Refinement of the Crystal Structure of VP$_2$

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Crystals of VP$_2$ have been prepared by the chemical transport technique, using iodine as the transport agent. The crystal structure has been refined from single crystal diffractometer data to a conventional R-value of 0.03. VP$_2$ belongs to the OsGe$_2$ (NbAs$_2$)-type structure (space group $C2/m$) and the unit cell dimensions are $a = 8.4641(6)$ Å, $b = 3.1054(4)$ Å, $c = 7.1698(4)$ Å, $\beta = 119.264(7)°$.

The occurrence of VP$_2$ was first reported by Zumbusch and Biltz.[1] They found by qualitative comparisons of the powder diffraction films that the three phosphides VP$_2$, NbP$_2$, and TaP$_2$ are structurally very similar. This observation was subsequently confirmed by Hulliger,[2] who indexed the powder patterns and concluded that the three diphosphides crystallize with the NbAs$_2$-type structure.[3-6]

According to Furuseth and Kjekshus,[6] NbAs$_2$ crystallizes with the non-centrosymmetric space group symmetry $C2$. The crystal structure of OsGe$_2$ is closely related to the NbAs$_2$ structure, and in discussions of the properties of NbAs$_2$-type compounds, Hulliger,[7] and Andres et al.[8] include OsGe$_2$ among the representatives. The structure of OsGe$_2$ was, however, described by Weitz et al.[9] in the centrosymmetric space group $C2/m$.

In the course of synthetic studies of transition metal phosphides by chemical transport methods we obtained VP$_2$ in single crystal form. In view of the space group problem of the NbAs$_2$-type compounds we decided to make an accurate refinement of the VP$_2$ structure. During this work Jeitschko and Donohue[10] published a report on the structures of the high-pressure phases CrP$_2$ and CrAs$_2$. Both compounds were found to crystallize with the OsGe$_2$-type structure, and for CrP$_2$, the space group was shown to be $C2/m$ within the (relatively high) accuracy of the diffraction data.

EXPERIMENTAL DETAILS

Preparation. The starting materials for the synthesis of VP$_2$ were red phosphorus of purity higher than 99 % and vanadium metal obtained from Materials Research Corporation, USA. The claimed purity was 99.95 % and according to the supplied analysis the major impurities were (in ppm): Fe 200, P 125, Ca 60, Cr 50, and Mn 50. Polycrystalline VP$_2$ was synthesized by heating red phosphorus and vanadium metal flakes in evacuated and sealed silica tubes at a temperature of 800 °C for 72 h. The product was then used as feedstock material in a chemical transport reaction with iodine as the transport agent. The iodine was introduced into the silica tubes in amounts corresponding to 5 mg I$_2$/cm^3, using an early version of the gas manipulation system as described by Richardson.[11] The silica tubes were inserted in a four-zone horizontal tube furnace, with the feedstock end at a temperature of about 800 °C and the growth zone at about 700 °C. Needle-shaped crystals, some of them with lengths up to 4 cm, were formed after a period of five days. The crystals were used for the X-ray diffraction work after rinsing in benzene.

X-Ray diffraction. Determination of the unit cell dimensions was carried out by X-ray powder methods using a Hägg-Guinier-type focussing camera with Cr$K\alpha_1$ radiation. Silicon ($a = 5.43054$ Å) was used as the internal calibration standard, and the cell dimensions were refined by the least squares method. The single crystal studies were performed with a Stoe four-circle computer-controlled diffractometer with a graphite monochromator and Mo$K\alpha$ radiation. The crystal used for the structure determination was in the form of a parallelepiped and bounded by [100], [010], and [001] faces with the approximate dimensions $50 \times 120 \times 20$ μm in the a, b, and c directions, respectively. The intensities were recorded using the ω-2θ

Table 1. Structure data for VP$_2$. Space group $C2/m$; $a = 8.4641(6)$ Å, $b = 3.1054(4)$ Å, $c = 7.1698(4)$ Å, $\beta = 119.264(7)°$; $U = 164.4$ Å^3; $Z = 4$; all atoms in 4 i positions. The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)]$, $\beta_{12} = \beta_{23} = 0$.

| Atom | Positional parameters | | | Anisotropic thermal parameters $\beta_{ij} \times 10^4$ | | | |
	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
V	0.84301(6)	0	0.30163(7)	15(1)	86(4)	15(1)	8(1)
P(1)	0.59962(11)	0	0.39969(12)	24(1)	117(6)	26(1)	16(1)
P(2)	0.14074(11)	0	0.02893(12)	22(1)	122(6)	19(1)	9(1)

Table 2. Interatomic distances (Å) in VP$_2$. Distances up to 4 Å are included. When greater than one, the number of equivalent distances from a central atom to its neighbours precedes the notation for the neighbouring atom.

