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The Crystal Structure of Nb₂Se*

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The crystal structure of Nb₂Se has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the monoclinic space group *C2/m* with unit-cell dimensions: $a=13.992$, $b=3.422$, $c=9.283$ Å, $\beta=91.76^\circ$. The unit cell contains eight formula units. Refinement of the structure was performed by least-squares treatment of positional parameters and anisotropic temperature factor coefficients with three-dimensional data. All niobium atoms have distorted cubic coordination with additional near neighbors adjacent to the cube faces. The selenium atoms are bonded to between five and six niobium atoms. There is no selenium-selenium bonding in the compound. The similarities and differences between Nb₂Se and other metal-rich chalcogen compounds such as Nb₂₁S₈, Ti₅Te₄ and Ti₂S, are discussed.

Introduction

The monoselenide region of the niobium-selenium system has been investigated by Brixner (1962), by Revolinsky, Brown, Beerntsen & Armitage (1965), by Schäfer & Fuhr (1965), and by Selte, Bjerkelund & Kjekshus (1966). The region $Se/Nb < 1$, however, has received relatively little attention. Selte & Kjekshus (1963) reported a phase, Nb₅Se₄, isostructural with Ti₅Te₄ (Grønvold, Kjekshus & Raaum, 1961). They indexed all lines on the powder pattern of Nb₅Se₄ on a tetragonal basis with parameters: $a=9.871$, $c=3.4529$ Å. No other compounds have been reported below the ratio $Se/Nb=0.8$.

The application of high temperature techniques has been successful in the preparation of many metal-rich chalconides (*cf.* Franzen, Smeggil & Conard, 1967). The crystal structures of these compounds have been consistent with an interpretation of the bonding in mono- and lower chalconides of transition metals (Franzen, 1966). Comparisons of the metal-rich com-

pounds of the Group IV transition metals with those of Group V have suggested that the roles of the chalcogen in bonding in these groups of compounds are somewhat different. For example, compare Ta₂S (Franzen & Smeggil, 1969) with the Ti₂S structure type (Owens, Conard & Franzen, 1967).

The purpose of the present work was to investigate the metal-rich region of the Nb-Se system, with the use of high temperature preparative techniques, to ascertain whether a metal-rich selenide of niobium could be synthesized, and to determine whether its structure was in accord with the above mentioned ideas concerning bonding in metal-rich chalconides and phosphides.

Experimental

The method of high temperature preparation has been described previously (Franzen, Smeggil & Conard, 1967). The Nb₂Se sample was prepared at a final annealing temperature of 1515°C. The niobium metal was obtained from E. I. Du Pont de Nemours & Co. The 99.999% selenium was obtained from Alfa Inorganics, Inc.

X-ray investigation of the sample was performed with Guinier powder and Weissenberg single-crystal techniques. For the Weissenberg exposures the crystal

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was rotated around the unique axis. The single-crystal X-ray diffraction data used in the structure determination were collected with a Hilger-Watts four circle automatic diffractometer coupled to an SDS 910 computer (Dahm, Benson, Nimrod, Fitzwater & Jacobson, 1967). Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), filtered by Zr, was used to measure the integrated intensities of 1563 reflections at $2\theta < 80^\circ$. Small corrections (less than 5%) for the non-linearity of the detector were applied to the strongest observed intensities. With the use of parameters obtained from the single-crystal diffractometer, accurate lattice parameters were determined by a least-squares treatment of the 2θ values from Guinier powder diffraction patterns obtained at 25°C. Cu $K\alpha$ radiation ($\lambda=1.54050$ Å), filtered by Ni, was used to obtain Guinier patterns. KCl was employed as an internal standard, $a=6.2930$ Å at 25°C (Hambling, 1953). Table 1 contains the $\sin^2\theta$ observed, $\sin^2\theta$ calculated, and the relative intensity of each reflection from the Guinier powder pattern.

Table 1. Guinier X-ray data for Nb₂SeMonoclinic, $a=13.992$, $b=3.422$, $c=9.283$ Å, $\beta=91.76^\circ$.

<i>hkl</i>	$\sin^2\theta(\text{obs})$	$\sin^2\theta(\text{calc})$	<i>I/I</i> ₀
001	0.00678	0.00689	10
200	0.01208	0.01214	10
201	0.01968	0.01959	5
310	0.07802	0.07798	10
112	0.08171	0.08181	5
311	0.08577	0.08568	20
31 $\bar{2}$	0.10338	0.10385	100
40 $\bar{3}$	0.10713	0.10718	80
312		0.10723	
600	0.10957	0.10918	100
004		0.11028	
60 $\bar{1}$	0.11441	0.11441	20
510	0.12639	0.12651	1
51 $\bar{1}$	0.13213	0.13201	5
31 $\bar{3}$	0.13684	0.13743	90
020	0.20252	0.20266	70
80 $\bar{2}$	0.21716	0.21716	5
620	0.31189	0.31189	50
62 $\bar{1}$	0.31699	0.31707	20
225	0.38455	0.38430	30

Lorentz and polarization corrections were applied. From photographs ($\times 250$) of the crystal, it was estimated that the shape of the crystal was a parallelepiped with one corner missing, and its size was $88 \times 180 \times 60 \mu$. Absorption corrections were made by the

use of a program by Busing & Levy (1957) adapted to the IBM 360/50 computer. Transmission factors ranged between 0.14 and 0.37. No extinction corrections were made.

