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Layer Structure Polytypism Among Niobium and Tantalum Selenides

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Single crystals of several varieties of tantalum and niobium selenide layer structures have been grown by vapor transport methods. Two two-layer forms have the NbS₂ structure, a three-layer form is like rhombohedral MoS₂, and two four-layer forms are new structures with a selenium stacking sequence of *AABBAACC* . . . , and *AABABBAB* . . . , respectively. These have been refined by least-squares methods. Refinement adjusts the *c* coordinates of the selenium atoms 0.1 Å away from positions in which each atom sheet is spaced at equal intervals along *z*. This adjustment moves the selenium atoms away from the interleaving metal atoms.

The trigonal prism coordination units in the niobium and tantalum compounds tend to be slightly shorter in the *z* direction and longer in the *x* direction than similar molybdenum coordination units.

Introduction

The disulfides of molybdenum, tungsten and niobium (Jellinek, 1963) and the diselenides of molybdenum (James & Lavik, 1963) and tungsten (Glemser, Sauer & König, 1948) are layer structures in which each cation* has as nearest neighbors six anions arranged

at the apices of a trigonal prism. Disulfides of tantalum have been reported in which cations have trigonal prismatic and/or octahedral anion coordination (Jellinek, 1963). All of these structures can be considered as two-dimensionally infinite 'layer molecules' within which the bonding is quite strong. These 'layer molecules' are stacked in a close-packed manner and the bonding between them is weak.

The common notation used in the description of close packed structures, *i.e.* a hexagonal close

* It is recognized that there is probably a high degree of covalency in these compounds; nevertheless, the terms cation and anion will be used to designate the two species involved.

packing as $ABABAB \dots$, a cubic close packing as $ABCABCABC \dots$, etc., is applicable to the description of trigonal prism layer structures. A trigonal prism coordination layer of two directly superposed anion sheets is designated by a double letter such as AA , BB , or CC . These double anion layers are articulated to other double layers by the normal geometry of close packing. We can develop sequences such as the two-layer sequence $AABBAABB \dots$, or the three-layer sequence $AABBCCAABBCC \dots$, or the four layer sequence $AABBAACCAABBAACC \dots$, and so on.

A similar notation using lower case letters is used to designate cation locations in a given sequence. Three cation sites, a , b , and c , can be distinguished in a trigonal prism layer sequence whose x and y coordinates in the layer plane are identical with the x and y coordinates of A , B , and C anion sites. In a single trigonal prism layer of two anion sheets two of these three cation sites exist but both sites may not simultaneously be occupied. In an AA layer, the anions fill the a site and positions b and c may be occupied. Similarly, in a BB layer, positions a and c may be occupied and in a CC layer positions a or b may be occupied. The multiplicity of stacking types is greater in trigonal prism layer structures than in the octahedral types because of the existence of two possible cation sites in each layer. For example, in layer structures with octahedral packing of anions such as CdI_2 only one octahedral cation site is available in each layer.

Trial structures for these compounds were obtained by constructing the possible combinations of layers and eliminating duplicates. Thus all possible combinations of trigonal prismatic two-layer packings give, with their symmetries:

- (1) $AbA BaB$, $P6_3/mmc$
- (2) $AcA BcB$, $P6_3/mmc$
- (3) $AbA BcB$, $P\bar{6}m2$
- (4) $AcA BaB$, $P\bar{6}m2$.

Types 3 and 4 are equivalent, as can be shown by shifting the origin in 3 or 4, and so three different two-layer types are possible. Types 1 and 2 were recognized by Jellinek, Brauer & Muller (1960) and applied to known compounds. Type 1 is the $C7$ (MoS_2) structure and type 2 the NbS_2 structure. There are no known representatives of type 3. By a similar process one finds two different three-layer types:

- (1) $AbA BcB CaC$, $R3m$
- (2) $AbA BcB CcC$, $P3m1$.

Type 1 has been recognized in the literature as rhombohedral MoS_2 (Semiletov, 1960; Bell & Herfert, 1957; Traill, 1963) and NbS_2 (Jellinek *et al.*, 1960). There are no known representatives of the three-layer type 2.

