type seen in $Au_{22}Mn_6$ (Hiraga et al., 1982). In the present case, there is a sliding offset of Mn-column positions as indicated, for example, by the arrows in Fig. 7(b) and the width of $D1a$ along the long-period axis is different. Careful observation of these images enables a schematic model for this lattice 'side-step' to be obtained, as drawn in Fig. 7(c) where the difference in brightness of spots is indicated by the lined, half-filled or solid circles (and the regions of $D1a$ type are shown in screen-tone). The structure model of $Au_{22}Mn_6$ is also shown in Fig. 7(d) for comparison. Some apparent nearest-neighbour Mn-Mn pairs, the brightness of which is lower than that of other parts, are visible at the side-step. However, no nearest-neighbour Mn-Mn pairs are known to exist in this alloy. Moreover, the recorded image comes from the projection of the structure along the incident-beam direction. Thus, it can be concluded that the occupation probability of the Mn atoms in the columns is less than unity in order to avoid true nearest-neighbour Mn-Mn pairs, and this causes the lower contrast of the pairs, as discussed for the 'super-structure' image condition (Shindo, Hiraga & Hirabayashi, 1984). It is not possible to distinguish where the Mn atoms are located in the columns, whether there is perfect order along the tilt boundary or if the Mn atoms occupy the columns randomly along the beam direction. It should be noted that the superstructure shown in Fig. 7(c), which is effectively $Au_{14}Mn_4$, has not previously been reported.

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The Determination of the Incommensurately Modulated Structure of Niobium Tetratelluride

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Abstract

A complete analysis of the modulated structure of $NbTe_4$ is presented, using the newly developed formalism of de Wolff [Acta Cryst. (1974). A30, 777-785] and Yamamoto [Acta Cryst. (1982). A38, 87-92]. The diffraction pattern was measured at room temperature, including first-order and second-order satellites. The superspace group of the complete structure is $W^{P4/mcc}_{1\bar{1}11}$. The final R_F^2 value is 0·095 (0·044 for main reflections only), for a total of 3894 unique reflections (923 main reflections). The average structure found previously [Selte & Kjekshus (1964). Acta Chem. Scand. 18, 690-696] is confirmed. In addition, the modulation wave is determined; it resides mainly on the Nb atoms, which have an amplitude of 0·33 Å. The results show that the displacements are correlated in such a way as to keep the Te-Te bonding distance constant and to minimize the variation in the shortest Nb-Te distance. It is found possible to refine at least

up to the fifth harmonic in the modulation wave. However, the values found for higher harmonics do not describe the real modulation wave, but assume values to account for the variation in intensities due to experimental errors. Therefore, only the amplitudes up to the second order are considered to be reliable.

1. Introduction

In the last decades there has been growing interest in compounds with quasi-one-dimensional properties. Among these there is the class of organic conductors (*Proceedings of the International Conference on One-Dimensional Conductors*, 1983) which have an electron band confined almost to one direction in the crystal. Another class is that of the transition-metal tri- and tetrachalcogenides (*Proceedings*, 1983), which have a charge-density-wave (CDW) state. They also exhibit unique electronic properties along the directions of the CDW.

One of the latter compounds is NbTe$_4$, which is discussed here.

Selte & Kjekshus (1964) determined the average structure of NbTe$_4$. Their subcell is tetragonal with $a = b = 6\cdot499$ and $c = 6\cdot837$ Å. Additional spots in the diffraction pattern were attributed to a $2a \times 2b \times 3c$ superstructure. Later work (Mahy, Wiegers, van Landuyt & Amelinckx, 1984; Boswell, Prodan & Brandon, 1983; Böhm & von Schnering, 1983) showed that there is not an exact tripling of the c axis. A careful analysis of X-ray data (Böhm & von Schnering, 1983; Boswell & Prodan, 1984) and of electron diffraction photographs (Mahy *et al.*, 1984) showed that the satellite spots appear at $\frac{1}{2}a^* + \frac{1}{2}b^* + 0\cdot309c^*$, thus indicating a modulation which is incommensurate with the periodicity of the average structure.

In this paper we present the result of a full X-ray analysis of the incommensurately modulated structure of NbTe$_4$, using the method developed by de Wolff (1974) and Yamamoto (1982a). In particular, the use of the so-called superspace groups (de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983) will be shown to be very powerful in determining the nature of the modulation wave.

