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Modulated phases in the system $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_4$

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Abstract. Phases and phase transitions in the system $\text{Ta}_{1-x}\text{Nb}_x\text{Te}_4$ are studied for three compositions ($x = 0, 0.25, 0.5$). The various phases are characterized by commensurate and/or incommensurate satellite reflections; the intensity variation of these satellites is analysed and critical exponents are determined: they characterize the type of transition. A tentative phase diagram is proposed.

1. Introduction

Transition metal tetrachalcogenides such as NbTe_4 or TaTe_4 are compounds exhibiting a pseudo-one-dimensional character in the structure. The basic structure of NbTe_4 determined by Selte and Kjekshus [1] is shown in figure 1.

The Te atoms form 1D infinite columns of stacked tetragonal antiprisms along [001], which are centred by the Nb atoms ($P4/mcc$, figure 1(a)). In figure 1(b) projections of the columns along the c axis are depicted as a schematic diagram of Te squares. In the basic structure of Selte and Kjekshus [1] the columns denoted by A, B C and D are identical. Basically NbTe_4 is isostructural with TaTe_4 ; in addition, there exists a complete range of solid solutions $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$ with $0 \leq x \leq 1$. For NbTe_4 at RT the modulation is incommensurate with the wave vector $q_1 = (0.5, 0.5, 0.688)$ [2–4], whereas for TaTe_4 this modulation is commensurate [3–11] with $q_1 = (0.5, 0.5, \frac{2}{3})$. A first structure determination of NbTe_4 [4] was based on a threefold superstructure; it showed the characteristic deformation modes of the basic structure. Niobium is longitudinally modulated along the c axis; for tellurium both a longitudinal mode and a transversal breathing mode and a libration of the Te squares were found. The structure determination by van Smaalen *et al* [7] based on the superspace group $W_{1111}^{P4/mcc}$ is consistent with the distortion modes found by Böhm and von Schnering [4] for the threefold superstructure [14]. The system of solid solutions $\text{NbTe}_4/\text{TaTe}_4$ exhibits a variety of incommensurate and commensurate structures, which was initially investigated by electron diffraction by Boswell and Prodan [5]. Subsequent studies by Bennett *et al* [6] revealed that the modulation periodicity remains commensurate until a threshold concentration ($x \approx 0.3$) is exceeded and then jumps discontinuously to an incommensurate value. In this paper various phases are studied by x-rays for three compositions ($x = 0, 0.25, 0.5$) as a function of temperature.

The q -vector notation is based on the tetragonal cell of the basic structure with the unit cell (a_0, b_0, c_0) and the lattice constants $a_0 \times a_0 \times c_0$. The indexing of reflections in the reciprocal lattice, however, is for convenience based on a cell $(2a_0, 2b_0, 3c_0)$ in the

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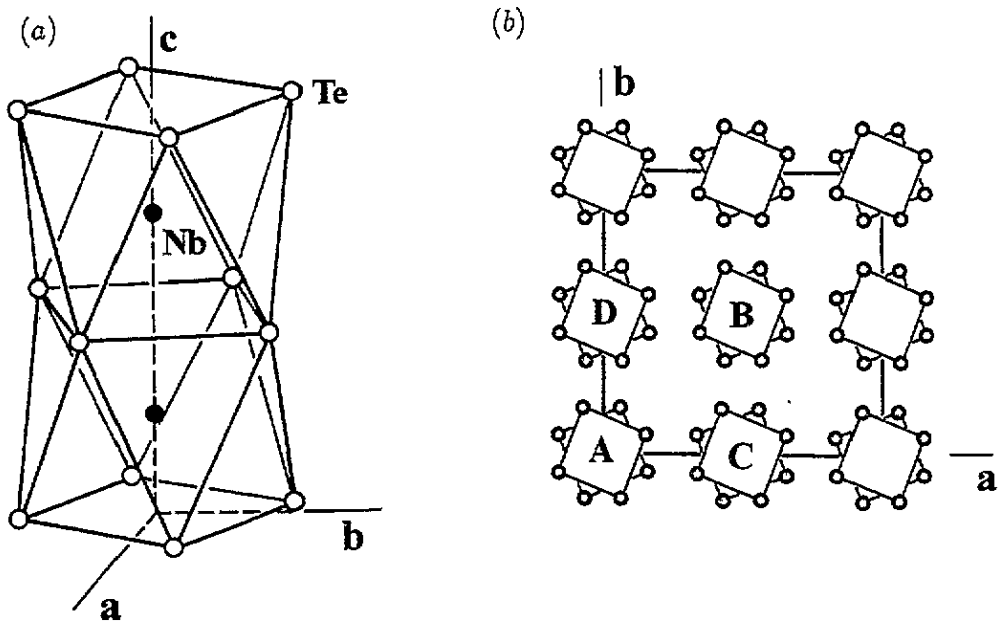


