b direction relative to the first, but its sulphur atom is displaced by $b/2+0.3$ Å. These relationships are probably responsible for the difficulties encountered in solving and refining the structure.

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The Crystal Structures of Niobium(III) Selenide and Tantalum(III) Selenide

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The crystal structures of the monoclinic phases Nb_2Se_3 ($a=6.503$, $b=3.434$, $c=9.215$ Å; $\beta=103.39°$) and Ta_2Se_3 ($a=6.495$, $b=3.408$, $c=9.206$ Å; $\beta=103.63°$) have been determined and refined from single-crystal data. All atoms are in the special position 2(e): $\pm(x\frac{1}{4}z)$ of space group $P2_1/m$. The metal atoms are in octahedral holes of a *chh* close packing of selenium, but the structures are deformed in such a way that zigzag metal–metal chains are formed. These chains are of two kinds; the metal–metal distances in half of the chains are comparable to those in the pure metals, in the other half of the chains the distances are considerably longer. In the isotypic phase Mo_2S_3 short metal–metal distances are found in all chains.

The phases Nb_2Se_3 and Ta_2Se_3

In our study of the system Nb–Se (*cf.* Selte, Bjerkelund & Kjekshus, 1966) we found needle-shaped crystals of a new phase (together with polycrystalline material of the same phase) in samples of compositions around Nb_2Se_3 that had been prepared by heating the mixed elements at 1000–1200°C, followed by quenching to room temperature (Huisman, Kadijk & Jellinek, 1967). Weissenberg diagrams showed the phase to crystallize in the monoclinic system, the needle axis coinciding with the *b* axis. In a sample of composition $Nb_{1.35}Se_2$ the new phase was contaminated by Nb_3Se_4 (Selte & Kjekshus, 1964*a*), while a sample of composition $Nb_{1.33}Se_2$ contained a trace of $2s(a)$–$Nb_{1+x}Se_2$ (Kadijk, Huisman & Jellinek, 1964; Selte & Kjekshus, 1964*b*) in addition to the new phase. The unit-cell dimensions of the new phase were not significantly different in the two samples. This indicates that the homogeneity range of the new phase is very narrow and that its composition is very close to Nb_2Se_3. The phase is a metallic conductor.

Needles of the corresponding tantalum selenide Ta_2Se_3, together with polycrystalline material, were obtained by heating the mixed elements at 1140°C and quenching to room temperature (Huisman *et al.*, 1967). The unit-cell dimensions determined at room temperature from diffractometer data with the use of Cu $K\alpha$ radiation ($\lambda\alpha_1=1.54050$ Å) and silicon ($a=5.4306$ Å) as internal standard are:

Nb_2Se_3 $a=6.503$, $b=3.434$, $c=9.215$ Å; $\beta=103.39°$

Ta_2Se_3 $a=6.495$, $b=3.408$, $c=9.206$ Å; $\beta=103.63°$.

Assuming unit-cell contents of Nb_4Se_6 and Ta_4Se_6 the densities are calculated as 7.012 g.cm⁻³ and 10.040 g.cm⁻³ respectively, which are reasonable values.

The phases Nb_2Se_3 and Ta_2Se_3 may correspond to γ-$Nb_{1.3}Se_2$ and γ-$Ta_{1.3}Se_2$ mentioned by Revolinsky, Brown, Beerntsen & Armitage (1965), although the latter phases were thought to possess layer-like structures.

Structure determination

The axial ratio $a:b:c$ and the angle β of Nb_2Se_3 and Ta_2Se_3 are very similar to those of monoclinic Mo_2S_3 (Jellinek, 1961, 1963) as is evident from the following table:

	a:	b:	c	β
Nb_2Se_3	1	0·5281	1·4171	103·39°
Ta_2Se_3	1	0·5247	1·4174	103·63
Mo_2S_3	1	0·5266	1·4172	102·43
Ideal	1	0·5774	1·4530	103·26 .

It seemed likely, therefore, that Nb_2Se_3 and Ta_2Se_3 are isotypic with monoclinic Mo_2S_3, the structure of which had been determined and refined from powder data (Jellinek, 1961; de Jonge, Wiegers & Jellinek, 1967). This conclusion was supported by the similarity of diffractograms of the three phases (Huisman *et al.*, 1967) and confirmed by Fourier syntheses. The structure of Mo_2S_3 was, therefore, taken as the starting point for the refinement of the structures of Nb_2Se_3 and Ta_2Se_3 from single-crystal data.

