LOEB, A. L. (1958). *Acta Cryst.* **11**, 469.
LOEB, A. L. (1962). *Acta Cryst.* **15**, 219.
MORRIS, I. L. & LOEB, A. L. (1960). *Acta Cryst.* **13**, 434.
PATTERSON, A. L. & KASPER, J. S. (1959). *International Tables for X-ray Crystallography*. Vol. II, p. 342. Birmingham: Kynoch Press.
SEITZ, F. (1934). *Z. Kristallogr.* **88**, 433.
SEITZ, F. (1935). *Z. Kristallogr.* **90**, 289; **91**, 336.
SEITZ, F. (1936). *Z. Kristallogr.* **94**, 100.
VERWEY, E. J. W. & HEILMANN, E. L. (1947). *J. Chem. Phys.* **15**, 174.
VERWEY, E. J. W., HAAYMAN, P. W. & ROMEIJN, F. C. (1947). *J. Chem. Phys.* **15**, 181.
WAREKOIS, E. P., LAVINE, M. C., MARIANO, A. N. & GATOS, H. C. (1962). *J. Appl. Phys.* **33**, 690.
WELLS, A. F. (1962). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.
ZHDANOV, G. S. (1945). *Compt. rend. acad. sci. URSS*, **48**, 39.

Acta Cryst. (1964). **17**, 1568

The Crystal Structures of Nb_3Se_4 and Nb_3Te_4

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The compounds Nb_3Se_4 and Nb_3Te_4 are isostructural. The hexagonal unit cells have the dimensions:

Nb_3Se_4: $a = 10{\cdot}012$, $c = 3{\cdot}4707$ Å;
Nb_3Te_4: $a = 10{\cdot}671$, $c = 3{\cdot}6468$ Å .

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

6Nb in (h) $\pm(x, y, \frac{1}{4};\ \bar{y}, x-y, \frac{1}{4};\ y-x, \bar{x}, \frac{1}{4})$
with $x_1 = 0{\cdot}4886$, $y_1 = 0{\cdot}1039$.
2Te in (c) $\pm(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$.
6Te in (h) with $x_2 = 0{\cdot}3389$, $y_2 = 0{\cdot}2731$.

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 Nb_5Te_4, Nb_5Se_4 and $Nb_{1+x}Se_2$ 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 Nb_3Se_4 and Nb_3Te_4 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 Nb_5Se_4, $Nb_{1+x}Se_2$, Nb_5Te_4 and $NbTe_2$ phases.

Unit cell and space group

Guinier photographs (taken with strictly monochromatized Cu $K\alpha_1$ radiation, $\lambda_{\alpha_1} = 1{\cdot}54050$ Å, with potassium chloride, $a = 6{\cdot}2919$ Å (Hambling, 1953) added as internal standard) could be indexed on hexagonal axes with the following unit cell dimensions (*cf.* Table 1):

Nb_3Se_4; $a = 10{\cdot}012$, $c = 3{\cdot}4707$ Å, $c/a = 0{\cdot}3467$.
Nb_3Te_4; $a = 10{\cdot}671$, $c = 3{\cdot}6468$ Å, $c/a = 0{\cdot}3418$.

The lattice dimensions were approximately constant

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* 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 $NbTe_{1{\cdot}00}$ to $NbTe_{1{\cdot}70}$. The available data indicate that their $NbTe_{1{\cdot}00-1{\cdot}70}$ 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} (Nb_3Se_4) and 7·20 g.cm^{-3} (Nb_3Te_4), the unit cell contains $2\,Nb_3X_4$ groups ($Z_c = 2{\cdot}04$ for Nb_3Se_4 and $Z_c = 1{\cdot}98$ for Nb_3Te_4).

The only systematically missing reflexions were of the type

$$00l \text{ when } l = 2n+1\ .$$

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* Nb_3Se_4 *and* Nb_3Te_4 *taken with strictly monochromatized* Cu $K\alpha_1$ *radiation*

