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## Determination of the Incommensurately Modulated Structure of Cu<sub>3-x</sub>Te<sub>2</sub>

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### Abstract

The incommensurately modulated structure of copper telluride Cu<sub>3-x</sub>Te<sub>2</sub> (Cu<sub>2.91</sub>Te<sub>2</sub>) with modulation wavevector  $\mathbf{q} = 0.397(1)\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$  has been determined by X-ray diffraction at room temperature (974 unique reflections). The lattice parameters of the primitive orthorhombic cell of the average structure are:  $a = 3.9727(4)$ ,  $b = 4.0020(5)$ ,  $c = 6.1066(3)$  Å,  $V = 97.1$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 304$  cm<sup>-1</sup> ( $\lambda = 0.7107$  Å),  $M_r = 440.1$ . The symmetry of the structure is given by the superspace group  $C_{2v}^{Pmn}11$ . The final  $R_F$  factor is 0.045. The modulated structure is related to the structure of Ni<sub>3±x</sub>Te<sub>2</sub> [Schutte & de Boer (1993). *Acta Cryst.* **B49**, 392–398] and, as in the latter compound, the occupation of the octahedral sites by metal atoms varies throughout the range 0 to 1. Different from the nickel telluride structure is the antiphase ordering along  $c$  together with a different displacement pattern of the atoms, which can be ascribed to a different interaction strength and a different charge transfer between the metal atom and Te.

### Introduction

The system Cu–Te has been studied by several authors (Anderko & Schubert, 1954; Stevels, 1969). One of the phases is Cu<sub>3-x</sub>Te<sub>2</sub> for which a tetragonal structure of the defective Cu<sub>2</sub>Sb type was reported (Forman & Peacock, 1949). This phase is known as the mineral rickardite.

Stevens (1969) investigated the thermal behaviour of the Cu–Te system by X-ray diffraction and DTA.

Cu<sub>3-x</sub>Te<sub>2</sub> ( $x \approx 0.2$ ) was found to be orthorhombic at room temperature, with a broad homogeneity range ( $0 < x < 0.26$ ). Above 633 K an f.c.c. structure with  $a = 6.032$  Å exists and below 623 K a tetragonal phase ( $a = 3.98$ ,  $c = 6.12$  Å) is stable. The structure of this phase is based on an f.c.c. arrangement of Te atoms, with Cu<sup>I</sup> atoms in tetrahedral sites and Cu<sup>II</sup> atoms in octahedral sites [for an overview see Fig. 1 of the analogous nickel compound (Schutte & de Boer, 1993)]. The tetrahedral sites are fully occupied by Cu atoms, the octahedral sites are partially occupied in a disordered way. By cooling the tetragonal phase

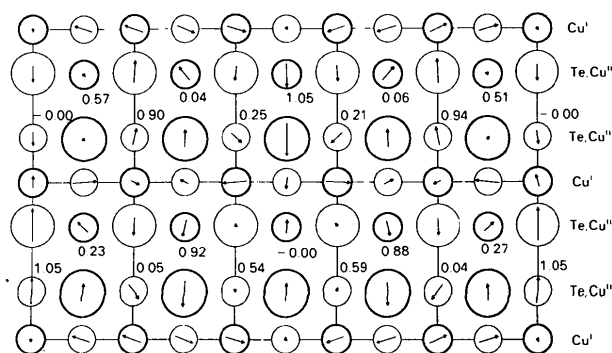


Fig. 1. Modulated structure of Cu<sub>3-x</sub>Te<sub>2</sub> ( $5a \times 2c$ ). Small circles are Cu atoms, larger ones are Te atoms. Bold circles are at  $y = 0$ , other circles are at  $y = \frac{1}{2}$ . Occupation numbers of the Cu<sup>II</sup> sites are indicated. Modulation displacements are represented, in direction and (factor 8 exaggerated) in length, by the arrows. Note that, by the presence of antiphase ordering along  $c$ , the height of this figure should be equal to that of the overview picture for Ni<sub>3±x</sub>Te<sub>2</sub>, as given in Fig. 1 of Schutte & de Boer (1993).

