

same $\%P(\theta)$ and L but different structure and symmetry. Among the m sequences, stacking by AB sequence yields structures of the highest symmetry. Between the two modes of stacking, stacking *via* the central mode results in structures of consistently higher $\%P(\theta)$ (Fig. 4) and L (Table 1). Hence, based on Laves principle (Laves, 1955) of maximum packing density, highest symmetry and largest coordination number, the three most probable structures arising from the three basic nets should be R_{AB}^c , S_{AB}^c and T_{AB}^c , which are b.c.t., c.c.p. and h.c.p., respectively. This principle is fully exemplified by the last two structures which are also the closest packing structures.

5. The b.c.c. structure

The packing density of a b.c.t. structure has its minimum value of 68% at $\theta = 70^\circ 32'$ (curve 1 in Fig. 4). The equation below relates θ to its axial ratio c/a :

$$c/a = 0.71(1 + \cos\theta)/\sin\theta. \quad (4)$$

At $70^\circ 32'$ the ratio equals 1 and b.c.t. becomes b.c.c. It is interesting to note that although b.c.t. is more densely packed than b.c.c., it rarely occurs whereas the latter is the third most frequently adopted struc-

ture after c.c.p. and h.c.p. This preferential adoption of b.c.c. is obviously due to its higher symmetry (isometric). Thus symmetry factors strongly outweigh packing density in determining the most probable structure. This rationale is consistent with the central force of interaction which favours highly symmetrical arrangements rather than the densest packing structures. For example, simple hexagonal (s.h.p.) structure is occasionally adopted (Pearson, 1972) even though its $\%P(\theta)$ is smaller *vis-à-vis* other close-packing structures of lower symmetry.

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Modulated Structure of $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$

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Abstract

The commensurately modulated structure of tantalum niobium tetratelluride, $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$, was

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determined by X-ray ($\text{Mo } K\alpha$, $\lambda = 0.71069 \text{ \AA}$) diffraction at room temperature. The symmetry is described by superspace group $P_{111}^{P4/acc}(00\gamma)$ ($t = 0$) with a $(2a \times 2a \times c)$ basic unit cell or equivalently by

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space group $P4/ncc$ in a superstructure approximation with a $(2a \times 2a \times 3c)$ supercell, $V = 3469.5 \text{ \AA}^3$, $Z = 24$. The structure of the $(a \times a \times c)$ subcell is described by $P4/mcc$. The structure was refined to $R = 0.058$, tetragonal unit cell, $2a = 13.024(6)$, $c = 6.818(5) \text{ \AA}$ and modulation vector $\mathbf{q} = 2/3\mathbf{c}^*$. It is shown that this room-temperature lock-in phase is very similar to TaTe_4 . A comparison of basic and modulated structure parameters of TaTe_4 , $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ and NbTe_4 is presented. The interchain distance between Te atoms in the basic structure decreased with increasing Nb content. This change seems to be responsible for the elongation of modulation wavevector from $q = 2/3c^*$ for TaTe_4 to $q = 0.688 c^*$ for NbTe_4 . The same Te—Te interchain distance has been found hardly disturbed by the modulation. Some other conclusions regarding the physical mechanism and the nature of distortions for the NbTe_4 structural archetype are also given.

1. Introduction

Transition-metal tetrachalcogenides are compounds exhibiting a pseudo-one-dimensional character. In many of them charge-density-wave (CDW)-like distortions are observed. In VS_4 these distortions, forming metal dimers along the c axis (Allmann, Baumann, Kutoglu, Rösch & Hellner, 1964), can be explained by the Peierls mechanism (Peierls, 1955).

This, however, is not adequate for chalcogenides of the NbTe_4 structural archetype. The refined structures of two members of this group: incommensurate NbTe_4 (van Smaalen, 1985; Böhm & von Schnering, 1985; van Smaalen, Bronsema & Mahy, 1986) and commensurate TaTe_4 (Bronsema, van Smaalen, de Boer, Wiegers, Jellinek & Mahy, 1987; Budkowski, Prodan, Marinković, Kucharczyk, Uszyński & Boswell, 1989) contain a modulation with wavelength λ close or equal to $3/2c$. The formation of metal-atom 'triplets' indicates a one-third filled d_{z^2} band, whereas the formal oxidation state $M^{4+}(\text{Te}_2^{2-})_2$ (identical to that for VS_4) gives a half-filled band (Whangbo, 1986). Some theoretical works (Bullet, 1984; Whangbo & Gressier, 1984; Whangbo, 1986) could not solve this discrepancy owing to incomplete structural information.

