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The Crystal Structures of Nb₃Se₄ and Nb₃Te₄

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The compounds Nb₃Se₄ and Nb₃Te₄ are isostructural. The hexagonal unit cells have the dimensions:

$$Nb_3Se_4: a = 10.012, c = 3.4707 \text{ Å};$$

 $Nb_3Te_4: a = 10.671, c = 3.6468 \text{ Å}.$

The space group is $P6_3/m$ (C_{6h}^2) and the unit cell contains 6Nb and 8Te(Se) in the positions:

 $\begin{array}{l} 6 \mbox{ Nb in } (h) \pm (x, \, y, \, \frac{1}{4}; \, \overline{y}, \, x-y, \, \frac{1}{4}; \, y-x, \, \overline{x}, \, \frac{1}{4}) \\ \mbox{ with } x_1 = 0.4886, \, y_1 = 0.1039. \\ 2 \mbox{ Te in } (c) \pm (\frac{2}{3}, \, \frac{1}{3}, \, \frac{3}{4}). \\ 6 \mbox{ Te in } (h) \mbox{ with } x_2 = 0.3389, \, y_2 = 0.2731. \end{array}$

The relationships to the Ti_5Te_4 type structure of the Nb_5Se_4 and Nb_5Te_4 phases and the NbS_2 (H)like structure of the $Nb_{1+x}Se_2$ phase are discussed.

Introduction

In recent communications by Selte & Kjekshus (1963, 1964) the crystallographic properties of the Nb₅Te₄, Nb₅Se₄ and Nb_{1+x}Se₂ phases have been described. The present paper is concerned with the crystal structures of two previously unknown niobium selenide and telluride* phases. The compositions were found to be Nb₃Se₄ and Nb₃Te₄ by X-ray and density measurements.

A variety of samples were prepared by heating accurately weighed quantities of the components (in different proportions) in evacuated and sealed silica tubes. The samples were heated at various temperatures between 500 and 1350 °C and quenching in ice water as well as slow cooling was used. Single crystals, grown from the vapour phase, were found in the telluride samples. Certain difficulties in the preparation of the samples resulted from reaction between the niobium and the silica (Selte & Kjekshus, 1963, 1964).

The atomic arrangement in these structures is of considerable interest, especially its resemblance to the neighbouring phases in the niobium-selenium and niobium-tellurium systems, *i.e.* the Nb₅Se₄, Nb_{1+x}Se₂, Nb₅Te₄ and NbTe₂ phases.

Unit cell and space group

Guinier photographs (taken with strictly monochromatized Cu $K\alpha_1$ radiation, $\lambda_{\alpha_1} = 1.54050$ Å, with potassium chloride, a = 6.2919 Å (Hambling, 1953) added as internal standard) could be indexed on hexagonal axes with the following unit cell dimensions (cf. Table 1):

Nb₃Se₄; a = 10.012, c = 3.4707 Å, c/a = 0.3467. Nb₃Te₄; a = 10.671, c = 3.6468 Å, c/a = 0.3418.

The lattice dimensions were approximately constant

^{*} The niobium tellurides have also been studied by Grigorjan, Simanov & Novoselova (1960) and by Novoselova, Grigorjan & Simanov (1960). They reported *inter alia* the existence of a phase with composition in the range $NbTe_{1.00}$ to $NbTe_{1.70}$. The available data indicate that their $NbTe_{1.00-1.70}$ phase is identical with the present Nb_3Te_4 phase.

over a range of composition of the starting material for each substance. This shows that the ranges of homogeneity must be rather narrow.

On the basis of the observed densities at 25.00 °C, 6.70 g.cm⁻³ (Nb₃Se₄) and 7.20 g.cm⁻³ (Nb₃Te₄), the unit cell contains $2 Nb_3 X_4$ groups ($Z_c = 2.04$ for Nb₃Se₄ and $Z_c = 1.98$ for Nb₃Te₄).

The only systematically missing reflexions were of the type

00*l* when
$$l = 2n + 1$$
.

The Laue symmetry is 6/m and the possible space groups are $P6_3$ (C_6^6) and $P6_3/m$ (C_{6h}^2).

Table 1. Guinier photograph data of Nb₃Se₄ and Nb₃Te₄ taken with strictly monochromatized Cu $K\alpha_1$ radiation

$\sin^2 \theta \times 10^5$	l _o	
$\mathrm{Ib}_3\mathrm{Se}_4$	Nb ₃ T	e ₄
) s	698	\$
ł vw	2088	w
vw	4858	vw
l w	5156	w
3 w	6258	m
ó vw	6545	m
i m	7248	vs
m	9035	8
3 8	9330	vs
ó w	10713	vw
i vw	11115	vw
) m	12799	m
vw	13192	vw
8 w	13486	w
8 w	14592	w
	17362	vw
8 m	17644	w
e m	17854	w
vw vw	18561	vw
	18721	vw
	19073	vw
w	19437	w
) vw	21515	vw
	21813	w
vw	23209	vw
vw	24121	vw
	$\sin^2 \theta \times 10^5$ $\log_3 Se_4$ vw ww ww ww m m s ww ww m www www wwwwwwwwwwwwwwwwwwwwww	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Determination of the structure of Nb₃Te₄

