

Table 2. Structure data for Zr_3As_5 . (x and y parameters $\times 10^4$, isotropic temperature factors $\times 10^3 \text{ \AA}^2$).

Atom	Position	x	y	z	B
Zr1	2a	0	0	0	59(10)
Zr2	4g	2155(1)	2495(5)	0	69(8)
Zr3	4g	3275(2)	4105(5)	0	65(8)
Zr4	4g*	0557(4)	4954(10)	0	80(15)
Zr5	4h	4936(2)	2414(5)	0.5	80(8)
Zr6	4h	0835(2)	0080(5)	0.5	45(7)
Zr7	4h	1209(2)	3224(6)	0.5	99(9)
Zr8	4h	2660(2)	0030(5)	0.5	47(6)
Zr9	4h	3731(2)	1643(5)	0.5	93(9)
As1	4g	0627(2)	2092(5)	0	65(8)
As2	4g	1616(2)	4811(5)	0	70(8)
As3	4g	4228(2)	3074(5)	0	65(8)
As4	4h	1724(2)	1003(5)	0.5	63(8)
As5	4h	2843(2)	2637(5)	0.5	63(8)

* Position filled to only 50 %.

values for the positional parameters were taken from the structure of Nb_3P_5 . The Zr4 position was assumed to be occupied to 50 % only, in analogy to the situation in Nb_3P_5 . The refinement converged, with the final conventional R -value of 0.14 for all 1272 reflexions measured. An attempt to refine the occupancy of the Zr4 position resulted in a value of 65 %, with a simultaneous increase in the isotropic temperature factor by a factor of two, the calculated correlation between the two parameters being of the order of 0.8. In view of the deficiencies in the intensity data, further refinements including, for instance, anisotropic thermal parameters were not considered worthwhile. The results of the refinement assuming a 50 % occupancy of the Zr4 position are presented in Table 2. The values of the isotropic temperature factors as given in Table 2 should be regarded with caution, while the values of the positional parameters can be treated with greater confidence.

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The Crystal Structure of V_2P

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In a previous communication the existence of V_2P was reported.¹ A complete single-crystal analysis has been performed, which shows that this compound is isotypic with Co_2P (*anti*- $PbCl_2$) as suggested. No deviation from the crystallographic formula was detected, but the phase may nevertheless be identical with the compound ascribed the approximate composition $V_{2.4}P$ reported by Boller.²

Experimental details. The compound was prepared in the following manner. Vanadium (Materials Research Corp., 99.95 % purity) and red phosphorus (KEBO, at least 99 % purity) were heated in an evacuated silica ampoule at 900 °C for 8 days and subsequently melted in an arc furnace under an argon atmosphere. The alloy was finally heat-treated in an alumina crucible for 8 h at 1175 °C under an argon atmosphere using an induction furnace. The X-ray powder pattern showed only the lines of V_2P together with blurred lines interpreted as belonging to traces of cubic VO_{1-x} .

The existence of V_2P had not been reported in earlier surveys of the V-P system, and the possibility could not be excluded that this phase was in fact a ternary compound. The alloy had been in contact with silica in the preliminary stages of the synthesis, and a small P-Si substitution would escape detection in the X-ray structure refinement. Therefore it was considered worthwhile to determine the silicon content by chemical analysis.

In all stages of the analysis glassware was avoided, using platinum or teflon vessels. The samples were dissolved in nitric acid, and vanadium and phosphorus were removed from the slightly acidic solution as vanadate and

Table 1. Structure data for V_2P from refinement based on F^2 . Standard deviations are given in parentheses. Space group $Pnma$ (No. 62). All atoms in 4(c) positions. Full occupancy. $a = 6.2045(2)$ Å, $b = 3.3052(1)$ Å, $c = 7.5440(2)$ Å, $V = 154.70(1)$ Å³; $Z = 4$. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^*)]$; $U_{12} = U_{23} = 0$.

