On the Crystal Structure of NbTe₄

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One of the phases in the niobium-tellurium system is identified as $NbTe_4$. This compound crystallizes tetragonally with

$$a = 2 \times 6.499 \text{ Å}; c = 3 \times 6.837 \text{ Å}; c/a = 3/2 \times 1.052$$

The pycnometric density is 6.88 g cm⁻³ at 25°C. There are 12×2 formula units per unit cell.
For the subcell

$$a' = 6.499 \text{ Å}; c' = 6.837 \text{ Å}$$

the space group is $P4/mcc$ and the atomic positions are:
2 Nb in $(a) \pm (0,0,1/4)$
8 Te in $(m) \pm (x,y,0; \bar{y},x,0; \bar{x},y,1/2; y,x,1/2)$
with $x = 0.1425, y = 0.3316$.

In recent communications from this Institute [1,2] some aspects of the properties of the polychalcogenide compounds of the subgroup IV, V, and VI elements have been described. The present knowledge of the properties of these substances is still too incomplete to describe their chemical bonding. For this reason it was considered of great interest to determine the detailed crystal structures of as many compounds as possible.

The present paper concerns the structural properties of $NbTe_4$. The existence of a higher niobium telluride with a broad range of homogeneity extending from 70 to 80 atomic % Te has previously been reported by Novoselova *et al.*[3] and Grigorjan *et al.*[4] as a result of X-ray and electrical measurements. The dimensions of a tetragonal unit cell were given.

EXPERIMENTAL

Samples were prepared from spectrographically standardized niobium (Johnson, Matthey & Co., Ltd.) and semiconductor grade tellurium (American Smelting and Refining Co.). A series of samples was prepared by heating accurately weighed quantities of the components in different compositions ranging from 66.7 to 100 atomic % Te. The samples were heated at a temperature of 900°C for 30 days and slowly cooled to room temperature over a period of 15 days.

All samples were crushed and X-ray photographs taken in a Guinier focusing camera of 80 mm diameter and strictly monochromatized $CuK\alpha_1$-radiation. For the calculation

of lattice constants potassium chloride (Analar, The British Drug Houses Ltd. a = 6.2919 Å[5]) was added to the specimen as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda(CuK\alpha_1)$ = 1.54050 Å.

X-Ray photographs were also taken in a Weissenberg camera of 57.3 mm diameter. Intensity measurements of the $hk0$ and $hk1$ reflections were carried out visually by comparison with a calibrated scale 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 calculation of F_c-values the atomic scattering factors were taken from Forsyth and Wells [6] for the $hk0$ reflections (Computer: IBM 1620) and from Vand et al.[7] for the $hk1$ reflections (Computer: Wegematic 1000). The agreement between F_o and F_c is expressed by the reliability index R = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. (Undetected reflections are not used in the calculation of R.)

The density measurements were carried out pycnometrically at 25°C with kerosene as displacement liquid. To remove gases absorbed by the sample the pycnometer was filled under vacuum with kerosene. The samples weighed from 1 to 2 g.

RESULTS

Unit cell and space group. Guinier photographs of samples with more than 66.7 atomic % Te show the presence of a phase designated NbTe₄. (The neighbouring phases are NbTe₂ and Te.) Guinier photographs of the NbTe₄ phase were indexed as tetragonal, *cf.* Table 1. The lattice constants of the NbTe₄ phase are:

$$a' = 6.499 \text{ Å}; c' = 6.837 \text{ Å}; c'/a' = 1.052.$$

As the lattice constants are almost invariant for specimens with different initial proportions of the components, no composition range of the NbTe₄ phase is indicated.

Table 1. Guinier photograph data of NbTe₄ taken with strictly monochromatized CuKα₁-radiation.

