

An Accurate Refinement of $1T\text{-VSe}_2$ at Room Temperature

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Abstract. $\text{V}_{1+x}\text{Se}_2$ is trigonal, space group $P\bar{3}m1$, with $a = 3.356$ (1), $c = 6.104$ (2) Å. The structure was refined to $R(F) = 0.022$ for 1441 observed reflections. The structure (CdI_2 type) consists of selenium layers perpendicular to the c axis, defining two octahedral sites ($000, 00\frac{1}{2}$). Vanadium atoms V(1) fill 000 sites and the small amount x of vanadium atoms V(2) occupies $00\frac{1}{2}$ sites.

Introduction. Among the layered compounds, the dichalcogenides of transition metals of groups IVb and Vb present much interest from at least two points of view.

Firstly, they have significant theoretical importance as two-dimensional compounds with particular band structure and properties (Wolley & Wexler, 1977). Secondly, alkali-metal intercalated dichalcogenides appear promising materials for non-aqueous cells (Wilson & Yoffe, 1969; Murphy, Cros, Di Salvo & Waszczak, 1977).

Unfortunately, these compounds are often affected by controversial non-stoichiometry and poor crystallinity, and are thus unsuitable for accurate determination of their charge density by X-ray diffraction (Coppens, 1977). However, for VSe_2 , the situation is clearer: the exact formula is $\text{V}_{1+x}\text{Se}_2$ and x can be very small (<1%) with optimum crystal growth conditions.

VSe_2 also shows sharp discontinuities in its electrical and magnetic properties near 100 K (Bayart & Sienko, 1976; Van Bruggen & Haas, 1976) which are not fully understood. A further reason for a new accurate crystallographic study of VSe_2 is that, until now, its structure is far from being well refined (Nakahira & Hayashi, 1978).

VSe_2 crystals were obtained by vapour-phase growth. A thin plate-shaped crystal of good crystalline

Table 1. *Experimental conditions for data collection* (293 K)

Apparatus:	Philips PW1100 four-circle diffractometer; monochromator: pyrolytic graphite ($\cos^2 2\theta_{\text{monoc}} = 0.9722$)
Wavelength	Ag $K\alpha_1 = 0.559407$ Å
Scanning mode	θ - 2θ step scanning: 90 steps of $0.02^\circ \theta$; counting time: 2 s per step
$(\sin \theta/\lambda)_{\text{max}}$	1.2 \AA^{-1}
Number of measured reflections	1441 (4 asymmetric units)
Sample size along a, b, c	$0.27 \times 0.13 \times 0.024$ (mm)

quality was selected by Laue and precession photographs to ensure that it contained no structural disorder. Table 1 gives information concerning the intensity data collection.

The reduction of step-scanning data was carried out by the program *STEPSCAN* described elsewhere (Rigault, 1979), which includes background subtraction and correction of Lorentz–polarization factors. The error which can arise from dynamic behaviour of the graphite monochromator is negligible because of the very small Bragg-angle reflection (Kerr & Ashmore, 1974). The variance of the observations was taken as

$$\sigma^2(F_o^2) = \sigma^2(F_o^2)' + (0.01 F_o^2)^2.$$

The second term was determined by statistics on three periodically measured reflections. It takes into account the agreement between symmetrical reflections, as appears later.

The influence of absorption [$\mu(\text{Ag } K\bar{\alpha}) = 218 \text{ cm}^{-1}$] has been carefully studied with the measurement of 101 reflections by rotation around the scattering vector (ψ scans). These observations were the basis of a

least-squares fit of the sample dimensions according to the procedure used in the program *FACIES* (Rigoult, Tomas & Guidi-Morosini, 1979). The residual factor $R^*(F^2)$ at the end of this treatment was 2%.

The absorption effect was corrected, using the previously adjusted dimensions, by numerical integration over an 864-point Gaussian grid (Coppens, Leiserowitz & Rabinovich, 1965). The transmission factor was found to be between 0.14 and 0.55.