2. Description of the diffraction pattern

In the reflection pattern of NbTe$_4$ one can distinguish two classes of reflections: a group of strong reflections and a group of weaker reflections. The reflections of the first group are at the nodes of the reciprocal lattice Λ^*, spanned by the vectors a^*, b^* and c^*, as was also used by Selte & Kjekshus (1964). The corresponding direct lattice gives the periodicity of the average structure. With use of the reciprocal lattice and a fourth vector $q' = \frac{1}{2}a^* + \frac{1}{2}b^* + 0\cdot309c^*$, all diffraction vectors can be described as an integral linear combination

of these four vectors,

$$S = ha^* + kb^* + lc^* + mq', \qquad (1)$$

where h, k, l and m are integers.

Diffraction spots with $m = 0$ are the so-called main reflections. From these the average structure can be determined. The reflections with $m \neq 0$ are the $|m|$th-order satellites. The combination of main reflections and satellites enables one to determine the modulated structure.

There are essentially two ways along which one can proceed to determine such a structure. Commonly used is the method in which a larger unit cell is chosen, in such a way that all reflections can be described with integer coefficients with respect to the new reciprocal base-vectors. Consequently a structure determination can be accomplished using the usual formulas for X-ray analysis. The difficulty now arises that the parameters of crystallographically independent atoms often become strongly correlated. Therefore some model has to be built to constrain the parameters to each other. A second difficulty of this supercell approach is that it is only possible exactly when the components of the modulation wave are rational numbers. In the case of NbTe$_4$ the c^* component of the modulation wavevector is irrational (or, a fraction with a very large denominator), so there is no true periodicity of NbTe$_4$ along this axis.

A more rigorous and more favourable description for an incommensurately modulated crystal is to describe it in the so-called modulated-crystal approach.† The reflections are then described according to (1). However, a modified form for the structure factor has to be used (de Wolff, 1974; Yamamoto, 1982a). The problem of dependent parameters does not now arise. Up to the mth-order harmonics of the modulation function can be determined, when the satellites up to the mth order are measured (van der Aalst, den Hollander, Peterse & de Wolff, 1976).

3. Experimental

The preparation of the crystals is described elsewhere (Mahy *et al.*, 1984).

Weissenberg photographs were taken with monochromatized Cu $K\alpha_1$ radiation, in order to have a preliminary scan of the symmetry and crystallographic data. The photographs clearly show the presence of satellite spots, with a wavevector of $(\frac{1}{2}, \frac{1}{2}, 0\cdot309)$.

The intensity data, necessary for the refinement, were collected on an Enraf-Nonius CAD-4 four-circle diffractometer with monochromatized Mo $K\alpha$

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† Frequently, the modulated-crystal formalism can also be of advantage for the description of commensurately modulated crystals [see Bronsema & Mahy (1985), Bronsema, van Smaalen & Mahy (1985) and van Smaalen, Bronsema & Wiegers (1985)].

Table 1. *The number of measured inequivalent reflections*

	Observed	Excluding less-than's*
Main reflections	972	923
First-order satellites	1846	1598
Second-order satellites	1935	1373
Total	4753	3894

* Less-than's are defined by $F_{obs} < 3\sigma_F$.

Table 2. *Lattice parameters of the average structure (tetragonal lattice)*

Selte & Kjekshus (1964) and Boswell *et al.* (1983) do not report standard deviations.

	This work	Selte & Kjekshus (1964)	Boswell *et al.* (1983)
$a = b$ (Å)	6·499 (2)	6·499	6·496
c (Å)	6·837 (2)	6·837	6·823

radiation, using the θ-2θ scan technique. In order to measure the satellite reflections a modified CAD-4 program (de Boer & Duisenberg, 1984) was used, which was able to measure reflections with non-integral indices. $\theta_{max} = 55°$; the *hkl* indices are in the range 0 to 15. Up to second-order satellites were measured; the third- and higher-order satellites were too weak to be observed. A crystal approximately $0.2 \times 0.1 \times 0.1$ mm was used. A total of 14 400 reflections (main reflections, first-order and second-order satellites) were measured. Corrections were made for the Lorentz–polarization effect and for absorption ($\mu = 224.1\ cm^{-1}$) (Spek, 1983). Finally, for the equivalent reflections the average value was taken and all systematic extinctions were removed. The number of inequivalent reflections and the number of reflections excluding those with $F_{obs} < 3\sigma_F$ (less-than's) are given in Table 1. Main reflections 211, 121 and 112 were used as standards: maximum variation 18%, between the several series measured over a period of 3 weeks.

