

Crystal Structures of Tungsten Disulfide and Diselenide*

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The crystal structures of the 2*H*- and 3*R*-forms of WS₂ and of WSe₂ have been refined from single-crystal data. The results are summarized and the interatomic distances are compared with those in related compounds. © 1987 Academic Press, Inc.

Introduction

It has been known for many years that tungsten disulfide, WS₂ (1), and diselenide, WSe₂ (2), have layer structures isotypic with hexagonal MoS₂ (3, 4). In addition to the common hexagonal 2*H*-form of WS₂ a rhombohedral form, 3*R*-WS₂, has also been reported (5), which is isotypic with the rhombohedral form of MoS₂ (6, 7). However, apart from a rough determination of the atomic positions in 2*H*-WS₂ and WSe₂ from powder X-ray diffraction data (8), no refinement of the structures of the tungsten compounds has been reported so far. We have undertaken such a study in connection with calculations of the electronic band structures of these compounds (9), for which the atomic positions had to be accurately known.

Experimental

Single crystals of the tungsten dichalcogenides had been prepared by J. C. Wil-

dervanck (10) by means of chemical transport using chlorine (2*H*-WS₂) or bromine (3*R*-WS₂, WSe₂) as transport agent. Very thin plate-like crystals were investigated by X-ray diffraction using a Nonius CAD4 diffractometer; monochromatized MoK α radiation ($\lambda = 0.71071 \text{ \AA}$) was employed. Unit cell parameters (Table I) were determined by least-squares fits of the optimized setting angles of about 20 reflections in the θ ranges 20–24° (2*H*-WS₂), 30–35° (WSe₂), and 27–31°, respectively; the parameters agree with those given by previous authors (5, 11).

Intensity data were collected in hemispheres up to θ values of 50° (2*H*-WS₂), 45° (3*R*-WS₂), and 35° (WSe₂), respectively. A modified version (12) of the CAD4 program was used to measure each reflection of the thin plate-shaped crystals in its position of minimal absorption; no absorption corrections were applied. The intensities of equivalent reflections were averaged and corrected for Lorentz and polarization effects; reflections with $I < 2.5 \sigma(I)$ were discarded. The structure factors of the remaining reflections (see Table I) were used

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TABLE I
CRYSTALLOGRAPHIC DATA OF WS₂ AND WSe₂
(STANDARD DEVIATIONS ARE
GIVEN IN PARENTHESES)

	2H-WS ₂	WSe ₂	3R-WS ₂
Space group	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>	<i>R3m</i>
<i>a</i> (Å)	3.1532(4)	3.282(1)	3.158(1)
<i>c</i> (Å)	12.323(5)	12.96(1)	18.49(1)
<i>c/a</i>	3.908	3.949	5.855
<i>V</i> (Å ³)	106.1	120.9	159.6
<i>Z</i>	2	2	3
Independent reflections	245	119	205
<i>z</i> (S, Se)	0.6225(6)	0.6211(4)	^a
<i>R_F</i> (%)	6.4	6.9	4.5

^a *z*(W) = 0.0000(5); *z*(S I) = 0.2497(6); *z*(S II) = 0.4190(7).

in the refinements by a full-matrix least-squares procedure. The atomic scattering factors were those of the XTAL system (13); anomalous dispersion factors were taken from the "International Tables for X-Ray Crystallography" (14). The final values of *R_F* are included in Table I.

Results and Discussion

It was confirmed that 2H-WS₂ and WSe₂ are isotypic with 2H-MoS₂ (3, 4), with space group *P6₃/mmc*. The tungsten atoms lie in 2(*c*): ± (1/3, 2/3, 1/4), and the chalcogen atoms in 4(*f*): ± (1/3, 2/3, *z*; 1/3, 2/3, 1/2-*z*). The final values of *z* are included in Table I and interatomic distances in Table II. The chalcogen parameter derived by Kalikham (8) for WSe₂ (*z* ≈ 0.620 in our setting) agrees with our results, but his value for 2H-WS₂ (*z* ≈ 0.614) is rather far off the mark. This is understandable because of the relatively small scattering factor of sulfur relative to tungsten.

Just as 3R-MoS₂ (6), the 3R-form of WS₂ crystallizes in space group *R3m* with tungsten and two independent sets of sulfur atoms all in positions 3(*a*): (00*z*; 2/3, 1/3, 1/3 + *z*; 1/3, 2/3, 2/3 + *z*). The final parameters

TABLE II
INTERATOMIC DISTANCES (Å) IN WX₂ (X = S, Se)
AND THEIR STANDARD DEVIATIONS
(IN PARENTHESES)

	2H-WS ₂	WSe ₂	3R-WS ₂
Within WX ₂ layers			
W-3X	2.405(5)	2.526(4)	2.39(1)
W-3X	2.405(5)	2.526(4)	2.42(1)
X-1X	3.14(2)	3.34(1)	3.13(2)
X-6X = W-6W	3.153	3.282	3.158
Between WX ₂ layers			
X-3X	3.53(1)	3.67(1)	3.54(1)

(and their standard deviations) are *z*(W) = 0.0000(5); *z*(S I) = 0.2497(6); *z*(S II) = 0.4190(7); interatomic distances are listed in Table II.

From Table II it is seen that the trigonal prisms formed by the chalcogen atoms around a tungsten atom are fairly regular, the prism edges parallel to *c*, X-1X (X = S, Se), being of about the same length or slightly longer than the edges X-6X perpendicular to *c*. The same is true of MoX₂ (4, 7), i.t. MoTe₂ (15, 16), and also ZrCl₂ (17); in all these phases the metal has a *d*²-configuration. In contrast, in NbS₂ (18), NbSe₂ (19, 20), and TaSe₂ (21), where the metal has *d*¹-configuration, the prism edges parallel to *c* are shorter than those perpendicular to *c*. It may be remarked that trigonal-prismatic coordination is expected to be stable only for metals with a *d*⁰, *d*¹, or *nd*² (*n* > 3) configuration (22). In the semi-conducting molybdenum and tungsten dichalcogenides the distances X-3X between the layers are considerably longer than the X-X distances within the layers; this difference is smaller in the metallic niobium and tantalum dichalcogenides.

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