below 413 K, transformation to an orthorhombic phase occurs in which the Cu atoms in the octahedral sites are partially ordered. This phase has a structure which resembles the structure of the orthorhombic phase of  $\text{Ni}_{3\pm x}\text{Te}_2$ . Weak extra lines were observed, which were indexed on Weissenberg photographs as  $h + \delta$ ,  $k$ ,  $l + \frac{1}{2}$  and  $\delta = 0.40$ . A complex arrangement of Cu atoms in the pseudo-octahedral sites in a  $5a \times 2c$  supercell was proposed.

Electron diffraction (Colaitis, Delavignette, van Dyck & Amelinckx, 1979; Colaitis, van Dyck, Delavignette & Amelinckx, 1979, 1980; van Dyck, Colaitis, Delavignette & Amelinckx, 1979) showed satellite reflections, the positions  $q_x$  of which shift continuously on cooling. In  $\text{Ni}_{3\pm x}\text{Te}_2$ , the positions shifted all the way to the limiting value of  $q_x = \frac{1}{3}$ , corresponding to a simple stacking of two types of layers; this behaviour was not observed for  $\text{Cu}_{3-x}\text{Te}_2$ . Incommensurate satellite reflections could be attributed to the occurrence of more complex intermediate phases.

In this work we determine, in the superspace-group description (de Wolff, 1974; Yamamoto, 1982), the incommensurately modulated structure of orthorhombic  $\text{Cu}_{3-x}\text{Te}_2$  at room temperature. We synthesized and carried out X-ray structure determinations on single crystals with slightly different compositions. We analyse the structural modulations and explain qualitatively the difference found between copper telluride and nickel telluride (Schutte & de Boer, 1993), in terms of the different interaction strengths and the different charge transfer between the metal atom and Te.

### Experimental

Weighted mixtures of the pure elements for compositions  $\text{Cu}_{3-x}\text{Te}_2$  ( $0.02 < x < 0.26$ ) were sealed in evacuated quartz-glass tubes and heated at 773 K for a week, followed by slow cooling to room temperature. All diffraction experiments were carried out with monochromatized  $\text{Mo K}\alpha$  radiation on an Enraf-Nonius CAD-4F diffractometer equipped with a modified CAD-4 program (de Boer & Duisenberg, 1984). From the batch with  $x=0.26$  we investigated a number of different crystals but found no significant differences between them, neither in cell dimensions nor in modulation vector  $\mathbf{q}$ .

For the final measurements we selected a crystal ( $x=0.26$ ) with approximate dimensions  $0.05 \times 0.1 \times 0.1$  mm. All observed reflections could be indexed as  $(h, k, l, m)$ , where  $h, k, l$  are the Miller indices of the orthorhombic unit cell of the average structure, and  $|m|$  is the order of the satellite reflections caused by a modulation characterized by a single modulation vector  $\mathbf{q}$ . Lattice parameters were obtained from the positions of higher-order reflections. The modulation

Table 1. Numbers of reflections and  $R_f$  values

	Observed	Unique	With $I > 2.5\sigma(I)$	$R_f^*$
Main reflections	822	248	230	0.109
First-order reflections	1762	492	442	0.095
Second-order reflections	1805	503	302	0.150
All reflections	4389	1243	974	

\*  $R_f = \{\sum_j [N_j \sum_i ((I_j) - (I_{i,j}))^2 / \sigma_{i,j}^2]^{1/2} / \sum_j [(N_j - 1) \sum_i I_{i,j}^2 / \sigma_{i,j}^2]^{1/2}\}$  where  $\sum_j$  is the summation over all independent reflections and  $\sum_i^{N_j}$  is the summation over all  $N_j$  symmetrically equivalent reflections for unique reflection  $j$ .