The compounds of NbTe_4 type are also of particular interest for other reasons. They have the same basic structure (Fig. 1), which is the simplest known in quasi-one-dimensional compounds. It consists of infinite columns of square antiprisms with metal atoms in their centres. The modulated phases are stable from liquid-helium temperatures up to temperatures at which the crystals disintegrate in air. However, by preventing decomposition using an argon atmosphere a nonmodulated phase of NbTe_4 has been observed at 793 K (Böhm, 1987). There is

also a series of phase transitions in NbTe_4 and TaTe_4 exhibiting marked similarity (Boswell, Prodan, Bennet, Corbett & Hiltz, 1987; Prodan & Boswell, 1987a). With increasing temperature a rearrangement in neighbouring columns occurs resulting in a change of the supercell base from $(2a \times 2a)$ to $(\sqrt{2}a \times \sqrt{2}a)$. This transition is abrupt in TaTe_4 and sluggish in NbTe_4 (Prodan & Boswell, 1987a,b).

Mixed crystals of $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$, existing with the complete range of $x \in (0,1)$ (Boswell & Prodan, 1984), could give answers to some of the physical problems related to this type of compounds. It was shown that with increasing Nb content, one of two satellites characteristic of TaTe_4 [$\mathbf{q}_1 = (1/202/3)$] vanishes, whereas the second one with $\mathbf{q}_2 = (1/2 \ 1/2 \ q)$ and its second harmonic $2\mathbf{q}_2$ increases linearly from $q = 2/3$ for TaTe_4 to $q = 0.688$ for NbTe_4 (Boswell & Prodan, 1984). Electron diffraction and satellite dark-field images (Eaglesham, 1985) proved that this change is continuous and that mixed crystals are not of a devil staircase type.

In this paper it is shown by a $(3+1)$ -dimensional refinement (§3, §4) that this phase is structurally equivalent to TaTe_4 . Some general conclusions on the nature of the modulation in the NbTe_4 family are derived from a comparison of the basic and modulated structures of $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ with those of the other members of the family, taking into account theoretical predictions by Whangbo (1986) (§4).

2. Experimental

The preparation of mixed crystals is described elsewhere (Boswell, Prodan & Brandon, 1983).

Weissenberg photographs show superstructure reflections at positions indicating a doubling of the a axis and a tripling of the c axis. Both types of

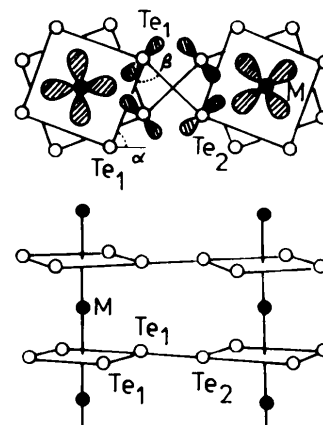


Fig. 1. The basic structure of the NbTe_4 structural archetype. $p\pi^*$ orbitals of Te_1 — Te_2 dimers overlap with $d_{x^2-y^2}$ and d_{xy} orbitals of M atoms.

Table 1. *Final parameters for the basic structure after refinement on main reflections only*

Standard deviations in the last decimal places are given in parentheses. Temperature tensor components U (\AA^2) are defined by $\exp(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*)$.