Well formed, needle-like, single crystals of Nb₃Te₄ with hexagonal cross-sections were investigated in an integrating Weissenberg camera with Cu K radiation. Intensity measurements of the hk0 and hk1reflexions were carried out microphotometrically (except for the weakest reflexions, which were estimated visually by comparison with a calibrated scale) on the Weissenberg photographs, using the multiple-film technique. Corrections for the combined Lorentz and polarization factor were made. No corrections for absorption, extinction or temperature factors were applied. For the calculation of F_c values the atomic scattering factors were taken from Forsyth & Wells (1959) for the hk0 reflexions and from Vand, Eiland & Pepinsky (1957) for the hk1 reflexions. The agreement between F_o and F_c is expressed by the reliability index $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. F_c values corresponding to the weakest reflexions, which were determined less accurately than the others, or to undetected reflexions, were not used in the calculation of R indices.

As both space groups have symmetry p6 in the (001) projection, it was decided to start with a Patterson projection on the basis of the corrected $F_{\alpha}^{2}(hk0)$ values. The [001] direction is specially suitable because of the short c axis and because the crystal has a section not far from circular along the caxis. Tentative atomic positions could be deduced from the Patterson map and a set of structure factors calculated on this basis gave R = 0.278. A Fourier synthesis was evaluated, which clearly showed all atoms resolved. The atomic parameters were refined further by means of two Fourier and two difference syntheses. R decreased to 0.155 after the Fourier syntheses and to 0.088 after the second difference synthesis. The observed and calculated F(hk0) values are listed in Table 2, and the final Fourier map is shown in Fig. 1. The corresponding parameters are:

$6\mathrm{Nb}$	in	$x_1 = 0.4886,$	$y_1 = 0.1039$,	etc.
$2{ m Te_I}$	in	$x = \frac{2}{3},$	$y = \frac{1}{3},$	etc.
6 Te _{II}	in	$x_2 = 0.3389,$	$y_2 = 0.2731$,	etc.

The short c axis indicates that the z parameters for all atoms are 0 and $\frac{1}{2}$ or $\frac{1}{4}$ and $\frac{3}{4}$.



Fig. 1. Electron-density projection of Nb₃Te₄ on (001). Contours are at intervals of 10 e.Å⁻². The zero contours are broken.

The crystals were needle-shaped in the direction of the *c* axis and the intensities for projections other than (001) would therefore suffer from absorption errors which are difficult to correct for. Intensities of *hk*1 reflexions were accordingly evaluated. R=0.141for F(hk1) was obtained on the basis of the arrangement suggested in Fig. 2, which in terms of the space group $P6_3/m$ (C_{6h}^2) is as follows:

