

Structures of Two Low-Temperature Incommensurate NbTe₄ Phases

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Abstract

The structures of two low-temperature incommensurate NbTe₄ phases, *LT*₁ and *LT*₂, were studied by computer simulations of electron diffraction patterns. The room-temperature ($2^{1/2}a_0 \times 16c_0$), *LT*₁ ($2a_0 \times 16c_0$) and *LT*₂ ($2a_0 \times 32c_0$) phases separately, as well as in combination ($2a_0 \times 32c_0$), were considered as long-period commensurate superstructures. The space groups of these phases were found to be *P4/m*, *P4/n*, *I4/m* and *P4₂/m*, respectively. The *LT*₁ phase is generated by the same modulation along columns with 11 periods in $16c_0$ as determined earlier for the room-temperature structure but with slight opposite longitudinal shifts of half of the columns. *LT*₂ is formed by a weak clockwise and anticlockwise rotation of alternate room-temperature or *LT*₁ modulation maxima resulting in a doubling of the *LT*₁ modulation length to 11 periods in $32c_0$. Both phases are considered as precursor effects to the low-temperature lock-in phase.

Introduction

The structures of NbTe₄ (Selte & Kjekshus, 1964) and TaTe₄ (Bjerkelund & Kjekshus, 1964) were first reported in the early 1960's. Little attention was paid to these tetrachalcogenides, however, until their room-temperature superstructures were found to be commensurate in TaTe₄ and incommensurate in

NbTe₄ (Boswell, Prodan & Brandon, 1981, 1983; Mahy, Wieggers, van Landuyt & Amelinckx, 1984; Böhm & Von Schnering, 1983, 1985). In an analysis of X-ray diffraction data using superspace groups (de Wolff, Janssen & Janner, 1981) and the corresponding structure-factor calculation (Yamamoto, 1982), van Smaalen, Bronsema & Mahy (1986) gave a description of the complete modulated room-temperature structure of NbTe₄. This belongs to $\mathcal{W}_{11}^{P4/mcc}$ which is equivalent to $\frac{P4/mc}{I4/mmm}c$ (Prodan & Boswell, 1987) in the dualistic notation (de Wolff, 1984a). Also, the space group of room-temperature TaTe₄ has been shown to be *P4/ncc* (Bronsema, van Smaalen, de Boer, Wieggers & Jellinek, 1987; Hiltz, 1987; Corbett, Hiltz, Boswell, Bennett & Prodan, 1988; Mahy, van Landuyt & Amelinckx, 1987).

Phase transitions in NbTe₄ (Eaglesham, Bird, Withers & Steeds, 1985; Eaglesham, 1985; Mahy, van Landuyt, Amelinckx, Bronsema & van Smaalen, 1986) and TaTe₄ (Boswell, Prodan, Bennett, Corbett & Hiltz, 1987) have been observed by electron diffraction and electron microscopy. NbTe₄ was found to undergo a lock-in transition at about 50 K to a ($2a_0 \times 3c_0$) unit cell while the unit cell of TaTe₄ transforms from ($2a_0 \times 3c_0$) at room temperature to ($2^{1/2}a_0 \times 3c_0$) above 450 K.

There are additional diffraction effects in NbTe₄ below room temperature and above the lock-in temperature. By electron diffraction, elongated streaks parallel to c_0^* were observed to develop gradually

during cooling (Boswell *et al.*, 1983; Mahy, van Landuyt, Amelinckx, Uchida, Bronsema & van Smaalen, 1985; Eaglesham, Bird *et al.*, 1985). Sharp, closely spaced satellite spots appeared in the streaks and increased in intensity as the temperature decreased from about 200 to 50 K. It was shown (Boswell & Prodan, 1986) that two sets of satellites, designated LT_1 and LT_2 , are observed singly or in combination along the streaks. Mahy *et al.* (1985) showed that the LT_1 set, together with the room-temperature incommensurate reflections, can be explained on the basis of a theory first developed for shear structures (van Landuyt, de Ridder, Gevers & Amelinckx, 1970), where the periodicity and the \mathbf{R} vector of planar defects were determined from the fractional shifts of the satellites from their commensurate positions. This model accounts for the positions of the LT_1 spots but the LT_2 spots were apparently not observed by these authors.