Seven different types can be derived from the four-layer $AABBAACC$ assemblage and three more

from the $AABBAABB$ arrangement which becomes four-layer by virtue of the cation arrangement. They are, with their space groups:

- (1) $AbA BaB AbA CaC$, $P\bar{6}m2$
- (2) $AbA BaB AbA CbC$, $P\bar{6}m2$
- (3) $AbA BcB AbA CaC$, $P\bar{6}m2$
- (4) $AbA BcB AbA CbC$, $P\bar{6}m2$
- (5) $AcA BcB AcA BaB$, $P\bar{6}m2$
- (6) $AbA BaB AbA BcB$, $P\bar{6}m2$
- (7) $AbA BaB AcA CaC$, $P3m1$
- (8) $AbA BcB AcA CaC$, $P3m1$
- (9) $AbA BcB AcA CbC$, $P3m1$
- (10) $AbA BaB AcA BcB$, $P3m1$

None of these types have been reported to date in the literature but an $NbSe_2$ polytype made in the course of this work exists as type 4 above.

Derivation of polytypes by actual construction is satisfactory if the number of layers is low as in the foregoing. It becomes tedious and error-prone as the number of possibilities rises. A paper is being prepared which will describe a systematic approach to delineation of geometrically distinguishable arrangements of any one type of layer packing.

Some new two-, three-, and four-layer selenides of tantalum and niobium

Single crystals of excellent quality have been prepared in this laboratory by vapor transport methods (Nitsche, Bolsterli & Lichtensteiger, 1961) among the tantalum and niobium selenide layer structures. The crystal habit of the two-layer forms differs noticeably from the polytypes having more than two layers in all of the samples we have so far encountered. The two-layer forms tend to be thin hexagonal plates with prominent (0001) faces. The three- and four-layer forms all have more strongly developed prism, pyramidal, or rhombohedral faces, so that they form thicker plates than the two-layer varieties.

The two- and four-layer $NbSe_2$ samples have compositions close to the ideal, but the crystallization temperature of the two-layer form was significantly lower (*ca.* 750 °C) than that of the four-layer (*ca.* 950 °C). The three-layer form crystallized with a composition richer in niobium (or poorer in selenium) than the ideal $NbSe_2$. A complete report on the growth

Table 1. Cell dimensions of some two-, three-, and four-layer $TaSe_2$ and $NbSe_2$ polytypes

H = hexagonal, R = rhombohedral			
Polytype	Space group	a (Å)	c (Å)
2H $NbSe_2$	$P6_3/mmc$	3.45 ± 0.01	12.54 ± 0.04
2H $TaSe_2$	$P6_3/mmc$	3.43 ± 0.01	12.71 ± 0.04
3R $NbSe_2^*$	$R3m$	3.45 ± 0.01	18.88 ± 0.04
4H $NbSe_2$	$P\bar{6}m2$	3.44 ± 0.01	25.24 ± 0.04
4H $TaSe_2$	$P6_3/mmc$	3.46 ± 0.01	25.18 ± 0.04

* Hexagonal axes.

conditions of these forms is to be published separately (Revolinsky, to be published).

precession photographs; Weissenberg photographs from four-layer NbSe₂ were made as well. Mo K α radiation was used in all cases. The cell dimensions