Composition analysis of the sample characterized as Nb₂Se was performed by igniting the sample to Nb₂O₅; the Se/Nb ratio was 0.44 ± 0.01 . The low value for this ratio, compared with the structurally determined value of 0.5, was probably a result of the presence of a small amount of Nb metal in the Nb₂Se sample, as evidenced by several faint lines observed in the powder pattern. In powder photographs of other samples lines from Nb₅Se₄ were observed together with lines from Nb₂Se. The density of Nb₂Se was measured by pycnometric techniques.

Crystal data

Nb₂Se, F. W. 264.77. Monoclinic, $a=13.992 \pm 0.006$, $b=3.422 \pm 0.001$, $c=9.283 \pm 0.007$ Å, $\beta=91.76 \pm 0.06^\circ$, $V=446.8$ Å³, $D_m=7.8$ g.cm⁻³ ± 0.1 , $Z=8$, $D_x=7.88$ g.cm⁻³. Mo $K\alpha$ ($\lambda=0.7107$ Å) $\mu=275.2$ cm⁻¹. Absent reflections, *hkl* when $h+k$ odd. Space group $C2$ (No. 5), Cm (No. 8), or $C2/m$ (No. 12). An intensity distribution analysis indicated $C2/m$, and this space group was confirmed by refinement of the structure.

Determination and refinement of the structure

A three-dimensional Patterson synthesis was performed with the use of all data; maxima were observed only at sections $y=0$ and $y=\frac{1}{2}$. The layering in the short axis direction ($b=3.422$ Å) was consistent with atoms occupying fourfold positions (*i*) $x, 0, z$ of $C2/m$. Accordingly, superposition methods were performed using the $y=0$ section. None of the trial structures obtained in this way refined satisfactorily with the use of the 166 reflections with the largest *U* values (*cf.* below). As was discovered later, the failure of the trial structure to refine was not the result of an incorrect model, but rather the result of not including in the refinement calculation a set of reflections of relatively low intensity.

Unitary structure factors were obtained from the observed structure factors by a graphical method (Woolfson, 1961). The unitary structure factors were found to depend on *k* only so far as *k* was even or odd, *i.e.* $U(h0l)=U(h2l)$ and $U(h1l)=U(h3l)$, in agreement with the proposed layering in the *y* direction; accord-

Table 2. Refined atomic parameters for Nb₂Se

The positional parameters and isotropic temperature factor coefficients were refined using 578 reflections of the zero and first levels. The anisotropic thermal parameters were refined using all data. All atoms occupy fourfold positions (*i*) $x, 0, z$ of space group $C2/m$. $\beta_{12}=\beta_{23}=0$.

	<i>x</i>	<i>z</i>	$\frac{B}{(\text{Å}^2)}$	β_{11}	β_{22}	β_{33}	β_{13}
Nb(1)	0.2155 (1)	0.1251 (2)	0.43 (3)	0.00049 (4)	0.0080 (8)	0.00128 (9)	0.00022 (4)
Nb(2)	0.0839 (1)	0.3988 (2)	0.39 (3)	0.00048 (4)	0.0064 (8)	0.00115 (9)	0.00028 (4)
Nb(3)	0.4127 (2)	0.3491 (2)	0.58 (4)	0.00063 (4)	0.0076 (8)	0.0020 (1)	0.00051 (4)
Nb(4)	0.2568 (1)	0.6228 (2)	0.32 (3)	0.00039 (4)	0.0058 (8)	0.00098 (9)	0.00015 (4)
Se(5)	0.1410 (2)	0.8627 (2)	0.44 (4)	0.00058 (5)	0.0065 (8)	0.0015 (1)	0.00023 (5)
Se(6)	0.4253 (2)	0.8157 (2)	0.54 (4)	0.00060 (5)	0.0077 (8)	0.0018 (1)	0.00041 (5)

ingly, only zero and first level data were used to assign phases. A set of eleven signs (Woolfson, 1961) was determined with a Harker-Kasper inequality (Harker & Kasper, 1948). The triple product sign relationship proposed by Zachariasen (1952),

$$s(\mathbf{h}) \approx s\{\sum_{\mathbf{h}'} s(\mathbf{h}') s(\mathbf{h}-\mathbf{h}')\}, \quad (1)$$

was used to extend the assignment of signs. In the case of an end-centered monoclinic crystal, the signs of two structure factors can be arbitrarily assigned (Haupt-

mann & Karle, 1953); $U_{3,1,2}$ and $U_{6,0,1}$ were taken to be positive.