hkl	Nb_3Se_4 $\sin^2\theta \times 10^5$	Nb_3Se_4 I_o	Nb_3Te_4 $\sin^2\theta \times 10^5$	Nb_3Te_4 I_o
100	790	*s*	698	*s*
110	2374	*vw*	2088	*w*
210	5521	*vw*	4858	*vw*
101	5714	*w*	5156	*w*
300	7106	*w*	6258	*m*
111	7295	*vw*	6545	*m*
201	8085	*m*	7248	*vs*
310	10261	*m*	9035	*s*
211	10458	*s*	9330	*vs*
301	12025	*w*	10713	*vw*
400	12625	*vw*	11115	*vw*
221	14390	*m*	12799	*m*
320	14976	*vw*	13192	*vw*
311	15173	*w*	13486	*w*
410	16543	*w*	14592	*w*
500			17362	*vw*
321	19913	*m*	17644	*w*
002	19704	*m*	17854	*w*
102	20512	*vw*	18561	*vw*
330			18721	*vw*
411			19073	*vw*
420	22091	*w*	19437	*w*
510	24439	*vw*	21515	*vw*
501			21813	*w*
331	26238	*vw*	23209	*vw*
302	26847	*vw*	24121	*vw*

Determination of the structure of Nb_3Te_4

Well formed, needle-like, single crystals of Nb_3Te_4 with hexagonal cross-sections were investigated in an integrating Weissenberg camera with Cu K radiation. Intensity measurements of the $hk0$ and $hk1$ reflexions 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 $F_o^2(hk0)$ 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 c axis. Tentative atomic positions could be deduced from the Patterson map and a set of structure factors calculated on this basis gave $R = 0{\cdot}278$. 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 Nb in $x_1 = 0{\cdot}4886$, $y_1 = 0{\cdot}1039$, *etc.*
2 Te_I in $x = \frac{2}{3}$, $y = \frac{1}{3}$, *etc.*
6 Te_{II} in $x_2 = 0{\cdot}3389$, $y_2 = 0{\cdot}2731$, *etc.*

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

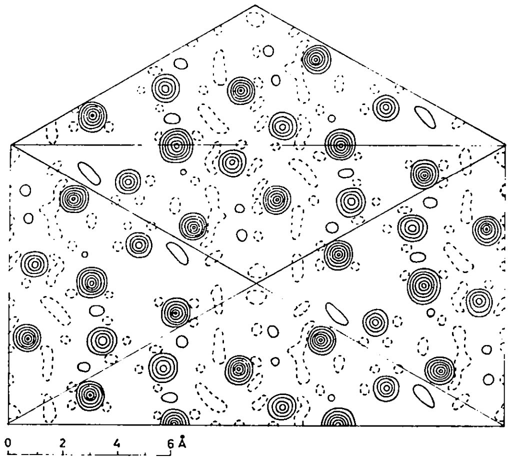

Fig. 1. Electron-density projection of Nb_3Te_4 on (001). Contours are at intervals of 10 e.Å^{-2}. The zero contours are broken.

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 $hk1$ reflexions were accordingly evaluated. $R = 0{\cdot}141$ for $F(hk1)$ 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 $10F_c$