Table 2. Observed and calculated structure factors for Nb_3Te_4

The three numbers in each column represent respectively $k,\;10F_o$ and $10F_c$

~	1780 -2029	7 0 <u>-124</u> 8 1474 -1681	-6 818 -758	3	3466	4010
ŝ	258 -276		-5 1818 1870	4	934 1478	-984 1628
4	1464 -1587	-13 1433 1241	-3 1635 1661	ć	1136	1090
2	3861 -3783	-12 0 413	-2 1843 -2069		b=3. 1	-1.
7	2544 -2544	-10 3091 3145	0 0 -429	-9		392
8	0 335	-9 575 -374	1 1111 -1274	-8 -7	4468	5398
9	0 -492	-7 2653 2221	3 876 1037	-6	2832	2760
••	h=1, 1=0.	-6 1955 2109	b-10 1-0	-5	5466 1008	
-9	1170 1131	-4 3762 3872	-11 0 -484	-3	1874	-1772
-8	0 427	-3 2193 -2463	-10 0 -152	-2 -1	1858	-5454
-6	1597 -1514	-1 567 -383	-8 3713 3527	ō	1870	1790
-5	3762 3879 3625 -3526	0 3861 -3785	-7 1643 -1492	2'	2524	-2020
-3	901 -967	2 2653 2752	-5 3091 3146	3	2832	2724
-2	1780 -2031	5 2700 -2040 4 1408 1886	-3 1837 -1839	5	3508	-2390
0	1780 -2026	5 3091 3145	-2 3241 3101		հաև 1	-1
2	698 -551	7 0 -345	0 0 -160	-9	0	-328
3	4621 5198	8 1519 1824	1 498 653	-8 -7	3466	-3424
5	1955 2114	h=6, 1=0.	2 0 -74	-6	934	-913
6	2543 2845	-13 1180 -1298	h=11, 1=0.	-5	1198	1294
έ	1170 -1020	-11 555 539	-9 2165 -2155	-3	2524	2990
9	587 -713	-10 0 -822 -0 1635 1674	-8 1692 -1854 -7 0 46	-2 -1	3902 1998	3990 1372
	h=2, 1=0.	-8 0 -50	-6 1111 -1437	ō	0	394
-11	2165 -2133	-7 2543 2851 -6 514 514	-5 785 552 -4 0 -117	1	0	-716
-9	1428 996	-5 1597 -1528	-3 1070 724	3	1456	-1730
-7	2653 2742	-4 2176 1849 -3 1386 1345	-2 1909 1922 -1 0 -489	4	9400	- 7072
-6	2176 1843	-2 3140 -3510	0 0 147	-9	h=5,] 0	.=1. 420
<u>_</u> 4	353 393	0 514 509		-á	3508	-24.54
-3	698 -551 258 -275	1 1038 -956	h=12, 1=0. -9 876 1026	-7 -6	1478	1638
-1	1277 -1121	3 578 -757	-8 1318 1178	-5	3846	-3916
1	258 -279 901 -968	4 0 - 309 5 1111 - 1437	-6 973 -964	-3	2496	1588
2	353 405	6 973 -950	-5 0 -351	-2	3466	-3914
4	3140 -3502	1 914 114	-3 619 -494	-0	3846	3786
5	2653 2225	h=7, 1=0.	hel3 1-0	1	0	-614
7	1843 -2060	-12 0 347	-8 1433 1251	3	4468	5272
8	3241 3108	-11 0 -134 -10 1837 -1848	-7 1055 -1299 -6 746 770		h⇔6. 1	=].
,	1,00 1,11	-9 1843 -2050	-5 1519 1826	-9	2128	2628
-12	h=3, 1=0. 876 1035	-8 0 227 -7 2544 -2529		-8 -7	1900	-1732
-11	1692 -1866	-6 1038 -942	b-0 1-1 <i>i</i>	-6	0	-204
-10 -9	818 -755	-5 2055 2752	1 088 1116	-?	910	-0,00
•	a=((a0ac		1 200 1110	-4	_ 0	
-8	2766 -2835	-3 492 -424	2 3632 -3960 3 1870 -1801	-4 -3 -2	0 2832 1322	-2742
-8 -7 -6	2766 -2835 1391 1416 1386 1359	-3 492 -424 -2 2653 2218 -1 2543 2846	2 3632 -3960 3 1870 -1801 4 0 -440	-4 -3 -2 -1	0 2832 1322 0	-2742 1458 -550
-8 -7 -6 -5	2766 -2855 1391 1416 1386 1359 1818 -1301 4621 5198	-3 492 424 -2 2653 2218 -1 2543 2846 0 2544 -2542 1 0 419	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-4 -3 -2 -1 0 1	0 2832 1322 0 1870	-2742 1458 -550 190 -1962
-76-54-50	2766 -2855 1391 1416 1386 1359 1818 -1301 4621 5198 3676 3674	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3652 -3960 3 1870 -1801 4 0 -440 5 3846 -3778 6 0 -114 7 4438 4392 8 1021 0078	-4 -3 -2 -1 0 1 2	0 2832 1322 0 1870 0	-2742 1458 -550 190 -1962 -426
-7 -6 -5 -4 -5 -2 -1	2766 -2835 1391 1416 1386 1359 1818 -1301 4621 5198 3676 3674 901 -970 698 -558	-3 462 -424 -2 2653 2218 -1 2543 2846 0 2544 -2542 1 0 419 2 1428 989 3 1643 -1496 4 0 43	2 362 -3960 3 1870 -1801 4 0 -440 5 3846 -3778 6 0 -114 7 4436 4392 8 3014 -2978	-4 -3 -2 -1 0 1 2	0 2832 1322 0 1870 0 h=7, 1	-2742 1458 -550 190 -1962 -426