After 25 signs had been determined with the use of the eleven signs, four electron density maps ($y=0$) were Fourier synthesized. These four maps resulted from assignment of signs to the two symbols used in the symbolic addition procedure. All maps had peaks in basically the same relative positions; one was selected as a trial structure on the basis of its similarity with a map obtained by the superposition method. Structure factors were then assigned signs and added to those originally used in groups of 10-20, in repeated attempts to refine the trial structure discussed above, and to obtain new electron density sections at $y=0$. Finally, after accepting 149 reflections, the structure refined to a reliability index

Table 3. Observed and calculated structure factors for Nb₂Se

H F ₀ F _c	H F ₀ F _c	H F ₀ F _c	H F ₀ F _c	H F ₀ F _c	H F ₀ F _c	H F ₀ F _c
K=0, L=0	K=0, L=8	K=0, L=16	K=0, L=24	K=0, L=32	K=0, L=40	K=0, L=48
2 108 -90	-12 28 20	-4 85 86	15 137 -132	3 80 -78	K=1, L=7	K=1, L=15
4 89 -72	K 181 196	-16 23 20	-105 -149	7 15 -13	-3 231 -235	-5 110 116
6 426 -615	2 244 -274	-18 38 -35	-10 41 -31	21 76 63	9 31 -39	-5 119 -113
8 0 18	6 67 67	-20 110 103	-20 110 103	23 6 62	12 12 101	-2 284 263
10 19 8	6 65 -69	-22 78 -76	-14 29 16	14 29 16	10 94 94	-10 286 263
12 208 185	10 72 76	-24 38 35	-16 38 -35	14 29 16	14 29 16	-13 211 178
14 200 177	10 72 76	-24 38 35	-16 38 -35	14 29 16	14 29 16	-13 211 178
16 81 -74	12 53 -54	K=0, L=31	K=0, L=31	3 89 99	3 81 -89	-15 166 -122
18 186 -176	14 81 -81	-4 32 31	-2 110 116	7 45 47	7 45 47	-11 93 -76
20 25 -29	16 81 -81	-4 32 31	-2 110 116	7 45 47	7 45 47	-11 93 -76
22 37 31	18 50 -50	-6 12 12	-4 137 -134	9 198 192	9 198 192	-10 105 -101
24 31 87	10 7 7	-8 130 -116	-6 12 12	11 209 225	9 46 50	-21 97 95
K=0, L=1	K=0, L=9	K=0, L=18	K=0, L=27	K=0, L=36	K=1, L=16	K=1, L=32
0 76 -72	0 52 -54	-12 168 162	-10 93 101	15 52 50	1 127 124	-1 67 71
2 82 -53	2 129 142	-14 108 -100	-14 96 -82	17 136 -132	3 42 -44	-3 92 -53
4 53 -49	4 119 126	-16 20 -20	-16 20 -20	19 36 24	5 12 7	-5 50 -55
6 14 12	6 15 8	-18 24 24	-18 24 24	21 29 -23	7 31 27	-7 50 -55
8 165 151	8 10 10	-20 44 42	-20 44 42	23 34 31	9 10 10	-9 42 -36
10 13 -5	10 10 -10	-22 28 45	-22 28 45	25 34 31	11 10 10	-11 50 -55
12 195 -136	12 126 -125	-24 10 10	-24 10 10	27 34 31	13 10 10	-13 50 -55
14 89 82	14 74 75	-26 28 45	-26 28 45	29 34 31	15 10 10	-15 50 -55
16 19 -18	16 53 49	-28 26 -25	-28 26 -25	31 34 31	17 10 10	-17 50 -55
18 26 28	18 77 67	-30 108 -102	-30 108 -102	33 34 31	19 10 10	-19 50 -55
20 68 -07	20 79 -73	-32 110 104	-32 110 104	35 34 31	21 10 10	-21 50 -55
22 34 40	22 74 -74	-34 110 104	-34 110 104	37 34 31	23 10 10	-23 50 -55
24 14 -7	24 74 -74	-36 110 104	-36 110 104	39 34 31	25 10 10	-25 50 -55
K=0, L=2	K=0, L=10	K=0, L=20	K=0, L=30	K=0, L=40	K=1, L=17	K=1, L=34
0 101 -103	4 88 110	-16 0 7	-2 31 -30	4 88 110	-16 0 7	-2 31 -30
2 45 -49	6 119 -123	-18 92 79	-4 40 -42	6 119 -123	-18 92 79	-4 40 -42
4 14 8	8 10 10	-20 27 18	-20 27 18	8 10 10	-20 27 18	-20 27 18
6 102 -115	10 27 -32	-22 33 -30	-22 33 -30	10 27 -32	-22 33 -30	-22 33 -30
8 190 206	12 22 49	-24 33 -30	-24 33 -30	12 22 49	-24 33 -30	-24 33 -30
10 59 56	14 33 33	-26 33 -30	-26 33 -30	14 33 33	-26 33 -30	-26 33 -30