		<i>P4/mcc</i>	<i>P4cc</i>
$M = (\text{Ta}_p\text{Nb}_{1-p})$	z	$\frac{1}{4}$	0.2454 (18)
	$U_{11} = U_{22}$	0.0050 (3)	0.0051 (2)
Te	U_{33}	0.074 (2)	0.072 (2)
	p	0.72 (2)	0.72 (fixed)
	x	0.1439 (1)	0.1440 (2)
	y	0.3275 (1)	0.3275 (1)
	U_{11}	0.0172 (4)	0.0176 (4)
	U_{22}	0.0098 (3)	0.0102 (3)
	U_{33}	0.0149 (3)	0.0156 (3)
	U_{12}	0.0039 (2)	0.0041 (2)
	U_{13}	0	-0.0029 (11)
	U_{23}	0	-0.0052 (7)
Isotropic extinction parameter	$3.3 (2) \times 10^{-4}$	$2.6 (2) \times 10^{-4}$	

satellites, q_1 and q_2 , together with their second harmonics, characteristic for the commensurate room-temperature TaTe_4 phase, are present. This indicates that at room temperature the crystal is below the potential lock-in transition temperature in agreement with electron diffraction observations for $(\text{Ta}_{0.75}\text{Nb}_{0.25})\text{Te}_4$ (Boswell *et al.*, 1983). The commensurability of the system was also checked by an unsuccessful attempt to perform structure refinement by the use of a program for incommensurately modulated structures (Paciorek & Uszyński, 1987).

A needle-shaped crystal, $0.05 \times 0.07 \times 0.18$ mm, was used for the intensity measurements. 20 365 reflections were recorded on a Philips PW 1100 diffractometer with monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), using ω/θ scans in the θ range $2\text{--}52^\circ$. 6, 6, 18, 249 and 429 were chosen as reference reflections. Their intensities fluctuated up to 2% during the measurements. Indices, on the basis of the $2a \times 2a \times 3c$ supercell, were in the range $0 \leq H, K \leq 28$ and $0 \leq L \leq 42$. After averaging the equivalent reflections and using a $2.5\sigma(F)$ limit 1890 (1534 observed) independent reflections were obtained. A spherical absorption correction ($\mu^*R = 3.6$) was applied. The minimum and maximum absorption correction factors A^* were 14.9 and 62.4, respectively.

For the $(a \times a \times c)$ basic structure, systematic absences were found for the reflections hhl and $0kl$ with l odd. The same systematic extinctions as well as the additional rule: $H = 2n$ and $K = 2n'$ if $L = 3n''$ were deduced for the $(2a \times 2a \times 3c)$ superstructure reflections HKL . The reciprocal lattice is identical to that found for TaTe_4 (Bronsema *et al.*, 1987).

The lattice parameters of the basic structure [$a = 6.512$ (3) and $c = 6.818$ (5) \AA] were determined from 25 independent reflections, $20 < \theta < 45^\circ$.

In all refinements a parameter for isotropic extinction was included and found to be influential. The

different refinements yielded values of about 2×10^{-4} (Tables 1, 2). To reduce the number of free parameters, especially when changing from centro- to noncentrosymmetric groups, anisotropic temperature factors were separately constrained to be equal for Ta/Nb and Te atoms (anisotropic overall model).

All the refinements were carried out using commensurate and incommensurate versions of the least-squares program *MSRLSQ* (Paciorek & Uszyński, 1987). The version for commensurate structures makes it possible to refine commensurate structures with $(3+1)$ -dimensional symmetries. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The refinements were performed by minimizing $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ using unit weights.

3. Structure determination

There are two possible space groups for the basic $(a \times a \times c)$ structure: *P4cc* and *P4/mcc*. We refine the basic structure in both space groups starting from values determined for TaTe_4 by Bronsema *et al.* (1987). The nominal metal composition $M = (\text{Ta}_x\text{Nb}_{1-x})$ was tested by refinement of suitably constrained population parameters for Ta/Nb atoms; the value obtained, $x = 0.72$ (2), is in good agreement with the nominal value of 0.75. The refinements yield R factors of 0.063 and 0.065 for *P4cc* (13 parameters) and *P4/mcc* (11 parameters), respectively. In *P4cc* the $z(\text{Te})$ coordinate was kept zero to fix the origin. Final parameters are summarized in Table 1. Both refinements seem to give different solutions especially regarding the $z(M)$ and $x(\text{Te})$ coordinates. In fact the correct values of these coordinates are influenced by large $U_{33}(M)$ and $U_{11}(\text{Te})$ tensor elements indicating the dominating amplitudes of the displacive modulations. Hence, it is not possible to determine the correct space group of the subcell as long as the satellites are neglected.

