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Crystal Structures of Tungsten Disulfide and Diselenide*

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The crystal structures of the 2*H*- and 3*R*-forms of WS_2 and of WSe_2 have been refined from single-crystal data. The results are summarized and the interatomic distances are compared with those in related compounds.

Introduction

It has been known for many years that tungsten disulfide, WS_2 (*1*), and diselenide, WSe_2 (*2*), have layer structures isotypic with hexagonal MoS_2 (*3, 4*). In addition to the common hexagonal 2*H*-form of WS_2 a rhombohedral form, 3*R*-WS_2, has also been reported (*5*), which is isotypic with the rhombohedral form of MoS_2 (*6, 7*). However, apart from a rough determination of the atomic positions in 2*H*-WS_2 and WSe_2 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. Wildervanck (*10*) by means of chemical transport using chlorine (2*H*-WS_2) or bromine (3*R*-WS_2, WSe_2) as transport agent. Very thin plate-like crystals were investigated by X-ray diffraction using a Nonius CAD4 diffractometer; monochromatized Mo$K\alpha$ radiation (λ = 0.71071 Å) 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*-WS_2), 30–35° (WSe_2), 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*-WS_2), 45° (3*R*-WS_2), and 35° (WSe_2), 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 WS_2 AND WSe_2 (STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

	2*H*-WS_2	WSe_2	3*R*-WS_2
Space group	$P6_3/mmc$	$P6_3/mmc$	$R3m$
a (Å)	3.1532(4)	3.282(1)	3.158(1)
c (Å)	12.323(5)	12.96(1)	18.49(1)
c/*a*	3.908	3.949	5.855
V (Å^3)	106.1	120.9	159.6
Z	2	2	3
Independent reflections	245	119	205
z (S, Se)	0.6225(6)	0.6211(4)	[a]
R_F (%)	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 2*H*-WS_2 and WSe_2 are isotypic with 2*H*-MoS_2 (*3*, *4*), with space group $P6_3/mmc$. 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 WSe_2 ($z \approx 0.620$ in our setting) agrees with our results, but his value for 2*H*-WS_2 ($z \approx 0.614$) is rather far off the mark. This is understandable because of the relatively small scattering factor of sulfur relative to tungsten.

Just as 3*R*-MoS_2 (*6*), the 3*R*-form of WS_2 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 WX_2 (*X* = S, Se) AND THEIR STANDARD DEVIATIONS (IN PARENTHESES)

	2*H*-WS_2	WSe_2	3*R*-WS_2
Within WX_2 layers			
W–3*X*	2.405(5)	2.526(4)	2.39(1)
W–3*X*	2.405(5)	2.526(4)	2.42(1)
X–1*X*	3.14(2)	3.34(1)	3.13(2)
X–6*X* = W–6W	3.153	3.282	3.158
Between WX_2 layers			
X–3*X*	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*–1*X* (*X* = S, Se), being of about the same length or slightly longer than the edges *X*–6*X* perpendicular to *c*. The same is true of MoX_2 (*4*, *7*), l.t. $MoTe_2$ (*15*, *16*), and also $ZrCl_2$ (*17*); in all these phases the metal has a d^2-configuration. In contrast, in NbS_2 (*18*), $NbSe_2$ (*19*, *20*), and $TaSe_2$ (*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 semiconducting molybdenum and tungsten dichalcogenides the distances *X*–3*X* 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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