4. Symmetry

The space group of the average structure is determined to be $P4/mcc$ with an inversion centre, or $P4cc$ without, in agreement with Selte & Kjekshus (1964). Boswell *et al.* (1983) proposed a group of lower symmetry, $P422$. Their argument was based on the fact that they observed some reflections which should be absent in $P4cc$. The presence of these reflections is probably due to the half-lambda effect. This is strongly suggested by the fact that we did observe these reflections on the diffractometer (using Mo $K\alpha$ radiation), while we did not observe them on the
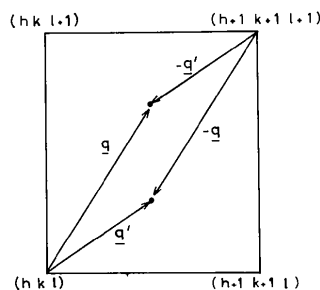
photographs (obtained with Cu $K\alpha$ radiation), even after long exposure times. Selte & Kjekshus (1964) used Cu $K\alpha$ radiation too, whereas Boswell *et al.* (1983) used Mo $K\alpha$ radiation.

The lattice parameters of the average structure were determined from 25 high-order reflections and are summarized in Table 2.

All satellites can be described with one modulation wavevector, $\mathbf{q}' = \frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{b}^* + 0.309\mathbf{c}^*$. Consideration of the whole diffraction pattern (both satellites and main reflections) leads to the four-dimensional Bravais class $W^{P4/\frac{mmm}{1\ 1\ 1}}_{1}$ (No. 20) of the classification of de Wolff *et al.* (1981). The possible space groups can then be obtained from the systematically extinct reflections. To arrive at a space group which is present in the tables of de Wolff *et al.* (1981), and not at one which is only equivalent to a space group in these tables, it is necessary to choose another modulation wavevector (de Wolff, 1984). The proper choice is:

$$\mathbf{q} = \mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^* - \mathbf{q}' = \frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{b}^* + 0.691\mathbf{c}^*. \quad (2)$$

The effect of this transformation is that a first-order satellite indexed with $(hkl\ +1)$ with respect to $\mathbf{q}' = (\frac{1}{2}\frac{1}{2}0.309)$, is indexed with $(h+1\ k+1\ l+1\ -1)$ with respect to the new modulation wavevector $\mathbf{q} = (\frac{1}{2}\frac{1}{2}0.691)$ (see Fig. 1). By this transformation, the second-order satellites are also assigned to another main reflection. One can refer to these different choices of modulation wavevector as the choice of different settings of the (four-dimensional) lattice.

In order to analyse the systematic extinctions, it is necessary to transform the subcell in such a way that only the irrational components of the modulation wavevector remain (de Wolff *et al.*, 1981). The required transformation is (see Fig. 2):

$$\mathbf{A} = (\mathbf{a} + \mathbf{b})$$
$$\mathbf{B} = (\mathbf{b} - \mathbf{a})$$
$$\mathbf{C} = \mathbf{c} \quad (3)$$
$$\mathbf{q}_i = (0, 0, 0.691)$$

The indices of the reflections *hklm* are transformed accordingly to *HKLM*. The systematic extinctions are: $L = 2n$, both for the $0KLM$ and the *HHLM* reflections. This indicates the presence of two distinct glide planes $\binom{c}{1}$. The latter symbol means a c glide in ordinary three-dimensional (3D) space, accompanied

Fig. 1. The two possible choices of the modulation wavevector.

by the identity transform in the fourth dimension. The only two possible superspace groups are then $W^{P4cc}_{11\bar{1}}$ and its centrosymmetric counterpart $W^{P4/mcc}_{1\,\bar{1}\,11}$.

5. Determination of the structure

The space group of the average structure is $P4/mcc$ or $P4cc$. In $P4/mcc$ Te lies at special position $8(m)$ at $(x, y, 0)$ and Nb at special position $2(a)$ at $(0\,0\,\frac{1}{4})$. The refinement was first performed in the centrosymmetric space group, starting from the values determined by Selte & Kjekshus (1964). Using the main reflections excluding less-than's an R_{F^2} factor of $0\cdot100$ was obtained. The atomic scattering factors are taken from *International Tables for X-ray Crystallography* (1974). The definitions used here are $R_F = \sum \|F_{obs}| - |F_{calc}\|/\sum |F_{obs}|$ and $R_{F^2} = [\sum (|F_{obs}| - |F_{calc}|)^2/\sum |F_{obs}|^2]^{1/2}$. The refinements are performed by minimizing R_{F^2}. All refinements were performed using unit weights. Inspection of the structure factor list showed that eight strong low-order reflections were heavily affected by extinction. Therefore, one additional parameter describing isotropic secondary extinction (Becker & Coppens, 1974; Yamamoto, 1982b) was used in the refinement. The R_{F^2} factor dropped to a value of $0\cdot065$, with an extinction parameter of 6×10^{-5}. The large drop in R factor, on addition of only one parameter, indicates that secondary extinction is indeed an important effect here. The final parameters are given in Table 3 (for all parameters $\Delta/\sigma = 0$).* The refinement was also performed using the restrictions imposed by the noncentrosymmetric space group $P4cc$. To fix the origin, the z parameter of Te was kept at zero. The R factor found for the noncentrosymmetric parameter set was not lower than that for the centrosymmetric