-7-6-5-4-3-2-10	2766 -2835 1391 1416 1386 1359 1818 -1301 4621 5198 3676 3674 901 -970 698 -558 3676 3675	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3652 -3360 3 1870 -1801 4 0 .440 5 3846 -3778 6 0 .114 7 4436 4392 8 3014 -2976 h=1, 1=1. 8 506	-4 -3 -2 -1 0 1 2 -9	0 2832 1322 0 1870 0 1870 0 h=7, 2 1660 2614	-2742 1458 -550 190 -1962 -426 L=1. 1684
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-87654321012345678 21109876	2/06-2655 1/921 1416 1/921 1416 1/926 13599 4621 5198 5676 5673 901 -970 698 -558 5676 5673 1957 -24588 1956 -552 1957 -24588 1957 -1858 1757 727 h=4, 1=0. 1918 1150 0 42 0 -319 1818 11855 1078 -1028 1078 -1028 10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3632 -3960 3 1870 -1801 4 0 _440 5 3846 -3778 6 0 _114 7 4436 4392 8 3014 -2978 h=1, 1=1. -8 0 596 -7 1870 -2992 -6 970 834 -5 0 398 -4 3524 -3934 -3 2858 -936 -2 2254 2284 2 4296 5378 3 1998 -1300 4 1196 1170 5 0 658 6 1900 -1676 7 2614 -5088	4321012 987654374101 876544	0 0 28322 1322 2322 1322 2322 1322 232 232 232	-2742 1458 -550 190 -1962 -426 -426 -426 -426 -428 -2992 -4492 20200 -1546 -1684 -2992 -1646 -1684 -518 H=1. -3056 -458 -458 -458 -458 -458 -558 -458 -5
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	2/66-2655 1/921 1416 1/921 1416 1/926 1259 6/76 3/67 901 -970 6/86 -558 5/76 3/675 5/25 -5525 2/95 -2458 1/936 1346 1/95 1665 1/951 1655 1/951 1/95 1/951 1/95	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-3-2-1012 -98-7-65-4-3-2-101 8-7-65-4-3-2-10	0 0 28322 1322 1322 1322 1322 1322 1322 1322 1322 1322	-2742 -2742 -2962 -550 -550 -1962 -2992 -1964 -2992 -1964 -2992 -1984 -1646 -1636 -1636 -4580 -4580 -4586 -4488 -45554 -45554 -4565 -456 -4
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3632 -3960 3 1870 -1801 4 0 .448 5 3846 -3778 6 0 .1114 7 4495 4392 8 3014 -2978 h=1, 1=1. -8 0 596 -7 1870 -2092 -7 0 398 -5 0 398 -4 3524 -2985 -2 2254 2284 -1 988 -1096 0 988 1090 1 2254 2258 2 4298 5378 3 1998 -1300 4 1108 1170 5 106 638 6 1900 -1676 7 2614 -3088 h=2, 1=1. -9 0 950 -7 0 -572 -7 0 -572 -7 0 -572 -7 0 -572	-32-1012 98-7654 34101 87-654 3410	0 0 28322 322 322 322 322 322 322 322 322 3	-2742 -2742 -2942 -550 -550 -1962 -2992 -1964 -2992 -1964 -1656 -198 -1646 -1656 -4580 -4580 -4580 -4580 -4580 -1026 -2450
	2/66-2655 1/921 1416 1/921 1416 1/926 1359 6/76 3/674 5/76 3/74 1/926 -358 5/76 3/74 1/936 1346 1/956 -358 1/936 1346 1/956 -358 1/936 1346 1/956 -358 1/956 1346 1/956 -358 1/956 1346 1/956 1346 1/956 -358 1/956 1346 1/956 -358 1/956 -35	$\begin{array}{c} -3 & 1652 & -424 \\ -2 & 2653 & 2218 \\ -1 & 2543 & 2846 \\ 0 & 2544 & -2542 \\ 1 & 0 & 439 \\ 2 & 1428 & 969 \\ 3 & 1643 & -1496 \\ 4 & 0 & 43 \\ 5 & 0 & 402 \\ 6 & 1055 & -1297 \\ \mathbf{h} = 3, 1 = 0, \\ -13 & 1520 & 1827 \\ -14 & 1520 & 1827 \\ -15 & 1520 & 1827 \\ -15 & 1520 & 1827 \\ -10 & 324 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 324 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 324 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 324 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 324 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 324 & 3108 \\ -5 & 2766 & -2846 \\ -4 & 1078 & -1014 \\ -3 & 2501 & -2053 \\ -2 & 0 & 0 & -355 \\ -1 & 0 & 242 \\ 0 & 0 & 333 \\ 1 & 1170 & 1136 \\ 2 & 3713 & 3524 \\ 4 & 