Atom	Positional parameters			$U_{ij} \times 10^5$ (Å ²)		U_{33}	U_{13}
	x	y	z	U_{11}	U_{22}		
V(1)	0.86148(8)	1/4	0.05891(7)	446(20)	558(20)	392(20)	-4(16)
V(2)	0.96041(9)	1/4	0.66624(7)	620(21)	584(22)	605(21)	-11(17)
P	0.24723(14)	1/4	0.14183(10)	524(29)	455(31)	570(31)	-4(25)

phosphate by anion exchange on Dowex 2 in its acetate form. The silicon content was determined spectrophotometrically.³

The silicon content was found to be 0.018 % in a crushed 43 mg sample and 0.013 % for the main part of the alloy (95 mg). The agreement between different aliquots was excellent. The discrepancy between the two samples might be due to inhomogeneity or due to the difference in specimen preparation and thus exposure to silicon-containing impurities. Preliminary tests of the analysis method using vanadate, phosphate and silicate indicated an accuracy better than 5 %.⁴

The cell dimensions were determined with a Guinier-Hägg type focussing camera, using strictly monochromatic $CuK\alpha_1$ radiation and silicon ($a = 5.431065$ Å)⁵ as internal calibration standard. The cell parameters given in Table 1 were refined using a least-squares method.

A small irregular fragment of the approximate dimensions $0.060 \times 0.020 \times 0.010$ mm picked from the final alloy proved to be a single crystal. A computer-controlled Stoe four-circle diffractometer equipped with a graphite monochromator to yield $MoK\alpha$ radiation was used for collecting the single-crystal intensity data. An $\omega-2\theta$ step-scan technique was utilized, and three standard reflexions were remeasured every 40 reflexions as a check of the stability. Reflexions were recorded up to 70° in 2θ , corresponding to $0 \leq h \leq 10$, $-5 \leq k \leq 5$ and $-12 \leq l \leq 12$. Because of the small size of the crystal and the calculated linear absorption ($\mu = 131$ cm⁻¹) it was considered that an absorption correction was not necessary.

The calculations were performed on IBM 370/155 and IBM 1800 computers. The crystallographic programs used have been described by Lundgren.⁶

Structure refinement. Reflexions that are equivalent according to the orthorhombic symmetry were averaged, and the structure was refined by a full-matrix least-squares method. As starting values for the positional parameters the coordinates of Co_2P were used.⁷ The atomic scattering factors were taken from Hanson *et al.*⁸ and the dispersion corrections from Cromer.⁹ Refinements on both F and F^2

were performed, where the function minimized was $w(|F_o^n| - |F_c^n|)^2$ with $n = 1$ or 2, respectively. The weights were assigned in accordance with the formula $w^{-1} = \sigma^2(F_o^n) + (p_n|F_o^n|)^2$; $\sigma^2(F_o^n)$ is based on counting statistics, and the empirical factor p_n was set to $p_1 = 0.007$ and $p_2 = 0.015$ for the two refinements. Anisotropic temperature factors were introduced, but there was no need for extinction corrections since the effects even on the very strongest reflexion were negligible. No significant differences in parameter values were found between the results of the two refinements. The F^2 refinement is recommended¹⁰ in order to preserve the assumed normal distribution in the intensity measurement, and the standard deviations obtained from the F^2 refinement were less than for the F refinement. The agreement factors were $R(F^2) = 0.029$, $R_w(F^2) = 0.039$ with the corresponding $R(F) = 0.032$ (371 reflexions), where

$$R(F^n) = \frac{\sum ||F_o^n| - |F_c^n||}{\sum |F_o^n|}$$

and

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

There were no indications of any appreciable deviation from the crystallographic formula. The isotropic temperature factors were quite similar to those obtained for other phosphides of this structure type.^{7,11} The occupancy factors were varied but the refinements invariably terminated with full occupancy. The parameter values from the final F^2 refinement are given in Table 1 together with refined cell parameters. A table of observed and calculated structure factors can be obtained from the authors on request.