wavevector  $\mathbf{q}$  was determined from accurately determined positions of first-order satellites, giving  $\mathbf{q} = [0.397(1), 0, \frac{1}{2}]$ . Intensity data were collected using the same methods as applied by Schutte & de Boer (1993) with  $\theta_{\max} = 33^\circ$  and scan-speed ratios 4:2:1 for  $|m| = 0, 1, 2$ , respectively. In this way we obtained a data file of 4685 reflections. Hereafter the data were corrected for Lorentz and polarization effects and for absorption (with absorption coefficient  $\mu = 304 \text{ cm}^{-1}$ ; transmission factors 0.14–0.34). The unique data set was subsequently obtained by averaging equivalent reflections; for details see Table 1.†

For a second crystal, prepared as  $x=0.02$ , a full data set was collected in an analogous way.

### Symmetry, refinement and results

From the symmetry of the diffraction pattern of the main reflections together with their systematic absences ( $h + k = \text{odd}$  for  $hk0$  reflections) the space group of the average structure is determined to be  $Pm\bar{m}n$ . All satellites can be described with one modulation wavevector  $\mathbf{q} = 0.397(1)\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$ . The diffraction symmetry of both main and satellite reflections is  $Pmmm$ , leading in a superspace description (de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983) to the four-dimensional Bravais class  $C_{111}^{Pm\bar{m}n}(\alpha, 0, \frac{1}{2})$ , which is different from that of the analogous nickel compound (Schutte & de Boer, 1993). The possible superspace group can be deduced from the systematic extinctions  $h + k = \text{odd}$  for  $hk00$  reflections. This indicates the presence of a glide mirror plane ( $\sigma$ ). If we assume that the superspace group is centrosymmetric (an assumption later justified by the refinement results) the superspace group for  $\text{Cu}_{3-x}\text{Te}_2$  is  $C_{111}^{Pm\bar{m}n}$ . We transform the subcell in such a way that only the irrational components of the modulation wavevector remain. So the  $c$  axis is doubled which results in the following

† Lists of structure factors and figures showing closest Cu—Cu and Cu—Te distances as a function of  $\varphi$  have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55334 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Symmetry restrictions on the components of the modulation function

It is indicated whether a particular component is even, odd or zero.

Atom	Component	Symmetry
Cu <sup>I</sup> , Cu <sup>II</sup> , Te	$u_x$	Odd
	$u_y$	Zero
	$u_z, P$	Even

Table 3.  $R_F$  and  $R_{F^2}$  values of the refinement for the final results

The numbers of parameters ( $n_p$ ) and the number of reflections ( $n_r$ ) used are also given.

	$R_F$	$R_{F^2}$	$n_p$	$n_r$
$m = 0$	0.022	0.026	15	230
$m = 1$	0.065	0.072	7	442
$m = 2$	0.153	0.176	7	302
Overall	0.046	0.038	29	974

symmetry elements with the corresponding equivalent positions (taking  $mm2/n$  at the origin):

$$\begin{aligned} & (E, 1|n_x n_y n_z n_4), (E, 1|00\frac{1}{2}\frac{1}{2}) + \\ & (2_z, \bar{1}|0000), (2_y, \bar{1}|\frac{1}{2}\frac{1}{2}00), (2_x, 1|\frac{1}{2}\frac{1}{2}00), \\ & (i, \bar{1}|\frac{1}{2}\frac{1}{2}00), (m_z, 1|\frac{1}{2}\frac{1}{2}00), (m_y, 1|0000), (m_x, \bar{1}|0000). \end{aligned} \quad (1)$$

$$\begin{aligned} & (x, y, z, x_4), (x, y, z + \frac{1}{2}, x_4 + \frac{1}{2}) + \\ & (-x, -y, z, -x_4), (-x + \frac{1}{2}, y + \frac{1}{2}, -z, -x_4), \\ & (x + \frac{1}{2}, -y + \frac{1}{2}, -z, x_4), (-x + \frac{1}{2}, -y + \frac{1}{2}, -z, -x_4), \\ & (x + \frac{1}{2}, y + \frac{1}{2}, -z, x_4), (x, -y, z, x_4), (-x, y, z, -x_4). \end{aligned} \quad (2)$$

We will describe here the modulation of the Cu compound using the same kind of parameters ( $P^\mu, u_i^\mu$ ) as for the Ni compound.