There are three possible space groups for the superstructure which are subgroups of the subcell space groups: *P4/mcc*, *P4/ncc* and *P4cc*. Trial refinements carried out with *P4/mcc* were unsuccessful. This was as expected, since the results obtained for TaTe_4 (Bronsema *et al.*, 1987; Corbett, Hiltz, Boswell, Bennet & Prodan, 1988) also exclude this space group. Landau theory calculations (Walker, 1985; Sahu & Walker, 1985) rule out this space group for commensurate modulations with $q = 2/3c^*$ as well.

A simple explanation of all extinction rules has been given in Budkowski *et al.* (1989). The superspace-group description, used in this work, allows a more accurate differentiation between superstructures resulting from the space groups *P4/ncc* and *P4cc*. To meet the formal superspace-

group requirement, the basic structure is described by a larger ($2a \times 2a \times c$) unit cell (Budkowski *et al.*, 1989). The main reflections (*HKL*) are now those in planes of reciprocal space with $L = 3n''$. In four-index notation they are (*hkl0*) with $h = H$, $k = K$ and $l = L/3$. For the chosen wavevector $\mathbf{q} = (0 \ 0 \ 2/3)$ satellites (*hk l m*) are reflections with $m = (L - 3l)/2$ lying in planes of reciprocal space with $L \neq 3n''$.

Several refinements were performed for two groups of models equivalent to centrosymmetrical ($P4/ncc$) and noncentrosymmetrical ($P4cc$) superstructure space groups.

First, a modulated structure refinement within the $P_{111}^{P4/ncc}$ superspace group and for the internal parameter $t = 0$ (Budkowski *et al.*, 1989) was carried out with initial parameters transformed from those of TaTe_4 . A final *R* factor of 0.058 was obtained with 33 free parameters. The results are summarized in Table 2.* *M* and *Te* atoms denoted *MAB* and *TeAB*, respectively, refer to $M\text{Te}_4$ square antiprismatic columns *A* and *B* and those denoted *MCD* and *TeCD* to columns *C* and *D* (Bronsema *et al.*, 1987). Displacement functions for the μ th atom and polarization $\alpha = x, y, z$ are defined by

$$u_{\alpha}^{\mu}(\bar{x}_4) = A_{1\alpha}^{\mu} \cos(2\pi\bar{x}_4) + B_{1\alpha}^{\mu} \sin(2\pi\bar{x}_4) \quad (1)$$

where $\bar{x}_4 = qr$ and r is the atomic position in the average structure. Trials with modulated anisotropic temperature factors (Yamamoto, 1982) did not reduce the *R* factor significantly. Moreover, their amplitudes were lower than three standard deviations. The same model has been refined in the corresponding three-dimensional description within $P4/ncc$ and with the same number of free parameters. In both cases the resulting *R* factors for different types of satellites (Table 3), as well as the atomic positions, are equal (within half a standard deviation for positions).

Further, two refinements were performed for noncentrosymmetric models (Table 3). 37 positional parameters (22 for $P4/ncc$ and 44 for $P4cc$) were needed if second harmonics of displacive waves for $t = 1/12$ and the $P_{111}^{P4/ncc}$ superspace were taken into account. The refinement converged to $R = 0.057$. P_{111}^{P4cc} with harmonic modulations requires the same number of positional parameters (44) as $P4cc$, where the refinement yielded $R = 0.055$ (Table 3). For both noncentrosymmetric models the formerly related atomic positions differ from their hypothetical equivalent positions by more than three standard deviations. However, taking into account the number of structural parameters and the minor differences in

Table 2. Final structural parameters obtained with superspace group $P_{111}^{P4/ncc}$, $t = 0$, and for harmonic modulation

Isotropic extinction parameter: $2.8 (1) \times 10^{-4}$.

