

classic displacive behaviour is established. The description of the same mechanism on an increasing temperature scale leads to the following picture: a static, ferroelastic state with coarse domains exists at room temperature. Each type of domain relates to one scalar order parameter that decreases with increasing temperature. The spontaneous strain and the excess volume decrease accordingly. When the order parameter falls below a threshold at temperatures sufficiently close to T_c , flip oscillations appear and microdomains are formed. These are correlated with a relative increase of the excess volume. The excess volume then decreases continuously above T_c and merges with the classical thermal expansion at $T \gg T_c$.

This picture leads to a further question: are the local lattice relaxations near T_c replaced by a further symmetry breaking near 430 K? If so, is this additional symmetry breaking related to an offset of $e_{13} > e_{11}$ near the transition point? Further work on the symmetry change on a local scale in pure lead phosphate and Ba-doped Pb₃(PO₄)₂ is underway.

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Determination of the Incommensurately Modulated Structure of Ni_{3±x}Te₂

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Abstract

The modulated structure of nickel telluride Ni_{3±x}Te₂ (Ni_{2.76}Te₂) is stabilized at 300 K by the substitution of a small amount of Fe (prepared as Ni_{2.57}Fe_{0.29}Te₂). The structure of this compound has been determined by X-ray diffraction at room temperature (1311 unique reflections). The structure is incommensurately modulated with wavevector $\mathbf{q} = 0.378(1)\mathbf{a}^*$. The lattice parameters of the primitive orthorhombic cell of the average structure are: $a = 3.761(1)$, $b = 3.796(1)$, $c = 6.084(4)$ Å with $V = 86.9$ Å³, $Z = 2$, $\mu = 317$ cm⁻¹ ($\lambda = 0.7107$ Å), $M_r = 416.4$. The symmetry of the structure is given by the superspace group P_{115}^{Pmmn} . Unlike the analogous Cu compound [Schutte & de Boer (1993). *Acta Cryst.* **B49**, 398–403]

there is no antiphase ordering along c . The final R_F factor is 0.047. Both occupational and displacive modulation functions are needed to describe the structure. The occupation of the distorted octahedral sites by Ni atoms is fully modulated ($P^{\text{Ni}^{\text{II}}}$ varying between 0 and 1). The Ni and Te atoms are slightly displaced, incommensurately with the basic lattice.

Introduction

The existence of a large number of phases in the Ni–Te system was reported by Kok, Wieggers & Jellinek (1965), Barstad, Grønbold, Røst & Vestersjø (1966) and Stevels (1969). Phases with composition Ni_{3±x}Te₂ are based on an f.c.c. arrangement of Te atoms, with Ni^I atoms in tetrahedral sites and Ni^{II}

atoms in octahedral sites, the Ni^{II} atoms being partially ordered depending on the temperature. In this way planes with only Ni^I atoms alternate along the *c* axis with planes occupied by Te and Ni^{II} atoms. For an overview of the packing, see Fig. 1.

Kok *et al.* (1965) found a tetragonal phase at room temperature for samples with composition Ni_{3-x}Te₂ whereas in Ni_{3+x}Te₂ samples a monoclinic phase was found. Both these phases are ordered superstructures derived from the Cu₂Sb type with partial disordering in the occupation of the nickel sites. The existence of an orthorhombic phase in quenched samples with composition Ni_{3±x}Te₂ was found by Barstad *et al.* (1966), who also found an f.c.c. high-temperature phase above 1073 K.

Stevens (1969) investigated the phase relations in Ni_{3±x}Te₂ more extensively using DTA and high-temperature Guinier photographs. Above 1043 K an f.c.c. phase with *a* ≈ 5.70 Å (depending on *x*) exists. Between 573 and 1043 K a tetragonal phase is found [similar to that of the rickardite Cu_{3-x}Te₂ and of the tetragonal iron chalcogenides Fe_{1+x}X with X = S, Se, Te (Grønvold, Haraldsen & Vihovde, 1954)]. The structure of this tetragonal high-temperature phase (*a* ≈ 3.82, *c* ≈ 6.06 Å, depending on *x*) with space group *P4/nmm* has an ordered arrangement of nickel in the tetrahedral sites while the Ni atoms in the pseudo-octahedral sites are occupied to the extent of about 50% in a disordered way.