h=0, l=0.		
1	1780	-2029
2	258	-276
3	3676	3675
4	1464	-1587
5	3861	-3783
6	514	511
7	2544	-2544
8	0	335
9	0	-432
h=1, l=0.		
-10	1111	-1281
-9	1170	1131
-8	0	427
-7	1038	-959
-6	1597	-1514
-5	3762	3879
-4	3625	-3526
-3	901	-967
-2	1277	-1118
-1	1780	-2031
0	1780	-2026
1	1277	-1119
2	698	-551
3	4621	5198
4	567	-385
5	1955	2114
6	2543	2845
7	0	233
8	1170	-1020
9	587	-713
h=2, l=0.		
-11	2165	-2133
-10	3713	3519
-9	1428	998
-8	584	-741
-7	2653	2742
-6	2176	1843
-5	2193	-2455
-4	353	393
-3	698	-551
-2	258	275
-1	1277	-1121
0	258	-279
1	901	-968
2	353	405
3	1818	-1303
4	3140	-3502
5	2653	2225
6	0	-46
7	1843	-2060
8	3241	3108
9	1900	1911
h=3, l=0.		
-12	876	1035
-11	1692	-1866
-10	1643	-1496
-9	818	-755
-8	2766	-2835
-7	1391	1416
-6	1386	1359
-5	1818	-1301
-4	4621	5198
-3	3676	3674
-2	901	-970
-1	698	-558
0	3676	3673
1	3625	-3525
2	2193	-2458
3	1386	1346
4	495	-431
5	2301	-2051
6	1635	1663
7	1837	-1838
8	757	727
h=4, l=0.		
-12	1318	1190
-11	0	42
-10	0	-319
-9	1818	1885
-8	1078	-1028
-7	492	-435
-6	3140	-3503
-5	567	-381
-4	1464	-1588
-3	3625	-3510
-2	353	407
-1	4621	5200
0	1464	-1581
1	3762	3877
2	2176	1842
3	1391	1414
4	762	-1021
5	575	-379
6	616	-835
7	0	-124
8	1474	-1681
h=5, l=0.		
-13	1433	1241
-12	0	413
-11	1111	-1444
-10	3091	3145
-9	575	-374
-8	2301	-2058
-7	2653	2221
-6	1955	2109
-5	3861	-3788
-4	3762	3872
-3	2193	-2463
-2	1818	-1301
-1	567	-383
0	3861	-3785
1	1597	-1508
2	2653	2752
3	2766	-2840
4	1408	1886
5	3091	3145
6	785	540
7	0	-345
8	1519	1824
h=6, l=0.		
-13	1180	-1298
-12	973	-941
-11	555	539
-10	0	-822
-9	1635	1674
-8	0	-50
-7	2543	2851
-6	514	514
-5	1597	-1528
-4	2176	1849
-3	1386	1345
-2	3140	-3510
-1	1955	2109
0	514	509
1	1038	-956
2	0	-744
3	578	-757
4	0	-309
5	1111	-1437
6	973	-950
7	914	774
h=7, l=0.		
-13	746	766
-12	0	347
-11	0	-134
-10	1837	-1848
-9	1843	-2050
-8	0	227
-7	2544	-2529
-6	1038	-942
-5	2653	2752
-4	1391	1421
-3	492	-424
-2	2653	2218
-1	2543	2846
0	2544	-2542
1	0	419
2	1428	989
3	1643	-1496
4	0	43
5	0	402
6	1055	-1297
h=8, l=0.		
-13	1520	1827
-12	1474	-1675
-11	757	720
-10	3241	3108
-9	1170	-1030
-8	0	325
-7	0	415
-6	585	-748
-5	2766	-2846
-4	1078	-1014
-3	2301	-2053
-2	0	-35
-1	0	242
0	0	333
1	1170	1136
2	3713	3524
3	1692	-1864
4	1318	1186
5	1432	1238
h=9, l=0.		
-12	620	-498
-11	1909	1914
-10	587	707
-9	0	-427
-8	1170	1124
-7	1428	1001
-6	818	-758
-5	1818	1870
-4	813	-376
-3	1635	1661
-2	1843	-2069
-1	1170	-1022
0	0	-429
1	1111	-1274
2	2165	-2134
3	876	1037
h=10, l=0.		
-11	0	-484
-10	0	-152
-9	1111	-1269
-8	3713	3527
-7	1643	-1492
-6	0	-309
-5	3091	3146
-4	0	-834
-3	1837	-1839
-2	3241	3101
-1	0	-716
0	0	-160
1	498	653
2	0	-34
h=11, l=0.		
-10	0	657
-9	2165	-2155
-8	1692	-1854
-7	0	46
-6	1111	-1437
-5	785	552
-4	0	-117
-3	1070	724
-2	1909	1922
-1	0	-489
0	0	147
1	686	968
h=12, l=0.		
-9	876	1026
-8	1318	1178
-7	0	405
-6	973	-964
-5	0	-351
-4	1474	-1681
-3	619	-494
h=13, l=0.		
-8	1433	1251
-7	1055	-1299
-6	746	770
-5	1519	1826
h=0, l=1.		
1	988	1116
2	3632	-3960
3	1870	-1801
4	0	-440
5	3846	-3778
6	0	-114
7	4438	4392
8	3014	-2978
h=1, l=1.		
-8	0	596
-7	1870	-2092
-6	970	834
-5	0	398
-4	3524	-3934
-3	2858	-936
-2	2254	2284
-1	988	-1096
0	988	1090
1	2254	2258
2	4298	5378
3	1998	-1300
4	1198	1170
5	0	638
6	1900	-1676
7	2614	-3088
h=2, l=1.		
-9	0	950
-8	0	-520
-7	0	-672
-6	934	-1244
-5	2496	-1580
-4	3902	-4014
-3	4298	5408
-2	3632	-3980
-1	2254	-2220
0	3632	4020
1	2862	-902
2	3902	-3990
3	3466	4010
4	934	-984
5	1478	1628
6	1136	1090
h=3, l=1.		
-9	0	392
-8	4468	5398
-7	1456	1792
-6	2832	2760
-5	3466	3966
-4	1998	-1388
-3	1874	-1772
-2	1858	866
-1	4298	-5454
0	1870	1790
1	2524	-3038
2	2496	-1516
3	2832	2724
4	0	-202
5	3508	-2390
h=4, l=1.		
-9	0	-328
-8	3466	-3424
-7	0	-284
-6	934	-913
-5	1198	1294
-4	0	-478
-3	2524	2990
-2	3902	3990
-1	1998	1372
0	0	394
1	0	434
2	0	-716
3	1456	-1730
4	3488	-3652
h=5, l=1.		
-9	0	420
-8	3508	-2434
-7	1478	1638
-6	0	572
-5	3846	-3916
-4	0	-334
-3	2496	1588
-2	3466	-3914
-1	1186	-1218
0	3846	3786
1	0	730
2	0	-614
3	4468	5272
h=6, l=1.		
-9	2128	2628
-8	1136	1086
-7	1900	-1732
-6	0	-204
-5	970	-856
-4	0	564
-3	2832	-2742
-2	1322	1458
-1	0	-550
0	0	190
1	1870	-1962
2	0	-426
h=7, l=1.		
-9	1660	1684
-8	2614	-2992
-7	4438	4492
-6	1870	2020
-5	0	742
-4	1456	1546
-3	0	198
-2	1478	-1646
-1	1900	1636
0	4438	-4580
1	0	518
h=8, l=1.		
-8	3014	-3056
-7	0	-418
-6	0	514
-5	4468	-5354
-4	3488	3650
-3	3508	2332
-2	1136	-1026
-1	2614	3040
0	3014	3068
h=9, l=1.		
-7	1174	-996
-6	0	-402
-5	0	308
-4	0	-484
-3	2128	-2508
-2	1660	-1654