In the superspace group  $C_{2111}^{Pmnm}$  all atoms occupy special positions. The restrictions on modulation parameters are listed in Table 2. We see that in this superspace group all allowed modulation functions are either even or odd, the displacements  $u_y$  are all zero. There is no phase shift between  $P^\mu$  and  $u_x^\mu$  and a phase difference of  $90^\circ$  between  $u_x^\mu$  and  $u_z^\mu$ . Moreover, note the phase difference of the modulation wave of  $180^\circ$ , between neighbouring unit cells along  $c$ .

Using the least-squares program REMOS85 (Yamamoto, 1985), we started our calculations with coordinates from Forman & Peacock (1949) for the tetragonal structure, which are transformed to our orthorhombic cell ( $c$  axis doubled): Cu<sup>I</sup> at (0,0,0.000), Cu<sup>II</sup> at (0, $\frac{1}{2}$ ,0.135) and Te at (0, $\frac{1}{2}$ ,0.3575). Next the possible occupation and displacive waves were included. For all reflections with  $I > 2.5\sigma(I)$

Table 4. Final values for the amplitudes of the modulation functions

The form of the anisotropic thermal vibrations is:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$ . (All values are with respect to the doubled- $c$  unit cell.)

$\mu, i$	$x_{0,i}^\mu, P_0^\mu$	$u_{1,i}^\mu, P_1^{\mu,c}$	$u_{1,i}^{\mu,s}$	$u_{2,i}^\mu, P_2^{\mu,c}$	$u_{2,i}^{\mu,s}$
Cu <sup>I</sup>					
$x$	0		-0.0262 (3)		0.0063 (5)
$y$	0				
$z$	0.00010 (7)	-0.0026 (1)		0.0018 (1)	
$\beta_{11}$	0.0230 (5)				
$\beta_{22}$	0.0221 (5)				
$\beta_{33}$	0.00209 (4)				
$P$	1				
Cu <sup>II</sup>					
$x$	0		0.007 (2)		-0.009 (2)
$y$	$\frac{1}{2}$				
$z$	0.143 (1)	0.007 (2)		0.002 (1)	
$\beta_{11}$	0.031 (1)				
$\beta_{22}$	0.028 (1)				
$\beta_{33}$	0.0025 (1)				
$P$	0.455 (4)	0.529 (5)		0.070 (5)	
Te					
$x$	0		-0.0021 (2)		-0.0004 (2)
$y$	$\frac{1}{2}$				
$z$	0.35795 (3)	0.00954 (5)		0.00345 (5)	
$\beta_{11}$	0.0182 (3)				
$\beta_{22}$	0.0161 (2)				
$\beta_{33}$	0.00163 (3)				
$P$	1				

Table 5. Interatomic distances (Å) in the average structure of orthorhombic Cu<sub>3-x</sub>Te<sub>2</sub>

Numbers between parentheses refer to Ni<sub>3-x</sub>Te<sub>2</sub>.

	Coordination	Distance		Coordination	Distance
Cu <sup>I</sup>	2 × Te	2.64 (2.56)	Te	1 × Cu <sup>II</sup>	2.63 (2.56)
	2 × Te	2.65 (2.57)		2 × Cu <sup>I</sup>	2.64 (2.56)
	2 × Cu <sup>II</sup>	2.65 (2.60)		2 × Cu <sup>I</sup>	2.65 (2.57)
	2 × Cu <sup>II</sup>	2.66 (2.61)		4 × Cu <sup>II</sup>	2.82 (2.67)
	4 × Cu <sup>I</sup>	2.82 (2.67)		2 × Cu <sup>II</sup>	3.48 (3.53)
Cu <sup>II</sup>	1 × Te	2.63 (2.56)	4 × Te	3.86 (3.74)	
	4 × Te	2.82 (2.67)	2 × Te	3.97 (3.76)	
	1 × Te	3.48 (3.53)	2 × Te	4.00 (3.80)	
	2 × Cu <sup>I</sup>	2.65 (2.60)			
	2 × Cu <sup>I</sup>	2.66 (2.61)			