Recently, three theoretical papers appeared which deal with the incommensurate-to-incommensurate phase transition in NbTe₄. On the basis of a Landau free-energy calculation, Walker & Morelli (1988) proposed a model in which discommensurations separate commensurate regions. In this model, the temperature-dependent driving mechanism of the phase transition involves a competition between nearest-neighbour and next-nearest-neighbour column interactions (Morelli & Walker, 1989). It was found that both single- \mathbf{q} and double- \mathbf{q} states are energetically acceptable but the former was chosen on the basis of a better fit to previous results (Mahy *et al.*, 1986). In addition, Chen & Walker (1989) have described LT_1 in terms of phason and amplitudon symmetry-mode distortions of the (3+1)-dimensional room-temperature supercrystal. Only the Nb atoms were taken into account and the calculation was carried out for the single- \mathbf{q} state.

As yet, the actual structures of the LT_1 and LT_2 phases remain unknown. It is thus appropriate that both incommensurate and discommensurate models be considered for these phases. We have examined various models by comparing computer-simulated electron diffraction patterns with the geometry of those observed. This approach was employed as there is currently no X-ray data for the low-temperature phases and such information would be difficult to obtain since the separation of the closely spaced satellites is beyond the resolution of conventional X-ray diffraction methods. As discussed below, only the incommensurate (long-period commensurate) models were found to give satisfactory results. We believe that development of the structural models for the LT_1 and LT_2 phases will contribute to a more complete understanding of the mechanism driving the phase transitions in the NbTe₄/TaTe₄ system.

Table 1. *Calculated intensities for the LT_1 and LT_2 phases of NbTe₄ based on a $2a \times 32c$ unit cell and for $\delta_1 = 0.00008$ and $\delta_2 = 0.03$*

The calculated intensities are rounded to the first figure. Intensities $< 10^{-3}$ are not given.