Figure 1. The basic structure of NbTe_4 after [1]: (a) the contents of the unit cell; (b) a projection of the structure along the tetragonal c axis on the basal plane of $2a_0 \times 2a_0$ (only the Te squares are shown).

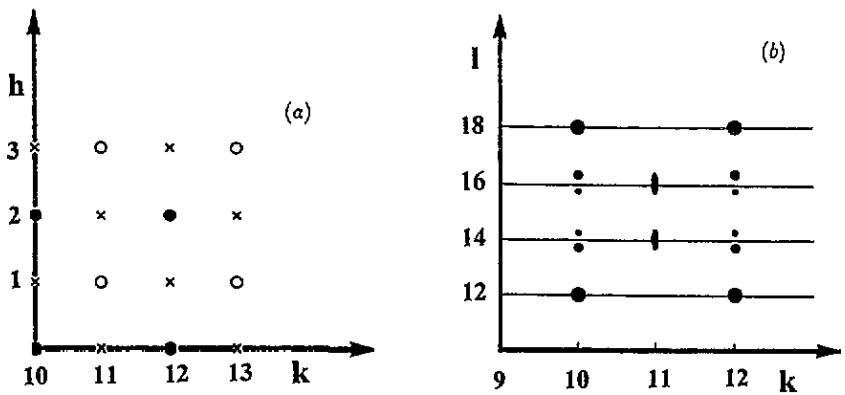


Figure 2. A schematic diagram of the reflection pattern: (a) the projection on the (a_0^*, b_0^*) plane, main reflections (solid circles), q_1 satellites (open circles) and (q_2, q_3) satellites (crosses); (b) the (b_0^*, c_0^*) plane, q_1 satellites of second order and fourth order are drawn separately (small solid circles), the (q_2, q_3) satellites are elongated [2].

incommensurate case as well, i.e. the incommensurate satellites are indexed as threefold superstructure reflections.

In general, the diffraction patterns in the system are characterized by three classes of reflections as shown in the schematic diagram of figure 2:

- (i) by main reflections, which are related to the average structure; the cell is (a_0, b_0, c_0) ;
- (ii) by one class of satellite reflections having a q vector $q_1 = (\frac{1}{2}, \frac{1}{2}, q_1(z))$ and

(iii) by another class of satellite reflection, which are diffuse for $NbTe_4$ and sharp for $TaTe_4$ at RT. These reflections are described by the q vectors $q_2 = (\frac{1}{2}, 0, q_2(z))$, $q_3 = (0, \frac{1}{2}, q_3(z))$.

$NbTe_4/TaTe_4$ compounds are characterized by sequences of phase transitions from non-modulated to incommensurately modulated and to commensurately modulated structures depending on temperature and composition. A non-modulated phase exhibits the main reflections alone; the incommensurate and commensurate phases are characterized by the first and second classes of satellites.

2. Experimental procedure

The crystals were grown by vapour transport in evacuated quartz tubes, using iodine as a transport agent, as described previously [3]. Needle-shaped single crystals were used to study the temperature dependence of the intensities as well as the variation of the q vectors for the different classes of satellite reflections. The size of the crystals used was approximately $0.1 \times 0.1 \times 0.6$ mm with the longest edge being the c axis. In order to prevent decomposition at higher temperatures ($T \sim 380^\circ\text{C}$), however, the crystals must be sealed in quartz capillaries filled with argon before heating.

The reflections were measured on a four-circle diffractometer with graphite monochromator (Mo $K\alpha$ radiation) and with devices for heating and cooling.

