnmm$ (No. 58). Unit cell: $a = 16.715(1)$ Å, $b = 27.572(2)$ Å, $c = 3.6742(3)$ Å; $U = 1693.3(2)$ Å³; $Z = 4$. Full occupancy for all positions. Standard deviations are given in parentheses. The temperature factor is $\exp[-B \sin^2\theta/\lambda^2]$.

Atom	Position	Positional parameters			B (Å ²)
		x	y	z	
Zr(1)	4g	0.0507(1)	0.5801(1)	0	0.10(3)
Zr(2)	4g	0.0987(1)	0.1047(1)	0	0.12(3)
Zr(3)	4g	0.1189(1)	0.7557(1)	0	0.04(3)
Zr(4)	4g	0.1363(1)	0.4692(1)	0	0.13(3)
Zr(5)	4g	0.1374(1)	0.3532(1)	0	0.10(3)
Zr(6)	4g	0.1992(1)	0.9904(1)	0	0.18(3)
Zr(7)	4g	0.2016(2)	0.8578(1)	0	0.30(4)
Zr(8)	4g	0.2451(1)	0.5836(1)	0	0.04(3)
Zr(9)	4g	0.2673(2)	0.1872(1)	0	0.18(3)
Zr(10)	4g	0.3334(1)	0.7621(1)	0	0.11(3)
Zr(11)	4g	0.4305(1)	0.4236(1)	0	0.16(3)
Zr(12)	4g	0.4805(1)	0.1774(1)	0	0.14(3)
Zr(13)	4g	0.4865(1)	0.6959(1)	0	0.19(3)
Zr(14)	2d	0	$\frac{1}{2}$	$\frac{1}{2}$	0.10(4)
Zr(15)	2a	0	0	0	0.03(4)
P(1)	4g	0.1323(5)	0.6580(3)	0	0.42(10)
P(2)	4g	0.3423(4)	0.6652(2)	0	0.07(8)
P(3)	4g	0.0484(5)	0.8571(3)	0	0.46(10)
P(4)	4g	0.2688(4)	0.4222(3)	0	0.33(10)
P(5)	4g	0.2736(4)	0.2859(3)	0	0.38(10)
P(6)	4g	0.0475(4)	0.2667(3)	0	0.21(9)
P(7)	4g	0.4371(4)	0.9080(2)	0	0.09(8)
P(8)	4g	0.3443(4)	0.0378(2)	0	0.06(8)
P(9)	4g	0.3959(4)	0.5333(3)	0	0.32(10)

As mentioned above the frequency distribution of the intensities indicated an acentric structure while the phase angles obtained indicated a centric structure. We believe that this can be ascribed to the incomplete intensity material (only the $hk0$ and $hk1$ reflections were measured) and to the fact that the strongest observed intensities were consistently lower than the calculated ones. In view of the extinction effects the final agreement between the observed and calculated structure factors was regarded as very satisfactory and no attempt to refine the structure in the lower space group was therefore considered necessary.

In the refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights were assigned according to the formula $w = 1/(a + |F_o| + c|F_o|^2)$. After some adjustments based on the weight analyses calculated after each refinement the constants were given the values $a = 14.0$ and $c = 0.012$. In the final refinement the following parameters were varied: two scale factors, 44 positional parameters and 24 isotropic temperature factors. The final agreement indices, based on 1891 reflections in the $(hk0)$ and $(hk1)$ layers, were:

$$R(F) = \sum (||F_o| - |F_c||) / \sum |F_o| = 0.108$$

and

$$R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.143.$$

Complex neutral-atom scattering factors were used.³

The measured and calculated structure factors

were compared after the last refinement cycle in a normal probability δR plot according to Abrahams and Keve.⁷ The majority of the points gave a linear plot with slope of 0.72 and an intercept of 0.16 on the experimental δR axis. Only two reflections fell outside the range $\pm 4\delta R$. The result shows that the standard deviations were overestimated by nearly 30 %.