For Nb_2Se_3 integrated Weissenberg diagrams of the first three layer lines about the *b* axis were taken, applying the multiple-film technique (Cu $K\alpha$ radiation). The intensities were measured photometrically; intensities of weak reflexions were visually estimated from non-integrated films. Since μR was about 0·25, no absorption correction was considered necessary. For Ta_2Se_3 all intensities were visually estimated from non-integrated Weissenberg diagrams (Cu $K\alpha$ radiation); in this case a correction for absorption had to be applied. The usual corrections for Lorentz and polarization factors were applied in all cases.

The intensity sequence of the $h2l$ reflexions was found to be the same as that of the $h0l$ reflexions, confirming that all atoms are in the special position $2(e)$: $\pm(x\frac{1}{4}z)$ of space group $P2_1/m$ (C_{2h}^2) (Jellinek, 1961).

Table 1. *Atomic parameters of* Nb_2Se_3 *and* Ta_2Se_3

	Nb_2Se_3			Ta_2Se_3			Ideal	
	x	z	B	x	z	B	x	z
Nb, Ta(1)	0·3147	0·0036	0·38 Å²	0·3190	0·0034	0·1 Å²	0·2500	0·0000
Nb, Ta(2)	0·1138	0·6369	0·29	0·1134	0·6365	0·4	0·1389	0·6667
Se(1)	0·5211	0·7967	0·36	0·5304	0·7973	0·1	0·5278	0·8333
Se(2)	0·9733	0·1564	0·48	0·9724	0·1554	0·3	0·9722	0·1667
Se(3)	0·7279	0·5144	0·43	0·7284	0·5144	0·3	0·7500	0·5000
e.s.d. Nb, Ta	0·0006	0·0004		0·0015	0·0010			
e.s.d. Se	0·0007	0·0005		0·0032	0·0022			