Position*		Average structure	A_1	B_1
<i>MAB</i> 4(a)	z	$\frac{1}{4}$	—	0.0491 (4)
($x = \frac{1}{2}, y = \frac{1}{2}$)				
<i>MCD</i> 4(c)	z	0.2469 (3)	0.0308 (4)	-0.0254 (4)
($x = \frac{1}{2}, y = \frac{1}{2}$)				
<i>MAB</i> and <i>MCD</i>	$U_{11} = U_{22}$	0.0049 (1)	—	—
	U_{33}	0.0102 (3)	—	—
[4(a) only]	U_{12}	0.0005 (30)	—	—
<i>TeAB</i> 16(g)	x	0.8211 (2)	-0.0110 (1)	-0.0025 (2)
	y	0.4138 (2)	-0.0058 (2)	0.0001 (2)
	z	0.0000 (5)	-0.0008 (4)	0.0086 (3)
<i>TeCD</i> 16(g)	x	0.3224 (2)	0.0086 (2)	0.0023 (2)
	y	0.4133 (2)	0.0015 (2)	0.0061 (2)
	z	-0.0025 (5)	0.0053 (4)	-0.0054 (3)
<i>TeAB</i> and <i>TeCD</i>	U_{11}	0.0067 (2)	—	—
	U_{22}	0.0062 (2)	—	—
	U_{33}	0.0129 (2)	—	—
	U_{12}	-0.0003 (1)	—	—
	U_{13}	-0.0014 (4)	—	—
	U_{23}	-0.0018 (9)	—	—

*The notation used in this column is explained in Budkowski *et al.* (1989).

Table 3. Number of free parameters and *R* values obtained for different superspace- and space-group models

n_{\max} is the highest harmonic used during refinement.

Model	No. of parameters		<i>R</i> values		
	Positional	All	$R_{m=0}$	$R_{m=\pm 1}$	R_{total}
Basic structure					
$P4/mcc$	2	11	0.065	—	0.065
$P4cc$	3	13	0.063	—	0.063
Modulated structure					
$P4/ncc$	22	33	0.44	0.075	0.058
$P_{111}^{P4/ncc}$ $t = 0, n_{\max} = 1$	22	33	0.044	0.075	0.058
$P_{111}^{P4/ncc}$ $t = 1/12, n_{\max} = 2$	37	48	0.044	0.073	0.057
P_{111}^{P4cc} $n_{\max} = 1$	44	55	0.043	0.071	0.055

R values obtained by different models, it can be concluded that the superspace-group description of the room-temperature $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ structure with $P_{111}^{P4/ncc}$ ($t = 0$), as well as the corresponding $P4/ncc$, represents a very good approximation. $P4/ncc$, which is a subgroup of $P4/mcc$, describes the symmetry of the proposed superstructure. This suggests that $P4/mcc$ is the most-probable space group of the subcell.

4. Discussion

4.1. Basic structure

A comparison of crystallographic data for TaTe_4 , $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ and NbTe_4 is given in Table 4. With decreasing x for the metal site $M = (\text{Ta}_x\text{Nb}_{1-x})$ systematic changes of lattice constants and bond

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52427 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Lattice constants a (Å), interatomic distances (Å) and important bond angles ($^\circ$) for compounds of the NbTe₄ structural type

$M = (\text{Ta}_{0.72}\text{Nb}_{0.28})$, $\alpha = \angle(x\text{—Te1—Te1})$, $\beta = \angle(\text{Te1—Te1—Te2})$. For notation see Fig. 1. Bonding distances were calculated for TaTe₄ and NbTe₄ from structural parameters reported by Bronsema *et al.* (1987) and van Smaalen *et al.* (1986).

	a	$M\text{—}M$	Te1—Te1	Te1—Te2	$M\text{—}M$	α	β
TaTe ₄	6.514	3.406	3.295	2.927	2.886	68.71	71.49
MTe ₄	6.512	3.409	3.294	2.925	2.886	68.72	74.45
NbTe ₄	6.499	3.419	3.292	2.917	2.888	68.72	71.34

lengths are observed in spite of identical Ta and Nb ionic radii (Fig. 1). Lattice constant a as well as Te1—Te2 distances between neighbouring columns decrease, while those between metals along the c axis ($c/2$) increase. Changes in the length of Te1—Te1 square edges and of $M\text{—}M$ bonds are one order of magnitude smaller.