12 86 -83	16 40 -38	-28 33 -30	-28 33 -30	16 40 -38	-28 33 -30	-28 33 -30
14 60 -38	18 49 77	-30 33 -30	-30 33 -30	18 49 77	-30 33 -30	-30 33 -30
16 39 -31	20 122 -101	-32 33 -30	-32 33 -30	20 122 -101	-32 33 -30	-32 33 -30
18 89 77	22 114 105	-34 33 -30	-34 33 -30	22 114 105	-34 33 -30	-34 33 -30
20 122 -101	24 63 -63	-36 33 -30	-36 33 -30	24 63 -63	-36 33 -30	-36 33 -30
22 114 105	26 44 -44	-38 33 -30	-38 33 -30	26 44 -44	-38 33 -30	-38 33 -30
24 63 -63	28 44 -44	-40 33 -30	-40 33 -30	28 44 -44	-40 33 -30	-40 33 -30
26 44 -44	30 44 -44	-42 33 -30	-42 33 -30	30 44 -44	-42 33 -30	-42 33 -30
28 44 -44	32 44 -44	-44 33 -30	-44 33 -30	32 44 -44	-44 33 -30	-44 33 -30
30 44 -44	34 44 -44	-46 33 -30	-46 33 -30	34 44 -44	-46 33 -30	-46 33 -30
32 44 -44	36 44 -44	-48 33 -30	-48 33 -30	36 44 -44	-48 33 -30	-48 33 -30
34 44 -44	38 44 -44	-50 33 -30	-50 33 -30	38 44 -44	-50 33 -30	-50 33 -30
36 44 -44	40 44 -44	-52 33 -30	-52 33 -30	40 44 -44	-52 33 -30	-52 33 -30
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48 44 -44	52 44 -44	-64 33 -30	-64 33 -30	52 44 -44	-64 33 -30	-64 33 -30
50 44 -44	54 44 -44	-66 33 -30	-66 33 -30	54 44 -44	-66 33 -30	-66 33 -30
52 44 -44	56 44 -44	-68 33 -30	-68 33 -30	56 44 -44	-68 33 -30	-68 33 -30
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144 44 -44	148 44 -44	-160 33 -30	-160 33 -30	148 44 -44	-160 33 -30	-160 33 -30
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148 44 -44	152 44 -44	-164 33 -30	-164 33 -30	152 44 -44	-164 33 -30	-164 33 -30
150 44 -44	154 44 -44	-166 33 -30	-166 33 -30	154 44 -44	-166 33 -30	-166 33 -30
152 44 -44	156 44 -44	-168 33 -30	-168 33 -30	156 44 -44	-168 33 -30	-168 33 -30
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156 44 -44	160 44 -44	-172 33 -30	-172 33 -30	160 44 -44	-172 33 -30	-172 33 -30
158 44 -44	162 44 -44	-174 33 -30	-174 33 -30	162 44 -44	-174 33 -30	-174 33 -30
160 44 -44	164 44 -44	-176 33 -30	-176 33 -30	164 44 -44	-176 33 -30	-176 33 -30
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164 44 -44	168 44 -44	-180 33 -30	-180 33 -30	168 44 -44	-180 33 -30	-180 33 -30
166 44 -44	170 44 -44	-182 33 -30	-182 33 -30	170 44 -44	-182 33 -30	-182 33 -30
168 44 -44	172 44 -44	-184 33 -30	-184 33 -30	172 44 -44	-184 33 -30	-184 33 -30
170 44 -44	174 44 -44	-186 33 -30	-186 33 -30	174 44 -44	-186 33 -30	-186 33 -30
172 44 -44	176 44 -44	-188 33 -30	-188 33 -30	176 44 -44	-188 33 -30	-188 33 -30
174 44 -44	178 44 -44	-190 33 -30	-190 33 -30	178 44 -44	-190 33 -30	-190 33 -30
176 44 -44	180 44 -44	-192 33 -30	-192 33 -30	180		

the parameters and their standard deviations are given in Table 2. The standard deviation of an observation of unit weight,

$$[\sum w \Delta^2 / m - n]^{1/2}, \quad (3)$$

was 1.03. In expression (3), w is the revised weight of an observation, Δ is $(F_o - F_c)$, m is the number of observations (578), and n is the number of variables (19). The positional parameters obtained from the refinement described above were used to calculate all structure factors in the zero and first levels, including those observations which had been taken as unobserved, as discussed above. The list of observed and calculated

structure factors are tabulated in Table 3. The reliability index for these data was 0.111.