At this stage, some strong reflections showed large disagreement which may have arisen from different extinction effects on the equivalent reflections. Thus, the first refinements were carried out with the whole set (1441 reflections) to ensure an unbiased extinction correction which was performed with the refinement program *LINEX* according to the model described by Becker & Coppens (1975). The best fit was found for a type I crystal with a Lorentzian mosaic described by an isotropic parameter $g = 0.423 \times 10^{-4}$. The strongest extinction corrections are respectively 0.52 and 0.59 for reflections $\bar{1}01$ and 002 .

The four asymmetric units measured in reciprocal space were then averaged by the program *BABAR* (Rigoult & Guidi-Morosini, 1980), leading to an agreement factor $R(F^2) = 2.6\%$. The statistical variances are close to the theoretical ones showing that the data are not affected by systematic errors. No TDS correction was applied.

The 389 independent reflections were the basis of full-matrix least-squares refinements based on F_o^2 with $\sigma^{-2}(F_o^2)$ as weights (Becker & Coppens, 1975).

The scattering factors including anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974).

The refinement was started based on V(1) and Se atoms corresponding to the ideal CdI₂ structure type. The V(1) atom is located in the special position (000), and two Se atoms are at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, -z)$; only the z parameter must be determined.

A least-squares refinement of the z coordinate of the Se atoms and of isotropic temperature factors led to an $R(F)$ of 4%.

Table 2. Refinement of 1T-VSe₂

Fractional coordinates and U_{ij} ($\times 10^4 \text{ \AA}^2$) ($U_{11} = U_{22} = 2U_{12}$)						
	x	y	z	U_{11}	U_{33}	Occupancy
V(1)	0	0	0	150 (1)	115 (2)	1.0
V(2)	0	0	$\frac{1}{2}$	150	115	0.005 (1)
Se	$\frac{1}{3}$	$\frac{2}{3}$	0.25665 (4)	86 (1)	102 (1)	1.0

Agreement factors*

$R(F) = 0.022$; $R_w(F) = 0.018$; $R(F^2) = 0.038$; $R_w(F^2) = 0.035$;
 $\delta = 2.68$

* $R(F) = \sum |F_o - F_c| / \sum |F_o|$; $R_w(F) = [\sum W(F_o - F_c)^2 / \sum WF_o^2]^{1/2}$; $R(F^2) = \sum |F_o^2 - F_c^2| / \sum |F_o^2|$; $R_w(F^2) = [\sum W(F_o^2 - F_c^2)^2 / \sum WF_o^4]^{1/2}$; $\delta = [\sum W(F_o^2 - F_c^2)^2 / (N_o - N_c)]^{1/2}$.

Table 3. Interatomic distances (\AA) and bond angles ($^\circ$) in octahedral coordination around vanadium atoms

Octahedron V(1 ^b)		Octahedron V(1 ^a)	
V(1 ^b)-Se(1)	2.4917 (2)	V(1 ^a)-Se(1)	2.4414 (2)
Se(1)-Se(1 ^b)	3.6839 (4)	Se(1)-Se(1 ⁱⁱⁱ)	3.5468 (4)
Se(1)-Se(1 ⁱ)	3.3560 (4)	Se(1)-Se(1 ^{iv})	3.3560 (4)
Se(1 ^b)-V(1 ^b)-Se(1 ⁱ)	95.334 (6)	Se(1)-V(1 ^a)-Se(1 ⁱⁱⁱ)	93.167 (6)
Se(1 ^b)-V(1 ^b)-Se(1 ⁱⁱⁱ)	84.666 (8)	Se(1)-V(1 ^a)-Se(1 ⁱ)	86.833 (8)

Symmetry code

(-)	$\frac{1}{3}, \frac{2}{3}, z$	(vi)	$-\frac{1}{3}, -\frac{2}{3}, 1-z$
(i)	$\frac{2}{3}, -\frac{1}{3}, z$	(vii)	$\frac{2}{3}, \frac{1}{3}, 1-z$
(ii)	$-\frac{2}{3}, -\frac{1}{3}, z$	(viii)	$-\frac{1}{3}, \frac{1}{3}, 1-z$
(iii)	$-\frac{1}{3}, \frac{2}{3}, z$	(ix)	0,0,0
(iv)	$\frac{2}{3}, \frac{1}{3}, z$	(x)	0,0, $\frac{1}{2}$
(v)	$-\frac{1}{3}, -\frac{2}{3}, z$		

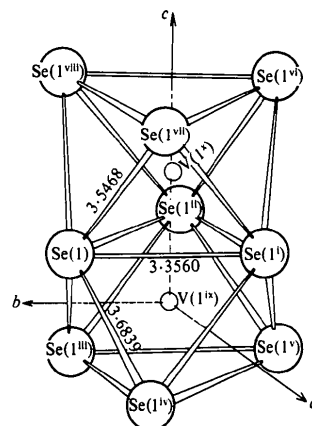


Fig. 1. Octahedral coordination in VSe₂. Symmetry code as in Table 3.