The X-ray data were derived principally from

Table 2. Comparison of observed and calculated intensities

2H NbSe ₂			4L NbSe ₂			3R NbSe ₂												
hk	F _o	F _c	hk	F _o	F _c	hk	F _o	F _c	A	B	hk	F _o	F _c	A	B			
30.0	55	51	30.0	42	29	20.0	151	118	10.0	29	59	56	-19	10.1	170	125	-121	-34
11.0	73	72	20.1	35	24	20.3	109	92	10.1	42	39	-25	15	10.4	198	163	-1	163
22.0	48	45	20.2	50	-50	20.4	182	207	10.2	125	125	5	125	10.7	186	168	11	168
00.2	23	-31	20.3	37	27	20.5	109	99	10.3	47	29	25	-15	10.10	158	85	-85	-10
00.4	27	-21	20.4	56	66	20.6	260	273	10.4	61	88	83	32	10.13	115	71	-71	-1
00.6	47	-45	20.5	24	-18	20.11	94	-76	10.5	117	101	87	-53	10.16	256	120	11	120
00.8	75	64	20.6	42	-40	20.12	182	167	10.6	148	136	-111	-80	10.19	160	83	-4	83
00.14	48	38	20.7	25	-28	20.13	120	-93	10.7	166	141	127	-60	10.22	166	60	-58	-16
00.16	35	30	20.8	31	26	20.16	156	107	10.8	126	122	101	68	10.5	189	204	23	203
11.2	28	-21	20.9	13	11	30.0	270	299	10.9	146	117	97	-66	10.8	82	111	-22	109
11.4	21	-17	20.10	55	-44	30.4	145	154	10.10	109	87	-78	-38	10.11	86	102	-95	-38
11.6	39	-37	30.0	68	70	30.12	182	184	10.11	73	28	51	-28	10.17	89	132	16	131
11.8	56	53	30.2	41	-36	30.16	224	262	10.12	46	87	66	14	20.2	84	67	-64	-17
11.14	39	-34	30.6	46	-43				10.14	150	121	19	120	20.5	202	156	17	-155
11.16	23	28		48	60				10.18	44	56	-19	54	20.8	100	89	-17	-87
22.6	23	-24							10.19	45	49	45	-22	20.11	116	84	-78	31
22.8	33	37							10.20	55	66	59	31	20.14	80	51	-34	-37
01.1	34	32							10.21	90	84	66	-52	20.17	256	115	13	-114
01.2	33	-36							10.22	107	100	-79	-64	20.1	117	92	-89	26
01.3	38	37							10.23	86	92	88	-31	20.4	137	123	-1	-123
01.4	49	54							10.24	49	74	64	39	20.7	128	132	8	-132
01.5	24	-20							10.25	62	55	42	-36	20.10	63	69	69	8
01.6	21	-19							10.30	80	79	13	80	20.13	84	59	-59	1
01.7	33	-35												20.16	86	104	9	-104
01.8	7	5							20.2	102	24	3	-95	20.19	57	72	-4	-72
01.9	8	9							20.3	39	23	19	12					
01.10	33	-31							20.4	68	68	64	-25					
01.11	31	30							20.5	83	76	66	41					
01.12	32	30							20.6	108	104	-85	62					
12.1	26	21							20.7	114	109	98	50					
12.2	26	-22							20.8	85	95	79	-54					
12.3	31	25							20.9	109	93	77	53					
12.4	39	32							20.10	61	69	-63	31					
12.5	12	-14							20.11	44	46	41	23					
12.6	12	-12							20.14	113	100	15	-101					
12.7	27	-26							20.21	73	72	58	46					
12.10	18	-23							20.22	91	87	-69	56					
12.11	18	24							20.23	66	80	77	28					
12.12	18	24							20.24	39	65	56	-35					
									20.25	57	49	37	34					
									30.0	214	204	204	--					
									30.4	61	65	65	--					
									30.8	63	42	-42	--					
									30.12	115	106	106	--					
									30.16	199	166	166	--					
									30.28	95	107	107	--					
									30.32	96	99	99	--					

2H TaSe ₂			4H TaSe ₂		
hk	F _o	F _c	hk	F _o	F _c
10.0	45	35	10.0	130	139
10.1	39	-32	10.1	62	50
10.2	58	-63	10.3	135	-120
10.3	35	-35	10.4	260	254
10.4	64	82	10.5	161	-126
10.5	28	22	10.7	99	62
10.6	35	-47	10.8	310	330
10.7	34	32	10.11	130	92
10.8	33	29	10.12	203	193
			10.13	135	110

2H TaSe ₂			4H TaSe ₂		
hk	F _o	F _c	hk	F _o	F _c
10.0	45	35	10.0	130	139
10.1	39	-32	10.1	62	50
10.2	58	-63	10.3	135	-120
10.3	35	-35	10.4	260	254
10.4	64	82	10.5	161	-126
10.5	28	22	10.7	99	62
10.6	35	-47	10.8	310	330
10.7	34	32	10.11	130	92
10.8	33	29	10.12	203	193
			10.13	135	110