unit weight and for those with  $I < 2.5\sigma(I)$  zero weight is taken. Refinement of the occupation  $P$  of the Cu<sup>II</sup> sites leads to a maximum value of  $P$  slightly greater than 1.00 at  $\bar{x}_4^{\text{Cu}^{\text{II}}} = 0$ . This unphysical result is probably caused by the fact that we used only first- and second-order harmonics, as third- and higher-order satellites were too weak to be measured. The final refinement results are listed in Table 3 (for  $R$  factors) and Table 4 (for parameters). The relatively high  $R$  factor for the second-order satellites is due to the fact that the intensities of these satellites are much weaker than the intensities of the first-order satellites. An analogous structure determination of the copper telluride prepared as  $x \approx 0.02$  leads remarkably enough to nearly the same structural parameters ( $P_0^{\text{Cu}^{\text{II}}} = 0.434$ ).

### Discussion

The average structure of orthorhombic  $\text{Cu}_{3-x}\text{Te}_2$  is a distorted defective  $\text{Cu}_2\text{Sb}$ -type structure in which the  $\text{Cu}^{\text{I}}$  atoms occupy the tetrahedral holes and the  $\text{Cu}^{\text{II}}$  atoms the pseudo-octahedral holes of the Te lattice. The  $\text{Cu}^{\text{II}}$  atoms are statistically distributed over the pseudo-octahedral holes with a mean occupation of 45.5%. The coordination is very similar to that in the orthorhombic nickel telluride (for interatomic distances, see Table 5).

In the modulated structure (Fig. 1) the strongest modulation is just as in the case of  $\text{Ni}_{3\pm x}\text{Te}_2$ , the occupation of the octahedral sites, which varies between empty and completely occupied. The displacive modulations are different from those in  $\text{Ni}_{3\pm x}\text{Te}_2$ . The strongest displacive modulation is observed for the  $\text{Cu}^{\text{I}}$  atoms along  $a$ , and for the Te atoms along  $c$ . The Te atoms move in the direction of the empty  $\text{Cu}^{\text{II}}$  octahedral sites and away from occupied  $\text{Cu}^{\text{II}}$  sites.

In Fig. 2 the occupation of the  $\text{Cu}^{\text{II}}$  sites is plotted as function of the phase parameter  $\varphi = \bar{x}_4^{\text{II}} - \mathbf{q} \cdot \mathbf{x}_0^{\text{II}}$ . The Cu—Cu and Cu—Te interatomic distances were also calculated (deposited as Figs. 4 and 5) together with those for Te—Te (see Fig. 3). The occupation of the  $\text{Cu}^{\text{II}}$  sites deviates, in contrast to the analogous situation in the nickel compound, only slightly from a simple harmonic modulation and the emptier the site, the more  $\text{Cu}^{\text{I}}$  moves towards it. The distances between the Te atoms vary considerably, but no Te—Te bonds are formed (bond distance in the Te metal chain is 2.87 Å). The Cu<sup>I</sup>—Te distances vary between 2.58 and 2.70 Å. The displacive modulations for the Cu<sup>II</sup>—Te distances are also small; smaller than the octahedral distortion.

The temperature factors for all atoms are nearly isotropic and the differences between the temperature factors of different types of atoms are small. A structure refinement with one temperature factor for all atoms gave a higher  $R_{Fz} = 0.056$  with  $B_{\text{Overall}} =$

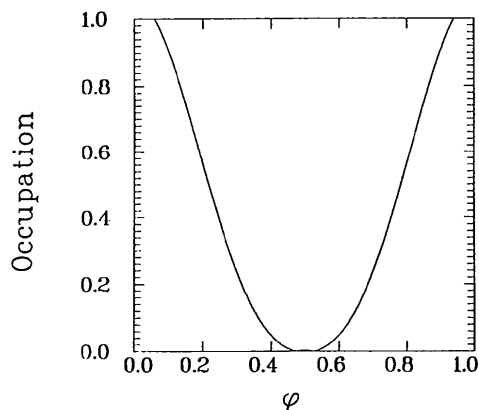


Fig. 2. Occupation of the  $\text{Cu}^{\text{II}}$  site as a function of  $\varphi$ .