V – 2P(2)	2.427(1)	P(1) – P(1)	2.699(2)	P(2) – P(2)	2.210(2)
P(2)	2.440(1)	2P(1)	2.717(1)	2P(2)	2.599(1)
2P(1)	2.476(1)	2P(1)	3.105(0)	2P(2)	3.105(0)
P(1)	2.481(1)	2P(2)	3.143(1)	2P(2)	3.811(1)
2P(1)	2.493(1)	2P(2)	3.241(1)		
V	2.786(1)	P(2)	3.472(1)		
2V	3.105(0)	P(2)	3.579(1)		
P(2)	3.872(1)				
2P(2)	3.912(1)				
2P(2)	3.949(1)				
2P(1)	3.975(1)				

step scan technique. Within the range of $0° \le 2\theta \le 120°$, reflexions were recorded corresponding to $0 \le h \le +15$, $0 \le k \le +6$ and $-13 \le l \le +15$. Measurements of three reference reflexions recorded every 38th reflexion indicated that the diffractometer operated in a stable manner during the whole intensity measurement period.

Numerical calculations. The numerical calculations were performed on an IBM 1800 and an IBM 370/155 computer using standard-type crystallographic programs as described in detail by Lundgren.[12]

STRUCTURE REFINEMENT

609 non-equivalent reflexions were recorded. Absorption corrections were applied, using the value of 76.3 cm^{-1} for the linear absorption coefficient. The minimum and maximum transmission factors were 0.66 and 0.87, respectively.

The structure was refined by the least squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights were assigned according to the formula
$$w^{-1} = \sigma^2(F_o) + (0.05|F_o|)^2$$
with $\sigma(F_o)$ based on counting statistics. 93 reflexions with $|F_o| < 3\sigma(F_o)$ were omitted from the refinements.

The refinement was started assuming $C2$ symmetry with the initial positional parameters taken from the values for NbAs$_2$ as given by Furuseth and Kjekshus.[6] Atomic scattering factors were taken from Hanson *et al.*[13] and corrections for anomalous dispersion from the International Tables.[14] Anisotropic temperature factors and an isotropic extinction correction according to Coppens and Hamilton[15] were included in the refinement.

The non-centrosymmetric refinement converged with the final agreement factors

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0336$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}} = 0.0476$$

An inspection of the results of the refinement showed that the deviations from centrosymmetry were negligible, and a final refinement was accordingly made assuming $C2/m$ symmetry. The final agreement factors were $R = 0.0339$ and $R_w = 0.0478$.

The structure data obtained are presented in Table 1. A list of interatomic distances is given in Table 2. In both tables, numbers in parentheses are the estimated standard deviations in the

least significant digits. Lists of observed and calculated structure factors can be obtained from the authors on request.

CONCLUDING REMARKS

In connection with their structure analysis of CrP_2, Jeitschko and Donohue [10] gave a thorough description and discussion of the $NbAs_2$-type structure. Only a few comments on the VP_2 structure are therefore given here.

The atomic arrangements in VP_2 and CrP_2 are very similar. As a consequence of the larger size of the vanadium atoms in comparison with the chromium atoms, the $V-V$ and $V-P$ distances are on an average 0.05 Å larger than the corresponding distances in CrP_2. The $P-P$ distances are also somewhat larger in VP_2, the shortest $P(2)-P(2)$ distance being 2.210(2) Å in VP_2 and 2.189(2) Å in CrP_2.

Concerning the space group symmetry of $NbAs_2$-type compounds we conclude, in agreement with Jeitschko and Donohue, that there is no convincing evidence for the lower space group $C2$. The structures of CrP_2 and VP_2 both conform to the $C2/m$ symmetry to a high degree of accuracy, and for NbP_2 and TaP_2, powder diffractometer data clearly indicate [16] that there can be no major deviation from the higher symmetry.

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