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42427 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
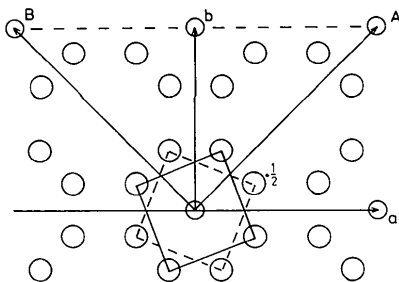

Fig. 2. Projection of the average structure along **c**. The two different unit cells used in this paper [equation (3)] are shown. Large circles denote Te atoms, small circles denote Nb atoms. [See equation (3) and Fig. 2 for the relation between (**A**, **B**, **C**) and (**a**, **b**, **c**).]

Table 3. *Final parameters for the average structure after refinement on main reflections only*

The temperature factor has the form $\exp(-W)$, with $W = \sum_i \sum_j h_i h_j \beta_{ij}$. The e.s.d.'s are given in parentheses. All values refer to the larger (A, B, C) unit cell [equation (3)].

Nb	x	$0\cdot$	Te	x	$0\cdot23599\,(9)$
	y	$0\cdot$		y	$0\cdot09193\,(8)$
	z	$\frac{1}{4}$		z	$0\cdot$
	$\beta_{11} = \beta_{22}$	$0\cdot00116\,(7)$		β_{11}	$0\cdot00374\,(7)$
	β_{33}	$0\cdot02891\,(93)$		β_{22}	$0\cdot00189\,(5)$
				β_{33}	$0\cdot00389\,(9)$
				β_{12}	$-0\cdot00109\,(4)$

one. From this we conclude that, as far as the average structure is concerned, there is a centre of symmetry.

For the refinement of the average structure both the *XRAY* system (Stewart, 1976) and the least-squares program *REMOS* (Yamamoto, 1982b) lead to the same results.

The average structure contains two independent atoms in the unit cell. In the modulated structure the additional parameters are the amplitudes of the modulation wave belonging to these two atoms. In principle one has to consider both occupation modulation and displacive modulation. The stoichiometry and the dependence of the satellite intensities on HKL strongly indicates that only a displacive modulation is present. Consequently, it is the only kind of modulation considered here. For a displacive modulation, the modulation function of each atom can be described as,

$$\mathbf{u}^\mu = \mathbf{u}^\mu(\bar{x}_4), \qquad (4)$$

where $\bar{x}_4 = \mathbf{q} \cdot \mathbf{r}_0^\mu$ is the fourth coordinate, $\mathbf{r}_0^\mu = \mathbf{n} + \mathbf{x}_0^\mu$ is the position of the μth atom in the nth unit cell in the average structure and $\mathbf{u}^\mu$ is its displacement in the real structure.

A symmetry operator of the modulated structure transforms the 3D space coordinates according to a 3D point-group operator R and a 3D translation τ. This transformation is accompanied by a transformation of the fourth coordinate as follows: $x_4 \rightarrow \varepsilon x_4 + \tau_4$, where τ_4 is the fourth translation component and $\varepsilon = \pm 1$ according to $\mathsf{R}\mathbf{q} = \pm \mathbf{q}$. For a particular supersymmetry group a notation for such an operator is $(\mathsf{R}|\tau)$, where τ stands for the four translation components and the value of ε is understood to follow from $\mathsf{R}\mathbf{q} = \varepsilon \mathbf{q}$.

Now, let K_μ be the group of symmetry operators $(\mathsf{R}|\tau)$ which leave the position of the μth atom invariant. Then, the symmetry restrictions on the components of the modulation wave are obtained from

$$\mathbf{u}^\mu(x_4) = (\mathsf{R}|\tau)\mathbf{u}^\mu(x_4) \qquad (5)$$

with $(\mathsf{R}|\tau) \in \mathsf{K}_\mu$. Only the generators of K_μ have to be considered here.