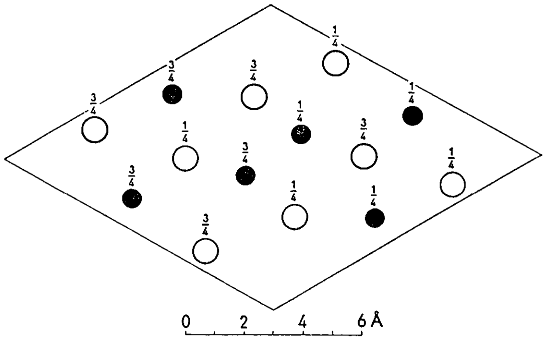

Fig. 2. The structure of Nb_3Te_4 viewed along the c axis. Filled circles represent niobium atoms and open circles represent tellurium atoms. The z parameters of the atoms are either $\frac{1}{4}$ or $\frac{3}{4}$ as indicated.

$6\,\text{Nb}$ in (h) $\pm(x, y, \frac{1}{4};\ \bar{y}, x-y, \frac{1}{4};\ y-x, \bar{x}, \frac{1}{4})$
with $x_1=0{\cdot}4886$, $y_1=0{\cdot}1039$.
$2\,\text{Te}_{\text{I}}$ in (c) $\pm(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$.
$6\,\text{Te}_{\text{II}}$ in (h) with $x_2=0{\cdot}3389$, $y_2=0{\cdot}2731$.

The space group and atomic parameters are therefore correctly chosen.

An alternative origin, shifted $0, 0, \frac{\bar{1}}{4}$, 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 Nb_3Se_4

Attempts to obtain single crystals of the Nb_3Se_4 phase were unsuccessful. There are obvious relationships between the intensities of the reflexions from Nb_3Se_4 and Nb_3Te_4 (Table 1) which indicate that the two compounds are isotructural. The rounded off values for the variable parameters ($x_1=0{\cdot}49$, $y_1=0{\cdot}10$, $x_2=0{\cdot}34$ and $y_2=0{\cdot}27$) in Nb_3Te_4 give reasonable agreement between observed and calculated intensities on the Guinier photographs. The parameters for Nb_3Se_4 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 $NbSe_6$ ($NbTe_6$) 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 Se_{I} atom is surrounded by six niobium atoms at