I_{obs}	sin² Θ × 10⁵		hkl	I_{obs}	sin² Θ × 10⁵		hkl
	obs	calc			obs	calc	
vst	1 397	1 405	100	w	18 284	18 260	320
w	2 803	2 809	110	vst	18 449	18 446	213
st	5 066	5 077	002	w	19 124	19 123	312
w	5 605	5 618	200	m	20 322	20 308	004
w	6 484	6 482	102	vw	21 698	21 713	104
m	7 887	7 886	112	vw	22 465	22 474	400
vst	8 289	8 292	211	vw	23 890	23 878	410
m	10 699	10 695	202	w	25 129	25 147	411
w	11 258	11 237	220	vw	25 292	25 284	330
m	12 110	12 100	212	vw	25 466	25 469	313
w	12 654	12 641	300	vw	25 951	25 923	204
m	14 039	14 046	310	m	27 546	27 551	402
w	15 320	15 315	311	w	28 105	28 093	420
vw	17 690	17 718	302	vw	29 365	29 362	421

Table 2. Observed and calculated structure factors for $NbTe_4$.

hkl	F_o	F_c	hkl	F_o	F_c
010	106.2	105.1	370	136.1	173.1
020	86.6	− 62.7	440	106.8	141.2
030	101.4	75.3	450	93.2	107.2
040	136.6	−135.3	460	70.9	− 82.6
050	57.2	− 49.7	550	73.5	65.1
060	227.7	224.7			
070	108.7	98.0	121	204.8	256.4
110	45.0	− 42.9	131	86.8	59.2
120	33.1	29.1	141	148.4	−142.8
130	179.7	220.5	151	0	− 22.8
140	93.7	72.1	161	72.8	− 71.2
150	0	18.4	171	75.2	− 71.2
160	94.7	78.7	231	38.8	− 48.8
170	0	− 39.7	241	86.4	− 62.4
220	99.7	97.1	251	156.0	196.4
230	97.8	90.2	261	108.0	78.4
240	128.6	123.3	271	96.4	− 88.4
250	80.8	73.7	341	48.8	− 45.2
260	0	− 17.4	351	51.6	44.4
270	0	− 5.0	361	0	4.4
330	159.8	−188.7	371	26.8	− 37.6
340	0	− 13.8	451	128.8	−133.6
350	89.1	72.8	461	75.6	− 72.0
360	0	9.8			

The observed density, 6.88 g cm^{-3}, corresponds to 2 ($Z_c = 1.99$) $NbTe_4$-groups in the unit cell. The calculated density of $NbTe_4$ from the X-ray measurements is 6.94 g cm^{-3}. (It should be noticed that the specific volume was found to be an approximately linear function of weight % Te in the concentration range from 66.7 to 100 atomic %. Density determinations alone would therefore fail to show the existence of this phase. X-Ray and density data together ascertained, however, the composition to be $NbTe_4$.)

Needle-shaped single crystals were grown from the vapour phase. Oscillation and Weissenberg photographs confirmed a tetragonal symmetry with the c-axis along the needle axis. The photographs clearly demonstrated a doubled a-axis and a tripled c-axis, i.e.

$$a = 2 \times a' = 12.998 \text{ Å}; \quad c = 3 \times c' = 20.511 \text{ Å}.$$

Since these additional reflections were faint, the full cell might be regarded as a superstructure of the smaller cell. (The X-ray data in Tables 1 and 2 are therefore listed in accordance with the smaller cell.)

The missing reflections were

hhl when $l = 2n + 1$ and
0*kl* when $l = 2n + 1$,

the Laue symmetry is 4/*mmm* and the possible space groups are accordingly P4cc and P̄4/mcc. The large and the smaller cell have the same extinctions and therefore the same possible space groups.

The X-ray data of Novoselova *et al.*[3] and Grigorjan *et al.*[4] leave little doubt that their $NbTe_{2.33-4.00}$ (70 to 80 atomic % Te) phase is identical with the present $NbTe_4$ phase. The disagreement with respect to the range of homogeneity reflects the weakness of the disappearing phase method in phase-analytical work by X-ray powder methods. The unit cell dimensions $a = 9.10 \pm 0.05$ Å; $c = 21.35 \pm 0.05$ Å given by Grigorjan *et al.*[4] agree reasonably well with the present value for the a-axis after multiplication of their a-axis by $\sqrt{2}$ (*i.e.* 12.85 ± 0.07 Å) whereas the marked difference between the length of the c-axes must be attributed to the fact that Grigorjan *et al.*[4] estimated their value from single crystal data.

Determination of the structure. In the present paper the determination of the crystal structure of $NbTe_4$ will be described regardless of the doubling of the a-axis and the tripling of the c-axis. Work is in progress to relate the superstructure cell with the subcell.