In the centrosymmetric point group, Nb is left invariant by $(C_4|0000)$ and $(C_2|00\frac{1}{2}0)$. The latter

Table 4. *Symmetry restrictions on the components*
of the modulation function
$$\mathbf{u}(\bar{x}_4) = u_1(\bar{x}_4)\mathbf{A} + u_2(\bar{x}_4)\mathbf{B} + u_3(\bar{x}_4)\mathbf{C}$$

Depicted is whether a particular component is an even function, an odd function, has to be zero, or is not restricted.

		Nb	Te
$W'^{P4/mcc}_{1\ \bar{1}11}$	u_1	zero	even
	u_2	zero	even
	u_3	odd	odd
W'^{P4cc}_{111}	u_1	zero	none
	u_2	zero	none
	u_3	none	none

operator is only present in the centrosymmetric group. Te lies only on a special position in the centrosymmetric group. It is then left invariant by $(m|0000)$, the horizontal mirror plane. From these operators the symmetry restrictions on the functions describing the modulation wave were obtained. They are summarized in Table 4.

With the restrictions on the components of the modulation function thus obtained, the refinement of the structure could be performed. For the refinement a least-squares program written by Yamamoto (1982b) was used. The parameters in the refinement were the average position parameters, the components of the temperature tensor, the Fourier amplitudes of the modulation wave and the extinction parameter. The Fourier amplitudes are defined by,

$$u_\alpha^\mu(\bar{x}_4) = \sum_{n=1}^{\infty} [A_{n\alpha}^\mu \cos (2\pi n\bar{x}_4)$$
$$+ B_{n\alpha}^\mu \sin (2\pi n\bar{x}_4)] \tag{6}$$

$(\alpha = x, y, z)$, where $A_{n\alpha}^\mu$ and $B_{n\alpha}^\mu$ are the amplitudes of the nth-order Fourier component of the μth atom. Note that A refers to the even component and B refers to the odd component of the modulation wave.

As shown by van der Aalst *et al.* (1976) the intensities of the nth-order satellites are dominated by the Fourier components up to the nth order. Therefore, the most feasible procedure to determine the Fourier amplitudes is to start the refinement with the first harmonic and then to add the other harmonics consecutively. First an attempt was made to test whether the centre of symmetry is absent or not. To this end, three refinements were performed using the main reflections and the first-order satellites. Initially the first-order harmonics were refined in the centrosymmetric space group, starting from the parameters of the average structure and a small offset of one of the modulation parameters. A smooth convergence was obtained to the final parameters in eight least-squares cycles. Using this result, a refinement was performed in the centrosymmetric space group of the harmonics up to the second order and a refinement was carried out in the noncentrosymmetric space group of the harmonics up to the first order.

Table 5. *R values for different centrosymmetric and noncentrosymmetric refinements, showing the effect of a centre of symmetry*

(a) Refinement on main reflections and first-order satellites

		$1, c^*$	$2, c$	$1, nc$
†R_F	0	0·054	0·039	0·042
	1	0·127	0·072	0·100
	overall	0·086	0·054	0·068
R_{F^2}	0	0·055	0·045	0·046
	1	0·133	0·080	0·109
	overall	0·080	0·055	0·066
Number of parameters		14	18	20

(b) Refinement on main reflections and first- and second-order satellites

		$2, c$	$3, c$	$2, nc$
R_F	0	0·044	0·046	0·040
	1	0·102	0·077	0·091
	2	0·319	0·229	0·242
	overall	0·106	0·084	0·090
R_{F^2}	0	0·047	0·050	0·044
	1	0·110	0·086	0·097
	2	0·378	0·262	0·295
	overall	0·095	0·077	0·080
Number of parameters		18	24	24

* The highest harmonic used in the refinement is given, and also whether the centrosymmetric (c) or noncentrosymmetric (nc) group is used.

† For the definition of R_F and R_{F^2} see text.

In the latter refinement the z parameter of the average position of Te was fixed as choice of origin and the cosine part, A_{1z}, of the modulation wave of Nb was kept at zero to fix the phase of the modulation wave. The resulting R_{F^2} values are displayed in Table 5(a). This shows that the addition of the second harmonic in the centrosymmetric space group gives a larger drop in R factor than does going from the centrosymmetric to the noncentrosymmetric space group, whereas the latter refers to more parameters. The same effect is observed for refinement on all reflections (Table 5b). From this we conclude that the structure is centrosymmetric.