1538 & 1186 \\ 5 & 1432 & 1238 \\ \mathbf{he0} & 1=0 \\ \end{array}$	2 3632 - 3960 3 1870 - 1801 4 0 .440 5 3846 - 3778 6 0 .1114 7 4439 4392 8 3014 - 2976 h=1, 1=1. -8 0 596 -7 1870 - 2092 -6 970 834 -3 2858 - 3934 -3 2858 - 3934 -2 2254 2284 -1 998 1090 1 2294 2258 3 1998 - 1096 1 2294 2258 3 1998 - 1300 1 2294 2258 3 1998 - 1300 1 2294 2258 6 1900 - 1676 6 1900 - 1676 7 2614 - 3088 h=2, 1=1. -9 0 950 -7 0 -572 -6 954 - 12844 -5 2496 - 1580	-4,-3,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,	0 0 28322 0 28322 0 28322 0 0 2 1322 0 0 2 1322 0 1870 0 0 1870 0 1670 26514 4438 0 1456 6 26514 4438 0 0 1478 1390 0 1478 3914 0 0 1478 3914 0 0 0 0 1478 3914 0 0 0 0 0 14568 39488 35508 25514 35514 1135 25514 1151 1151 1151 1151 1151 1151 11	-2742 1458 -550 1900 -1962 -1962 -1962 -1968 -2992 742 1988 -2992 742 1988 -1646 1636 -4580 -4580 -1646 -45800 -45800 -4580 -45800 -45800 -
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} -3 & 1652 & -424 \\ -2 & 2653 & 2218 \\ -1 & 2543 & 2894 \\ 0 & 2544 & -2542 \\ 1 & 0 & 439 \\ 2 & 1428 & 939 \\ 3 & 1643 & -1495 \\ 4 & 0 & 43 \\ 5 & 0 & 402 \\ 6 & 1055 & -1297 \\ \\ h -8, 1 = 0, \\ -15 & 1520 & 1827 \\ -16 & 1520 & 1827 \\ -12 & 1474 & -1675 \\ -11 & 1520 & 1827 \\ -12 & 1474 & -1675 \\ -11 & 1520 & 1827 \\ -10 & 3241 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 3241 & 3108 \\ -9 & 1170 & -1030 \\ -10 & 325 & -748 \\ -5 & 2766 & -2846 \\ -4 & 1078 & -1014 \\ -3 & 2301 & -2055 \\ -2 & 0 & -355 \\ -2 & 0 & -355 \\ -2 & 0 & -355 \\ -2 & 0 & -355 \\ -1 & 0 & 242 \\ 0 & 0 & 3333 \\ 1 & 1170 & 1136 \\ 2 & 3713 & 3524 \\ 3 & 1652 & -1864 \\ 4 & 1518 & 1186 \\ 5 & 1432 & 1238 \\ h =9, 1 =0, \\ -12 & h =9, 1 =0, \\ -12 & h =9, 1 =0, \\ \end{array}$	2 3632 -3960 3 1870 -1801 5 3846 -3778 6 0 -1114 7 44.98 4392 8 3014 -2978 h=1, 1=1. -8 0 596 -7 1870 -2092 -6 970 834 -5 2094 -3934 -3 368 -1096 1 2254 -2384 -1 988 -1096 1 2254 -2284 -1 988 -1096 1 2254 -2284 -2 2284 -2384 -1 988 -1096 1 2254 -2284 -3 1998 -1109 1 2254 -2384 -1 988 -1096 1 2254 -2384 -1 988 -1096 1 2254 -2384 -2 2294 -3368 h=2, 1=1. -9 0 950 -7 0 -672 -7 0	-4 -4 -3 -3 -2 -2 -1 -1 -0 -1 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	0 0 28322 0 28322 0 2 1870 0 0 1870 0 0 1650 2614 4438 0 1456 6 2614 4 4438 0 0 1456 6 1478 0 1478 0 0 0 1478 0 2614 3 3014 1 1130 0 2614 3 3014 1 1130 0 2614 3 3014 1 1130 0 2614 1 3014 1 1130 0 2614 1 1130 0 2614 1 1130 0 2614 1 1130 0 2614 1 1130 0 2614 1 1130 0 1130 0 11174 0	-2742 1458 -550 1900 -1962 -1962 -1964 -2992 -2920 742 1986 -4580 -4580 -4580 -4580 -4580 -4580 -1066 -4580 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -4580 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -1066 -2070 -1066 -
	$\begin{array}{c} 2 & (66 - 265)5\\ 1 & (96 - 265)5\\ 1 & (96 - 135)6\\ 1 & (96 - 135)6\\ 1 & (196 - 135)1\\ 1 & (1818 - 1301)\\ 1 & (1818 - 130$	$\begin{array}{c} -3 & 1652 & -424 \\ -2 & 2653 & 2218 \\ -1 & 2543 & 2894 \\ 0 & 2544 & -2542 \\ 1 & 0 & 419 \\ 2 & 1428 & 939 \\ 3 & 1643 & -1496 \\ 4 & 0 & 43 \\ 5 & 0 & 402 \\ 6 & 1055 & -1297 \\ \\ h -8, 1 = 0, \\ -15 & 1520 & 1827 \\ -16 & 1520 & 1827 \\ -12 & 1474 & -1675 \\ -111 & 1577 & 720 \\ -10 & 3241 & 5108 \\ -9 & 1170 & -1030 \\ -10 & 3241 & 5108 \\ -9 & 1170 & -1030 \\ -10 & 3241 & 5108 \\ -9 & 1170 & -1030 \\ -10 & 3241 & 5108 \\ -9 & 1170 & -1030 \\ -10 & 