1.18 (1) [versus 0.038 for anisotropic and 0.041 for isotropic refinement with  $B_{\text{iso}}^{\text{Cu}^{\text{I}}} = 1.39$  (1),  $B_{\text{iso}}^{\text{Cu}^{\text{II}}} = 1.69$  (3),  $B_{\text{iso}}^{\text{Te}} = 1.07$  (1)]. The structure can thus approximately be represented as a close packing of Te spheres, without strong anisotropic interactions. Compared with the corresponding nickel telluride phase, all atoms have larger temperature factors in the copper compound and show a stronger deviation from isotropy. In both compounds the heavier Te atom has smaller temperature factors than the metal atoms.

Colaitis, Delavignette *et al.* (1979) and Colaitis, van Dyck *et al.* (1979) described the structure of  $\text{Cu}_{3-x}\text{Te}_2$  in terms of a model with a partial ordering of  $\text{Cu}^{\text{II}}$  atoms in long-period superstructures, in order to explain the observed satellite reflections. No displacements of the atoms were taken into account in these superstructures. These superstructures correspond to the periodical removal or insertion of filled  $\text{Cu}^{\text{II}}$  layers. In an original and different way from that used for nickel telluride, a reference phase is taken, now with  $\mathbf{q} = \frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$  and only one site filled with a  $\text{Cu}^{\text{II}}$  atom. By carrying out the shear operations  $z_1$  or  $-z_1$ , defined by Colaitis *et al.* (1980), different superstructures can be created. The most simple superstructure explaining the satellites has the stacking sequences  $(5)^n$  [notation Colaitis *et al.* (1980)]. This superstructure resembles in some respects the modulated structure we deduced from our structure refinement. A more precise superstructure representation of the incommensurate structure is  $3\ 5^{17}\ 3\ 5^{17}$ , which has 88 unit cells along  $a$  ( $\mathbf{q} = 0.398\mathbf{a}^*$ ).

We now compare the structural modulations in nickel and copper telluride. Considering the occupational modulation of the metal(II) atom, we remark that it is more sinusoidal in the copper compound. The displacive modulation is much stronger for all atoms in the copper compound. Especially the Te

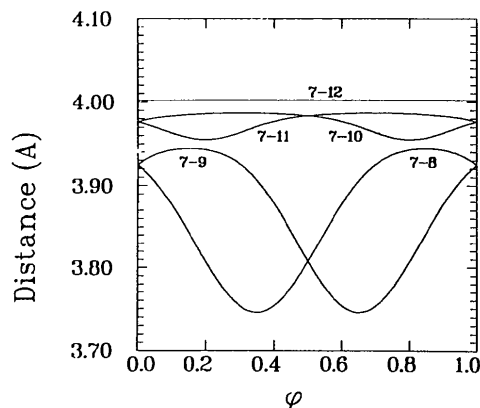


Fig. 3. Closest Te—Te distances as a function of  $\varphi$ . The numbers correspond with the atomic positions indicated in Fig. 1 of Schutte & de Boer (1993); primed numbers have  $z' = z - 1$ .

atoms move towards the empty octahedral sites along  $c$ , while in the nickel telluride the Te atoms were hardly affected. The metal atoms in the tetrahedral sites do not move towards the empty octahedral sites (as was the case in the nickel telluride), but mainly follow the modulation of the Te neighbours, resulting in strong displacements along  $a$ .