3. Phase transitions

In general, the undistorted phase (basic structure) exhibits no satellite reflections. The unit cell (a_0, b_0, c_0) consists of identical columns of antiprisms ($A=B=C=D$ in figure 1(b)). A modulated phase is characterized by satellite reflections q_1 ; in most phases of the system these are located at incommensurate positions. Because of the position of the q_1 satellites the structure must be described in a new unit cell:

$$a_1 = a_0 + b_0 \quad b_1 = a_0 - b_0 \quad c_1 = \mu c_0 \quad \mu = 1/q_1(z).$$

The metric of the unit cell is given by $\sqrt{2}a_0 \times \sqrt{2}a_0 \times \mu c_0$ ($A=B$ and $C=D$ in figure 1(b)); $\mu = 3$ for a commensurate structure and $\mu \neq 3$ for an incommensurate structure. If the temperature or composition is changed appropriately, (q_2, q_3) satellites may occur in addition to the q_1 satellites; in this case the unit cell for describing the structures is

$$a_2 = 2a_0 \quad b_2 = 2b_0 \quad c_2 = \mu c_0.$$

The metric of the cell is $2a_0 \times 2a_0 \times \mu c_0$ and the unit cell is characterized by four independent columns A, B, C, and D. However, the tetragonal symmetry (fourfold axis in column A) requires that $C=D$ ($A \neq B$); other symmetry elements may impose further restrictions.

For $NbTe_4$, the sequence of phases as a function of temperature is reported elsewhere [2, 8]. In TEM experiments the mixed crystals $(Ta_{1-x}Nb_x)Te_4$, $0 \leq x \leq 1$, have been studied extensively by Bennett *et al* [6]. Below the critical Nb concentration ($x < 0.3$), the diffraction patterns at RT correspond to those of $TaTe_4$, i.e. q_1 and (q_2, q_3) satellites are at commensurate positions. As x increases, a commensurate to incommensurate (C to IC) phase transition at $x \sim 0.3$ is marked by the abrupt change of the q_1 satellites to an incommensurate

value whereas the (q_2, q_3) satellites remain centred at commensurate positions. Further changes occur in the positions and appearance of the satellites in the electron diffraction patterns (EDPs) with increasing x . The (q_2, q_3) satellites become progressively fainter and more diffuse; this may be interpreted as a second-order phase transition as x is increased. The q_1 satellites in all cases remain sharp. There is an indication in the $q_1(z)$ against x curve that increase of x in the incommensurate region leads to a discontinuous variation of $q_1(z)$ proceeding through a sequence of discrete jumps [6]. This would imply that these plateaux indicate the existence of a series of long-period commensurate phases.

In this article, x-ray investigations with mixed crystals ($x = 0.25$ and $x = 0.5$) and with TaTe_4 are reported. The compositions are nominal; a range of compositions about the nominal value as a mean is found by TEM microanalysis for crystallites prepared by cleaving a single macrocrystal. At higher temperatures the structures are incommensurately modulated (IC phase). On cooling, phase transitions from the IC phase into a low-temperature phase (LT phase) are observed. The transitions are associated with the occurrence of (q_2, q_3) satellites at ~ 480 K for $x = 0.25$ and at ~ 390 K for $x = 0.5$. For RT NbTe_4 these satellites are diffuse [2]; in the mixed crystals studied here they appear sharp (see figure 3); however, Bennett *et al* [6] observed in TEM experiments that the (q_2, q_3) satellites become progressively fainter and more diffuse when the Nb content in the mixed crystals is varied from $x = 0$ to $x = 1$. Apparently there is a gradual loss of correlations when the composition is changed from Ta rich to Nb rich.