Table 2. *Structure factors of* Nb_2Se_3

```
h k = 0 0          h k = 3 0          h k = 5 0          h k = -8 0         h k = -2 1         h k = 5 1
   F_obs   F_calc     F_obs   F_calc     F_obs   F_calc     F_obs   F_calc     F_obs   F_calc     F_obs   F_calc
l= 1  36.9  + 35.6  l= 0  91.1  + 81.3  l= 0 256.5 -226.4  l= 0  58.6 + 52.2  l= 1 206.9 -187.0  l= 0 239.2 +224.7
   2  89.0  + 97.8     1 235.4 +220.5     1   6.4  - 2.5     1 135.7 -158.9     2 125.8 -116.2     1 162.0 -147.9
   3  48.8  - 50.3     2 119.3 +103.1     2  16.9  - 8.1     2 171.5 -184.5     3  93.6 - 67.9     2  55.0 + 44.9
   4  69.3  + 65.7     3 107.4 +105.5     3 105.2 - 98.6     3  33.6 - 16.5     4 106.2 -103.0     3  72.4 - 78.2
   5 183.4  +183.0     4 100.9 +101.6     4  82.4 - 72.9     4  25.0 - 27.0     5   0.0 +  4.5     4  99.2 +101.0
   6 295.1  +305.0     5 100.9 - 93.6     5 146.5 -136.8     5  17.4 -  4.5     6 130.6 +121.1     5 144.8 +137.0
   7  65.1  - 55.0     6 120.4 +126.5     6 143.2 -150.2                        7 224.2 -230.9     6  66.0 + 59.7
   8 170.4  +153.9     7 250.6 +219.8     7  95.5 + 90.1  h k = 0 1            8  65.3 - 53.2
   9   0.0  +  5.3     8  59.7 + 71.4                     l= 1 103.8 +120.7     9 137.6 -143.5  h k = -5 1
  10  66.1  + 54.9     9 110.7 +116.7  h k = -5 0           2 162.8 -188.9    10  35.4 + 16.7  l= 1 174.6 -156.7
  11  82.4  + 94.0                     l= 1  77.1 + 64.5     3   0.0 -  0.7    11  71.6 + 70.6     2   0.0 - 15.6
                    h k = -3 0            2 179.0 -165.9     4  24.4 - 28.6                        3  37.8 + 41.5
h k = 1 0          l= 1  68.3 + 48.9     3 129.1 -116.9     5  32.2 + 23.4  h k = 3 1             4  38.6 + 45.2
l= 0  43.4  + 37.5     2 296.2 +291.4     4 119.3 -111.5     6 155.3 +153.6  l= 0  66.0 - 57.3     5  44.8 + 41.0
   1  25.0  - 22.1     3 109.6 -104.8     5  79.2 - 69.4     7   0.0 -  3.5     1  45.6 + 25.2     6 169.6 -195.6
   2 113.9  -102.3     4 103.0 +104.0     6  68.3 - 52.1     8 206.1 -206.5     2 155.8 -134.5     7   0.0 - 11.1
   3  51.0  + 45.3     5  65.1 + 68.2     7  86.8 +106.7     9  32.2 + 11.7     3   0.0 - 15.4     8   0.0 -  3.9
   4 193.1  -199.6     6 130.2 +144.8     8 224.6 -227.4    10  55.6 - 66.0     4  99.2 +106.7     9  46.4 - 33.2
   5 185.5  -195.0     7 172.4 +180.2     9  68.3 - 73.9                        5 183.3 +189.7    10  49.6 + 52.3
   6 126.9  +111.0     8 119.0 +119.5    10 135.7 -131.8  h k = 1 1             6   0.0 -115.8
   7  36.9  - 36.7     9 153.0 -147.6                     l= 0  76.3 - 67.6     7  77.8 + 88.3  h k = 6 1
   8  79.2  + 69.8    10 103.0 + 96.1  h k = 6 0           1 284.8 -274.5     8  61.0 - 90.5  l= 0  77.1 + 83.9
   9 106.3  -101.1    11   0.0 +  5.6  l= 0  51.0 + 64.0     2 265.1 -254.9                        1  54.2 + 48.4
  10 186.6  -179.2                        1 189.9 +192.1     3 192.0 -199.3  h k = -3 1            2  38.6 + 41.9
  11  58.6  - 55.9  h k = 4 0             2 113.9 +115.8     4 216.3 +211.5  l= 1 414.6 -401.8     3  65.3 + 66.9
                    l= 0 132.4 +102.5     3  43.4 - 38.6     5 165.2 -173.3     2   0.0 +  3.9     4 105.4 -116.1
h k = -1 0            1 154.0 +146.6     4  55.3 - 57.3     6   0.0 -  9.5     3  50.4 + 33.1     5  94.4 +106.4
l= 1 150.8  -149.8     2  39.1 + 56.2     5 149.7 +157.2     7 160.4 -161.8     4  65.0 + 54.4
   2  31.4  + 32.3     3 267.9 -272.9                       8  96.0 -113.9     5   0.0 +  6.8  h k = -6 1
   3   0.0  +  1.8     4  45.5 + 65.9  h k = -6 0           9  52.7 - 35.0     6  93.6 - 87.5  l= 1  91.2 - 81.7
   4 265.8  -305.3     5  96.6 -100.8  l= 1 137.7 +124.5    10  41.6 - 18.7     7 192.8 -191.6     2  45.6 + 19.0
   5  57.5  + 63.5     6  98.8 +102.7     2 184.4 -172.5                        8  59.8 + 56.8     3 204.6 -199.2
   6  35.8  - 28.4     7  29.3 + 21.5     3  68.3 + 49.0  h k = -1 1            9  73.2 - 70.2     4  96.0 + 94.7
   7  92.2  + 99.7     8  63.0 - 55.9     4 156.2 +154.5  l= 1  48.0 + 44.7    10  27.6 - 19.9     5  46.4 - 45.5
   8  45.5  + 41.2                        5  88.5 + 83.9     2 221.8 -217.0                        6  46.4 - 38.5
   9 120.4  -115.9  h k = -4 0            6 107.4 +100.4     3 329.6 +385.6  h k = 4 1             7 101.4 -136.3
  10 173.5  -157.7  l= 1  39.1 - 53.9     7   0.0 + 11.5     4 133.8 +136.3  l= 0  96.8 - 75.4     8 111.0 -100.5
  11  83.5  + 80.4     2  80.3 - 51.6     8  32.5 - 56.8     5 185.6 +187.1     1 176.2 -155.8     9  96.8 -105.5
                      3 263.6 -255.7     9  65.7 + 87.1     6 108.6 + 65.8     2  39.4 + 21.3
h k = 2 0             4 181.2 +187.7    10  39.1 + 33.5     7   0.0 -  5.5     3 246.2 -242.0  h k = 7 1
l= 0  35.6  + 31.6     5  72.7 + 69.3                       8  41.0 + 34.1     4 152.2 -134.3  l= 0  60.6 + 63.2
   1 253.9  +249.7     6  46.6 + 26.8  h k = 7 0            9 173.8 +173.9     5   0.0 +  4.1     1  65.3 - 68.5
   2 350.5  -382.9     7  40.2 + 23.3  l= 0  95.5 + 76.5    10   0.0 -  7.3     6  54.2 - 50.7     2 192.8 -218.1
   3  86.8  - 74.2     8  83.5 - 75.0     1  84.6 - 90.7    11 116.4 +122.0     7  29.6 + 21.6
   4 206.2  -203.2     9  38.0 - 24.2     2 154.0 +161.2                        8  81.0 -107.7  h k = -7 1
   5   0.0  -  0.5    10  90.0 + 78.7     3   0.0 +  6.2  h k = 2 1             l= 1   0.0 + 10.6
   6  69.4  + 54.1                                        l= 0  63.0 - 49.2  h k = -4 1            2  98.4 + 94.5
   7   0.0  -  5.5                     h k = -7 0           1 236.6 +219.8  l= 1  54.2 + 57.5     3 114.8 + 97.0
   8 172.6  -162.5                     l= 1  41.3 + 15.8     2  63.8 + 57.3     2 118.0 + 93.7     4 158.2 +200.8
   9  57.5  + 52.9                        2   0.0 -  2.0     3   0.0 -  2.0     3 101.4 + 93.4     5  40.2 - 26.7
  10 123.7  -126.0                        3   0.0 -  6.3     4 146.2 -140.3     4   0.0 + 15.3     6  36.2 - 17.9
                                         4  52.1 + 53.0     5  85.0 + 79.0     5 295.8 +320.1     7  54.2 + 76.3
h k = -2 0                               5  61.9 + 52.8     6 166.4 +173.7     6   0.0 +  5.6
l= 1  84.6  - 76.7                        6 190.9 +211.8     7 122.0 +146.1     7  61.6 + 77.4
   2 242.0  -242.3                        7  31.4 - 24.3     8  49.6 - 62.2     8  41.0 - 25.8
   3 218.1  -217.6                        8   0.0 -  6.1     9  29.2 - 44.3     9  38.6 + 36.4
                                                                              10 129.0 +118.1
```