325 & -7 & 0 & 415 \\ -10 & 3241 & 5108 \\ -5 & 2766 & -28946 \\ -4 & 1078 & -1014 \\ -3 & 2301 & -2055 \\ -2 & 0 & -355 \\ -1 & 0 & 242 \\ 0 & 0 & 3333 \\ 1 & 1170 & 1136 \\ 2 & 5713 & 5524 \\ 3 & 1652 & -1864 \\ 4 & 1518 & 1186 \\ 5 & 1452 & 1239 \\ h =9, 1 =0, \\ -12 & 620 & -498 \\ -11 & 1509 & 1914 \\ -10 & 87 & 707 \\ \end{array}$	2 3632 -3960 3 1870 -1801 4 0 -1440 5 3846 -3778 6 0 -1114 7 44.96 4392 8 3014 -2978 h=1, 1=1. -8 0 596 -7 1870 -2092 -6 970 834 -5 2858 -936 -4 3524 -2984 -1 988 -1096 1 2254 -2284 2 4295 578 3 1998 -1300 4 1198 1170 5 0 658 6 1900 -1676 7 2614 -3088 h=2, 1=1. -9 0 950 -6 9540 -7 0 -672 -6 954 -1244 -5 2496 5408 -2 3632 -3960 -7 0 -672 -6 9540 -1244 -5 2496 5408 -2 3632 -3960 -1 2254 -2220	-4 -3 -3 -2 -3 -2 -2 -3 -2 -2 -1 -1 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	0 0 21322 0 21322 0 0 0 11320 18700 h=7, 1660 26114 44538 18700 1456 0 1456 0 1456 0 1458 13000 44538 1300 0 1456 0 0 1456 0 0 0 1456 0 0 0 1456 0 0 0 1456 0 0 0 1456 0 0 0 1456 0 0 0 1456 0 0 0 0 1456 0 0 0 0 0 1456 0 0 0 0 0 0 0 1456 0 0 0 0 0 0 0 0 0 1456 0 0 0 0 0 0 0 0 0 1456 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	-2742 -2742 -550 -550 -962 -1962 -1962 -1962 -2992 -1426 -2992 -1456 -2992 -1456 -2992 -1456
	$\begin{array}{c} 2 & (66 - 265)^{\circ} \\ 1 & 991 & 1416 \\ 1 & 196 & 1359 \\ 1 & 196 & 1359 \\ 1 & 196 & 1359 \\ 1 & 5168 & 1361 \\ 901 & -970 \\ 698 & -558 \\ 5676 & 5675 \\ 2195 & -2458 \\ 1 & 5676 & 5675 \\ 2195 & -2458 \\ 1 & 2501 & -2051 \\ 1 & 1555 & 1665 \\ 1 & 354 \\ 2501 & -2051 \\ 1 & 1655 & 1665 \\ 1 & 357 & -1858 \\ 2501 & -2051 \\ 1 & 1655 \\ 1 & 1655 \\ 1 & 1655 \\ 1 & 1655 \\ 1 & 1655 \\ 1 & 1551 \\ 1 & 1561 \\ 1 & 1561 \\ 1 & 1561 \\ 1 & 5567 \\ -381 \\ 1 & 1568 \\ 5675 & -381 \\ 1 & 1568 \\ 5675 & -381 \\ 1 & 1568 \\ 1 & 1568 \\ 5675 & -381 \\ 1 & 1568 \\$	$\begin{array}{c} -3 & 1652 & -424 \\ -2 & 22633 & 2218 \\ -1 & 2543 & 2894 \\ 0 & 2544 & -2542 \\ 1 & 0 & 419 \\ 2 & 1428 & 969 \\ 3 & 1643 & -1496 \\ 4 & 0 & 43 \\ 5 & 0 & 402 \\ 6 & 1055 & -1297 \\ \hline & heb, 1=0, \\ -15 & 1520 & 1827 \\ -12 & 1474 & -1675 \\ -111 & 757 & 720 \\ -10 & 5241 & 5108 \\ -9 & 1170 & -1030 \\ -9 & 1170 & -1030 \\ -10 & 525 & -746 \\ -4 & 1078 & -1014 \\ -5 & 2766 & -2846 \\ -4 & 1078 & -1014 \\ -5 & 2766 & -2846 \\ -4 & 1078 & -1014 \\ -5 & 2766 & -2846 \\ -4 & 1078 & -1014 \\ -5 & 2501 & -2053 \\ -2 & 0 & -355 \\ -1 & 0 & 242 \\ 0 & 0 & 3335 \\ 1 & 1070 & 1136 \\ 2 & 5713 & 3524 \\ 3 & 1692 & -1864 \\ 4 & 1318 & 1126 \\ 5 & 1432 & 1239 \\ \hline & h=9, 1=0, \\ -12 & 620 & -498 \\ -11 & 1909 & 1914 \\ -10 & 587 & 707 \\ -9 & 0 & -127 \end{array}$	2 3632 -3960 3 1870 -1801 4 0 -440 5 3846 -3778 6 0 -1114 7 4436 4392 8 3014 -2978 h=1, 1=1. -8 0 596 -7 1870 -394 -5 0 394 -5 0 394 -5 0 394 -3 2858 -936 -2 2254 2258 2 4958 -1096 1 2254 2258 2 4958 -1096 1 2254 2258 2 4958 -1300 4 1196 1170 5 0 658 6 1900 -1676 7 2614 -3088 h=2, 1=1. -9 0 950 -8 0 -520 -7 0 -521 -6 934, -1244 -5 2496 -1580 -2 2254 -2280 -5 2496 -1580 -2 2254 -2280 -5 2496 -1580 -2 254 -2280 -5 2496 -1580 -2 254 -2280 -5 2496 -1580 -2 254 -2280 -5 254 -2280 -5 264 -2088 -5 265 -3980 -5 265 -3980	-4,3,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,-2,	0 0 21322 0 21322 0 2 1322 0 2 1370 0 0 1 3700 0	-2742 -2742 -550 -550 -1962 -1962 -1962 -2992 -1962 -2992 -126 -138 -2505