The subcell contains two niobium and eight tellurium atoms. The two niobium atoms must thus be located in a twofold position and as no other
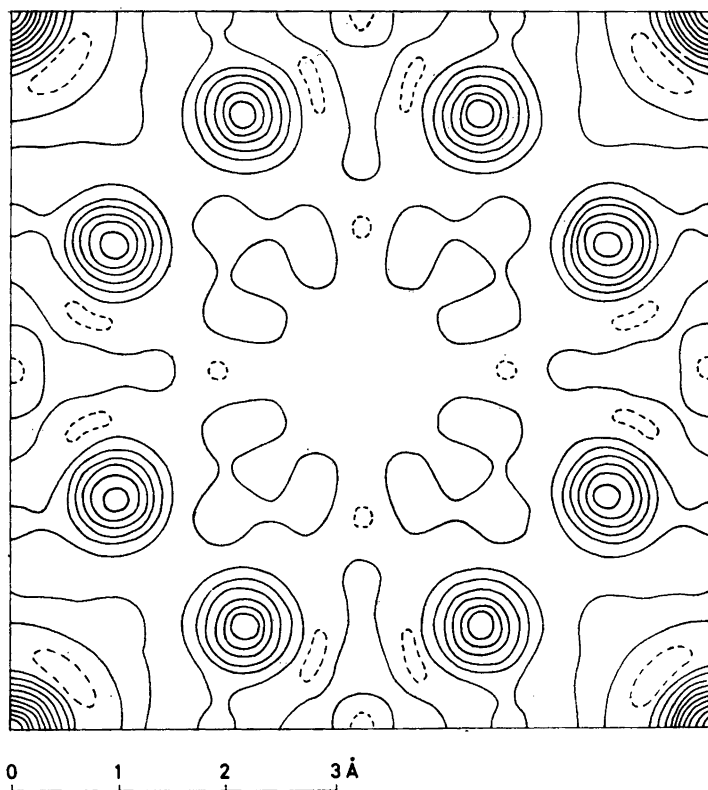

0 1 2 3 Å

Fig. 1. Electron density projection of $NbTe_4$ on (001). Contours are at intervals of 10 e.Å⁻². The zero contours are broken.

extinctions have been observed the eight tellurium atoms accordingly must be in an eightfold position. Both space groups have symmetry $p4m$ in the [001]-projection. (The [001]-direction is also suitable because the crystal has a cross-section not far from circular along the c-axis.)

Tentative atomic positions could easily be deduced from a Patterson projection on (001). Based on these approximate atomic parameters, structure factors were calculated giving $R = 0.376$. A Fourier projection was evaluated, which clearly showed all atoms resolved. The atomic parameters were refined by means of two Fourier and one difference syntheses. R decreased to 0.157 after the Fourier syntheses and to 0.138 after the 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:

2 Nb in 0, 0
8 Te in $x = 0.1425$, $y = 0.3316$; etc.

In terms of the highest symmetric space group $P4/mcc$ the atoms would have fixed z-coordinates. With the 8 Te atoms in (m) the 2 Nb atoms must be in (a), as (b) was unreasonable considering the interatomic Nb-Te distances. In order to verify these z-parameters, a comparison of $F_o(hk1)$ and $F_c(hk1)$ was carried out. $R = 0.164$, cf. Table 2, was obtained on the basis of the sug-
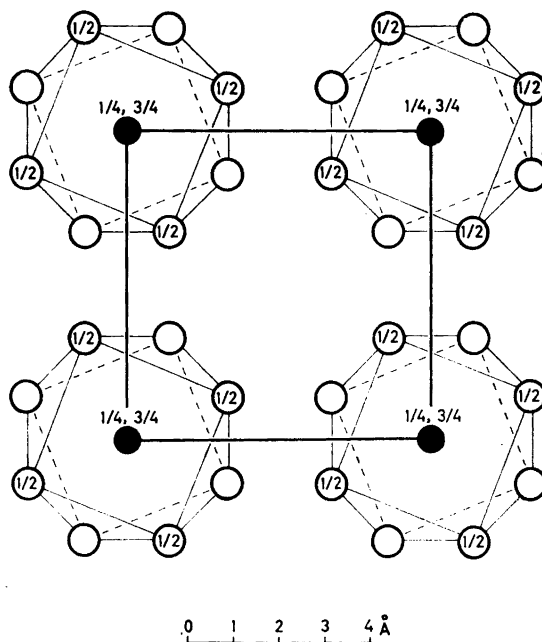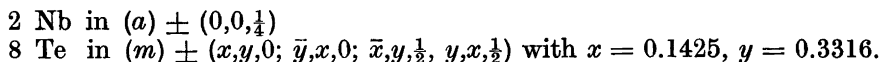