A final difference Fourier map was calculated using the parameters obtained in the last refinement cycle. It exhibited no abnormal features and no positive or negative peak exceeding 8 % of a phosphorus maximum in the corresponding F_o synthesis. A list of observed and calculated structure factors can be obtained on request from the Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

The structure data, presented in Table 1, are based on a refinement of 1861 reflections excluding the 30 strongest. The interatomic distances are given in Table 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A projection of the structure of $Zr_{14}P_9$ along the c axis is illustrated in Fig. 1. The most conspicuous feature of the structure is the abundant occurrence of triangular prisms, consisting of a phosphorus atom at the centre and six zirconium atoms at the prism corners. There are nine non-equivalent phosphorus atoms in the structure, of which all coordinate between one and three additional zirconium atoms

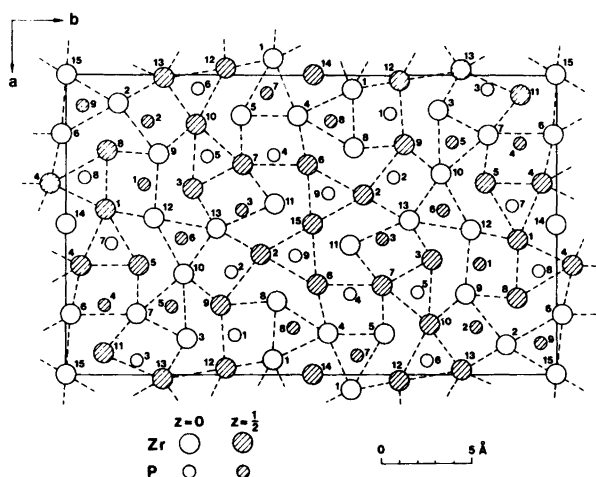


Fig. 1. The crystal structure of $Zr_{14}P_9$ projected on (001) .

Table 2. Interatomic distances and standard deviations for $Zr_{14}P_9$ (Å units). Distances listed are <4.3 and <3.5 Å for Zr and P respectively.

Zr(1)–P(1)	2.543(8)	Zr(6)–2P(4)	2.683(6)
–2P(7)	2.663(5)	–2P(9)	2.703(6)
–2P(8)	2.794(5)	–P(8)	2.755(7)
–2Zr(14)	2.995(2)	–2Zr(8)	3.293(3)
–Zr(8)	3.251(3)	–Zr(15)	3.340(2)
–2Zr(12)	3.292(3)	–2Zr(4)	3.358(3)
–Zr(4)	3.375(4)	–2Zr(11)	3.387(3)
–Zr(4)	3.409(3)	–Zr(2)	3.569(4)
–Zr(5)	3.643(3)	–Zr(7)	3.657(4)
–2Zr(1)	3.674(0)	–2Zr(6)	3.674(0)
Zr(2)–2P(2)	2.671(5)	Zr(7)–P(3)	2.561(8)
–P(3)	2.676(8)	–2P(4)	2.602(6)
–2P(9)	2.692(6)	–2P(5)	2.735(6)
–2Zr(8)	3.244(3)	–Zr(3)	3.136(4)
–Zr(15)	3.324(3)	–2Zr(5)	3.260(3)
–2Zr(13)	3.425(3)	–2Zr(11)	3.398(3)
–2Zr(11)	3.448(3)	–Zr(10)	3.437(4)
–Zr(6)	3.569(4)	–Zr(6)	3.657(4)
–Zr(9)	3.623(4)	–2Zr(7)	3.674(0)
–2Zr(2)	3.674(0)		
Zr(3)–2P(5)	2.701(6)	Zr(8)–2P(8)	2.685(5)
–P(1)	2.705(8)	–P(2)	2.773(7)
–P(6)	2.848(7)	–P(1)	2.786(8)
–P(3)	3.032(8)	–P(9)	2.877(8)
–Zr(7)	3.136(4)	–2Zr(2)	3.244(3)
–2Zr(13)	3.170(3)	–Zr(1)	3.251(3)
–2Zr(9)	3.250(3)	–2Zr(6)	3.293(3)
–2Zr(12)	3.287(3)	–2Zr(9)	3.402(3)
–Zr(10)	3.591(3)	–Zr(4)	3.642(4)
–2Zr(3)	3.674(0)	–2Zr(8)	3.674(0)
Zr(4)–P(4)	2.566(8)	Zr(9)–2P(1)	2.615(6)
–2P(8)	2.657(5)	–2P(2)	2.665(5)
–2P(7)	2.780(5)	–P(5)	2.722(8)
–2Zr(14)	3.047(2)	–2Zr(10)	3.237(3)
–Zr(5)	3.198(4)	–2Zr(3)	3.250(3)
–2Zr(6)	3.358(3)	–2Zr(8)	3.402(3)
–Zr(1)	3.375(4)	–Zr(12)	3.573(4)
–Zr(1)	3.409(3)	–Zr(2)	3.623(4)
–Zr(8)	3.642(4)	–2Zr(9)	3.674(0)
–2Zr(4)	3.674(0)		
Zr(5)–2P(7)	2.685(5)	Zr(10)–2P(5)	2.647(6)
–P(6)	2.820(8)	–P(2)	2.677(7)
–P(4)	2.905(8)	–2P(6)	2.712(5)
–P(5)	2.938(8)	–Zr(13)	3.144(4)
–2Zr(10)	3.150(3)	–2Zr(5)	3.150(3)
–Zr(4)	3.198(4)	–2Zr(9)	3.237(3)
–2Zr(7)	3.260(3)	–Zr(7)	3.437(4)
–2Zr(12)	3.311(3)	–Zr(12)	3.529(3)
–Zr(1)	3.643(3)	–Zr(3)	3.591(3)
–2Zr(5)	3.674(0)	–2Zr(10)	3.674(0)