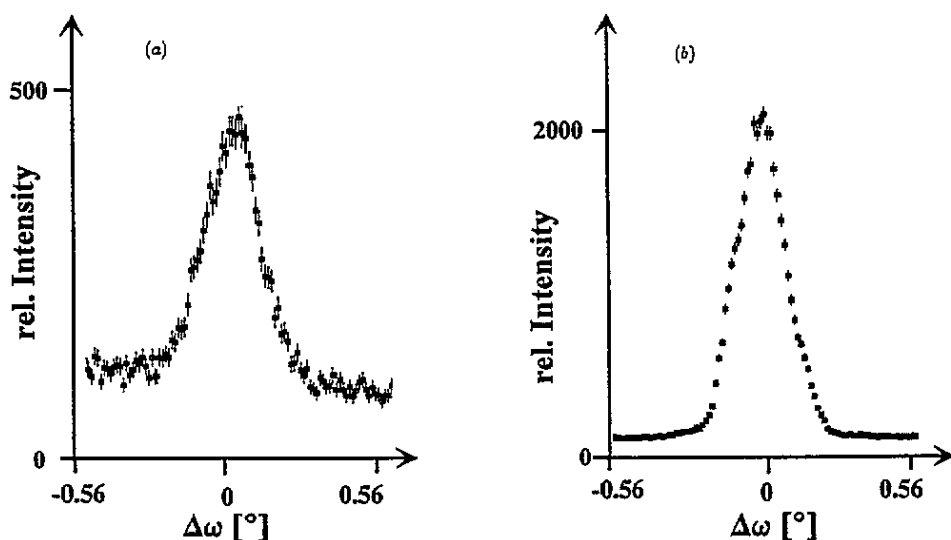


Figure 3. The reflection profile (ω scan) for (a) the q_3 satellite (0 11 9) and (b) the main reflection (0 10 6) for $\text{Nb}_{0.25}\text{Ta}_{0.75}\text{Te}_4$ at RT.

The intensity variation of the q_3 reflection (0 11 4) with temperature is shown in figure 4 for $x = 0.25$. A fit with the equation

$$I = a(T_c - T)^{2\beta} \quad (1)$$

will yield the parameters $T_c = 480$ K and $\beta = 0.21(1)$ (the curve in figure 4). The critical exponent β is clearly different from $\beta = 0.5$ for a mean-field second-order transition or

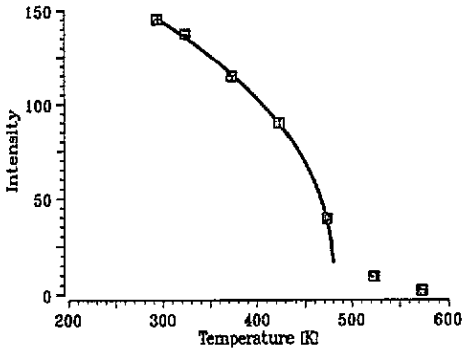


Figure 4. The integral intensity variation of the q_3 satellite (0114) for $Nb_{0.25}Ta_{0.75}Te_4$.

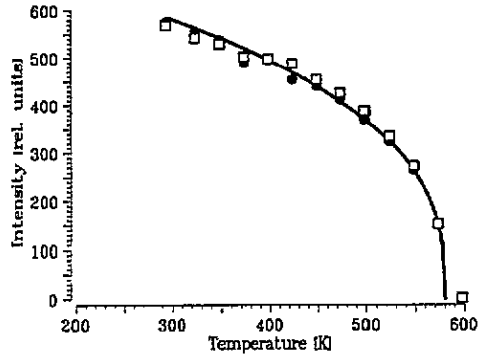


Figure 5. The integral intensity variation of the q_3 satellite (0112) of $TaTe_4$ in an x-ray experiment on heating (●) and cooling (□).

$\beta = 0.33$ for 3D Ising behaviour [12]. From the few data it cannot be concluded that a first-order phase transition occurs. A value with $\beta < 0.25$ was observed by Schmahl and Salje [13] in $NaNO_3$; these authors interpret their value ($\beta = 0.22$) in terms of a crossover between two thermal regimes with different critical behaviour. This crossover regime can be described by two coupled order parameters. More detailed data are required to distinguish between these cases. It is interesting to note that a pronounced scattering is observed also above the phase transition (figure 4). The values of $\beta = 0.21(1)$ and $T_c = 390$ K are obtained for $x = 0.5$. The q_1 satellites are at incommensurate positions in both the LT and IC phases (see figure 6 below).