Below about 573 K an orthorhombic phase (*a* ≈ 3.80, *b* ≈ 3.82, *c* ≈ 6.07 Å, depending on *x*) is formed whose structure is very similar to the tetragonal structure. In powder photographs weak lines were found which could not be indexed on the basis of the orthorhombic unit cell or by a simple supercell. This modification can be stabilized at room

temperature by incorporation of about 10% iron [Stevens (1969) used Ni_{3.01}Fe_{0.32}Te₂]. On Weissenberg photographs these extra reflections are indexed by (*h* + δ, *k*, *l*) with δ = 0.425. The existence of the satellite reflections could be explained by assuming a modulated structure. A complicated arrangement of the Ni atoms in the pseudo-octahedral sites was proposed, which was responsible for the orthorhombic distortion of the cell. When cooling the high-temperature tetragonal phase of Cu_{3-x}Te₂ (*x* = 0.2) (Stevens, 1969; Schutte & de Boer, 1993a) an orthorhombic modulated structure is found which had a number of features in common with the modulated structure of Ni_{3±x}Te₂. Similar satellite reflections also occur in orthorhombic eucairite CuAgSe (Früh, Czamanske & Knight, 1957).

Below about 423 K two different phases with simple ordered arrangements of Ni atoms exist in Ni_{3±x}Te₂ (Stevens, 1969). In the Ni-rich region, a monoclinic superstructure (2*a* × *b* × *c*) is observed, in which alternating rows of pseudo-octahedral Ni atoms and vacancies are formed, all running in the *b* direction. This structure can be described in space group *P2₁/m*. In the Te-rich region, a tetragonal superstructure (2*a* × *c*) is reported, with space group *P4m2* (Stevens, 1969).

Electron diffraction studies on Ni_{3±x}Te₂ (van Dyck, Colaitis, Delavignette & Amelinckx, 1979; Colaitis, Delavignette, van Dyck & Amelinckx, 1979; Colaitis, van Dyck, Delavignette & Amelinckx, 1979) showed that the ordering process is characterized by the appearance of a small number of quasi-incommensurable superlattice reflections, the positions of which shift continuously with composition and temperature. The diffraction features were interpreted in terms of long-period superstructures with partial ordering of the atoms. High-resolution electron microscopy with *in situ* heating was used to study the dynamical formation of these superstructures. The stacking sequences, as deduced from the observed structure images, were in agreement with the proposed structure models in which subsequent phases are considered as being constructed from two kinds of layers for the octahedral sites in a distorted cubic close-packed arrangement of Te atoms: planes filled predominantly with Ni atoms and planes occupied predominantly by vacancies.

In this paper we describe the incommensurately modulated structure of orthorhombic Ni_{3±x}Te₂ in which we have incorporated 10% Fe in order to stabilize the modulated structure at room temperature. We present the results of an X-ray analysis with up to second-order satellites using the methods developed by de Wolff (1974) and Yamamoto (1982). We compare our results with the structure models of the electron diffraction studies and qualitatively interpret the origin of the modulation.

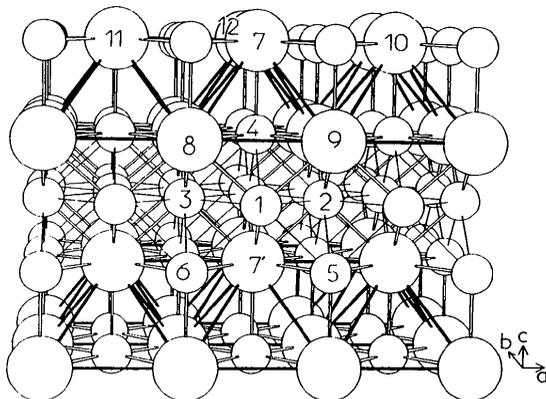


Fig. 1. Average structure of the orthorhombic form of Ni_{3±x}Te₂ (3*a* × 2*b* × 2*c* unit cells). Small circles represent Ni atoms, the larger circles Te atoms. Thick lines give *r*_{Te-Te} < 4.0 Å, double lines give *r*_{Ni-Te} < 2.7 Å and single lines give *r*_{Ni-Ni} < 2.7 Å. Atoms labeled 1, 2, 3 are Ni^I atoms, those labeled 4, 5, 6 are Ni^{II} atoms and those labeled 7–12 are Te atoms.