Table 2. Continued.

Zr(11)–2P(3)	2.620(6)	Zr(13)–P(2)	2.555(7)
–P(4)	2.703(8)	–2P(3)	2.564(6)
–2Zr(15)	3.027(2)	–2P(6)	2.741(6)
–P(9)	3.080(8)	–Zr(10)	3.144(4)
–P(9)	3.134(8)	–2Zr(3)	3.170(3)
–2Zr(6)	3.387(3)	–2Zr(2)	3.425(3)
–2Zr(7)	3.398(3)	–Zr(12)	3.539(4)
–2Zr(2)	3.448(3)	–Zr(11)	3.574(4)
–Zr(13)	3.574(4)	–2Zr(13)	3.674(0)
–2Zr(11)	3.674(0)		
Zr(12)–2P(6)	2.647(5)	Zr(14)–2P(7)	2.745(7)
–2P(1)	2.686(6)	–2P(8)	2.803(6)
–P(7)	2.727(7)	–4Zr(1)	2.995(2)
–2Zr(3)	3.287(3)	–4Zr(4)	3.047(2)
–2Zr(1)	3.292(3)	–2Zr(14)	3.674(0)
–2Zr(5)	3.311(3)		
–Zr(10)	3.529(3)	Zr(15)–4P(9)	2.692(5)
–Zr(13)	3.539(4)	–4Zr(11)	3.027(2)
–Zr(9)	3.573(4)	–2Zr(2)	3.324(3)
–2Zr(12)	3.674(0)	–2Zr(6)	3.340(2)
		–2Zr(15)	3.674(0)
P(1)–Zr(1)	2.543(8)	P(5)–2Zr(10)	2.647(6)
–2Zr(9)	2.615(6)	–2Zr(3)	2.701(6)
–2Zr(12)	2.686(6)	–Zr(9)	2.722(8)
–Zr(3)	2.705(8)	–2Zr(7)	2.735(6)
–Zr(8)	2.786(8)	–Zr(5)	2.938(8)
P(2)–Zr(13)	2.555(7)	P(6)–2Zr(12)	2.647(5)
–2Zr(9)	2.665(5)	–2Zr(10)	2.712(5)
–2Zr(2)	2.671(5)	–2Zr(13)	2.741(6)
–Zr(10)	2.677(7)	–Zr(5)	2.820(8)
–Zr(8)	2.773(7)	–Zr(3)	2.848(7)
P(3)–Zr(7)	2.561(8)	P(7)–2Zr(1)	2.663(5)
–2Zr(13)	2.564(6)	–2Zr(5)	2.685(5)
–2Zr(11)	2.620(6)	–Zr(12)	2.727(7)
–Zr(2)	2.676(8)	–Zr(14)	2.745(7)
–Zr(3)	3.032(8)	–2Zr(4)	2.780(5)
P(4)–Zr(4)	2.566(8)	P(8)–2Zr(4)	2.657(5)
–2Zr(7)	2.602(6)	–2Zr(8)	2.685(5)
–2Zr(6)	2.683(6)	–Zr(6)	2.755(7)
–Zr(11)	2.703(8)	–2Zr(1)	2.794(5)
–Zr(5)	2.905(8)	–Zr(14)	2.803(6)
		P(9)–2Zr(15)	2.692(5)
		–2Zr(2)	2.692(6)
		–2Zr(6)	2.703(6)
		–Zr(8)	2.877(8)
		–Zr(11)	3.080(8)
		–Zr(11)	3.134(8)