Refinement of the structure was also performed with anisotropic thermal parameters by use of all 1563 data (maximum $k=6$). The anisotropic components of the thermal parameters are given in Table 2. The positional parameters obtained in this refinement were the same, within the standard deviations, as those listed in Table 2. In this case the R value was 0.100, and the 'goodness of fit', as defined by (3), was 0.94.* Refinements were

* A total listing of F_{obs} and F_{calc} for the anisotropic refinement will be furnished upon request.

Table 4. *Interatomic distances in Nb₂Se ($\pm 0.003 \text{ \AA}$) and angles around Se atoms*

Reference atom	Neighbor	No. of neighbors	Distance
Nb(1)	Se(5)	1	2.618
	Se(5)	2	2.642
	Se(6)	2	2.682
	Nb(4)	2	2.923
	Nb(1)	2	3.074
	Nb(2)	1	3.197
	Nb(3)	1	3.404
Nb(2)	Se(6)	2	2.630
	Nb(4)	2	2.826
	Nb(3)	2	2.904
	Nb(3)	2	2.967
	Nb(2)	1	3.060
	Nb(4)	1	3.138
	Nb(1)	1	3.197
Nb(3)	Se(5)	2	2.701
	Se(6)	1	2.782
	Nb(2)	2	2.904
	Nb(4)	2	2.947
	Nb(2)	2	2.967
	Nb(1)	1	3.404
	Nb(4)	1	3.411
Nb(4)	Se(5)	1	2.805
	Nb(2)	2	2.826
	Nb(4)	2	2.857
	Se(6)	1	2.911
	Nb(1)	2	2.923
	Nb(3)	2	2.947
	Nb(2)	1	3.138
	Nb(3)	1	3.411
Se(5)	Nb(1)	1	2.618
	Nb(1)	2	2.642
	Nb(3)	2	2.701
	Nb(4)	1	2.805
Se(6)	Nb(2)	2	2.630
	Nb(1)	2	2.682
	Nb(3)	1	2.782
	Nb(4)	1	2.911

Angle	Degrees	Angle	Degrees
Nb(1)-Se(5)-Nb(1)	71.51	Nb(3)-Se(6)-Nb(2)	66.41
Nb(1)-Se(5)-Nb(1)	80.96	Nb(2)-Se(6)-Nb(2)	81.39
Nb(3)-Se(5)-Nb(3)	78.84	Nb(1)-Se(6)-Nb(1)	79.49
Nb(1)-Se(5)-Nb(4)	121.36	Nb(3)-Se(6)-Nb(4)	108.53
Nb(1)-Se(5)-Nb(4)	64.83	Nb(2)-Se(6)-Nb(4)	61.09
Nb(1)-Se(5)-Nb(3)	140.53	Nb(3)-Se(6)-Nb(1)	137.04
Nb(1)-Se(5)-Nb(3)	79.16	Nb(2)-Se(6)-Nb(1)	73.99
Nb(3)-Se(5)-Nb(4)	64.70	Nb(1)-Se(6)-Nb(4)	62.86

also carried out in the acentric space groups. In each case the hypothesis that the acentric structure was correct rather than the centric one could be rejected according to Hamilton's (1965) criterion at the 99.5% confidence level.

For the purpose of checking the correctness of the refinement, a difference electron density synthesis was performed with 578 reflections of the zero and first levels. The synthesis had maxima, corresponding to about 2 electrons at the $y=0$ section; these maxima were all at atomic positions. Interatomic distances and angles, obtained by the use of the *Thermal Ellipsoid Plot* computer program written by Johnson (1965), are listed in Table 4. Johnson's program was used with Slater's (1964) atomic radii to draw the stereoscopic view of the structure along the b axis. The illustration is presented in Fig. 1.

Description and discussion of the structure

The four independent Nb atoms have similar coordination polyhedra, namely, a distorted cubic arrangement of eight atoms with additional bonded atoms adjacent to the faces of the cube. For example, as shown in Fig. 2, the most distorted cubic arrangement is around the Nb(1) atom which is coordinated by 2 Nb(1), 2 Nb(4), 2 Se(5), and 2 Se(6), forming the distorted cube, and Nb(2), Nb(3), and Se(5) are located adjacent to the faces of the cube. The least distorted cubic arrangement is found around Nb(4).

The coordination polyhedra of the two independent Se atoms are difficult to describe. One can see, however, by comparing angles and distances in Table 4 that the arrangement of Nb atoms around each Se is similar, namely, that each Se atom is bonded to six Nb atoms. In addition, it is noted that the Nb atoms are not arranged so as to spatially surround the Se atoms; rather, in the vicinity of each Se there are relatively large regions which are unoccupied by either Nb or Se atoms. Referring to Fig. 2, these 'holes' occur on the twofold axes.