After establishing the presence of a centre of symmetry, a series of refinements of the parameters up to the nth-order harmonics, for $n = 2, 3, 4, 5$, using both the first- and second-order satellites and the main reflections, was carried out. The resulting R values for all these refinements are given in Table 6. It seems that one can go on and on adding modulation-wave harmonics. However, we think that the higher harmonics are not meaningful. The first reason is that the addition of each harmonic introduces four more parameters, whereas it appears from Table 6 that on going to higher order the drop in R factor becomes less on addition of one more harmonic. Secondly, the contribution from a harmonic to the structure factor of a particular reflection will decrease rapidly on increasing the order of the harmonic (van der Aalst *et al.*, 1976). Although no numerical estimate was made, it can be said safely that harmonics higher

Table 6. *R values for the final results of a series of refinements*

		*$n = 2$	$n = 3$	$n = 4$	$n = 5$
†R_F	0	0·044	0·046	0·037	0·035
	1	0·102	0·077	0·073	0·055
	2	0·319	0·229	0·166	0·165
	overall	0·106	0·084	0·070	0·061
R_{F^2}	0	0·047	0·050	0·043	0·042
	1	0·110	0·086	0·083	0·067
	2	0·378	0·262	0·194	0·196
	overall	0·095	0·077	0·064	0·060
Number of parameters		18	22	26	30

* Up to the nth-order harmonic is used in the refinement.
† For definition of R_F and R_{F^2}, see text.

than the fifth do not give any appreciable contribution to the structure factor of reflections up to the second order. Finally, and even more important, an argument lies in the values of the Fourier amplitudes obtained in the different refinements (Table 7). When we look, for example, at the Fourier amplitudes B_{nz} of Nb (all other Fourier amplitudes of Nb are zero by symmetry), we see that the first and second harmonics are not much affected by the number of harmonics taken into account in the refinement. However, the higher harmonics change markedly on adding additional harmonics in the refinement. The most striking example is the B_{4z} and B_{5z} amplitudes. In the refinement up to the fourth order the B_{4z} amplitude becomes extraordinarily large. In the refinement up to the fifth order, it drops by a factor of ten, but now the B_{5z} amplitude becomes very large. We think that the effects observed here can be attributed to the experimental errors in the measured intensities. The higher harmonics do not represent a real modulation of the atoms in the crystal, but their numerical values account for the deviations in the structure factors from their true values. It is stressed that we do not intend to say that the higher harmonics cannot have an important contribution to the modulation function. Our conclusion is that the order up to which the satellites can be measured, limits the order up to which the harmonics can be determined. Because of these reasons, we have taken the refinement up to the second-order harmonic as the final result. The final parameters are given in Table 8. Note that all values refer to the larger unit cell defined in equation (3).

One point still needs discussion: the large R factor of the second-order satellites. Inspection of the structure factor list shows that the values $|\Delta F| = \||F_{obs}| - |F_{calc}|\|$ are not larger for the second-order satellites than for the first-order satellites and main reflections. However, the intensities of the second-order satellites are much lower than those of the other reflections, indicating that the relative errors in these reflections are much higher. Consequently the best fit of the second-order satellites will be reached at a higher R factor than the best fit of the other reflections.

Table 7. *The B_{nz} values of the Nb amplitudes for the various refinements*

	*$n = 2$	$n = 3$	$n = 4$	$n = 5$
B_{1z}	−0·0390 (2)	−0·0379 (1)	−0·0368 (1)	−0·0363 (1)
B_{2z}	0·0164 (2)	0·0173 (2)	0·0167 (2)	0·0169 (1)
B_{3z}	—	−0·0090 (2)	−0·0044 (1)	−0·0067 (1)
B_{4z}	—	—	0·0209 (4)	0·0023 (3)
B_{5z}	—	—	—	−0·0197 (5)

* Up to the nth-order harmonic is used in the refinement.
† Values quoted are given with respect to the **A, B, C** unit cell [equation (3)].

With the final structure model (Table 8), the intensities at the positions of the third-order satellites were calculated. They were found to be of the order of the differences $|\Delta F|$ in the second-order satellites, and are indeed 'less-than's'.

6. Discussion

Here the general features of the modulation wave in NbTe$_4$ are described. A more extensive discussion and a comparison with other compounds, in particular TaTe$_4$, will be given elsewhere (Bronsema *et al.*, 1985).