Fig. 2. The structure of $NbTe_4$ (subcell) projected along [001]. Filled circles represent niobium atoms and open circles represent tellurium atoms. The numbers indicate fractions of the c-axis.

gested arrangement, which indicates that the choice of the space group and parameters is correct *. The deduced atomic arrangement, *cf*. Fig. 2, is thus:

2 Nb in $(a) \pm (0,0,\frac{1}{4})$
8 Te in $(m) \pm (x,y,0; \bar{y},x,0; \bar{x},y,\frac{1}{2}, y,x,\frac{1}{2})$ with $x = 0.1425$, $y = 0.3316$.

* *Note added in proof:* A recent determination of the isostructural compound TaTe₄ by Bjerkelund and Kjekshus [12] indicates a slight deviation from $z = 1/4$ for the metal atoms. This suggests the lower symmetric space group *P4cc*. Further comments will have to await the interpretation of the superstructure.

DISCUSSION

The coordination around the niobium and tellurium atoms can be seen from Fig. 2. Each niobium atom is surrounded by eight tellurium atoms. The configuration of the eight tellurium atoms is that of a slightly distorted square antiprism. Each tellurium atom is coordinated to two niobium atoms and eleven tellurium atoms. Five of the tellurium atoms form a planar, irregular pentagon and six a trigonal prism.

Table 3. Interatomic distances in NbTe₄ (Å).

$$
\begin{array}{llll}
\text{Nb} & - & 2 \text{ Nb} & : 3.419 \\
& - & 8 \text{ Te} & : 2.902 \\
\\
\text{Te} & - & 2 \text{ Nb} & : 2.902 \\
& - & 1 \text{ Te} & : 2.867 \\
& - & 2 \text{ Te} & : 3.318 \\
& - & 2 \text{ Te} & : 3.633 \\
& - & 2 \text{ Te} & : 3.836 \\
& - & 2 \text{ Te} & : 3.888 \\
& - & 2 \text{ Te} & : 4.059 \\
\end{array}
$$

The interatomic distances between nearest neighbours are listed in Table 3. On the basis of these distances, bonds are considered to exist between niobium and the eight surrounding tellurium atoms, and between each tellurium and two niobium and one of the other tellurium atoms.

The existence of Te-Te bonds is of considerable interest in relation to the connection between valence, crystal chemistry and semiconductivity. This relationship is described in the general $(8-N)$ rule:[8-10]

$$(n_e + b_a - b_c)/n_a = 8$$

where per formula unit n_e is the number of valence electrons, b_a is the number of valence electrons involved in anion-anion bond formation, b_c is the number of valence electrons involved in cation-cation bond formation (together with any unshared electrons on the cations) and n_a the number of anions. Compounds being semiconductors and having anions to the right of the Zintl border are known to obey this rule. The rule is used as a criterion for occurrence of semiconductivity (picking out the valence structures that lead to filled subshells on the anions, *i.e.* a filled valence band) or it affords a prediction of the coordination configurations in a given compound.

The application of the general $(8-N)$ rule to describe transition metal compounds is doubtful, if valences and electrical conductivity have not been established. Nevertheless, many compounds containing transition metals are semiconductors and satisfy the rule with reasonable assumptions concerning valence.

With a valence of 5 for Nb and 6 for Te the predicted value of b_a/n_a from the rule is 3/4 for $NbTe_4$. This value is to be compared with the value $b_a/n_a = 4/4 = 1$ according to the crystal structure.

This discrepancy would have been satisfactorily accounted for by assuming one unpaired d-electron on each Nb atom. Localized, unpaired d-electrons are inconsistent with $NbTe_4$ being diamagnetic.[11] If the general $(8-N)$ rule is to be satisfied for $NbTe_4$ the explanation must evidently be sought in the occurring superstructure. With the information from the general $(8-N)$ rule we are proceeding with an interpretation of the superstructure.

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