Fig. 2. The structure of Nb_3Te_4 viewed along the *c* axis. Filled circles represent niobium atoms and open circles represent tellurium atoms. The *z* parameters of the atoms are either $\frac{1}{4}$ or $\frac{3}{4}$ as indicated.

$6\mathrm{Nb}$	in (h)	$\pm (x, y, \frac{1}{4}; \bar{y}, x-y, \frac{1}{4}; y-x, \bar{x}, \frac{1}{4})$
		with $x_1 = 0.4886$, $y_1 = 0.1039$.
$2\mathrm{Te_{I}}$	in (c)	$\pm (\frac{2}{3}, \frac{1}{3}, \frac{3}{4}).$
$6\mathrm{Te_{II}}$	in (h)	with $x_2 = 0.3389$, $y_2 = 0.2731$.

The space group and atomic parameters are therefore correctly chosen.

An alternative origin, shifted $0, 0, \frac{1}{4}$, is possible and more reasonable for describing the atomic arrangement in this structure. As this origin furthermore is more convenient for bringing out relationships to other structures it is adopted in the rest of this paper.

Determination of the structure of Nb₃Se₄

Attempts to obtain single crystals of the Nb₃Se₄ phase were unsuccessful. There are obvious relationships between the intensities of the reflexions from Nb₃Se₄ and Nb₃Te₄ (Table 1) which indicate that the two compounds are isotructural. The rounded off values for the variable parameters $(x_1=0.49, y_1=0.10, x_2=0.34$ and $y_2=0.27)$ in Nb₃Te₄ give reasonable agreement between observed and calculated intensities on the Guinier photographs. The parameters for Nb₃Se₄ cannot be considered very accurate.

Discussion of the structures

The coordination around the niobium and selenium (tellurium) atoms can be seen from Fig. 2. The interatomic distances between nearest neighbours are listed in Table 3.

Each niobium atom is surrounded by six selenium (tellurium) atoms at the corners of a deformed octahedron. The structure might be looked upon as built up by these NbSe₆ (NbTe₆) octahedra coupled together by common edges. The niobium atoms are shifted from the centres of the selenium (tellurium) octahedra in a manner which produces alternately longer and shorter niobium-niobium distances. Each Se₁ atom is surrounded by six niobium atoms at

Table	3.	Interatomic distar	ıces (Å) i	n
		Nb ₂ Se ₄ and Nb ₂ Te	ea , ,	

Nb ₃ Se	94	Nb_3Te	4
$\begin{array}{c} \rm Nb-2 \ Nb \\ -2 \ Nb \\ -2 \ Nb \\ -2 \ Se_{\rm I} \\ -1 \ Se_{\rm II} \\ -2 \ Se_{\rm II} \\ -1 \ Se_{\rm II} \\ -1 \ Se_{\rm II} \end{array}$: $2 \cdot 80$: $3 \cdot 471$: $3 \cdot 61$: $2 \cdot 71$: $2 \cdot 60$: $2 \cdot 62$: $2 \cdot 76$	Nb-2 Nb -2 Nb -2 Nb -2 Te _I -1 Te _{II} -2 Te _{II} -1 Te _{II}	$\begin{array}{c} : \ 2 \cdot 973 \\ : \ 3 \cdot 647 \\ : \ 3 \cdot 854 \\ : \ 2 \cdot 877 \\ : \ 2 \cdot 768 \\ : \ 2 \cdot 781 \\ : \ 2 \cdot 950 \end{array}$
$egin{array}{c} { m Se_I-6~Nb} \ -2~{ m Se_I} \ -6~{ m Se_{II}} \ -6~{ m Se_{II}} \end{array}$: 2·71 : 3·471 : 3·48	$egin{array}{c} { m Te_I-6} \ { m Nb} \ -2 \ { m Te_I} \ -6 \ { m Te_{II}} \ -6 \ { m Te_{II}} \end{array}$: 2.877 : 3.647 : 3.705
$\begin{array}{c} \mathrm{Se_{II}-l} \ \mathrm{Nb} \\ -2 \ \mathrm{Nb} \\ -1 \ \mathrm{Nb} \\ -2 \ \mathrm{Se_{I}} \\ -2 \ \mathrm{Se_{II}} \\ -4 \ \mathrm{Se_{II}} \end{array}$: 2.60 : 2.62 : 2.76 : 3.48 : 3.471 : 3.56	${f Te_{II}-l \ Nb} \ -2 \ Nb} \ -1 \ Nb} \ -2 \ Te_{I} \ -2 \ Te_{I} \ -2 \ Te_{II} \ -4 \ Te_{II}$: 2.768 : 2.781 : 2.950 : 3.705 : 3.647 : 3.789

the corners of a trigonal prism and each Se_{II} atom by four niobium atoms and one hole at the corners of a deformed trigonal bipyramid.