In Figs. 3 and 4 drawings of the structure are presented. Fig. 3 gives the projection along **A + B** of several unit cells of the basic structure [**A, B, C** are the lattice vectors of the larger unit cell as defined in equation (3)]. The displacement of the atoms along **C** is represented by arrows; note that the actual displacement is one fifth of the length of the arrows. The phase of the modulation wave at $x = y = \frac{1}{2}$ differs by one-half from the phase at $x = y = 0$. (The periodicity of the modulation wave is one by definition.) For
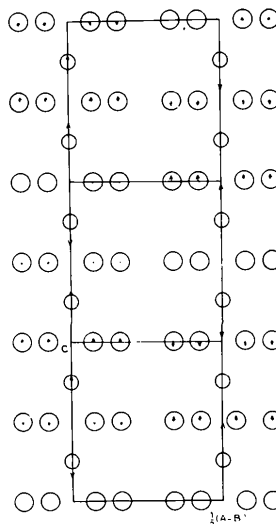

Fig. 3. Projection of the structure along **A + B**. The atoms are drawn at their average positions. The displacement along **C** is given by arrows; the actual displacement is one-fifth of the length of the arrow. [See equation (3) and Fig. 2 for the relation between (**A, B, C**) and (**a, b, c**).]

Table 8. *Final values for the structural parameters*

		Average structure	A_1*	B_1	A_2	B_2
Nb,	z	$\frac{1}{4}$	—	0·03899 (22)	—	0·01640 (24)
	†$\beta_{11} = \beta_{22}$	0·00188 (4)	—	—	—	—
	β_{33}	0·00463 (13)	—	—	—	—
Te	x	0·23589 (4)	0·01389 (5)	—	−0·00386 (6)	—
	y	0·09195 (4)	−0·00669 (5)	—	−0·00103 (6)	—
	z	—	—	−0·00637 (8)	—	−0·00236 (7)
	β_{11}	0·00192 (3)	—	—	—	—
	β_{22}	0·00187 (3)	—	—	—	—
	β_{33}	0·00408 (4)	—	—	—	—
	β_{12}	−0·00008 (2)	—	—	—	—

* A_n and B_n are the nth-order Fourier amplitudes as defined in equation (6). All values are with respect to the, larger, **A**, **B**, **C** unit cell [equation (3)].
† For Nb, $x = y = 0$; $\beta_{12} = \beta_{23} = \beta_{13} = 0$. For Te, $\beta_{13} = \beta_{23} = 0$.

the first harmonic this gives a reversal of sign of the amplitude; for the second harmonic the amplitudes on different chains are the same. The result is that there is no simple relationship between the amplitudes of the modulation wave on different chains.

It is well known that the average positions of different atoms can be related to each other by the symmetry of the three-dimensional space group. Similarly, the amplitudes of the modulation wave of the different atoms are related to each other by the

symmetry elements of the superspace group. Between each pair of Nb atoms there are four Te atoms with the same z coordinate, the average positions of which are related to each other by the fourfold axis (Fig. 3). The same fourfold axis requires the amplitudes of the modulation wave along z of these Te atoms to be equal; the amplitudes in the AB-plane have to be equal in magnitude, but have a different direction as given by the rotation axis (Fig. 4). Treating each such square of Te atoms as one entity one can decompose the displacements of the atoms involved into three modes. As a whole the square of Te atoms can have a displacement along **C**. In addition, there are the shrinking and expansion of the square and the rotation of the square around **C**. The presence of all three deformations is clearly visible in Figs. 3 and 4. This form of displacement was also suggested by Böhm & von Schnering (1983). However, we would like to emphasize here that this form is merely a result of the symmetry of the structure.

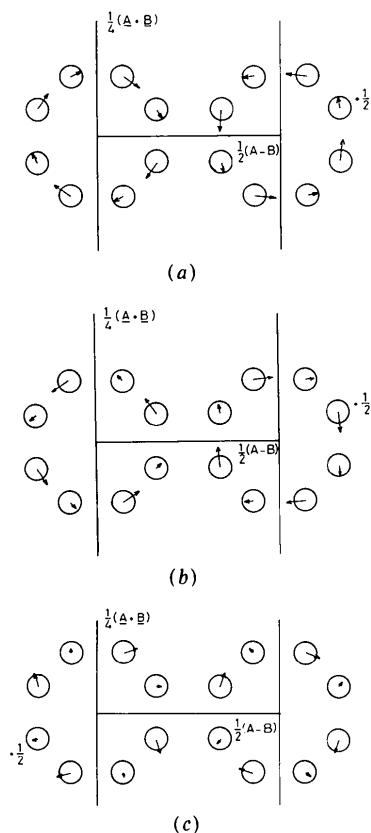In Fig. 5 we present for a number of interatomic distances the dependence of this distance on t. t is