| Room temperature | | | | Room temperature | | | |
|------------------|----------|----------|---------------------------|------------------|----------|----------|---------------------------|
| <i>h</i> | <i>k</i> | <i>l</i> | | <i>h</i> | <i>k</i> | <i>l</i> | |
| 0 | 0 | 0 | $2 \times 10^{0*}$ | 2 | 2 | 0 | $2 \times 10^{5*}$ |
| 0 | 0 | 20 | $2 \times 10^{\dagger}$ | 2 | 2 | 1 | |
| 0 | 0 | 24 | $2 \times 10^{\dagger}$ | 2 | 2 | 20 | $4 \times 10^{\dagger}$ |
| 0 | 0 | 40 | $7 \times 10^{\dagger}$ | 2 | 2 | 24 | $3 \times 10^{-2\dagger}$ |
| 0 | 0 | 44 | $9 \times 10^{\dagger}$ | 2 | 2 | 40 | $7 \times 10^{\dagger}$ |
| 0 | 0 | 60 | $6 \times 10^{-1\dagger}$ | 2 | 2 | 44 | $1 \times 10^{\dagger}$ |
| 0 | 0 | 64 | $8 \times 10^{*}$ | 2 | 2 | 60 | $6 \times 10^{-1\dagger}$ |
| 0 | 1 | 1 | | 2 | 2 | 63 | |
| 0 | 1 | 20 | 1×10^0 | 2 | 2 | 64 | 3×10^{-1} |
| 0 | 1 | 21 | | 2 | 4 | 0 | $2 \times 10^{6*}$ |
| 0 | 1 | 22 | 1×10^0 | 2 | 4 | 1 | |
| 0 | 1 | 23 | | 2 | 4 | 8 | $6 \times 10^{\dagger}$ |
| 0 | 1 | 40 | 3×10^{-2} | 2 | 4 | 12 | $4 \times 10^{\dagger}$ |
| 0 | 1 | 41 | | 2 | 4 | 20 | $7 \times 10^{\dagger}$ |
| 0 | 1 | 42 | 2×10^{-1} | 2 | 4 | 24 | $2 \times 10^{-2\dagger}$ |
| 0 | 1 | 43 | | 2 | 4 | 28 | $3 \times 10^{-3\dagger}$ |
| 0 | 1 | 44 | 8×10^{-2} | 2 | 4 | 32 | $7 \times 10^{*}$ |
| 0 | 1 | 62 | 1×10^0 | 2 | 4 | 40 | $1 \times 10^{\dagger}$ |
| 0 | 1 | 63 | | 2 | 4 | 44 | $1 \times 10^{\dagger}$ |
| 0 | 2 | 0 | $1 \times 10^{7*}$ | 2 | 4 | 52 | $3 \times 10^{\dagger}$ |
| 0 | 2 | 20 | $2 \times 10^{\dagger}$ | 2 | 4 | 56 | $5 \times 10^{\dagger}$ |
| 0 | 2 | 24 | $8 \times 10^{-1\dagger}$ | 2 | 4 | 60 | $6 \times 10^{-1\dagger}$ |
| 0 | 2 | 40 | $4 \times 10^{\dagger}$ | 2 | 4 | 63 | |
| 0 | 2 | 44 | $2 \times 10^{\dagger}$ | 2 | 4 | 64 | $1 \times 10^{*}$ |
| 0 | 2 | 60 | $5 \times 10^{-1\dagger}$ | 2 | 6 | 0 | $7 \times 10^{*}$ |
| 0 | 2 | 64 | $3 \times 10^{*}$ | 2 | 6 | 8 | $4 \times 10^{\dagger}$ |
| 1 | 1 | 2 | $1 \times 10^{-2\dagger}$ | 2 | 6 | 9 | |
| 1 | 1 | 18 | $4 \times 10^{-2\dagger}$ | 2 | 6 | 10 | |
| 1 | 1 | 22 | $2 \times 10^{\dagger}$ | 2 | 6 | 12 | $8 \times 10^{\dagger}$ |
| 1 | 1 | 42 | $8 \times 10^{\dagger}$ | 2 | 6 | 20 | $6 \times 10^{\dagger}$ |
| 1 | 1 | 46 | $1 \times 10^{\dagger}$ | 2 | 6 | 24 | $2 \times 10^{\dagger}$ |
| 1 | 1 | 62 | $4 \times 10^{\dagger}$ | 2 | 6 | 28 | $2 \times 10^{-3\dagger}$ |
| 1 | 2 | 1 | | 2 | 6 | 31 | |
| 1 | 2 | 2 | 2×10^{-3} | 2 | 6 | 32 | $6 \times 10^{*}$ |
| 1 | 2 | 9 | | 2 | 6 | 33 | |
| 1 | 2 | 10 | 8×10^{-1} | 2 | 6 | 36 | $7 \times 10^{-3\dagger}$ |
| 1 | 2 | 11 | | 2 | 6 | 40 | $3 \times 10^{\dagger}$ |
| 1 | 2 | 12 | 1×10^{-1} | 2 | 6 | 44 | $5 \times 10^{\dagger}$ |
| 1 | 2 | 13 | | 2 | 6 | 52 | $8 \times 10^{\dagger}$ |
| 1 | 2 | 19 | | 2 | 6 | 55 | |
| 1 | 2 | 20 | 1×10^{-1} | 2 | 6 | 56 | $2 \times 10^{\dagger}$ |
| 1 | 2 | 21 | | 2 | 6 | 60 | $5 \times 10^{-1\dagger}$ |
| 1 | 2 | 22 | 4×10^{-2} | 2 | 6 | 64 | $1 \times 10^{*}$ |
| 1 | 2 | 23 | | 1 | 3 | 2 | $6 \times 10^{\dagger}$ |
| 1 | 2 | 31 | | 1 | 3 | 10 | $3 \times 10^{\dagger}$ |
| 1 | 2 | 33 | | 1 | 3 | 14 | $6 \times 10^{-3\dagger}$ |
| 1 | 2 | 40 | 2×10^{-2} | 1 | 3 | 18 | $1 \times 10^{-3\dagger}$ |
| 1 | 2 | 41 | | 1 | 3 | 22 | $2 \times 10^{\dagger}$ |
| 1 | 2 | 42 | 4×10^{-1} | 1 | 3 | 30 | $4 \times 10^{\dagger}$ |
| 1 | 2 | 43 | | 1 | 3 | 34 | $1 \times 10^{\dagger}$ |
| 1 | 2 | 44 | 4×10^{-1} | 1 | 3 | 42 | $9 \times 10^{\dagger}$ |
| 1 | 2 | 51 | | 1 | 3 | 46 | $1 \times 10^{\dagger}$ |
| 1 | 2 | 52 | 1×10^{-1} | 1 | 3 | 50 | $2 \times 10^{-2\dagger}$ |
| 1 | 2 | 53 | | 1 | 3 | 54 | $1 \times 10^{\dagger}$ |
| 1 | 2 | 54 | 3×10^0 | 1 | 3 | 62 | $5 \times 10^{\dagger}$ |
| 1 | 2 | 55 | | | | | |
| 1 | 2 | 62 | 1×10^0 | | | | |
| 1 | 2 | 63 | | | | | |