A thorough discussion of the Co_2P structure and its features were given by Rundqvist,¹² who made a sub-division of the *anti*- $PbCl_2$ structure type into two subclasses according to slightly different atomic arrangement. Typical representatives for the two sub-classes are Co_2P and Co_2Si , respectively. In the Co_2P sub-class the phosphorus atoms have nine near neighbours. A classifying feature^{12,13} is the axial ratio a/c , which in V_2P is 0.823, consistent with the Co_2P sub-class. The complete

Table 2. Interatomic distances in V_2P (Å units). Distances shorter than 3.5 Å are listed. The estimated standard deviations are smaller than 0.001 Å for all distances.

$V(1)-2P$	2.341	$V(2)-2P$	2.461
- P	2.366	- 2P	2.547
- P	2.474	- P	2.674
- 2V(1)	2.545	- 2V(1)	2.716
- 2V(2)	2.716	- 2V(1)	2.872
- 2V(2)	2.872	- V(1)	3.013
- V(2)	3.013	- V(1)	3.025
- V(2)	3.025	- 2V(2)	3.043
- 2V(1)	3.305	- 2V(2)	3.305
		- 2V(2)	3.349
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P - 2P	3.305		

single-crystal analysis showed that V_2P is indeed a new member of this class.

It is interesting to compare the atomic arrangement of V_2P with that of the isotypic Ru_2P ,⁷ since the metal radii are approximately equal. Different arrangements are found, which implies that the radius ratio is not the governing factor. The *b*-axis of Ru_2P is 3.859 Å while that of V_2P is only 3.305 Å. Thus the trigonal prisms in V_2P are contracted compared to those in Ru_2P , which demand the metal atoms outside the prism faces to be positioned further away from the central phosphorus atom. These M-P distances are then longer while within the prisms the M-P distances as well as the M-M distances are shorter than in Ru_2P . This leads to a more even distribution of the M-P distances but a larger spread of the M-M distances in V_2P . These geometrical aspects were introduced and thoroughly discussed by Rundqvist.¹² The interatomic distances in V_2P are presented in Table 2, using the same notation as Rundqvist. The mean $V(1)-P$ distance is 2.38 Å and the mean $Ru(1)-P$ distance is 2.34 Å. Corresponding averages for the $M(2)-P$ distances are 2.54 and 2.61 Å for V_2P and Ru_2P , respectively. The shortest M-M distance in Ru_2P is 2.74 Å as compared to 2.55 Å in V_2P , the latter distance being shorter than a normal metal contact. Short intermetallic distances are not uncommon in vanadium-rich compounds with Group 4 or 5 elements.

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On the Compound $La_4Co_3O_{10}$

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Some binary oxides, of general formulae AO and BO_2 , form ternary compounds $AO(ABO_3)_n$, where one at the one end finds the perovskite ABO_3 ($n = \infty$) type structure and at the other the A_2BO_4 ($n = 1$) the K_2NiF_4 type. Two further members of a series are known, viz. $A_2B_2O_7$ ($n = 2$) and $A_4B_3O_{10}$ ($n = 3$), but none has reported examples for n between 3 and ∞ . The structure of $AO(ABO_3)_n$ contains n perovskite sheets separated by an AO sheet of NaCl like structure. Such series are known in the systems $CaO-MnO_2$, $CaO-TiO_2$, $SrO-MnO_2$, $SrO-TiO_2$, and $SrO-ZrO_2$.¹

In the system $La-Co-O$ $LaCoO_3$ and La_2CoO_4 with rhombohedrally modified perovskite and orthorhombic K_2NiF_4 type structures^{2,3} are known. We have prepared $La_4Co_3O_{10}$,⁴ which also has been reported quite recently by Janecek and Wirtz.⁵

Experimental. Initial batches of $LaCoO_3$ and La_2CoO_4 were prepared from 99.99% La_2O_3 (Kemira OY) and 99.95% CoO (Sheritt Gordon). Powder mixtures were coldpressed at 9.8 kN/cm². $LaCoO_3$ -specimens were fired for one week at 1100 °C in oxygen atmosphere and La_2CoO_4 -tablets for four days at 1300 °C in argon ($PO_2 \approx 10^{-6}$ bar) with frequent inter-