Fig. 4. Projection of the structure along **C**. The displacements in the AB plane are given by arrows; the actual displacement is one-fifth of the length of the arrow. (a) Unit cell with $z = 0$. (b) Unit cell with $z = 1$. (c) Unit cell with $z = 2$.
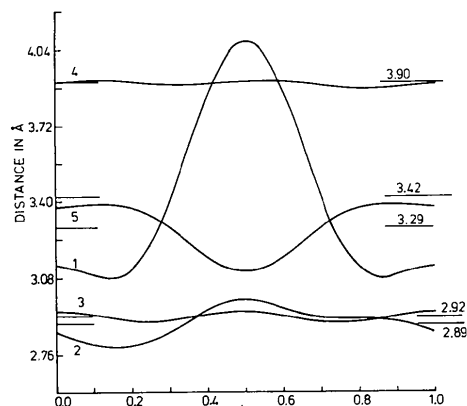

Fig. 5. Some interatomic distances as a function of the phase factor, t, in the modulation wavefunction. (1) Nb($z = \frac{1}{4}$)–Nb($z = -\frac{1}{4}$), av. 3·418 Å; (2) Nb($z = \frac{1}{4}$)–Te($xy0$), av. 2·887 Å; (3) Te($xy0$)–Te($\frac{1}{2} - x, \frac{1}{2} - y, 0$), av. 2·918 Å; (4) Te($x, y, 0$)–Te($y, x, \frac{1}{2}$), av. 3·897 Å; (5) Te($x, y, 0$)–Te($\bar{y}, x, 0$), av. 3·291 Å.

defined by $x_4 = \mathbf{q} \cdot \mathbf{r}^0 + t$, where x_4 is the argument of the modulation wavefunction. For example, $t = 0$ corresponds to the distances between the atoms given in the caption of Fig. 5. The distances between the same atoms, shifted n unit cells along $\mathbf{c}$, is given by $t = n\mathbf{q} \cdot \mathbf{c}$ (mod 1). Since the modulation is incommensurate the probability for a distance to be in a certain interval is directly proportional to the interval on the t axis to which it corresponds.

First, the Nb-Nb distance along $\mathbf{c}$ is considered (No. 1 in Fig. 5). When only the first harmonic of the modulation wave is present, the occurrence of a certain lengthening of the bond is of equal probability as the occurrence of a shortening by the same amount. From Fig. 5 it appears that the effect of the second harmonic is to increase the probability for a bond shortening (60% of the bonds are shorter than average), while at the same time the average lengthening is, of course, larger than the average shortening.

The shortest Nb-Te distance is between a Te at $z = 0$ and the Nb at $z = \frac{1}{4}$. From heuristic reasoning it is expected that there is some coherence between the displacements of the Nb atoms and the neighbouring Te atoms. This is also found experimentally, as can be deduced from Fig. 5. Fig. 5 shows that the lengthening of the Nb$(00\frac{1}{4})$-Nb$(00-\frac{1}{4})$ distance is accompanied by a lengthening of the Nb$(00\frac{1}{4})$-Te$(xy0)$ distance; for a shortening of the bonds the same correlation is found. In more detail, we can look at the values for the lengthening and shortening of the Nb-Te distance. The maximum lengthening/shortening of this distance can be calculated with the amplitudes of Table 8, but with a maximal anti-phase displacement of the atoms. Then values are found of 0·34 and 0·32 Å respectively. If a maximum positive correlation is assumed, the maximum lengthening/shortening is found to be 0·12/0·09 Å. These latter values are also found experimentally (0·12/0·10 Å, Fig. 5). From this it can be concluded that there is indeed a large coherence in the displacement of the Nb and Te atoms.

In Fig. 5, No. 3 shows the shortest Te-Te distance. The average distance is 2·92 Å which is only slightly larger than the distance in Te crystals (2·84 Å) (Cherin & Unger, 1967). This, and the fact that there is only a small variation in this distance ($\pm0·04$ Å), supports the assertion of Selte & Kjekshus (1964) and Mahy *et al.* (1984) that it is a Te-Te bond.

No. 4 is the distance between Te$(xy0)$ and Te$(yx\frac{1}{2})$. There is hardly any variation in this distance ($\pm0·015$ Å). Apparently, the displacements of the Te atoms are coupled in such a way as to keep this distance constant.

Finally, No. 5 is the distance between Te$(xy0)$ and Te$(\bar{y}x0)$, *i.e.* the length of an edge of the Te square. The value $x\sqrt{2}$ gives the length of the diagonal of the Te square. The variation in the latter distance, which amounts to 0·4 Å, gives directly the amplitude of the shrinking/expansion mode of the Te square. Again, a large correlation with the variation in the Nb-Nb distance is found. A lengthening of this latter distance is accompanied by a shrinking of the Te square.

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