* Average intensities.

† Modulated intensities.

Calculation of the LT_1 and LT_2 phases

In principle any incommensurate structure can be described as long-period commensurate, with the periodicity dependent on the accuracy with which the modulation wavevector can be determined (de Wolff, 1984b), which leads to a periodicity of $16c_0$ for the case of room-temperature NbTe₄. During the

calculation† the average structure of NbTe₄, as determined by Selte & Kjekshus (1964), was first modified into an equivalent enlarged unit cell ($2^{1/2}a_0 \times 16c_0$) ($\mathbf{A} = \mathbf{a}_0 + \mathbf{b}_0$, $\mathbf{B} = \mathbf{b}_0 - \mathbf{a}_0$, $\mathbf{C} = 16c_0$). The original average positions [2(a) for Nb and 8(m) for Te, space group $P4/mcc$] were multiplied into 64 Nb and 256 Te positions.

In this enlarged cell the position of each atom was changed according to the modulation function (Yamamoto, 1982; van Smaalen *et al.*, 1986), limited to first and second harmonics:

$$u_{\alpha}^{\mu}(\mathbf{x}_4) = \sum_{n=1}^2 [P_{n\alpha}^{\mu} \cos(2\pi n\mathbf{x}_4) + Q_{n\alpha}^{\mu} \sin(2\pi n\mathbf{x}_4)],$$

where $\mu = \text{Nb, Te}$, and $\alpha = x, y, z$. The amplitudes are those given by van Smaalen *et al.* (1986),§ with all z components multiplied by 1/16. If $u_{\alpha}^{\mu}(\mathbf{x}_4) = 0$, only the average structure reflections are obtained (marked by * in Table 1). The presence of modulation, $u_{\alpha}^{\mu}(z)$ for column (I) and $u_{\alpha}^{\mu}(z + \frac{1}{2})$ for column (II) (see below), results in additional satellites († in Table 1) characteristic for room-temperature NbTe₄. This long-period superlattice with unit cell ($\mathbf{A} = \mathbf{a}_0 + \mathbf{b}_0$, $\mathbf{B} = \mathbf{b}_0 - \mathbf{a}_0$, $\mathbf{C} = 16c_0$) gives an equivalent result to that of van Smaalen *et al.* (1986), carried out for an incommensurate modulation with ($\mathbf{A} = \mathbf{a}_0 + \mathbf{b}_0$, $\mathbf{B} = \mathbf{b}_0 - \mathbf{a}_0$, $\mathbf{C} = c_0$, $\mathbf{q}_i = 0, 0, 0.691$). As compared to the average structure, the symmetry elements of this long-period superstructure, perpendicular to the fourfold axis, are lost and the resulting space group is $P4/m$. A further unit-cell enlargement is needed if the room-temperature structure is to be used as the basis for the calculation of LT_1 and LT_2 phases. For LT_1 the base has to be further enlarged into $\mathbf{A} = 2\mathbf{a}_0$, $\mathbf{B} = 2\mathbf{b}_0$, so that the original positions (x, y, z) are changed into $[(x+y)/2, (y-x)/2, z]$, giving four columns [(I), (II), (III), (IV)] instead of two [(I), (II)]:

| | | |
|---|---|-------|
| Nb: 0, 0, z | \rightarrow 0, 0, z | (I) |
| 1, 0, z | \rightarrow $\frac{1}{2}, \frac{1}{2}, z$ | (II) |
| 0, 0, $z + (\frac{1}{2}, \frac{1}{2}, 0)$ | \rightarrow $\frac{1}{2}, 0, z$ | (III) |
| 1, 0, $z + (\frac{1}{2}, \frac{1}{2}, 0)$ | \rightarrow $0, \frac{1}{2}, z$ | (IV) |
| Te: x, y, z | \rightarrow $(x+y)/2, (y-x)/2, z$ | (I) |
| $x+1, y, z$ | \rightarrow $(x+y+1)/2, (y-x-1)/2, z$ | (II) |
| $x, y, z + (\frac{1}{2}, \frac{1}{2}, 0)$ | \rightarrow $(x+y+1)/2, (y-x)/2, z$ | (III) |
| $x+1, y, z + (\frac{1}{2}, \frac{1}{2}, 0)$ | \rightarrow $(x+y)/2, (y-x-1)/2, z$ | (IV) |

The x and y amplitudes must also be changed accordingly. As expected, applying the modulation function $u_{\alpha}^{\mu}(z)$ to the new columns (I) and (II) and

† The source program listing and a program description have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52947 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

§ The correct value of $Q_{1z}^{\text{Nb}} = -0.03899$ (van Smaalen, 1988).

$u_{\alpha}^{\mu}(z + \frac{1}{2})$ to (III) and (IV), the room-temperature result is obtained. For the calculation of LT_1 , changes either between columns (I) and (II), and/or between (III) and (IV) are required.

A calculation was first performed with the ($2a_0 \times 16c_0$) unit cell, where the positions were commensurately modulated and with a discommensuration introduced after each $16c_0$ ($10 \times 1.5c_0 + c_0$). The parameters were determined from those of room-temperature TaTe₄ (Bronsema *et al.*, 1987). It was found however that the envelope, determining the number of satellites which form one streak, became too wide, resulting in more satellites than were actually observed in the vicinity of $\frac{1}{3}c_0^*$.

Calculations for various incommensurate (long-period) models were also carried out. The only satisfactory result was obtained when half of the columns [in our case (III) and (IV)] were further shifted in opposite directions: $u_{\alpha}^{\mu}(z + \frac{1}{2} + \delta_1)$ and $u_{\alpha}^{\mu}(z + \frac{1}{2} - \delta_1)$ for columns (III) and (IV). This is similar to the shifts that occur in the structure of room-temperature TaTe₄ (Bronsema *et al.*, 1987); see also Table 2 of Budkowski, Prodan, Kucharczyk, Uszynski, Marinković & Boswell (1989), where the result of these shifts is a ($2a_0 \times 3c_0$) commensurate superstructure. For a value of $\delta_1 = 0.00016$, which produces displacements similar to those in TaTe₄, the calculated LT_1 satellite positions are in agreement with those observed (Table 1 and Fig. 1). It should