Table 3. *Interatomic distances* (Å) *in* Nb_3Se_4 *and* Nb_3Te_4

Nb_3Se_4		Nb_3Te_4	
Nb–2 Nb	: 2·80	Nb–2 Nb	: 2·973
–2 Nb	: 3·471	–2 Nb	: 3·647
–2 Nb	: 3·61	–2 Nb	: 3·854
–2 Se_I	: 2·71	–2 Te_I	: 2·877
–1 Se_{II}	: 2·60	–1 Te_{II}	: 2·768
–2 Se_{II}	: 2·62	–2 Te_{II}	: 2·781
–1 Se_{II}	: 2·76	–1 Te_{II}	: 2·950
Se_I–6 Nb	: 2·71	Te_I–6 Nb	: 2·877
–2 Se_I	: 3·471	–2 Te_I	: 3·647
–6 Se_{II}	: 3·48	–6 Te_{II}	: 3·705
Se_{II}–1 Nb	: 2·60	Te_{II}–1 Nb	: 2·768
–2 Nb	: 2·62	–2 Nb	: 2·781
–1 Nb	: 2·76	–1 Nb	: 2·950
–2 Se_I	: 3·48	–2 Te_I	: 3·705
–2 Se_{II}	: 3·471	–2 Te_{II}	: 3·647
–4 Se_{II}	: 3·56	–4 Te_{II}	: 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