For $TaTe_4$ the sequence of phases is different. On cooling from high temperature the incommensurate phase (IC) transforms into a commensurate phase (C^*) at 650 K with q_1 satellites at commensurate positions; from the present experiments it cannot be decided whether this 'lock-in transition' is first order. On further cooling, the C^* structure undergoes a reversible phase transition (C^* to C transition), which is characterized by the occurrence of (q_2, q_3) satellites (the metric of the unit cell is $2a_0 \times 2a_0 \times 3c_0$); however, they are not diffuse as in $NbTe_4$. The transition temperature is ~ 580 K. The intensity variation of the q_3 reflection (0112) in an x-ray experiment is shown in figure 5. Since no hysteresis for the C^* to C transition is observed the transition might be interpreted as of second order; however, TEM results [10] indicate a first-order phase transition since the two phases can coexist. If the intensity variation in figure 5 is fitted with equation (1) the parameters are $T_c = 579$ K, $\beta = 0.17(1)$. The exponent $\beta = 0.17$ is close to $\frac{1}{8}$, which is characteristic of a 2D Ising model. The same behaviour of a structural phase transition was found in $CaTiSiO_5$ [13]. The deviation of the experimental value from $\frac{1}{8}$ may be related to weak interlayer coupling in the 2D structural phase transition. The temperature variation of the component $q_1(z)$ of the q_1 satellites is depicted in figure 6. For $TaTe_4$ (curve d), the q vector is at the commensurate position $q_1(z) = \frac{2}{3}$ (C^* phase') and temperature independent up to the C^* to IC phase transition at 650 K. Above that temperature $q_1(z)$ is incommensurate, temperature dependent and has a value of less than $\frac{2}{3}$. This is in contrast to the other cases and to $NbTe_4$ (curves a-c), where $q_1(z) > \frac{2}{3}$.

As for $NbTe_4$ (curve a) the specimen with $x = 0.5$ (curve b) exhibits no temperature dependence, whereas the crystal with $x = 0.25$ (curve c) shows a significant variation with temperature. From an extrapolation of curve c to lower temperatures, one would conjecture that a lock-in transition into the commensurate phase ('C phase') below 100 K might occur.

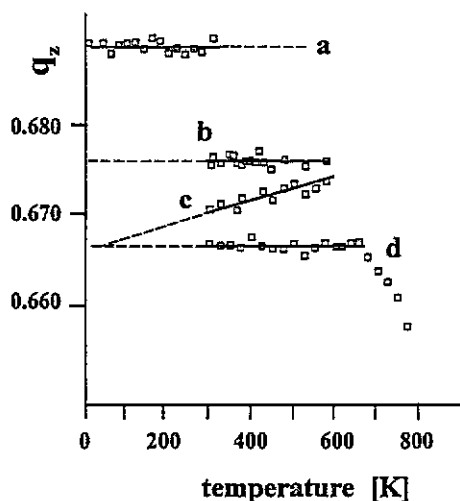


Figure 6. The variation of the q_z component of the q_1 satellite with temperature in $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$ for four compositions (nominal values) in an x-ray experiment: $x = 1$ (after [2]) (a); $x = 0.5$ (b); $x = 0.25$ (c) and $x = 0$ (d).

In NbTe_4 this transition is inhibited for a macroscopic crystal [2] (i.e. $q_1(z) > \frac{2}{3}$ even at 10 K), but it has been verified under the electron microscope [3]. For the composition $x = 0.25$, the structure is still incommensurate (LT phase) at RT while according to Bennett *et al* [6] the C to LT transition occurs for $x \geq 0.3$. However, the compositions are nominal values and the actual composition may be slightly different; the observed behaviour is very sensitive to the actual composition.

Above 793 K, NbTe_4 exhibits the undistorted basic structure (high-temperature (HT) modification) with the unit cell (a_0, b_0, c_0) [9]. A reversible phase transition (second order) is observed from the incommensurately modulated (IC) RT phase to the HT phase. The value is $\beta = 0.35(1)$. For the three compounds containing tantalum, the temperature increase was intentionally stopped to avoid decomposition, i.e. for none of these compounds was an attempt made to verify an HT phase although the crystals were kept in sealed capillaries filled with argon.

From the known facts about the system $(\text{Ta}_{1-x}\text{Nb}_x)\text{Te}_4$ with $0 \leq x \leq 1$, one is tempted to propose a tentative phase diagram. Such a diagram is depicted in figure 7.

The following phases can be distinguished.

HT phase. Only verified for $x = 1$; basic unit cell (a_0, b_0, c_0) (metric $a_0 \times a_0 \times c_0$); no satellites.

IC phase. Verified for all compositions; unit cell (a_1, b_1, c_1) (metric $\sqrt{2}a_0 \times \sqrt{2}a_0 \times \mu c_0$); incommensurate q_1 satellites.