Only the $h0l$ and $h1l$ intensities were used for the refinement of the structures by least squares which was carried out on the Telefunken TR4 computer of this University (program H-562); atomic scattering factors were taken from Moore (1963). For Nb_2Se_3 281 independent reflexions (26 of which had zero intensity) were included in the refinement, all with equal weight. For Ta_2Se_3 only 160 independent reflexions were used in the refinement; 77 weak reflexions (the intensities of which were difficult to estimate accurately) and 39 non-observed reflexions were given zero weight. Several isotropic and anisotropic cycles of refinement were computed; after the last cycle the shifts in the coordinates were less than one tenth of the e.s.d.'s.

The final positional parameters and isotropic temperature factors are listed in Table 1. (Because of uncertainties in the absorption corrections and the scaling factors, the temperature factors are not very reliable; this is especially true of the anisotropic thermal parameters.) The final value of the disagreement index R was 0·0935 for 281 independent $h0l$ and $h1l$ reflexions of Nb_2Se_3 ($R = 0·0877$ for the 255 observed reflexions). For the 160 independent reflexions of Ta_2Se_3 used in the refinement $R = 0·128$; for all 237 observed reflexions of Ta_2Se_3 $R = 0·143$. The final structure factors are listed in Tables 2 and 3. For identification purposes, low-angle powder diffraction data are given in Table 4.

Discussion of the structures

The structure of Nb_2Se_3 and Ta_2Se_3 is shown in Fig. 1; interatomic distances are listed in Table 5. The struc-
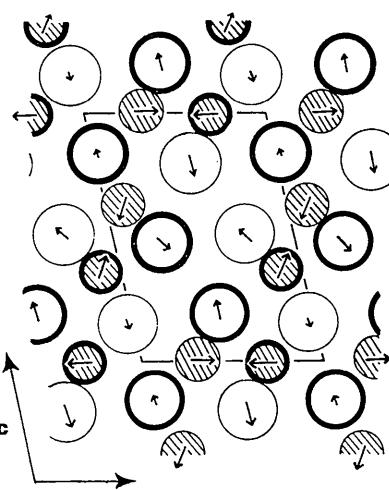

Fig. 1. The structure of Nb_2Se_3 projected along the b axis. Metal atoms are indicated by hatched circles, selenium by open circles. Atoms at $y = \frac{1}{4}$ are drawn with light contours, atoms at $y = \frac{3}{4}$ with heavy contours. The arrows indicate the displacement of the atoms from their 'ideal positions' $2\frac{1}{2}$ times enlarged.
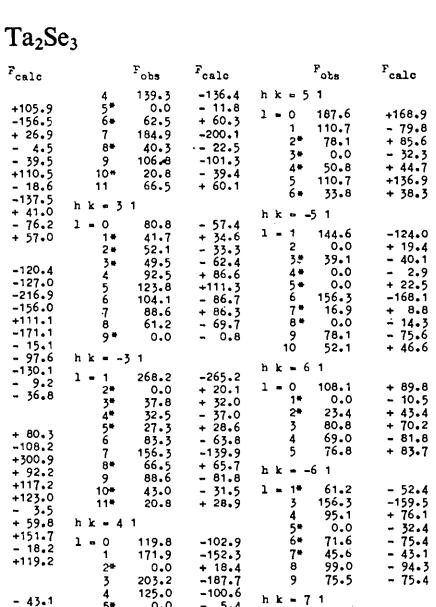
Table 3. *Structure factors of* Ta_2Se_3