The Nb₂Se structure-type is new, but the metal and non-metal environments in Nb₂Se are similar to those

in Nb₅Se₄, which has the Ti₅Te₄ type structure (Selte & Kjekshus, 1963). The coordination polyhedra of the non-metal in Nb₂Se and Nb₅Se₄ are related to those observed in Nb₃Se₄ (Selte & Kjekshus, 1964), perhaps suggesting a basis for understanding the relationship of metal-rich chalcogenides to mono- and higher chalcogenides.

The tendency for metal atoms to form body-centered coordination polyhedra has been correlated with the promotion energies from the ground electronic states to the sd^{n-1} configurations (n denotes the number of valence electrons) in the gaseous atoms (Brewer, 1963). The metal coordination in metal-rich compounds has recently been discussed from this point of view (Franzen, Smeggil & Conard, 1967). The Nb₂Se structure type provides further corroboration of this correlation, for elemental Nb crystallizes in the b.c.c. structure type, and the Nb atoms in Nb₂Se are surrounded by eight atoms, both Se and Nb, in distorted cubes.

The Nb₂Se structure can be compared with the Nb₂₁S₈ structure (Franzen, Beineke & Conard, 1968). Fig. 2 shows the Nb₂Se structure projected along the short axis (3.42 Å). Fig. 3 shows the Nb₂₁S₈ structure also projected along its short axis (3.36 Å). There is a mirror plane parallel to the plane of the Figure in each structure. The structural similarity between Nb₂Se and Nb₂₁S₈ is outlined by exactly equivalent bold-lined parallelograms in each Figure. In Nb₂Se the bold parallelogram is almost an asymmetric unit of the structure, whereas in Nb₂₁S₈ the same parallelogram is only a portion of an asymmetric unit. The projected atom positions in each bold-lined parallelogram are approximately the same with the exception that in Nb₂₁S₈ there are two projected atom positions which are not present in Nb₂Se, namely, the Nb atom at $z=0$ in the upper right-hand corner and the Nb atom at $z=\frac{1}{2}$ in the lower right-hand corner of the bold-lined parallelogram. It is seen, however, that these two additional projected positions in Nb₂₁S₈ occur in the 'hole' regions of Nb₂Se. Nonetheless, Nb₂Se is seen to have a basic structural similarity with Nb₂₁S₈, and thus with a number of lower chalcogenides (and, it should be mentioned, phosphides) as well.

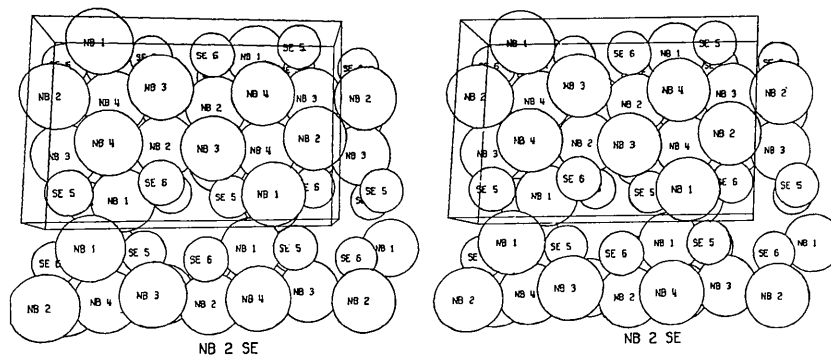


Fig. 1. Stereoscopic illustration of the Nb₂Se structure viewed along the b axis. The box indicates a unit cell.

Nb₂Se does exhibit, however, some significant differences from other metal-rich transition metal compounds. For example, the Nb₂₁S₈ structure does not contain regions with non-bonded sulfur arrangements. On the other hand, while, as is generally true of metal-rich chalcogenides, there are no selenium-selenium bonds in the Nb₂Se structure (the closest Se-Se distance is 3.43 Å), the Se atoms are, nonetheless, arranged in non-bonded tetrahedra. These tetrahedra share edges so as to form chains of tetrahedra in the *b* direction. The non-bonded Se atom arrangements in Nb₂Se differentiate this structure from the structures of the Group IV transition metal subchalcogenides and subphosphides, for in all of the Group IV compounds a high degree of coordination (six to nine) of the non-metal by metal atoms is observed. This feature of Nb₂Se is shared by Ta₂S (Franzen & Smeggil, 1969), for in Ta₂S the sulfur atoms are similarly located in a non-bonded fashion in regions of the structure.