2H MoSe₂ 2H NbSe₂ 3R NbSe₂ 4L NbSe₂ 4H TaSe₂

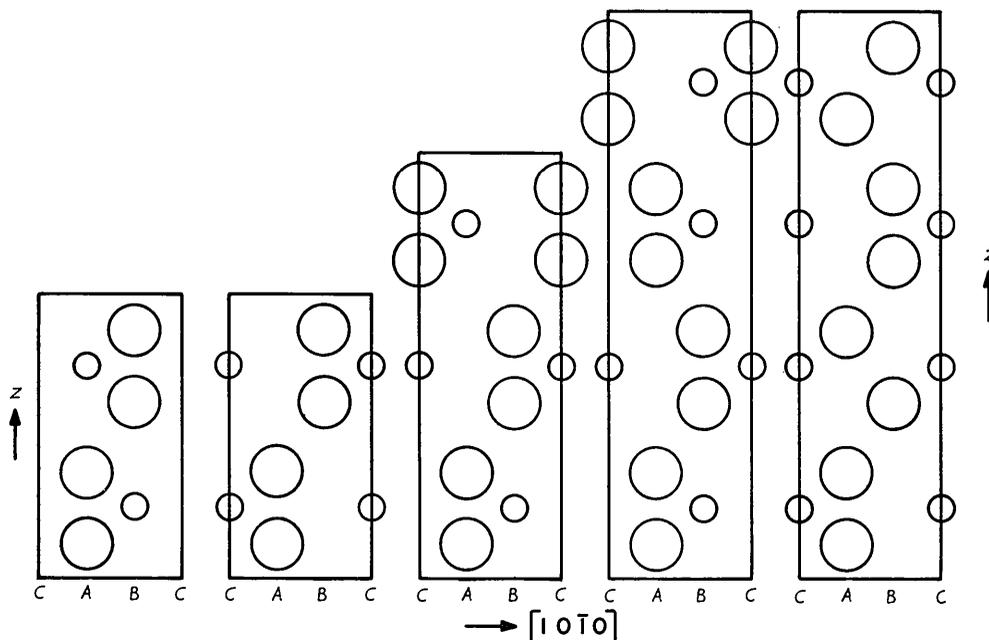


Fig. 1. Sections through the origin parallel to (1120). Anions are represented by the larger circles and cations by the smaller.

derived from precession photographs corrected for film shrinkage are listed in Table 1. The intensities were read from precession and Weissenberg films by visual means using a standard intensity scale for comparison. Lorentz and polarization corrections were done graphically for the precession photographs and analytically for the Weissenberg photographs with an IBM 704 computer. Absorption corrections were applied to the TaSe₂ intensities by the use of an effect noted by Takeuchi (1957). He has shown how precession photographs of plate-like crystals can be divided into areas containing surface reflection fields and transmission reflection fields. The $h0\bar{h}l$ reflections from precession photographs for two- and four-layer TaSe₂ were split into transmission and reflection groups and a separate scale factor was assigned to each. The introduction of this device improved the reliability index from 27% to 14% for the two-layer type and from 20% to 14% for the four-layer type. Absorption

is low enough in NbSe₂ compounds so that adequate agreement was obtained without absorption corrections.

The refinements were done with the least-squares program of Busing & Levy (1959), using scattering factors from Thomas & Umeda (1957). F_o and F_c values are listed in Table 2, refined parameters are listed in Table 3, and bond distances in Table 4. A section through the origin parallel to (11 $\bar{2}$ 0) (Fig. 1) illustrates the similarities and differences in the four structures. The reliability index for the three-layer NbSe₂ polymorph is not as satisfactory as for the two- and four-layer samples so the results reported here must be considered tentative.

Two-layer polytypes

Comparisons of calculated and observed intensities showed that NbSe₂ ($R=11.5\%$) and TaSe₂ ($R=14.3\%$) have the NbS₂ structure (Jelinek, 1960) with the stacking sequence $AcA BcB \dots$ and the space group $P6_3/mmc$. The cation environment in the NbS₂ structure differs from MoS₂ by virtue of the relation of a given cation to next nearest neighbors rather than near neighbors, and therefore differences in the two structures involve relatively large distances. This is illustrated by calculating some bond distance for structures of both types, choosing the cell dimensions of MoS₂ ($a=3.15$, $c=12.30$ Å) and letting the z parameter = $\frac{1}{2}$. Then the cation-nearest neighbor anion distance is 2.4 Å, and a cation-next neighbor anion distance is, for the MoS₂ structure, 4.6 Å, and for the NbS₂ structure, 5.0 Å. In addition, the cations in a given layer of the MoS₂ structure are not completely screened from the next nearest neighbor anions by nearest neighbor anions while such screening in the NbS₂ structure is complete. The other possible two-layer structure, the $P\bar{6}m2 AbA BcB$ type (no known examples), has two types of cation sites. The 'b' cations are in an environment similar to Mo in MoS₂ and the 'c' cations are in an environment similar to Nb in NbS₂. Mixing of cations may tend to stabilize such a structure.