h k l	F_{obs}	F_{calc}
h k = 0 0		
1 = 1	39.2	+ 39.8
2	72.0	+101.8
3	70.4	+ 79.4
4*	42.2	+ 31.6
5	150.2	+161.5
6	223.8	+220.7
7*	36.0	- 31.8
8	180.0	+156.1
9*	29.7	+ 28.8
10*	50.1	+ 33.8
11	108.0	+113.5
h k = 1 0		
1 = 0	54.7	+ 38.9
1	56.3	- 42.9
2	123.6	-124.6
3	64.1	+ 52.6
4	140.8	-158.7
5	148.6	-137.7
6	89.2	+ 72.6
7*	75.1	- 84.6
8*	31.3	+ 31.5
9*	70.4	- 47.5
10	136.1	-148.4
h k = -1 0		
1 = 1	126.7	-159.9
2*	32.8	+ 26.0
3*	0.0	- 7.3
4	167.5	-227.7
5	73.6	+ 61.8
6*	40.7	- 43.6
7*	45.4	+ 14.6
8*	48.5	+ 54.7
9	126.7	-103.3
10	112.6	- 93.9
11	84.5	+ 64.9
h k = 2 0		
1 = 0*	0.0	- 11.9
1	161.1	+134.8
2	226.9	-270.2
3*	43.8	- 30.4
4	137.7	-128.0
5*	70.4	- 65.6
6*	29.7	+ 52.9
7*	31.3	- 33.7
8	147.0	-114.9
9*	54.7	+ 48.6
10	108.0	-111.9
h k = -2 0		
1 = 1	147.0	-129.9
2	131.5	-104.5

h k l	F_{obs}	F_{calc}
3	145.6	-164.2
4	136.1	-154.2
5	108.0	+123.2
6	144.0	-149.1
7*	46.9	- 44.8
8*	76.6	- 49.0
9	165.9	-135.0
10*	0.0	- 16.0
11*	51.7	- 36.7
h k = 3 0		
1 = 0	95.5	+ 68.0
1	220.6	+208.0
2	92.3	+ 54.4
3	117.4	+101.4
4	137.7	+134.9
5*	51.7	- 48.4
6	118.9	+119.1
7	148.6	+150.6
8*	46.9	+ 34.2
9	117.4	+129.7
h k = -3 0		
1 = 1	86.1	+ 69.0
2	226.9	+248.0
3	79.8	- 58.2
4	108.0	+109.2
5	98.6	+110.4
6*	82.9	+ 75.7
7	159.6	+171.0
8*	82.9	+ 96.1
9	98.6	- 82.6
10	142.4	+123.1
11*	0.0	+ 10.7
h k = 4 0		
1 = 0*	0.0	- 14.5
1	120.5	+106.5
2*	0.0	+ 7.4
3	173.7	-178.1
4*	68.8	+ 53.8
5*	86.1	-100.9
6*	56.3	+ 37.2
7*	0.0	+ 35.7
8	75.1	- 70.5
h k = -4 0		
1 = 1*	0.0	- 30.2
2*	0.0	- 16.8
3	198.7	-180.8
4	150.2	+133.3
5*	0.0	+ 16.7
6*	0.0	- 29.9
7*	48.5	+ 51.4
8*	57.9	- 65.2
9*	0.0	- 20.0

h k l	F_{obs}	F_{calc}
10*	75.1	+ 70.6
11	75.1	- 66.6
h k = 5 0		
1 = 0	189.3	-178.2
1*	0.0	- 20.9
2*	0.0	- 18.6
3	128.3	-118.4
4*	31.3	- 22.0
5	106.4	- 86.4
6	129.9	-125.8
7*	48.5	+ 53.8
h k = -5 0		
1 = 1*	59.5	+ 48.8
2	145.6	-132.5
3	158.0	-130.6
4*	67.3	- 49.5
5	101.7	- 95.6
6*	50.1	- 50.5
7*	31.3	+ 58.4
8	156.5	-200.7
9*	68.8	- 51.1
10	93.9	- 84.8
h k = 6 0		
1 = 0*	57.9	+ 39.5
1	136.1	+120.3
2	123.6	+141.0
3*	0.0	- 13.3
5	108.0	+119.4
h k = -6 0		
1 = 1	167.5	+130.0
2	108.0	- 85.0
3*	86.1	+ 76.7
4	151.8	+146.8
5*	70.4	+ 29.4
6	97.0	+104.5
9	108.0	+113.8
10	31.3	+ 21.2
h k = 7 0		
1 = 0*	65.7	+ 54.7
1	72.0	- 81.2
2	90.7	+100.7
h k = -7 0		
1 = 1*	0.0	+ 33.4
5*	26.6	- 45.9
6	114.2	+160.2
h k = -8 0		
1 = 1	90.7	-120.4
2	108.0	-140.9