On the basis of these and similar observations, the following classification can be made of the metal-rich chalcogenides of transition metals: Class I refers to group IV transition metal compounds with chalcogen/metal (*C/M*)=0.5, which form with high chalcogen coordination numbers (six to nine); to Class II belong the Group V compounds with *C/M* < 0.5 and high chalcogen coordination numbers; and to Class III belong other Group V compounds which have *C/M* = 0.5 and lower chalcogen coordination numbers (five to six). In addition, the structures of Class III compounds exhibit regions containing non-bonded chalcogen atoms and regions with extensive metal-metal bonding.

Table 5. *Known metal-rich chalcogenide compounds, listed according to their class (defined in text)*

Average chalcogen coordination numbers (C.N.) and calculated chalcogen valences are given.

	Class	Average C.N.	Average calculated valence
Ti ₂ S	I	7.7	4.5
Ti ₂ Se ^(a)	I	7.7	—
Zr ₂ S ^(a)	I	7.7	—
Zr ₂ Se ^(b)	I	7.7	4.3
Hf ₂ S ^(c)	I	6	3.4
Hf ₂ Se ^(a)	I	6	—
α-V ₃ S ^(d)	II	8	5.0
β-V ₃ S ^(d)	II	8	5.0
Nb ₂ S ₃	II	7.5	4.1
Nb ₂ Se	III	6	3.0
Ta ₂ S	III	5	3.0

References not given in text:

(a) Franzen, Smeggil & Conard (1967).

(b) Franzen & Norrby (1968).

(c) Franzen & Graham (1966).

(d) Pedersen & Grønvold (1959).

Table 5 lists all known subchalcogenides of the Group IV and V transition metals, together with their classes (as defined above), their average chalcogen coordination numbers, and their average chalcogen valences, as given by the Pauling empirical relationship (Pauling, 1960). While these valences are probably not absolutely correct, the trends in the calculated valences clearly are significant in this case.

The coordination numbers and valences of the chalcogens in the various classes strongly suggest an elec-

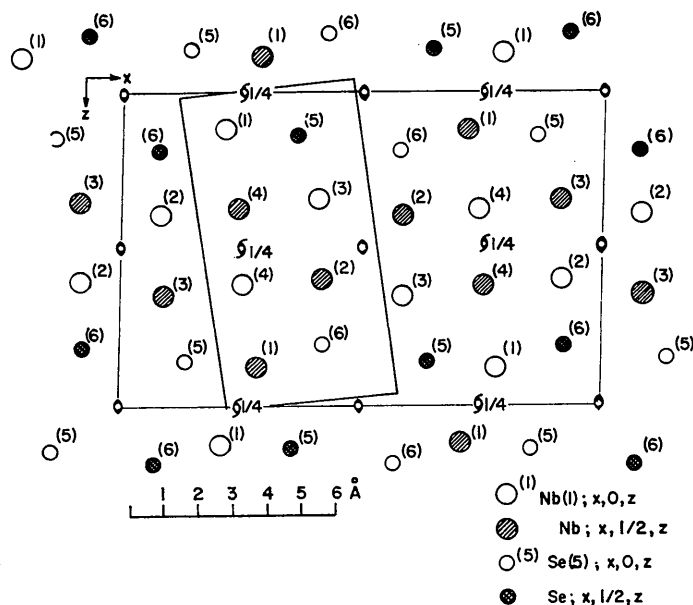


Fig. 2. A unit cell of Nb₂Se projected on (010). Bold-lined parallelogram contains structural similarities to Nb₂₁S₈.

tron concentration interpretation of the differences between the classes. All Group IV subchalcogenides belong to Class I, as would be expected from this viewpoint, since all have the same valence electron concentration. On the other hand, the valence electron concentration is increased if the stoichiometry is unchanged but a Group V element replaces a Group IV element. Since no Group V subchalcogenides are isostructural with Group IV subchalcogenides, this replacement appears to result in compounds unstable either with respect to disproportionation into a still lower chalcogenide (forming a Class II compound) and a higher chalcogenide, or with respect to a structure type in which the chalcogen contributes fewer electrons to the conduction band (forming a Class III compound).