It seems that the Te1—Te2 interchain distance is the most important of all these changes. Although varying for different compounds, this distance is, in contrast to other bonds, hardly disturbed by the modulation. This appears to be the boundary condition for the modulated structures of NbTe₄ structural type (Böhm & von Schnering, 1985; Bronsema *et al.*, 1987). Te1—Te2 contacts represent Te₂²⁻ dimers. As a consequence, in a first approximation, the metal atom of MTe₄ exists as an M^{4+} (d^0) ion. The $p\pi^*$ orbitals of Te₂²⁻ units interact effectively with all the d orbitals of M^{4+} except with z^2 (Fig. 1) (Whangbo, 1986). Hence, the d_{z^2} level is well separated in energy from other d levels. The overlapping of p and d orbitals stabilizes the NbTe₄-type structure as compared with the VS₄ type (Bullet, 1984; Bronsema *et al.*, 1987). The decrease of the a lattice constant with increasing Nb content is caused by a shortening of the Te1—Te2 interchain distance (Te₂²⁻), whereas Te1—Te1 distances remain practically unchanged. The mutual angular orientation of these square edges (expressed by the angle α) is also kept constant. As a result the angle β between the Te square edge and the Te₂²⁻ pair decreases (Fig. 1). This in turn means that the $p\pi^*$ orbitals of Te₂²⁻ dimers are shifted in the xy planes towards the d orbitals of M^{4+} . Such an effect is accompanied by shifts of metal atoms outwards in the z direction, if p, d overlapping is assumed to be constant for all members of the NbTe₄—TaTe₄ family. However, it is difficult to decide which of these two effects is the driving one, since available band-structure calculations (Bullet, 1984; Whangbo & Gressier, 1984; Whangbo, 1986) are not sufficiently detailed.

In our opinion the evident shortening of the Te₂²⁻ pair length with increasing Nb content is responsible for the linear increase of the modulation wavevector

from $q = 2/3c^*$ for TaTe₄ to $q = 0.688c^*$ for NbTe₄ (Boswell & Prodan, 1984). The charge-density-wave wavevectors $q = 2k_F$ (Wilson, 1979; Boswell *et al.*, 1983) rewritten into the units of $M\text{—}M$ distance d along the chain give: $q = 1/3d^*$ and $0.344d^*$, and lead to 33.3% and 34.4% d_{z^2} band filling ($f = 2k_F/d^*$) for TaTe₄ and NbTe₄, respectively. These experimental values differ from the theoretical one of 50%, resulting from the oxidation state $M^{4+}(\text{Te}_2^{2-})_2$. This discrepancy can be explained (Whangbo, 1986) assuming that not all of Te—Te bonds are of the Te₂²⁻ type and that a certain fraction w is in the 2Te^{2-} oxidation state. This assumption is reasonable because the interchain Te—Te distance of ~ 2.92 Å for MTe₄ is longer than the Te₂²⁻ pair distance, for example in ZrTe₃ (2.761 Å) (Furuset, Brattås & Kjekhus, 1975), Nb₂Te₂Br₆ (2.670 Å) or Nb₂Te₂I₆ (2.685 Å) (Franzen, Hönle & von Schnering, 1983). For the necessary enlargement of the q vector the fraction w has to be changed from 8.3 (3)% for TaTe₄ to 7.8% for NbTe₄. The process $2\text{Te}^{2-} \rightarrow \text{Te}_2^{2-}$, associated with the reduction of the Te1—Te2 distance, releases electrons, which are transferred to the d_{z^2} band of the M atom, increasing the modulation wavevector.

4.2. Modulated structure

In the ($2a \times 2a \times 3c$) superstructure of (Ta_{0.72}Nb_{0.28})Te₄ four columns A, B, C, D can be distinguished. Only two are independent in $P4/ncc$, since chains C and D are related by a centre of symmetry and chains A and B by fourfold rotations C_4 . This is why Te squares in these columns are rectangularly deformed. All important interatomic distances in (Ta_{0.72}Nb_{0.28})Te₄ are shown in Fig. 2. All modulations — a longitudinal one for M atoms as well as