As to the origin of the incommensurate phase, we propose a mechanism similar to that proposed for the nickel telluride (Schutte & de Boer, 1993), in which the ordering of the Ni<sup>II</sup> is responsible for the phase transition tetragonal → orthorhombic. Together with the atomic displacements and the strong polarizability of the Te lattice the incommensurable ordering of these metal atoms is stabilized. The most simple ordering of the partially occupied sites will be empty–full, seen in the low-temperature superstructures of the nickel telluride. In the incommensurable structure of nickel telluride the ordering also tends to this scheme: the modulation wave of the symmetrically equivalent Ni<sup>II</sup> atom given by the  $n$  glide, is in antiphase. Both the temperature and the average occupation of the octahedral sites affect the wavelength of the modulation in the structure. For the copper telluride the ordering is different from that in the nickel compound. We ascribe this to a different interaction strength and a different charge transfer between the metal atom and Te.

The interaction strength between the metal atom and Te is larger in the nickel compound than in the copper compound, as the Ni–Te distances (average distance 2.56 Å) are considerably shorter than the Cu–Te distances (average distance 2.64 Å). We can qualitatively estimate the charge transfer by considering the interatomic Te distances. The Te–Te distance in the neutral Te metal is 3.74 Å, while the distance between Te<sup>2-</sup> ions is about 4.38 Å. In the copper and nickel telluride the Te atoms forming the distorted f.c.c. lattice have interatomic distances of 4.00 and 3.80 Å, respectively, along the  $b$  axis. Thus in the copper telluride the Te lattice has acquired more negative charge. The formal charge on the Te atoms in the nickel telluride is much smaller (Schutte & de Boer, 1993). In Cu<sub>3-x</sub>Te<sub>2</sub> the Cu atoms presumably have a full 3d shell (Cu<sup>+</sup>, 3d<sup>10</sup>), as in all other copper sulfides, selenides and tellurides (Jellinek, 1972). This would correspond in Cu<sub>3-x</sub>Te<sub>2</sub> to a formal charge of -1.4 on the Te atoms.

We can now explain the difference in the modulation between the copper and nickel compounds. By the strong Ni–Te interaction in Ni<sub>3±x</sub>Te<sub>2</sub> the Te lattice is strongly coupled. There is then no possibility of large Te displacements, but only small displacements of the metal atoms in the tetrahedral and octahedral holes. In Cu<sub>3-x</sub>Te<sub>2</sub>, with a weak Cu–Te interaction, displacements of the Te atoms are possible. The way in which these displacements

can be accommodated can be explained by considering the charge transfer between the metal atom and Te. By ordering of the metal atoms in the octahedral sites the valency of the closest neighbouring Te atoms changes. When a Cu<sup>II</sup> site is occupied this Te atom acquires extra charge, thereby enlarging its effective ionic radius. A displacement of the Te atom along  $c$  is the result. The whole orthorhombic Te lattice is affected and to balance this displacement the neighbouring Te atom in the next unit cell along  $c$  must move in the opposite direction. It is then necessary for the neighbouring octahedral site to be empty, and this leads to the antiphase ordering along  $c$  of the Cu<sup>II</sup> atoms. In the nickel telluride, which shows a much smaller charge transfer from Ni to Te, this antiphase ordering is not necessary because the charge on the Te atoms is hardly affected by the presence of the metal atoms in the octahedral sites. Here the strong Ni–Te interaction is more important. The displacements of the Ni atoms in the tetrahedral sites of the tellurium lattice are obvious. In the nickel telluride the Ni<sup>I</sup> atoms stabilize the incommensurable ordering by moving to the empty Ni<sup>II</sup> sites and away from occupied sites. In the copper telluride the Cu<sup>I</sup> atoms also stabilize the modulated structure by moving in the  $xy$  plane, reacting on the Te displacements (see Fig. 1).

We find that the incommensurable structure of the copper telluride is hardly affected by variation ( $x \approx 0.02, 0.26$ ) in the compound preparation conditions. Both structure determinations lead to nearly the same occupation of the Cu<sup>II</sup> sites ( $P^{\text{Cu}^{\text{II}}} = 0.455$  and 0.434) and the same modulation displacements for the atoms. In electron diffraction studies Colaitis *et al.* (1980) have already observed that the modulation wavevector  $q_x$  varies little as a function of temperature ( $463 < T < 403$  K), between  $q_x = 0.387$  and  $q_x = 0.40$ , which is much less than in the nickel telluride. Probably the range of existence of the modulated orthorhombic phase is much more limited ( $x \approx 0.11 \pm 0.03$ ) than previously proposed (Stevens, 1969).