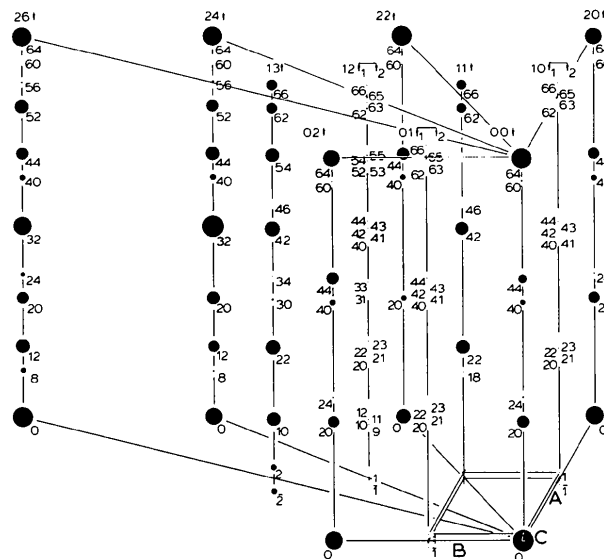


Fig. 1. The calculated reciprocal space of LT_1 and LT_2 NbTe₄. Only reflections for which the intensity I exceeds 0.01 are shown. The diameters of the reflections are proportional to $\log(I)$ for $I \geq 1$ while weaker reflections are simply indicated by a point. The faintest satellites have been somewhat enlarged for better visibility. Table 1 should be referred to for quantitative data.

be noted that δ_1 varies the intensities of LT_1 satellites with no significant effect on the room-temperature satellites or the matrix reflections, again in good agreement with experiment. In summary, the suggested LT_1 superstructure is derived from that of the room-temperature phase by shifting the complete columns (III) and (IV) while columns (I) and (II) remain unshifted. In this process, the modulation along the individual columns is unchanged except for a slight deformation of the Te squares in columns (I) and (II). These distortions (up and down shifts by $\delta_1/4$ in the calculation) allow the maintenance of nearly constant intercolumn Te—Te distances for the LT_1 superstructure. For the $(2a_0 \times 16c_0)$ unit cell, the symmetry of LT_1 is described by space group $P4/n$.

To explain the LT_2 satellites, a further enlargement of the unit cell was necessary, since corresponding satellites appear at positions exactly half-way between those of LT_1 (*i.e.* $2a_0 \times 32c_0$). Thus the final unit cell contains 1280 atoms (256 Nb plus 1024 Te). Several models, based on this enlarged unit cell, were studied. We could not account for the LT_2 spots by considering c shifts only and it was concluded that the LT_2 phase must involve transverse modes modulating Te x and y coordinates as well. In developing a satisfactory model, the following factors must be considered: the modulation periodicity, the phase shift between adjacent columns and the displacement modes along individual columns.

Although it is possible to obtain the observed extinctions using models based on either a single or 11 modulations within $32c_0$, only the latter has an acceptable physical meaning since the interactions driving the modulation are unlikely to involve distances as large as 200 Å. It is also reasonable to expect the LT_2 modulation periodicity to be closely related to that of LT_1 , which means that these distances should be related by a small rational number. It should however be pointed out that, due to this shorter modulation period, the LT_2 intensities are more sensitive to changes in modulation amplitudes, which are difficult to estimate exactly in this procedure. Regarding phase shifts between columns, the required extinctions are obtained for a shift of $\pi/2$ between all four neighbouring columns. The columns are then related by a 4_1 or a 4_3 screw axis. Finally, properly chosen modulation modes on a single column are essential. Only a deformation mode involving further alternate clockwise and anticlockwise rotations around the c axis, superimposed on the room-temperature modulation, gave results in agreement with experiment. The calculation was carried out by applying an additional modulation onto the room-temperature x and y amplitudes of Te atoms with an amplitude δ_2 . The value of δ_2 can be varied, resulting in stronger or weaker LT_2 satellites in the vicinity of $\frac{1}{3}c_0^*$ only, without significantly affect-

ing those of the room-temperature (or LT_1) phase. A value of $\delta_2 = 0.03$ was found to give the best agreement with the experimental results. Thus, the in-phase LT_1 maxima of columns (I) and (II) at $z = 0$ are rotated clockwise and anticlockwise, while columns (III) and (IV), being at LT_1 minima, are at their rotation minima as well. At $z = 1/44$ the situation is reversed, columns (III) and (IV) are rotated while columns (I) and (II) are not. At $z = 1/22$ (I) and (II) are again rotated but in an opposite direction as compared to $z = 0$. At $z = 1/11$ the modulation period is completed. The symmetry of this LT_2 phase, with $(2a_0 \times 32c_0)$ unit cell, belongs to space group $I4/m$.