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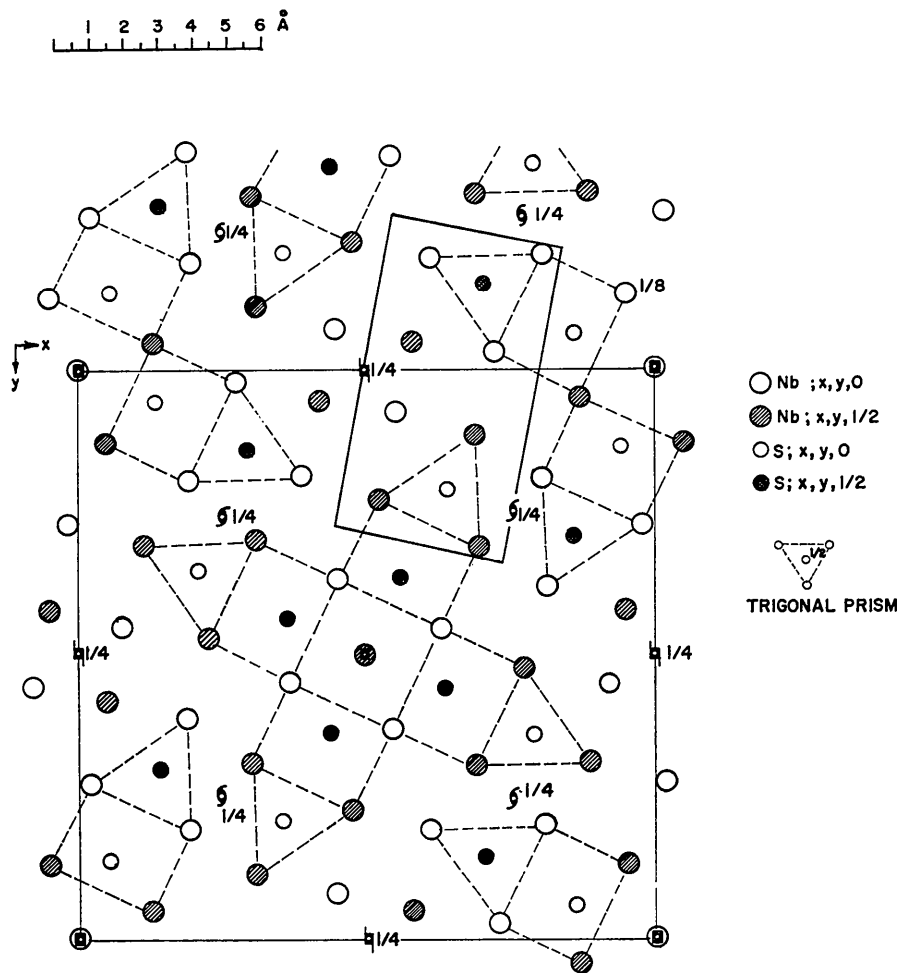


Fig. 3. Approximately one and one-half unit cells of Nb_{21}S_8 projected on (001). All sulfur atoms are coordinated to six niobium atoms at the corners of trigonal prisms, shown by the dotted lines, and to additional niobium atoms adjacent to rectangular faces of the prisms. The bold-lined parallelogram contains structural similarities to Nb_2Se .

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The Crystal Structure of Ta₂S*

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The crystal structure of ditantalum sulfide, Ta₂S, has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic system, space group *Pbcm*, with unit-cell dimensions: $a=7.379$, $b=5.574$, and $c=15.19$ Å. The unit cell contains 12 formula units. Refinement of the structure was performed by a least-squares treatment of the positional parameters and the temperature factor coefficients. The Ta₂S structure is fundamentally different from other known metal-rich chalconide structures. The structure can be viewed as chains of body-centered pentagonal antiprisms of tantalum atoms sharing faces in one direction and interconnected *via* sulfur atoms in the other two directions.

Introduction

The crystal structures of the sulfides of tantalum have been reviewed by Jellinek (1963). It was concluded that an early claim of the preparation of a subsulfide of tantalum by Biltz & Kocher (1938) was incorrectly based on powder patterns of a mixture of phases. Preparations at relatively low temperatures (less than about 1000°C) have generally failed to produce metal-rich sulfides such as have been prepared by high-temperature techniques in recent years in the Hf-S system (Franzen & Graham, 1966), in the Ti-S system (Owens, Conard & Franzen, 1967), and in the Nb-S system (Franzen, Beineke & Conard, 1968). The work reported here was performed with the purpose of extending the application of high-temperature preparation techniques to the Ta-S system in order to prepare and determine the structure of a lower sulfide of tantalum.

Experimental

The ditantalum sulfide samples were prepared in a manner analogous to that previously described (Owens, Conard & Franzen, 1967). The sulfur obtained from the American Smelting and Refining Co. was 99.999% pure. The tantalum obtained from the National Research Corporation was 99.99% pure. The final annealing temperature in the case of the Ta₂S preparation was 1600°C. Single-crystal X-ray diffraction data were initially collected with a General Electric spectrometer and nickel filtered Cu $K\alpha$ radiation. Data were collected for 767 reflections in the range $0^\circ < 2\theta \leq 160^\circ$. A second set of data was collected using a Hilger-Watts diffractometer coupled with an SDS(910-IBM) (1401) computer configuration described elsewhere (Dahm, Benson, Nimrod, Fitzwater & Jacobson, 1967). Mo $K\alpha$ radiation was used with a Zr filter to collect data for 1104 reflections in the range $0^\circ < 2\theta \leq 60^\circ$. Lorentz and polarization corrections were applied to both sets of data. Absorption corrections, based on the crystal's approximately rectangular prismatic shape

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