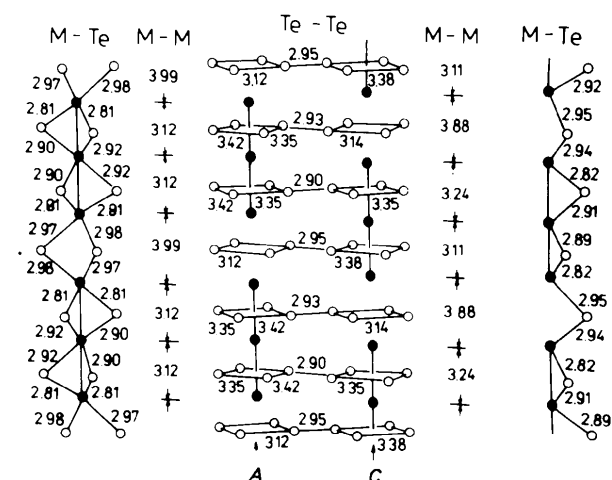


Fig. 2. Schematic sketch of two nonequivalent columns A and C with interatomic distances in Å.

three deformation modes for Te 'squares' – are similar to that determined for TaTe_4 [see Böhm & von Schnering (1985) and Bronsema *et al.* (1987)].

Obviously, there is a strong coupling between the longitudinal modulation of M atoms and displacements of Te atoms. This was found also in TaTe_4 (Bronsema *et al.*, 1987) and in NbTe_4 (Böhm & von Schnering, 1985; van Smaalen *et al.*, 1986). One can compare important interatomic distances of $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ with the corresponding ones of commensurate TaTe_4 and incommensurate NbTe_4 (Bronsema *et al.*, 1987). A comparison is presented in Fig. 3. The internal parameter $t = \bar{x}_4 - qr$ is shifted by $\Delta t = 1/6$ so that the present results can be compared with those of Bronsema *et al.* (1987).

It is also of interest to compare modulation amplitudes and phases for these three compounds explicitly. To avoid problems during transformation of modulation parameters between incommensurate and commensurate systems structural data for NbTe_4 obtained by Böhm & von Schnering (1985) were used. They refined the NbTe_4 modulated structure as a superstructure with space group $P4$. Table 5 presents a comparison of the modulation parameters recalculated according to the function:

$$u_\alpha^\mu(\bar{x}_4) = u_{0\alpha}^\mu + C_\alpha^\mu \cos(2\pi\bar{x}_4 + \varphi_\alpha) \quad (2)$$

where $u_{0\alpha}^\mu$ is the zero-order Fourier term, $\bar{x}_4 = qr$ and r is the atomic position in the basic structure. Parameters for TaTe_4 are transformed from the results of Bronsema *et al.* (1987). The two columns A_H and B_H of room-temperature NbTe_4 are related to the two column pairs: A, B and C, D of room-temperature TaTe_4 , respectively. Two sets of parameters are given in the case of NbTe_4 . They correspond to the atomic positions (xyz) and $(yxz + 1/2)$, because of the lack of a glide mirror in $P4$.

It is easy to notice that modulation parameters are hardly affected by the composition of

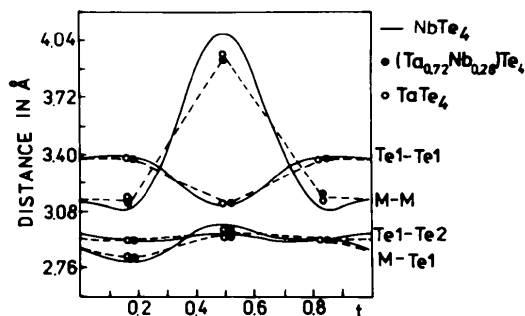


Fig. 3. Comparison between important distances for representatives of the NbTe_4 structural type: incommensurate NbTe_4 , commensurate $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ and commensurate TaTe_4 (Bronsema *et al.*, 1987).

Table 5. Modulation-function parameters for compounds of the NbTe_4 structural type

The modulation-function parameters are given with reference to the $(2a \times 2a \times c)$ unit cell.

