

Short Communications

Two New Zirconium Arsenides,
 Zr_3As_2 and Zr_8As_5 BERTIL CARLSSON,* MARGARETA GÖLIN and
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In connection with previous studies of the Hf-As, Nb-As and Ta-As systems,¹⁻³ an examination of the Zr-As system was begun, but subsequently left unfinished. The studies provided some information on two new compounds discovered, however, and the results obtained are reported in the present communication.

Turnings of zirconium (claimed purity 99.9 %) and arsenic (claimed purity 99.99 %), both *ex Koch-Light Laboratories Ltd.*, England, were heated in evacuated and sealed silica tubes at 900 °C for periods up to three days. The reaction products, consisting of mixtures of $ZrAs_2$, ZrAs and unreacted zirconium, were arc-melted under purified argon. The resulting alloys were crushed and examined by powder and single crystal X-ray diffraction methods.

Powder diffraction films were recorded in Hagg-Guinier type cameras, using $CuK\alpha_1$ or $CrK\alpha_1$ radiation. Silicon ($a = 5.431065 \text{ \AA}$)⁴ was used for internal calibration. Single crystal fragments were examined in a Weissenberg camera using filtered $MoK\alpha$ radiation. Single crystal intensity data were collected on a computer-controlled Stoe Philips four-circle diffractometer, using graphite-monochromatized $MoK\alpha$ radiation. An $\omega - 2\theta$ step scan procedure was used in the measurements, and instrumental stability was checked by re-measuring three standard reflexions at regular intervals. The calculations were performed on IBM 370/155 and IBM 1800 computers using standard-type crystallographic programs described in Ref. 5.

The powder diffraction studies showed that the arc-melted alloys were generally inhomogeneous and often contained more than two phases. In alloys with high zirconium contents, the presence of Zr_8As_5 , previously described by Lundström,⁶ was observed. The

lattice parameters of Zr_3As_2 were found to agree closely with those reported earlier.⁶ In more arsenic-rich preparations, two new phases were discovered. The first phase, Zr_3As_2 , was found to be isostructural with Hf_3As_2 and Hf_3P_2 by comparing its powder pattern with that for Hf_3As_2 ,¹ and by comparing the Weissenberg films recorded for a Zr_3As_2 crystal fragment with those obtained for Hf_3P_2 by Lundström.⁷ The second phase, Zr_8As_5 , was characterized in a corresponding manner by comparison with the powder and single crystal data for the phosphide Nb_8P_5 , investigated by Anugul *et al.*⁸ The unit cell dimensions for Zr_3As_2 and Zr_8As_5 are given in Table 1. Some of the powder diffraction patterns of the arc-melted alloys contained lines, which did not belong to Zr_3As_2 , Zr_8As_5 , or any of the previously reported zirconium arsenides Zr_2As , ZrAs and $ZrAs_2$.⁹ This indicates the presence of further phases in the Zr-As system.

The crystal structure of Zr_8As_5 was subjected to a closer examination, and diffractometer data were recorded for a single crystal fragment. Unfortunately, the crystal was accidentally lost before its dimensions had been measured, and no absorption correction could therefore be applied to the intensity values. A least-squares structure refinement was nevertheless performed using the uncorrected data. Atomic scattering factors and dispersion corrections were taken from Refs. 10 and 11, respectively. In the least-squares routine, the function $\sum [w(|F_o| - |F_c|)^2]$ was minimized, where the weights w were assigned according to the formula $w^{-1} = \sigma^2(F_o) + (0.05 F_o)^2$ with $\sigma(F_o)$ obtained from counting statistics. One scale factor, 26 positional parameters and 14 isotropic temperature factors were varied; initial

Table 1. Crystallographic data for Zr_3As_2 and Zr_8As_5 .

Compound	Zr_3As_2	Zr_8As_5
Structure type	Hf_3P_2	Nb_8P_5
Space group	$Pnma$	$Pbam$
a (Å)	10.5348(6)	28.3335(25)
b (Å)	3.7185(4)	10.2052(5)
c (Å)	10.3103(18)	3.7743(3)
Cell volume (Å ³)	403.9	1091.3

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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