Table 3. Prism orientation, coordination and average distance for the phosphorus atom in $Zr_{14}P_9$.

Atom	Coordination	Average P–Zr distance (Å)
Prism axis \perp to the c axis		
P(1)	7	2.66
P(2)	7	2.67
P(3)	7	2.66
P(4)	7	2.68
Prism axis \parallel to the c axis		
P(5)	8	2.73
P(6)	8	2.73
P(7)	8	2.72
P(8)	8	2.73
P(9)	9	2.81

situated outside the quadrilateral faces of the prisms. As shown in Table 3 the phosphorus atoms P(1)–P(4) coordinate seven zirconium atoms while P(5)–P(8) have eight and P(9) nine close zirconium neighbours. The triangular faces of the prisms are parallel to the c axis for the P(1)–P(4) atoms and perpendicular to the c axis for the P(5)–P(9) atoms.

The average distances P–Zr for the 7-coordinated phosphorus atoms are 2.66–2.68 Å (see Table 3), which is slightly shorter than the sum of the Goldschmidt 12-coordination radius for zirconium, 1.60 Å, and the tetrahedral covalent radius for phosphorus, 1.10 Å. The corresponding average distances for 8-coordinated phosphorus are 2.72–2.73 Å and for 9-coordinated phosphorus 2.81 Å. A higher coordination is thus associated with larger phosphorus–zirconium average distances. The linkage of the prisms leads to large distances between the phosphorus atoms, the shortest P–P distance exceeding 3.5 Å.

The zirconium atoms have high coordination numbers. If Zr–P distances shorter than 3.15 Å and Zr–Zr distances shorter than 3.70 Å are taken into account, then the Zr(1)–Zr(13) atoms coordinate 5 phosphorus atoms and 9–11 zirconium atoms. Zr(14) and Zr(15) coordinate 4 phosphorus and 10 zirconium atoms.

The arrangement of the atoms coordinated by Zr(1)–Zr(13) is irregular. Zr(14) is surrounded by eight zirconium atoms in a slightly distorted cubic arrangement (1 b.c.c. fragment), two additional zirconium atoms situated outside two of the cube faces and four phosphorus atoms situated outside

the remaining cube faces. Zr(15) is surrounded by eight zirconium atoms in a strongly distorted cubic arrangement with two additional zirconium atoms situated outside two of the cube edges and four phosphorus atoms situated outside four of the quadrilateral faces.

A structural feature of particular interest in the $Zr_{14}P_9$ type structure is the occurrence of two types of building blocks containing b.c.c. fragments as the central part.

One building block consists of a body-centred cube with Zr(14) at the centre and four PZr_6 prisms sharing quadrilateral faces with the cube and having their axes parallel to each other and to the c axis. This type of building block occurs in other phosphide structures, namely in the Nb_7P_4 ⁸ and Nb_8P_5 ⁹ type structures. Variations of the building block with other orientations of the prism axes occur, for instance, in the Nb_5P_3 ,¹⁰ Nb_4As_3 ¹¹ and V_3As_2 ¹² type structures.

The other type of building block with Zr(15) at the centre of the very distorted b.c.c. fragment has a face diagonal in the c direction. The adjoining P(9)Zr₆ prisms are partially situated inside the cube with Zr(15)–Zr(2)–Zr(6) forming the triangular faces and with the prism axes in the c direction. This type of building block is unique among phosphide structures.

It may finally be mentioned that there is an isostructural counterpart to $Zr_{14}P_9$ with the formula $(Ti_{1-x}Cu_x)_{14}P_9$ in the Ti–Cu–P system.¹³ An X-ray investigation of this compound is in progress at this institute and will be reported in this journal.

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