Table 1. Numbers of reflections and R_I values for the measurements at room temperature

	Measured	Unique	With $I > 2.5\sigma(I)$	R_I^*
Main reflections	1581	460	429	0.099
First-order reflections	3450	854	611	0.154
Second-order reflections	3461	792	271	0.266
All reflections	8492	2106	1311	

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

Experimental

We have not been able to prepare suitable single crystals of the orthorhombic phase of Ni_{3±x}Te₂ by heating mixtures of pure Ni and Te in evacuated quartz tubes at 1073 K, with subsequent quenching. However, good single crystals could be selected from a sample containing about 10% iron (Ni_{2.57}Fe_{0.29}Te₂). The properties of these stabilized phases are the same as those of the orthorhombic phase of Ni_{3±x}Te₂, although the Fe atoms have a stronger preference than nickel for tetrahedral coordination [11.7% tetrahedral Fe, 6.5% octahedral Fe, referring to the total amount of metal present (Stevens, 1969)].

All diffraction experiments were performed with monochromatized Mo $K\alpha$ radiation on an Enraf-Nonius CAD-4F diffractometer equipped with a modified CAD-4 program (de Boer & Duisenberg, 1984). All observed reflections could be indexed as (h,k,l,m) , where h,k,l are the Miller indices corresponding to the orthorhombic unit cell, and $|m|$ is the order of the satellite reflections caused by a modulation characterized by a single modulation vector \mathbf{q} . We investigated a large number of different crystals, both lumps and thin needles, but found no significant differences amongst them, neither in cell dimensions nor in modulation vector \mathbf{q} . For the final measurements we selected a crystal with dimensions of about $0.05 \times 0.10 \times 0.05$ mm. Lattice parameters were obtained from the positions of higher-order reflections, the modulation wavevector \mathbf{q} was determined from accurately determined positions of first-order satellites. Intensity data were collected using the θ - 2θ scan method, up to $\theta = 45^\circ$ for the main and satellite reflections. First- and second-order satellites could be measured, higher-order satellites were too weak to be observed. In view of the low intensities of higher-order satellites, reflections were measured with scan speeds in the ratio 3:2:1 for $|m| = 0, 1, 2$, respectively. Each data set was split into subsets of constant m (0, 1, -1, 2, -2) and the (h,k,l,m) measurement of each of these five subsets, defined in a unique sector of reciprocal space, was followed by measurement of the equivalent sector obtained by taking the $(-h,k,l,-m)$ reflections.

Throughout these ten subset measurements within one data file, three intensity-control reflections were monitored regularly every 2 h and used for slight drift corrections (within $\pm 1.5\%$). Including these reflections we obtained a data file of 8999 reflections. Hereafter the data were corrected for Lorentz and polarization effects and for absorption (with absorption coefficient $\mu = 317 \text{ cm}^{-1}$; transmission factors 0.1–0.3). Unique data sets were subsequently obtained by averaging equivalent reflections; for details see Table 1.†

Symmetry, refinement and structure results

The space group of the average structure obtained from the main reflections is determined to be $Pm\bar{m}n$. All satellites can be described with a single modulation wavevector $\mathbf{q} = 0.378(1)\mathbf{a}^*$. The diffraction symmetry of both main and satellite reflections is $Pm\bar{m}m$ leading in the superspace description (de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983) to the four-dimensional Bravais class $P_{\bar{1}11}^{Pm\bar{m}m}(\alpha, 0, 0)$. A $(3+1)$ -dimensional superspace group operator can be described by the symbol $(\mathcal{R}, \varepsilon | \tau)$ where \mathcal{R} and ε represent the point-group operations on the three-dimensional part and on the fourth coordinate, respectively. $\tau = (\tau_x, \tau_y, \tau_z, \tau_4)$ is the four-dimensional translational part of the operator. The systematic extinctions $h+k+m = \text{odd}$ for $hk0m$ reflections indicate the presence of a glide mirror plane (σ). If we assume that the superspace group is centrosymmetric (an assumption later justified by the refinement results), the superspace group for Ni_{3±x}Te₂ is $P_{\bar{1}11}^{Pm\bar{m}m}$, which has the following symmetry elements and corresponding equivalent positions (taking $mm2/n$ as the origin):