The calculated intensities of LT_1 and LT_2 show that the envelopes, giving rise to allowed reflections, are always centred at $\frac{1}{3}c_0^*$, although the satellites themselves are not. We also note that the calculated satellite intensities increase with higher order and so do the discrepancies between experiment and calculation. These discrepancies are attributed to the absence of a damping factor in the calculation which should increase with the diffraction angle. In contrast, at low diffraction angles the agreement with experiment is very good.

Finally, the calculation can be carried out for both deformations simultaneously, resulting in a superposition of the LT_1 and LT_2 satellites, as is most frequently observed. The closely spaced LT_1 and LT_2 satellites form nearly continuous diffuse streaks, centred at $\frac{1}{3}c_0^*$ positions. The resulting unit cell is again $(2a_0 \times 32c_0)$ as for LT_2 and the symmetry is described by the space group $P4_2/m$.

Discussion

The incommensurate state can in principle be modelled by discommensurations, which in their broad limit become essentially indistinguishable from the purely incommensurate case. The present calculation shows that for those models which presume sharp discommensurations, some satellite spot positions do not agree with observations for either the LT_1 or LT_2 phases. However, we note that the transition between LT_1/LT_2 and the lock-in phase must involve formation and annihilation of discommensurations, possibly very close to the transition temperature. Transmission electron microscopic observations have revealed such defects in NbTe₄ (Eaglesham, Bird *et al.*, 1985; Mahy *et al.*, 1986), but the defects appear to occur as islands and such a distribution is unlikely to account for the observed low-temperature satellites. Thus we conclude that the model should be based on an incommensurate rather than a sharp discommensurate modulation.

The calculated LT_1 and LT_2 phases resemble the modulation of room-temperature TaTe₄ (Bronsema

et al., 1987). The additional displacements associated with the LT_2 phase result in an effective extension of the Te cages, such that the intracolumn Te—Te distances change from the room-temperature $NbTe_4$ values to approach those expected for the lock-in phase. The displacements associated with LT_1 also resemble those in room-temperature $TaTe_4$, where they result in constant intercolumn Te—Te distances. Thus, although the phase shifts in incommensurate LT_1/LT_2 phases are different than those in room-temperature $TaTe_4$, it appears that they represent a precursor to the formation of the lock-in phase. Since both contain elements of the modulation present in room-temperature $TaTe_4$, it is reasonable to expect low-temperature $NbTe_4$ to be isostructural with room-temperature $TaTe_4$, which however has to be verified by a liquid helium X-ray analysis.

In general, different phases observed in $NbTe_4$ and $TaTe_4$ are a result of several competing mechanisms. If allowable, triplets are formed with the largest possible phase shift between neighbouring columns. Further, all columns are equivalent and the inter- and intracolumn Te—Te distances are maintained as constant as possible. In incommensurate room-temperature $NbTe_4$, a structure containing only Nb triplets cannot be formed and the largest possible phase difference between columns occurs, *i.e.* π . In contrast, low-temperature commensurate $NbTe_4$ and room-temperature $TaTe_4$ phases form triplets only, resulting in phase shifts of $2\pi/3$ between columns.

Regarding the theoretical analyses of the incommensurate-to-incommensurate phase transition in $NbTe_4$ (Walker & Morelli, 1988; Morelli & Walker, 1989; Chen & Walker, 1989), we note that the present model for LT_1 corresponds to their double- q state with equal shifts for both modulations but the structure of LT_2 appears to be outside the scope of their analysis, since it involves shifts of Te atoms, while they considered those of Nb atoms only.

Finally, calculations based on an incommensurate (long-period commensurate), rather than sharply discommensurate, model of the LT_1/LT_2 phases have been found to provide the best fit to the electron diffraction data. Only limited experimental data is currently available, however. Since the LT_1 -like shifts in room-temperature $TaTe_4$ result in $2\pi/3$ phase shifts between the columns, and discommensurations would also involve $2\pi/3$ phase shifts, it seems reasonable that discommensurations, whether sharp or extended, at least support the development of the LT_1 shifts in $NbTe_4$. Thus, a more sophisticated model involving discommensurations may also possibly lead to an acceptable fit to the diffraction data.

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