Table 3. Refined parameters of the two-, three-, and four-layer polytypes of NbSe₂ and TaSe₂

Polytype	Atom	Space group set	x	y	z
2H NbSe ₂	Nb	(b)	0	0	$\frac{1}{2}$
	Se	(f)	$\frac{1}{2}$	$\frac{2}{3}$	0.116 ± 0.001
2H TaSe ₂	Ta	(l)	0	0	$\frac{1}{2}$
	Se	(f)	$\frac{1}{2}$	$\frac{2}{3}$	0.118 ± 0.001
3R NbSe ₂	Nb ₁	(a)	$\frac{1}{3}$	$\frac{2}{3}$	0
	Se ₁	(a)	$\frac{2}{3}$	$\frac{1}{3}$	0.088 ± 0.003
	Se ₂	(a)	$\frac{1}{3}$	$\frac{2}{3}$	0.243 ± 0.003
4H NbSe ₂	Nb ₁	(a)	0	0	0
	Nb ₂	(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$
	Nb ₃	(g)	0	0	0.250 ± 0.001
	Se ₁	(h)	$\frac{1}{3}$	$\frac{2}{3}$	0.066 ± 0.002
	Se ₂	(i)	$\frac{2}{3}$	$\frac{1}{3}$	0.185 ± 0.004
	Se ₃	(i)	$\frac{2}{3}$	$\frac{1}{3}$	0.318 ± 0.004
	Se ₄	(g)	0	0	0.432 ± 0.002
4H TaSe ₂	Ta ₁ *	(a)	0	0	0
	Ta ₂ †	(b)	0	0	$\frac{1}{2}$
	Se ₁	(f)	$\frac{1}{2}$	$\frac{2}{3}$	0.065 ± 0.001
	Se ₂	(f)	$\frac{2}{3}$	$\frac{1}{2}$	0.184 ± 0.001

* Octahedral cation. † Trigonal prism cation.

Table 4. Interatomic distances for the two-, three-, and four-layer polytypes

Polytype	Between layers	Se-Se	In layer perpendicular to z	M-Se
		In layer parallel to z		Trigonal prism
2H NbSe ₂	$3.52_5 \pm 0.02$	3.36 ± 0.02	3.45^*	2.60 ± 0.01
2H TaSe ₂	3.59 ± 0.02	3.35 ± 0.02	3.43^*	2.59 ± 0.01
3R NbSe ₂	3.54 ± 0.08	3.32 ± 0.08	3.45^*	$2.59_5 \pm 0.06$
4H NbSe ₂	3.60 ± 0.13	3.34 ± 0.15	3.44^*	2.59 ± 0.08
	3.50 ± 0.11	3.36 ± 0.14		2.62 ± 0.08
		3.44 ± 0.10		2.58 ± 0.08
				2.62 ± 0.08
	Av. 3.55 ± 0.08	Av. 3.38 ± 0.08		Av. 2.60 ± 0.04
4H TaSe ₂	3.60 ± 0.03	3.32 ± 0.05	3.45^*	2.60 ± 0.02
		$3.84 \pm 0.05^\dagger$		$2.58 \pm 0.02^\dagger$

* Distances by direct measurement.

† Octahedral coordination.

As is evident from this and other work the *AbA BaB* structure is the form encountered in the disulfides and diselenides of the group 6B elements molybdenum and tungsten, while the *AcA BcB* is the two-layer form encountered most frequently among the disulfides and diselenides of the group 5B elements, niobium and tantalum.