$$(E, 1 | n_x, n_y, n_z, n_4), (2_z, \bar{1} | 0000), (2_x, \bar{1} | \frac{1}{2}\frac{1}{2}0\frac{1}{2}), (2_x, 1 | \frac{1}{2}\frac{1}{2}0\frac{1}{2}), \\ (i, \bar{1} | \frac{1}{2}\frac{1}{2}0\frac{1}{2}), (m_z, 1 | \frac{1}{2}\frac{1}{2}0\frac{1}{2}), (m_y, 1 | 0000), (m_x, 1 | 0000); \quad (1)$$

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

To arrive at the equivalent superspace group which is present in the table of de Wolff *et al.* (1981), it is necessary to choose another modulation vector (van Smaalen, Bronsema & Mahy, 1986). This choice is:

$$\mathbf{q}' = \mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^* - \mathbf{q} = 0.622\mathbf{a}. \quad (3)$$

† Lists of structure factors and figures showing closest Te—Te, Ni—Ni and Ni—Te distances as a function of φ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55333 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All satellites indexed as (h,k,l,m) with respect to $\mathbf{q} = 0.378\mathbf{a}^*$ are then indexed as $(h+m,k,l,-m)$ with respect to the modulation vector $\mathbf{q}' = 0.622\mathbf{a}^*$. The resulting superspace group is then $P_{\uparrow 1 1}^{Pmmn}$ [No. 59b in the tables of de Wolff *et al.* (1981)]. We perform the structure determination for the three-dimensional part of the superspace group in the first setting of *International Tables for Crystallography* (1987, Vol. A). In the internal space we choose for the modulation vector $\mathbf{q} = 0.378\mathbf{a}^*$.

We will consider two types of modulations: an occupational one for the partially occupied Ni^{II} positions and one of a displacive type for all atoms. To analyse this modulated structure we use the following notation for the modulation wave for the μ th atom:

$$P^\mu(\bar{x}_4^\mu) = P_0^\mu + \sum_{n=1}^N P_n^{\mu,c} \cos(2\pi n \bar{x}_4^\mu) + P_n^{\mu,s} \sin(2\pi n \bar{x}_4^\mu) \quad (4)$$

$$u_i^\mu(\bar{x}_4^\mu) = \sum_{n=1}^N u_{n,i}^{\mu,c} \cos(2\pi n \bar{x}_4^\mu) + u_{n,i}^{\mu,s} \sin(2\pi n \bar{x}_4^\mu) \quad i = x, y, z \quad (5)$$

with P_n^μ , $u_{n,i}^\mu$ the n th harmonic Fourier amplitudes of the modulation wave, with $N=2$ as we have observed up to second-order satellite reflections. P^μ refers to the occupation and u^μ to the displacement of the atom μ . For a displacive modulation the positions of the atoms are given by:

$$\begin{aligned} \mathbf{r}^\mu(\bar{x}_4^\mu) &= \mathbf{r}_0^\mu + \mathbf{u}^\mu(\bar{x}_4^\mu) \\ &= \mathbf{n} + \mathbf{x}^\mu(\bar{x}_4^\mu) \\ &= \mathbf{n} + \mathbf{x}_0^\mu + \mathbf{u}^\mu(\bar{x}_4^\mu) \end{aligned} \quad (6)$$

where \mathbf{n} ($n_x n_y n_z n_4$) is a basic structure lattice translation and \mathbf{x}_0^μ is the average position within the unit cell. The modulation is a periodic function of $\bar{x}_4^\mu = \mathbf{q} \cdot \mathbf{r}_0^\mu$.