LT phase. Verified for several compositions $x > 0$; unit cell (a_2, b_2, c_2) (metric $2a_0 \times 2a_0 \times \mu c_0$); incommensurate q_1 satellites; (q_2, q_3) satellites.

C phase.* Verified for $x = 0$; unit cell (a_1, b_1, c_1) (metric $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 3c_0$); commensurate q_1 satellites.

C phase. Verified for $x = 0$ and $x = 1$; unit cell (a_2, b_2, c_2) (metric $2a_0 \times 2a_0 \times 3c_0$); commensurate q_1 satellites; commensurate (q_2, q_3) satellites.

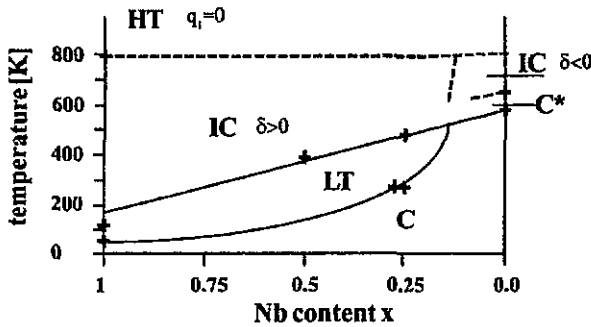


Figure 7. A tentative phase diagram of the system $(Ta_{1-x}Nb_x)Te_4$ with $0 \leq x \leq 1$; $q_1 = (\frac{1}{2}, \frac{1}{2}, \frac{2}{3} + \delta)$; crosses are verified compositions (nominal values).

4. Discussion

In the system $(Ta_{1-x}Nb_x)Te_4$, $0 \leq x \leq 1$ there is a sequence of phase transitions from a high-symmetry undistorted (HT) phase to an incommensurate (IC) phase and further to a commensurate low-temperature (C) phase as for many other modulated structures. Which structure is stable depends on temperature and composition. In general, the undistorted basic structure exhibits no satellite reflections. It transforms to a phase characterized by satellite reflections at incommensurate positions; in our system these are the q_1 satellites: $q_1 = (\frac{1}{2}, \frac{1}{2}, \frac{2}{3} + \delta)$. This phase transition is different for each of the two end members of the system: $\delta \leq 0$ for $TaTe_4$ and $\delta \geq 0$ for $NbTe_4$. When the composition is varied there is one range of compositions that behaves like $NbTe_4$ and another range that behaves like $TaTe_4$. If the appropriate temperature is chosen where both end members are incommensurate, a continuous variation of the composition with a continuous change from $\delta \leq 0$ to $\delta \geq 0$ will cross a line where δ happens to be zero (figure 7). This, however, has not yet been verified by experiment. On cooling, the IC phase undergoes a reversible phase transition. Again, it is different for the two end members: for $TaTe_4$ the q_1 satellites become commensurate ($\delta = 0$, IC to C^* transition), while for $NbTe_4$ an intermediate low-temperature phase (LT phase) is formed before the q_1 satellites become commensurate. This intermediate phase is characterized by the occurrence of (q_2, q_3) satellites. On further cooling the phase transforms to a commensurate structure (lock-in transition into the C phase). For $NbTe_4$ this transformation can only be verified under the electron microscope for very small specimens; in an x-ray experiment the LT to C transformation is inhibited. Kusz and Böhm [2] argue that kinetic effects are responsible for impeding the phase transition: discommensurations that are responsible for the discommensurability are hindered from migrating to the surface. It is still unknown whether kinetic effects also prevail in the mixed crystals (e.g. for $x = 0.5$, curve b in figure 6) and whether these effects depend on composition.

However, in general, in the Nb-rich range the IC phase transforms to the commensurate C phase only after forming the intermediate incommensurate LT phase. This seems to be true for all compositions with $x > 0.3$. On the other hand, the IC to C^* transition in $TaTe_4$ does not require an intermediate incommensurate phase. The q_1 satellites are commensurate (C^* phase), when the (q_2, q_3) satellites occur (C^* to C transition); they are, therefore, also commensurate. The C phase exists in the entire range of compositions. However, the Nb-rich range of the system and the Ta-rich range transform through different mechanisms

to the C phase. Therefore, a multicritical point must be postulated in the phase diagram (figure 7), which separates the two ranges.

Acknowledgments

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