A three-layer polytype

The systematic absences on the precession photographs of the three-layer NbSe₂ can be interpreted satisfactorily on the basis of a rhombohedral space lattice. There is one possible three-layer rhombohedral trigonal prism structure, the rhombohedral MoS₂ structure (Semiletov, 1961; Bell & Herfert, 1957). Refinement with this model fails to give a better agreement to date than 28% on 25 $h\bar{0}hl$ reflections. However, in the refinement process the atomic shifts were similar in direction and amount to atomic shifts in the two- and four-layer structures in which agreement is good. This variety has an apparent niobium excess, allowing a formula as high in niobium as Nb_{1.16}Se₂ to be calculated from our sample analyses. It is probable, as suggested by Jelinek *et al.* (1960), for NbS₂, that the extra niobium is accommodated in interlayer sites. Neither a Fourier nor a difference Fourier map showed any excess of scattering matter in the inter-layer sites, but the amount of niobium to be detected was of the order of the experimental error in the maps. More accurate data will be required to define this point. It is likely that the model is essentially correct and the main reason for poor agreement arises from the difficulty of getting good intensity measurements from these crystals which were invariably twinned. In space group *R3m* it is likely that the threefold axis is the twin axis or the (0001) plane is the twin plane. Either type explains the observed distribution of reflections. On point rows from an $h\bar{0}hl$ (hexagonal indexing) precession photograph where $h \neq 3n$ the absolute value of the l index increases in the sequence 1, 2, 4, 5, 7, 8 *etc.* with $l=3n$ absent. Were there no twinning, the sequence would be 1, 4, 7, *etc.* on one side of the photograph and 3, 5, 8, *etc.* on the other, following the requirement $-h+k+l=3n$, but twinning mixes the two sets on both sides of the film. Observation of the triangular growth steps on the (0001) faces of a few crystals shows that twinning about the threefold axis is present. Twinning across the (0001) plane may or may not be present. Both types can be explained structurally as the result of a change in stacking order. The sequence *AbA BcB CaC BaB AcA CbC* is twinned on the unique axis and the sequence *AbA BcB CaC BcB AbA CaC* is twinned with (0001) the twin plane.

A four-layer NbSe₂ structure

The reflection 10 $\bar{1}$ 2 from these crystals is strong, and so a likely model from the list of theoretical

four-layer trigonal prism stacking types was picked on the basis of a strong calculated 10 $\bar{1}$ 2 reflection. This model, the *AbA BcB AbA CbC* type, refined to 14.4% using 46 reflections of type $h\bar{0}hl$. This structure and the three-layer structure are both non-centric types. However, in the four-layer type both cations and anions are in an uncentered arrangement whereas in the rhombohedral three-layer modification the cations and anions considered separately are in a centered arrangement but the structure as a whole is non-centric.

A four-layer TaSe₂ structure

The intensities from a sharp, high quality, precession photograph from an exceptionally fine crystal of a four-layer TaSe₂ failed to agree with the calculated intensities from any of the ten possible four-layer trigonal prism types. A Patterson projection prepared from $h\bar{0}hl$ reflections indicated that all of the Ta-Ta vectors were parallel to the c axis, a condition not met in any of the four-layer trigonal prism stacking types. Experimentation with alternate layers of trigonal prism and octahedral coordination led to the conclusion that only one four-layer scheme of this type exists in which the superposition of cations along c is possible. This packing arrangement is as follows: *AcB AcA BcA BcB . . .*. The arrangement has the space group *P6₃/mmc* along with MoS₂ and the two-layer structures discussed earlier. With the use of 38 reflections of type $h\bar{0}hl$, this model refined to 14.3%.

Discussion

Certain generalizations can be made concerning the direction and amount of the change in position in the selenium atoms between the original model and the refined structure. In a two-layer sequence with cation and anion sheets at equal intervals along c , and the origin midway between anion sheets, the z coordinates of the anions are multiples of $\frac{1}{8}$. Similarly in the three- and four-layer structures the z coordinates are multiples of $\frac{1}{12}$ and $\frac{1}{16}$ respectively. The use of such z coordinates places the sheets of anions too close to the interleaving cation sheet. During refinement the anion sheets always moved away from their interleaving cations. As can be seen from the data in Table 5 this shift is about 0.11 Å in the NbSe₂ layer compounds and about 0.09 Å in the TaSe₂ compounds. The adjustments in other trigonal prism layer structures are in the same direction and are: for MoS₂ (Jelinek, 1963), 0.06 Å; for MoTe₂ (Puotinen & Newnham, 1961), 0.12₅ Å; and for NbS₂ (Jelinek, 1963), 0.08 Å.