	TaTe_4	$(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$	$\text{NbTe}_4(xyz)$	$\text{NbTe}_4(yxz + \frac{1}{2})$
MAB				
u_{z0}	0	0	0.0005	0.0013
C_z	0.0457	0.0491	0.0501	0.0341
φ_z	270°	270°	265.3°	263.6°
MCD				
u_{z0}	-0.0021	-0.0032	-0.0090	-0.0096
C_z	0.0461	0.0399	0.0475	0.0366
φ_z	33.4°	38.7°	40.7°	41.0°
TeAB				
u_{z0}	-0.0003	-0.0009	0.0012	0.0003
C_x	0.0107	0.0125	0.0111	0.0115
φ_x	167.0°	167.1°	165.5°	171.5°
u_{y0}	-0.0004	0.0001	0.0003	-0.0004
C_y	0.0055	0.0058	0.0047	0.0052
φ_y	185.5°	181.1°	187.1°	188.0°
u_{z0}	0.0008	0.0000	-0.0043	0.0013
C_z	0.0088	0.0087	0.0093	0.0036
φ_z	258.8°	265.1°	266.9°	249.1°
TeCD				
u_{z0}	-0.0002	0.0004	-0.0014	0.0000
C_x	0.0091	0.0089	0.0104	0.0099
φ_x	340.6°	344.6°	332.8°	340.1°
u_{y0}	-0.0003	-0.0004	-0.0023	-0.0010
C_y	0.0076	0.0063	0.0037	0.0034
φ_y	285.9°	282.9°	296.5°	306.8°
u_{z0}	-0.0025	-0.0025	-0.0086	-0.0048
C_z	0.0088	0.0076	0.0048	0.0072
φ_z	30.0°	44.9°	38.3°	51.2°

$(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$. For all atoms amplitudes for both types of columns are close to each other, with average values of: $C_z(MAB) \cong 0.045$ (4) [0.305 (25) Å] and $C_z(MCD) \cong 0.043$ (3) [0.290 (17) Å]; $C_x(\text{TeAB}) \cong 0.012$ (0) [0.149 (5) Å] and $C_x(\text{TeCD}) \cong 0.010$ (0) [0.125 (4) Å]; $C_y(\text{TeAB}) \cong 0.005$ (0) [0.069 (3) Å] and $C_y(\text{TeCD}) \cong 0.005$ (1) [0.068 (13) Å] as well as $C_z(\text{TeAB}) \cong 0.008$ (1) [0.052 (9) Å] and $C_z(\text{TeCD}) \cong 0.007$ (1) [0.048 (6) Å]. The mutual phase shift between modulation waves of the AB (A_H) and CD (B_H) chains of atoms is equal in all these compounds to within $\pm 4^\circ$, except for very weak y and z components of Te ($\pm 7^\circ$). The phase shift for longitudinal modulation of M atoms is approximately equal to $2\pi/3$ with $\varphi_z(MAB) \cong 267$ (2)° and $\varphi_z(MCD) \cong 38$ (2)°.

5. Concluding remarks

Space-group determination was crucial in the present crystal structure analysis of room-temperature $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$. Similar to room-temperature TaTe_4 (Bronsema *et al.*, 1987; Budkowski *et al.*, 1989) the deduced supercell space group, $P4/ncc$, is equivalent to the superspace group, $P_{111}^{P4/ncc}$, $t = 0$. It

is justified only on the basis of a reduced number of free parameters needed for the structure description with no influence on the discrepancy factor R . The same difficult choice between centro- and noncentrosymmetric space groups occurs in case of the ($a \times a \times c$) basic structure. If $P4/ncc$ is chosen to describe the modulated structure, then the correct space group for the basic structure is $P4/mcc$.

The commensurately modulated structure of $(\text{Ta}_{0.72}\text{Nb}_{0.28})\text{Te}_4$ at room temperature is very similar to that of the room-temperature phase of TaTe_4 . This is the first evidence of a lock-in phase continuity with changing stoichiometry x in the $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$ system.

Continuous changes of the lattice constants of the basic structure and of bonding distances across the $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$ series can be explained by a reduction in the interchain distance between Te atoms with increasing x . This change is also responsible for the elongation of the modulation wavevector from $q = 2/3c^*$ for TaTe_4 to $q = 0.688c^*$ for NbTe_4 .

A great similarity was found between all three commensurately and incommensurately modulated representatives of the NbTe_4 structural type. Modulation amplitudes and phases calculated for them in commensurate approximation (also for incommensurate NbTe_4) are almost constant. This points out the possible explanation of the phase transformations occurring when composition or temperature is changed. Namely, the structural differences within two pairs of columns (characteristic for the lock-in phase) disappear leading to two different columns in the incommensurate phase (Prodan, 1986; Walker & Morelli, 1988; Chen, Walker & Morelli, 1989; and references therein).

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