A three-dimensional difference Fourier synthesis with the parameters resulting from the refinement yielded the position $(00\frac{1}{2})$ for the V(2) atom. In order to adjust x [occupation factor of V(2) atoms], V(2) was constrained to have the same thermal parameters as V(1). This is a reasonable approximation because their sites are very similar. A least-squares refinement of positional and anisotropic thermal parameters and occupation factors reduced the R value to 0.022. During the refinement, the occupation factor of the V(1) atom remained equal to 1. The final positional and thermal parameters and occupation factors are given in Table 2, interatomic distances and angles in Table 3.*

Discussion. The crystal structure of VSe₂ is very close to the CdI₂ type. The CdI₂-type structure consists of selenium layers, stacked upon each other and perpendicular to the c axis. They define octahedral sites

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36637 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Comparison between the heights of layers *s* and *w*

s vanadium-full layer; *w* vanadium-deficient layer.

	<i>s</i>	<i>w</i>	<i>s</i> + <i>w</i>
Wolley & Wexler (a.u.) (1977)	5.803	5.736	11.539
Our study	(a.u.) 5.920 (2)	5.614 (2)	11.534 (4)
	(Å) 3.133 (1)	2.971 (1)	6.104 (2)

alternately empty or occupied, by vanadium atoms V(1) leading to the stacking sequence ... Se—V(1)—Se—□—Se—V(1)—Se— ... The specificity of the VSe₂ structure compared with the CdI₂ type comes from the existence of an additional octahedral site occupied by a small amount *x* of vanadium atoms V(2) between the Se—V(1)—Se sheets. The real stacking sequence, according to the formula V_{1+x}Se₂, is thus ... —Se—V(1)—Se—V(2)—Se—V(1) ... (Fig. 1). Table 3 shows that the octahedral sites are slightly trigonally distorted along the *c* axis. Contrary to Ti_{1.026}S₂ (Riekell & Schöllhorn, 1975) there is a contraction of the selenium planes toward the vanadium planes. The layer heights are largely different from those given by Wolley & Wexler (1977) for their band-structure calculations of 1T-VSe₂ (see Table 4). Their parameters *s* and *w* (the heights of full and deficient vanadium layers) are respectively too small and too large by 20%.

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Structure of α-BiAsO₄ (Rooseveltite)

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Abstract. α-BiAsO₄, monoclinic, *P*2₁/*n* (No. 14), *a* = 6.879 (1), *b* = 7.159 (1), *c* = 6.732 (1) Å, β = 104.84 (1)°, *V* = 320.4 (1) Å³, *Z* = 4, *D*_c = 7.21 Mg m⁻³. The structure has been refined to *R* = 0.027 for 772 observed reflections. α-BiAsO₄ crystallizes in the monazite (CePO₄) type structure. Bi exhibits an irregular one-sided coordination by eight O atoms: Bi—O = 2.332 (6)–2.646 (6) Å. The AsO₄ tetrahedron [As—O = 1.667 (6)–1.702 (6) Å] is, with O—As—O angles of 97.3 (3)–117.8 (3)°, considerably distorted.

Introduction. BiAsO₄ crystallizes in two different forms. The tetragonal β form adopts the scheelite structure (Mooney, 1948) while the monoclinic α form crystallizes with the monazite structure type (Frondele, 1951). In the course of studies on some secondary Bi minerals (Bedlivy & Mereiter, 1981), a structure analysis of α-BiAsO₄ was of interest, because it is known also as the mineral rooseveltite (Herzenberg, 1946; Bedlivy, Llambias & Astarloa, 1972). Since natural material was heretofore found only in microcrystalline form, synthetic crystals had to be used.