There appears to be a tendency in the two- and four-layer structures for the cations to align themselves so that they superpose when projected onto the (0001) plane. Maximum line-up is not found in the observed three-layer structure. The more symmetrical rhombo-

hedral form is adopted rather than the lower symmetry ($P3m1$) form in which two out of three cations are aligned. This may be due to the influence of interlayer niobium as suggested by Jellinek *et al.* (1960) for NbS_2 . In the four-layer $NbSe_2$ structure a perfect

Table 5. Selenium atom adjustment from initial z parameters at $\frac{1}{8}$ (two-layer), $\frac{1}{12}$ (three-layer), and $\frac{1}{16}$ (four-layer), during refinement

Polytype	Atom	z (fractional coordinates)	z (Å)	Average
2H $NbSe_2$	Se(1)	0.009	0.11	0.11
2H $TaSe_2$	Se(1)	0.007	0.09	0.09
3R $NbSe_2$	Se(1)	0.005	0.09	0.11
	Se(2)	0.007	0.13	
4H $NbSe_2$	Se(1)	0.004	0.10	0.11
	Se(2)	0.002	0.05	
	Se(3)	0.005	0.13	
	Se(4)	0.006	0.15	
4H $TaSe_2$	Se(1)*	0.002 ₅	0.06	0.09
	Se(2)†	0.003 ₅	0.09	

* Octahedron. † Trigonal prism.

overlap is not found either, but the $bbbc$ cation arrangement found is as close an approximation to such a line-up as is possible for the $AABBAACC$ anion stacking type. Two other theoretical four-layer arrangements, (2) and (5), give equally good line-up. The cation superposition is complete in the four-layer $TaSe_2$ as this is possible with the adoption of an alternating trigonal prism, octahedral coordination sequence. There are 18 geometrically possible four-layer, alternating trigonal prism, octahedral coordination sequences, but only the 4H $TaSe_2$ type has complete cation alignment.

As one would expect, the bond distances between near neighbors do not change significantly because of polytypic differences. Table 4 catalogues the near neighbor bond distances for the five polytypes under discussion.

In 4H $TaSe_2$ it is noted that the volumes of the trigonal prism coordination unit and an octahedral coordination unit are nearly equal. The volume of a single trigonal prism unit is 17.2 \AA^3 and the volume of an octahedral unit is 17.0 \AA^3 . The energy differences between octahedral and trigonal prism coordinations must be small as well, so that the alternate juxtaposition of each coordination forms a more stable

structure than one having purely trigonal prism or octahedral coordination.

The interbond angles in $NbSe_2$ and $TaSe_2$ compounds closely follow theoretical d^4sp hybrid bond angles ($81^\circ 47'$, $81^\circ 47'$, $135^\circ 35'$; Hultgren, 1932). However, the bond angles in Nb and Ta trigonal prisms apparently have consistent small differences from molybdenum trigonal prisms. The comparison in Table 6 illustrates that prisms containing niobium and tantalum tend to be shortened along c and lengthened along a when compared to the prisms containing molybdenum. The c/a ratios are significant in this regard and so molybdenum and tungsten structures whose exact atomic parameters have not been measured are given here also.

Table 6. Comparison of X-M-X bond angles and c/a ratios from molybdenum and tungsten and from niobium and tantalum layer structures

	X-X Parallel to z	X-X Perpendicular to z	$\frac{1}{2}(c/a)$
MoS_2	$82^\circ 30'$	$81^\circ 30'$	1.945
$MoSe_2$			1.96
$MoTe_2$	$83^\circ 30'$	$80^\circ 24'$	1.98
WS_2			1.96
WSe_2			1.97
NbS_2	$79^\circ 00'$	$84^\circ 10'$	1.796
$NbSe_2$	$80^\circ 10'$	$82^\circ 50'$	1.82
TaS_2			1.825
$TaSe_2$	$80^\circ 20'$	$82^\circ 46'$	1.85

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