h k l	F_{obs}	F_{calc}
h k = 0 1		
1 = 1	87.3	+105.9
2	125.0	-156.5
3*	22.2	+ 26.9
4*	0.0	- 4.5
5*	31.3	- 39.5
6	123.8	+110.5
7*	17.0	- 18.6
8	157.6	-137.5
9*	37.8	+ 41.0
10	79.5	- 76.2
11	59.9	+ 57.0
h k = 1 1		
1 = 0	123.8	-120.4
1	145.9	-127.0
2	209.7	-216.9
3	147.1	-156.0
4	121.1	+111.1
5	162.8	-171.1
6*	23.5	- 15.1
7	104.1	- 97.6
8	132.8	-130.1
9*	0.0	- 9.2
10	52.1	- 36.8
h k = -1 1		
1 = 1	79.5	+ 80.3
2	119.8	-108.2
3	221.4	+300.9
4	95.1	+ 92.2
5	125.0	+117.2
6	121.1	+123.0
7*	0.0	- 3.5
8	78.1	+ 59.8
9	179.7	+151.7
10*	0.0	- 18.2
11	123.8	+119.2
h k = 2 1		
1 = 0	50.8	- 43.1
1	230.5	+192.8
2	76.8	+ 72.5
3*	41.7	- 33.9
4	148.4	+158.1
5*	63.8	+ 44.2
6	123.8	+109.0
7	145.9	+148.7
8*	23.5	- 36.5
9*	0.0	+ 13.1
10	102.9	+100.4
h k = -2 1		
1 = 1	178.4	-167.6
2	115.9	-122.5
3	52.1	- 36.6

h k l	F_{obs}	F_{calc}
4	139.3	-136.4
5*	0.0	- 11.8
6*	62.5	+ 60.3
7	184.9	-200.1
8*	40.3	- 22.5
9	106.4	-101.3
10*	20.8	- 39.4
11	66.5	+ 60.1
h k = 3 1		
1 = 0	80.8	- 57.4
1*	41.7	+ 34.6
2*	52.1	- 33.3
3*	49.5	- 62.4
4	92.5	+ 86.6
5	123.8	+111.3
6	104.1	- 86.7
7	88.6	+ 86.3
8	61.2	- 69.7
9*	0.0	- 0.8
h k = -3 1		
1 = 1	268.2	-265.2
2*	0.0	+ 20.1
3*	37.8	+ 32.0
4*	32.5	- 37.0
5*	27.3	+ 28.6
6	83.5	- 63.8
7	156.3	-139.9
8*	66.5	+ 65.7
9	88.6	- 81.8
10*	43.0	- 31.5
11*	20.8	+ 28.9
h k = 4 1		
1 = 0	119.8	-102.9
1	171.9	-152.3
2*	0.0	+ 18.4
3	203.2	-187.7
4	125.0	-100.6
5*	0.0	- 5.4
6	87.3	-101.0
7*	0.0	+ 9.2
8	74.3	- 63.5
h k = -4 1		
1 = 1*	48.2	+ 23.1
2	164.1	+131.9
3	99.0	+ 75.7
4	45.6	+ 32.0
5	261.7	+263.8
6*	0.0	+ 6.3
7	69.0	+ 67.9
8*	45.6	+ 50.5
9*	0.0	+ 14.2
10	134.1	+122.1
11	131.6	+148.8