When the metal atoms in the octahedral sites in Cu<sub>3-x</sub>Te<sub>2</sub> are withdrawn another phase in the Cu–Te system becomes stable: vulcanite CuTe (Baranova & Pinsker, 1964), which has the same structure and space group  $Pm\bar{m}n$  ( $a = 3.149$ ,  $b = 4.089$ ,  $c = 6.946$  Å) and has  $P^{\text{Cu}^{\text{II}}} = 0$ . Here again we see the effect on the structure of a larger charge transfer to Te, as compared with the corresponding nickel compound NiTe, which has the NiAs structure. In CuTe the Te atoms form [Te–Te]<sup>-</sup> chains (with an interatomic distance of 3.16 Å) along  $a$ . In Cu<sub>3-x</sub>Te<sub>2</sub> the Cu<sup>II</sup> atoms in the tellurium layers prevent the formation of these Te–Te chains. When more copper is substituted in Cu<sub>3-x</sub>Te<sub>2</sub> ( $P^{\text{Cu}^{\text{II}}} > \frac{1}{2}$ ) another phase (Cu<sub>2-x</sub>Te) is formed for which several superstruc-

tures are reported with a hexagonal subcell. Probably distortion of the tellurium lattice becomes too large to be realized by an incommensurable modulation.

### Concluding remarks

The average orthorhombic phase of  $\text{Cu}_{3-x}\text{Te}_2$  is analogous to that of  $\text{Ni}_{3\pm x}\text{Te}_2$  and has a close packing of Te atoms in which partially occupied  $\text{Cu}^{\text{II}}$  sites become ordered along the  $a$  direction (still random along  $b$ ). The Te—Te distances indicate that, unlike in the nickel compound, there is considerable charge transfer from the Cu to the Te atoms. This is reflected in the modulation: the Te atoms are strongly displaced towards the empty  $\text{Cu}^{\text{II}}$  sites. The displacements of the  $\text{Cu}^{\text{I}}$  atoms follow the tellurium lattice. The ordering of the  $\text{Cu}^{\text{II}}$  sites along  $a$  (Fig. 1) is described by the modulation wavevector  $\mathbf{q} = 0.397\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$ , incommensurable with the basic lattice. The ordering is determined quantitatively with first- and second-order harmonics of the modulation wave; probably higher-order harmonics should be used for a more precise description. The representation of the occupation modulation with a shear-structure-like model is possible. An explanation of the origin of the incommensurable modulation can be given in terms of two competing interactions, between the ordering of the  $\text{Cu}^{\text{II}}$  sites and the polarizability of the Te lattice. The difference between this case and the nickel telluride originates from a different interaction strength and a different charge transfer between the metal atom and Te. The homogeneity range of the modulated phase seems to be much smaller (somewhere around  $x = 0.11$ ) than was previously proposed, as we found only small

differences in the modulation (including occupation) parameters for two samples prepared under rather different conditions ( $x = 0.26$  and  $x = 0.02$ ).

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## Neutron Powder Investigation of Tetragonal and Cubic Stabilized Zirconia, TZP and CSZ, at Temperatures up to 1400 K

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### Abstract

A comparative study of tetragonal (Y-TZP, 3 mol%  $\text{Y}_2\text{O}_3$ ) and cubic (CSZ, 15 mol% CaO) zirconia powder samples was carried out to learn about a possible structural origin of the superior ionic con-

ductivity of TZP at low temperatures. Structure refinements including anharmonic temperature factors and oxygen occupancies as well as a qualitative analysis of the diffuse background revealed large differences especially of the anisotropy of thermal motion and the underlying disorder in both samples.

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