The symmetry restrictions on the components of the modulation wave are obtained from the group of symmetry operations $(\rho, \varepsilon | \tau)$, which leave the position and the occupation of the μ th atom invariant:

$$\begin{aligned} \mathbf{u}^\mu(x_4^\mu) &= (\rho, \varepsilon | \tau) \mathbf{u}^\mu(x_4^\mu) \\ P^\mu(x_4^\mu) &= (\rho, \varepsilon | \tau) P^\mu(x_4^\mu). \end{aligned} \quad (7)$$

In the superspace group $P_{\uparrow 1 1}^{Pmmn}$ all atoms occupy special positions. As a consequence, in addition to the restrictions on positional [for example Ni^I on $(0,0,z)$] and thermal parameters there are also restrictions on the modulation parameters. All atom sites are left invariant by $(m_y, 1 | 0000)$, $(m_x, \bar{1} | 0000)$. From these operators the symmetry restrictions on the modulation wavefunctions are obtained and these are summarized in Table 2. We see that in this superspace group all allowed modulation functions

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
Ni ^I , Ni ^{II} , 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 number of parameters (n_p) and the number of reflections (n_r) used are also given in the table.

	R_F	R_{F^2}	n_p	n_r
$m = 0$	0.030	0.040	15	429
$m = 1$	0.081	0.090	7	611
$m = 2$	0.222	0.270	7	271
Overall	0.048	0.045	29	1311

are either even or odd, and that displacements u_y^μ are all zero. There is no phase shift between P^μ and u_z^μ , and there is a phase difference of 90° between u_x^μ and u_z^μ .

The least-squares program REMOS85 (Yamamoto, 1985), which calculates the structure factor in the four-dimensional analysis, has been used for the refinement. Refinement of the variables, with one extra parameter describing the secondary extinction, was performed by minimizing R_{F^2} . The definition of the R factors is

$$R_F = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|} \quad (8)$$

and

$$R_{F^2} = \left(\frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum |F_{\text{obs}}|^2} \right)^{1/2}. \quad (9)$$

The atomic scattering factors and the anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

We started our calculation with transformed coordinates of Stevels (1969) results for the tetragonal structure: Ni^I at $(0,0,0.000)$, Ni^{II} at $(0, \frac{1}{2}, 0.31)$ and Te at $(0, \frac{1}{2}, 0.71)$. Next the occupational and displacive waves were included. For all reflections with $I > 2.5\sigma(I)$ unit weight and for those with $I < 2.5\sigma(I)$ zero weight is taken. Refinement of the occupation of the Ni^{II} sites leads to a maximum value of 1.05 for the occupation at $\bar{x}_4^{\text{Ni}^{\text{II}}} = 0$. This unphysical result is probably caused by the fact that we used only first- and second-order harmonics, as third- and higher-order satellites are too weak to be measured. In order to avoid unrealistic occupation values, we hereafter used a penalty function which constrains the value of P between zero and one. The R factor is only very slightly affected by this condition. The final R_F values, using the penalty function, are listed in Table 3. The relatively high R factor for the second-

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

The factor for the anisotropic thermal vibrations is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$.

μ, i	$x_{0,0}^{\mu}, P_0^{\mu}$	$u_{1,0}^{\mu,c}, P_{1,0}^{\mu,c}$	$u_{1,0}^{\mu,d}$	$u_{2,0}^{\mu,c}, P_{2,0}^{\mu,c}$	$u_{2,0}^{\mu,d}$
Ni ^I					
<i>x</i>	0		0.0004 (3)		-0.0019 (6)
<i>y</i>	0				
<i>z</i>	-0.0005 (1)	-0.0091 (2)		-0.0024 (3)	
β_{11}	0.0165 (1)				
β_{22}	0.0165 (4)				
β_{33}	0.0063 (1)				
<i>P</i>	1				
Ni ^{II}					
<i>x</i>	0		0.002 (3)		-0.010 (3)
<i>y</i>	$\frac{1}{2}$				
<i>z</i>	0.295 (3)	0.000 (5)		0.001 (3)	
β_{11}	0.0158 (8)				
β_{22}	0.0152 (7)				
β_{33}	0.0053 (3)				
<i>P</i>	0.379 (3)	0.491 (4)		0.134 (4)	
Te					
<i>x</i>	0		-0.0035 (2)		-0.0037 (2)
<i>y</i>	$\frac{1}{2}$				
<i>z</i>	0.71505 (6)	-0.00268 (9)		0.0012 (1)	
β_{11}	0.0139 (2)				
β_{22}	0.0147 (2)				
β_{33}	0.00498 (7)				
<i>P</i>	1				

order satellites is due to the fact that the intensities of these satellites are much weaker than the intensities of the first-order satellites. The final structural parameters are given in Table 4.