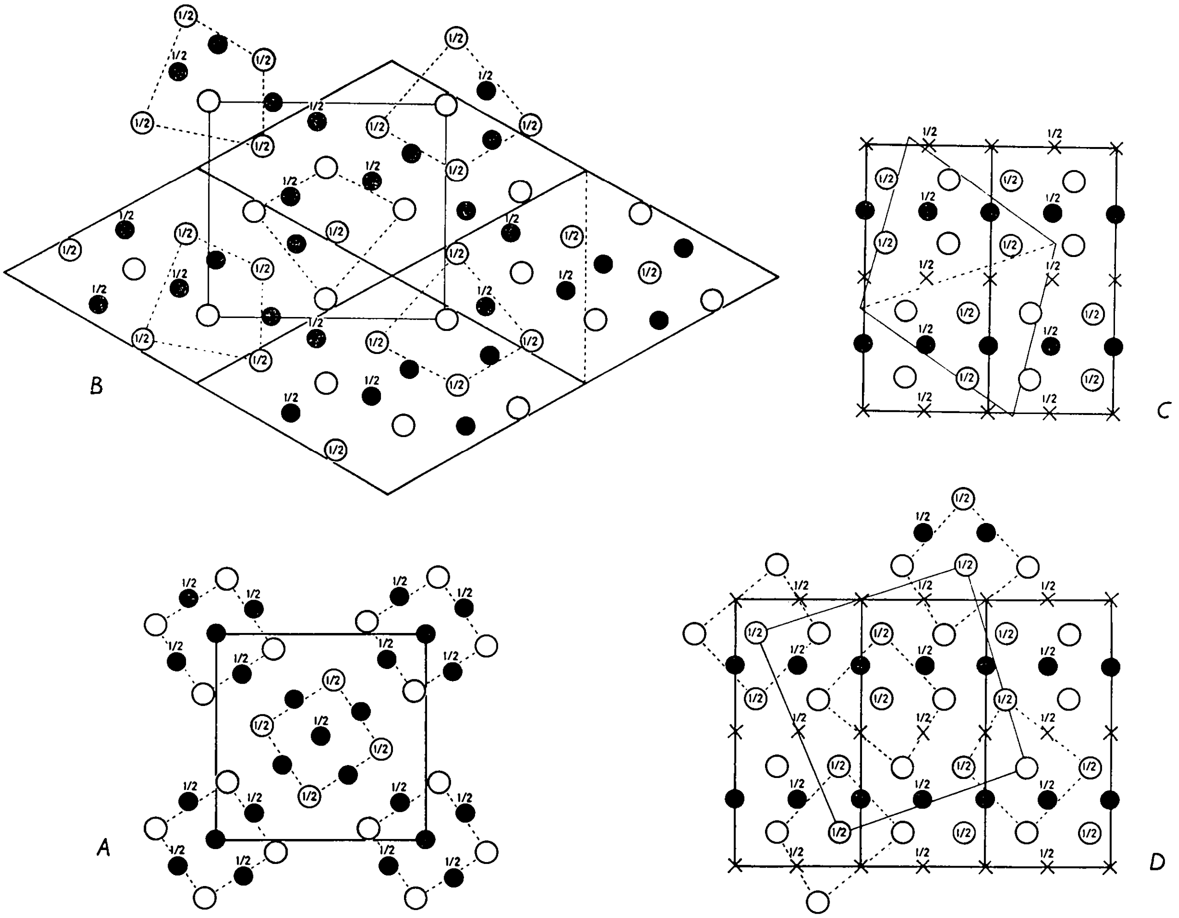

Fig. 3. The structural relationships between the Nb_5Se_4 phase (*A*: with Ti_5Te_4 type structure), the Nb_3Se_4 phase (*B*) and the $Nb_{1+x}Se_2$ phase (*C* and *D*: with filled-up NbS_2 (*H*)-type structure). Filled circles represent niobium atoms and open circles selenium atoms. The numbers indicate fractional heights of the atoms on the projection. Crosses indicate the positions of partially filled niobium lattice sites.

Dimensions:

Nb_5Se_4: Tetr. $a = 9{\cdot}871$, $c = 3{\cdot}4529$ Å.
Nb_5Te_4: Tetr. $a = 10{\cdot}231$, $c = 3{\cdot}7194$ Å.
$Nb_{1+x}Se_2$: Hex. $a = 3{\cdot}450$, $c = 13{\cdot}02$ Å for $x = 0{\cdot}29$.

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 Nb_3Se_4 phase shows interesting similarities to corresponding groups of atoms in the neighbouring Nb_5Se_4 and $Nb_{1+x}Se_2$ phases with respectively Ti_5Te_4 type and NbS_2 (*H*)-like structures (Selte & Kjekshus, 1963, 1964). Among the telluride phases the same kinds of relationship exist between the Nb_3Te_4 phase and the Nb_5Te_4 phase (these phases are isostructural with the corresponding selenide phases) whereas the structure of the $NbTe_2$ phase is not yet known.

In Fig. 3 the structure of Nb_5Se_4 (*A*) is shown in (001) projection, the structure of Nb_3Se_4 (*B*) in (001) projection and the structure of $Nb_{1+x}Se_2$ (*C*, *D*) in (110) projection for $x=0{\cdot}29$. The axes of projection are of similar dimensions ($c_{Nb_5Se_4}=3{\cdot}453$ Å, $c_{Nb_3Se_4}=3{\cdot}471$ Å and $a_{Nb_{1\cdot29}Se_2}=3{\cdot}450$ 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 Nb_3Se_4 phase, has its characteristic counterpart in the square plane cell with $a=9{\cdot}871$ 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 *B* and 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 Nb_3Se_4 structure from that of Nb_5Se_4 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 Nb_3Se_4 phase (*B*) and the $Nb_{1+x}Se_2$ phase (*C*) are rather closer than between the Nb_3Se_4 phase (*B*) and the Nb_5Se_4 phase (*A*). The slightly distorted hexagonal pseudo-unit indicated in *C* has edge lengths of 8·8 and 9·0 Å, *i.e.* somewhat smaller than the *a* axis ($a=10{\cdot}012$ Å for Nb_3Se_4) 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 Nb_5Se_4 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 $Nb_{1\cdot29}Se_2$ with the square in *A*. The smaller dashed quadrilaterals in *D* (as previously described for *B*) resemble those in *A* except that the central atoms are selenium atoms in *D* and 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 $Nb_{1\cdot29}Se_2$. In order to obtain the structure of the Nb_5Se_4 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 Nb_5Se_4 phase and the $Nb_{1+x}Se_2$ phase than between the Nb_5Se_4 phase and the Nb_3Se_4 phase.

No examples are at present known of compounds which are isostructural with Nb_3Se_4 and Nb_3Te_4.

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References

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

Grigorjan, L. A., Simanov, Yu. P. & Novoselova, A.V. (1960). *Dokl. Akad. Nauk SSSR*, **135**, 1133.

Hambling, P. G. (1953). *Acta Cryst.* **6**, 98.

Novoselova, A. V., Grigorjan, L. A. & Simanov, Yu. P. (1960). *Dokl. Akad. Nauk SSSR*, **135**, 864.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Pearson, W. B. (1964). *Acta Cryst.* **17**, 1.

Selte, K. & Kjekshus, A. (1963). *Acta Chem. Scand.* **17**, 2560.

Selte, K. & Kjekshus, A. (1964). *Acta Chem. Scand.* **18**, 697.

Vand, V., Eiland, P. F. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 303.