h k l	F_{obs}	F_{calc}
h k = 5 1		
1 = 0	187.6	+168.9
1	110.7	- 79.8
2*	78.1	+ 85.6
3*	0.0	- 32.3
4*	50.8	+ 44.7
5	110.7	+136.9
6*	33.8	+ 38.3
h k = -5 1		
1 = 1	144.6	-124.0
2	0.0	+ 19.4
3*	39.1	- 40.1
4*	0.0	- 2.9
5*	0.0	+ 22.5
6	156.3	-168.1
7*	16.9	+ 8.8
8*	0.0	- 14.3
9	78.1	- 75.6
10	52.1	+ 46.6
h k = 6 1		
1 = 0	108.1	+ 89.8
1*	0.0	- 10.5
2*	23.4	+ 43.4
3	80.8	+ 70.2
4	69.0	- 81.8
5	76.8	+ 83.7
h k = -6 1		
1 = 1*	61.2	- 52.4
3	156.3	-159.5
4	95.1	+ 76.1
5*	0.0	- 32.4
6*	71.6	- 75.4
7*	45.6	- 43.1
8	99.0	- 94.3
9	75.5	- 75.4
h k = 7 1		
1 = 0*	20.8	+ 42.8
1	69.0	- 70.0
2	113.3	-153.0
3*	0.0	- 17.0
h k = -7 1		
1 = 1	79.5	+ 77.4
2	86.0	+ 89.3
3*	66.5	+ 57.6
4	156.3	+171.0
5*	0.0	- 8.4
6*	0.0	+ 21.9
7	92.5	+112.1
h k = -8 1		
1 = 1	48.2	+ 62.0
2	78.1	-106.6
4*	28.7	+ 44.0

*not included in refinement.

ture may be regarded as based on a close packing of selenium of the type chh; Se(1) and Se(2) together form the h-packed layers, Se(3) the c-packed layers. (For a definition of the symbols c and h see e.g. Wells, 1962). The octahedral holes between adjacent h-packed selenium layers are filled by the Nb,Ta(1) atoms, while half of the octahedral holes between h- and c-packed selenium layers are occupied by Nb,Ta(2), the other half being vacant. An undistorted structure of this type would have an axial ratio $a:b:c=1:\frac{1}{3}\sqrt{3}:\frac{1}{3}\sqrt{19}$, a monoclinic angle $\beta = \arccos(-\sqrt{1/19})$, and the 'ideal' atomic parameters included in Table 1.

The deviations of the actual structures from the ideal one can be understood in terms of the formation of infinite zigzag metal–metal chains running in the **b** direction (cf. Fig. 1). The **b** axes are considerably shorter than in the ideal structure. Moreover, the Nb(1) atoms have moved from their ideal positions by 0·41 Å (Ta(1) by 0·44 Å) in the direction of the octahedron face formed by Se(1); the Se(1) atoms are pushed away from their ideal positions by 0·33 Å. In this way Nb(1)–

Nb(1) and Ta(1)–Ta(1) chains are formed with metal–metal distances comparable to those in the pure metals. (In b.c.c. Nb and Ta the shortest metal–metal distances are 2·86 Å; the derived metal radius for twelve-coordination is 1·47 Å).

The Nb(2) and Ta(2) atoms also form zigzag chains in the **b** direction, but in these chains the metal–metal distances are considerably longer (cf. Table 5). The Nb,Ta(2) atoms have moved by 0·29 Å from their ideal positions in the direction of the octahedron face formed by Se(3); the latter atoms are pushed away by 0·22 Å. The Se(2) atoms are only slightly – by 0·10 Å – displaced from their ideal positions.

Thus, each metal atom has three selenium neighbours at short distances (average 2·55 Å) and three more selenium neighbours at larger distances (average about 2·75 Å). The Se(2) atoms have five metal neighbours at long distances, Se(3) three metal neighbours at short distances, while Se(1) has three metal atoms at short distances and one at a long distance (cf. Table 5). The Nb(Ta)–Se distances may be compared

Table 4. *Low-angle powder data of* Nb_2Se_3 *and* Ta_2Se_3

Cu $K\alpha$ radiation.

	Nb_2Se_3					Ta_2Se_3	
$10^5 \sin^2\theta_{obs}$	d_{obs} (Å)	I^*	h k l		$10^5 \sin^2\theta_{obs}$	d_{obs} (Å)	I^*
739	8·96	5	0 0 1		754	8·87	11
1477	6·338	3	1 0 0		1502	6·29	9
1736	5·846	70	−1 0 1		1758	5·81	100
2701	4·686	1	1 0 1		2741	4·65	11
2956	4·480	20	0 0 2		2968	4·47	37
3479	4·129	3	−1 0 2				
5418	3·309	10	1 0 2		5450	3·299	35
5714	3·222	8	−2 0 1		5722	3·220	25
5787	3·201	7	0 1 1		5869	3·179	18
5943	3·159	3	2 0 0				
6508	3·019	3	1 1 0		6595	2·999	7
6655	2·985	5	{ 0 0 3 { −1 0 3				
6769	2·960	1	−1 1 1				
6936	2·924	96	−2 0 2		6972	2·917	23
7635	2·787	28	2 0 1		7718	2·772	21
7737	2·769	21	1 1 1		7849	2·749	18
7981	2·726	17	0 1 2		8104	2·706	25
8490	2·643	17	−1 1 2		8607	2·626	11
9662	2·477	58	−2 0 3		9673	2·477	30
10439	2·384	15	1 1 2		10546	2·372	26
10739	2·350	13	−2 1 1		10804	2·343 }	42
10816	2·342	61	2 0 2		10870	2·336 }	
11352	2·286	100	−1 0 4		11374	2·284	39
11698	2·252	31	−1 1 3		11777	2·245	58
11980	2·225	6	−2 1 2		12048	2·219	11
12668	2·164	9	2 1 1		12784	2·154	16
13385	2·105	46	−3 0 2		13409	2·103	35
13876	2·067	40	−2 0 4		13876	2·068	9
14620	2·014	8	1 1 3 }		14756	2·005	5
14694	2·009	5	−2 1 3 }				
15230	1·973	13	1 0 4		15342	1·966	12
15531	1·954	8	3 0 1 }		15620	1·949	18
15620	1·948	12	−3 0 3 }				
16388	1·902	4	−1 1 4		16492	1·897	7
17541	1·839	4	−1 0 5				
17660	1·832	48	−3 1 1		17740	1·829	28