One of the interesting features about these structures is the short niobium-niobium distances, which indicate that bonding exists between the niobium atoms. Niobium-niobium bonds, *i.e.* some short niobium-niobium distances, are predicted by Pauling's (1960) metallic-bond description assuming the usual 'metallic' valences for niobium and selenium (tellurium). However, the observed interatomic distances are not in quantitative agreement with the calculated values based on Pauling's description. The application of the general (8-N) rule (cf. Pearson, 1964) to describe transition metal compounds is doubtful when valences and electrical conductivity have not been established. Nevertheless, the rule seems in the present case to



Fig. 3. The structural relationships between the Nb₅Se₄ phase (A: with Ti₅Te₄ type structure), the Nb₃Se₄ phase (B) and the Nb_{1+x}Se₂ phase (C and D: with filled-up NbS₂ (H)-type structure). Filled circles represent niobium atoms and open circles selenium atoms. The numbers indicate fractional heights of the atoms on the projection. Crosses indicate the positions of partially filled niobium lattice sites.

]	Dimensions:
Nb_5Se_4 :	Tetr.	a = 9.871, c = 3.4529 Å.
Nb_5Te_4 :	Tetr.	a = 10.231, c = 3.7194 Å.
$Nb_{1+x}Se_2$:	Hex.	a = 3.450, c = 13.02 Å for $x = 0.29$

give an almost correct prediction for the number of niobium-niobium bonds. Further comments will have to await more experimental data.

The atomic arrangement in the Nb₃Se₄ phase shows interesting similarities to corresponding groups of atoms in the neighbouring Nb₅Se₄ and Nb_{1+x}Se₂ phases with respectively Ti₅Te₄ type and NbS₂ (*H*)like structures (Selte & Kjekshus, 1963, 1964). Among the telluride phases the same kinds of relationship exist between the Nb₃Te₄ phase and the Nb₅Te₄ phase (these phases are isostructural with the corresponding selenide phases) whereas the structure of the NbTe₂ phase is not yet known.

In Fig. 3 the structure of Nb₅Se₄ (A) is shown in (001) projection, the structure of Nb₃Se₄ (B) in (001) projection and the structure of Nb_{1+x}Se₂ (C, D) in (110) projection for x=0.29. The axes of projection are of similar dimensions ($c_{Nb_5Se_4}=3.453$ Å, $c_{Nb_3Se_4}=3.471$ Å and $a_{Nb_{1.29}Se_2}=3.450$ Å).

By comparing A and B it is seen that the rectangle outlined in B, with edge lengths of 10.4 and 11.2 Å for the Nb₃Se₄ phase, has its characteristic counterpart in the square plane cell with a=9.871 Å for the Nb_5Se_4 phase (A). The small dashed quadrilaterals in B resemble those in A. The most notable difference is that the 'central' atoms are selenium atoms in Band niobium atoms in A. Inside the unit formed by the rectangle in B there are seven niobium atoms and nine selenium atoms. In order to obtain the Nb₃Se₄ structure from that of Nb₅Se₄ it is necessary to replace the niobium atoms at the centres of the dashed squares by selenium atoms and to remove one niobium and one selenium atom from the square by a fairly large rearrangement of the surrounding atoms. (This includes twisting and distortion of the dashed squares and movement of one niobium atom from the central dashed square to a 'general' position in the rectangle.)

The structural relationships between the Nb₃Se₄ phase (B) and the Nb_{1+x}Se₂ phase (C) are rather closer than between the Nb₃Se₄ phase (B) and the Nb₅Se₄ phase (A). The slightly distorted hexagonal pseudounit indicated in C has edge lengths of 8.8 and 9.0 Å, *i.e.* somewhat smaller than the a axis (a=10.012 Å for Nb₃Se₄) in B. These units both contain the same number of atoms, *i.e.* six niobium and eight selenium atoms (including the partly occupied sites in C). The only difference is that one niobium and one selenium atom in each of the two triangles in C have changed their height by $\frac{1}{2}$ compared with the similar atoms in B. Within each triangle in B only the selenium atom located at centre of gravity of the triangle has a height differing from those of the rest of the atoms in the same triangle.

A structural relationship between the Nb₅Se₄ phase and the $Nb_{1+x}Se_2$ phase is seen by comparing the irregular quadrilateral in D (with edge lengths of 9.5, 10.3, 10.4 and 10.5 Å) for Nb_{1.29}Se₂ with the square in A. The smaller dashed quadrilaterals in D(as previously described for B) resemble those in Aexcept that the central atoms are selenium atoms in Dand niobium atoms in A, and that although the four niobium atoms in both cases show an almost square arrangement, two of them have different heights in the structure of the $Nb_{1+x}Se_2$ phase. Inside the unit formed by the large quadrilateral in D there are ten selenium atoms and approximately eight niobium atoms when the composition of the phase is $Nb_{1.29}Se_2$. In order to obtain the structure of the Nb₅Se₄ phase it is necessary to substitute the selenium atoms at the centres of the dashed quadrilaterals by niobium atoms and rearrange the vacancies (which occur in the positions indicated by crosses in the structure of the $Nb_{1+x}Se_2$ phase (D)) so that they are now on the sides of the large quadrilateral.

The structural relationship is much closer between the Nb₅Se₄ phase and the Nb_{1+x}Se₂ phase than between the Nb₅Se₄ phase and the Nb₃Se₄ phase.

No examples are at present known of compounds which are isostructural with Nb₃Se₄ and Nb₃Te₄.

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