* Peak intensities from diffractograms.

Table 5. *Interatomic distances* (Å) *in* Nb_2Se_3 *and* Ta_2Se_3

		Nb_2Se_3	Ta_2Se_3			Nb_2Se_3	Ta_2Se_3
Nb,Ta(1)-2 Se(1)		2·562	2·53	Se(1)-1 Se(3)		3·193	3·16
-1 Se(1)		2·573	2·59	-2 Se(3)		3·412	3·42
-2 Se(2)		2·711	2·71	-2 Se(1)		3·434	3·408
-1 Se(2)		2·891	2·92	-2 Se(2)		3·645	3·59
				-2 Se(2)		3·757	3·80
Nb,Ta(2)-1 Se(3)		2·502	2·49	-1 Se(2)		3·888	3·83
-2 Se(3)		2·572	2·56	-2 Se(1)		4·188	4·21
-2 Se(2)		2·720	2·72				
-1 Se(1)		2·716	2·76	Se(2)-2 Se(2)		3·434	3·408
				-2 Se(2)		3·441	3·42
e.s.d. Nb,Ta-Se		0·005–	0·02	-2 Se(3)		3·633	3·62
		0·006		-2 Se(1)		3·645	3·59
				-2 Se(1)		3·757	3·80
Nb,Ta(1)-2 Nb,Ta(1)		2·972	2·92	-1 Se(1)		3·888	3·83
-1 Nb,Ta(2)		3·329	3·33	-1 Se(3)		3·984	3·99
-2 Nb,Ta(1)		3·434	3·408				
				Se(3)-1 Se(1)		3·193	3·16
Nb,Ta(2)-2 Nb,Ta(2)		3·127	3·11	-2 Se(3)		3·382	3·38
-1 Nb,Ta(1)		3·329	3·33	-2 Se(1)		3·412	3·42
-2 Nb,Ta(2)		3·434	3·408	-2 Se(3)		3·434	3·408
				-2 Se(2)		3·633	3·62
e.s.d. Nb,Ta-Nb,Ta		0·006–	0·015	-1 Se(2)		3·984	3·99
		0·007		-2 Se(3)		3·997	3·98
				e.s.d. Se-Se		0·006–	0·03–
						0·009	0·04

with those in 2s–$NbSe_2$ (2·60 Å) and 2s–$TaSe_2$ (2·59 Å); in these phases, however, the metals have trigonal-prismatic coordination (Brown & Beerntsen, 1965).

It may be remarked that in Mo_2S_3, which is isotypic with Nb_2Se_3 and Ta_2Se_3, the metal–metal distances in both the Mo(1)–Mo(1) and Mo(2)–Mo(2) chains are comparable to those in pure molybdenum metal (Jellinek, 1961; de Jonge et al., 1967). This may be related to the fact that Mo has one more d-electron than Nb or Ta (Mo^{3+} has three d-electrons, Nb^{3+} and Ta^{3+} two d-electrons). Zigzag Nb–Nb chains quite similar to the Nb(1)–Nb(1) chains in Nb_2Se_3 are also found in Nb_3Te_4, Nb_3Se_4 and Nb_3S_4; the Nb–Nb distances are 2·97 Å in Nb_3Te_4 (Selte & Kjekshus, 1964a) and 2·881 Å in Nb_3S_4 (Ruysink, Kadijk, Wagner & Jellinek, 1968). In contrast to Nb_2Se_3, all metal atoms in the Nb_3X_4 phases are incorporated in the short-distance Nb–Nb chains; the average degree of oxidation of the metal is $Nb^{2·67+}$ corresponding to an average of 2·33 d-electrons left on the metal atoms which may be involved in metal–metal bonding.

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