Discussion

The average structure of orthorhombic Ni_{3±x}Te₂ (see Fig. 1) is a distorted defective Cu₂Sb-type structure. The Ni^I atoms occupy the tetrahedral holes (four equal distances Ni^I—Te of 2.56 Å) and the Ni^{II} atoms the pseudo-octahedral holes (four equal Ni^{II}—Te of 2.67 Å in the *ab* plane, and distances of 2.55 and 3.1 Å along *c*) of the Te lattice. The Ni^{II} atoms are distributed over the pseudo-octahedral holes with an average occupation of 37.9%. Each Te

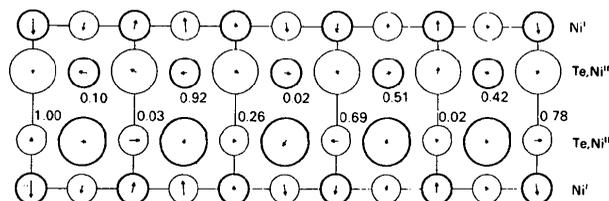


Fig. 2. Block $5a \times c$ of the modulated structure of Ni_{3±x}Te₂ projected onto the *ac* plane. Small circles are Ni atoms, larger ones are Te atoms. Bold circles are at $y = 0$, other circles are at $y = \frac{1}{2}$. Occupation numbers of the Ni^{II} sites are indicated. Modulation displacements are represented, in direction and (factor 8 exaggerated) in length, by the arrows. Note that, by the absence of antiphase ordering along *c*, the height of this figure could be limited to half of that of the overview picture for Ni_{3±x}Te₂ given in Fig. 1.

is surrounded by four Ni^I and five Ni^{II} atoms (four in the same layer, one in the next layer). The Te atoms form a distorted f.c.c. lattice with four Te neighbours at 3.75, two at 3.77 and two at 3.80 Å, all in the same layer, and four at 4.30 Å between the layers. In this intermetallic compound the distances between like and unlike atoms are not very different. Each Ni^I is surrounded by four Ni^I atoms in the same plane at 2.67 Å and by four Ni^{II} atoms in a tetrahedral manner at 2.60 Å. Each Ni^{II} atom is surrounded by four Ni^I atoms at 2.60 Å.

In the modulated structure (see Fig. 2) the strongest modulation is the occupation of the Ni^{II} sites, where the occupation varies over the full range from empty to fully occupied. The strongest displacive modulation is that of the Ni^I atom along *z*, in such a way that it moves in the direction of the empty Ni^{II} sites and away from occupied Ni^{II} sites.

Fig. 3 shows the occupation of the Ni^{II} sites as a function of the phase parameter $\varphi = \bar{x}_4^{\mu} - \mathbf{q} \cdot \mathbf{x}_0^{\mu}$. The characteristics of the occupation of the Ni^{II} sites resemble a block-wave with $P = 0$ for $\frac{1}{4} < \varphi < \frac{3}{4}$ and $P = 1$ for $\varphi < \frac{1}{4}, \varphi > \frac{3}{4}$. Also, the Te—Te, Ni—Ni and the Ni—Te interatomic distances were calculated (deposited as Figs. 4, 5 and 6). The Ni^{II} sites have an asymmetric coordination along *a*. Variations in the Ni^{II}—Te distances are small. Modulation of the Te—Te distances is also small, leaving the distorted close-packed Te structure nearly unaffected. Therefore correlation between the occupation of the Ni^{II} sites and the displacement of the Te atoms is weak.

From the interatomic distances we can obtain some indications about the degree of charge transfer between Ni and Te atoms. The distance between neutral Te atoms is about 3.74 Å (from nearest distances between atoms in different chains in Te metal), the smallest distance between two Te²⁻ ions is about 4.38 Å [ionic radii from O'Keeffe & Navrotsky (1981)]. In Ni_{3±x}Te₂ the Te—Te distance is 3.80 Å, only slightly larger than in the neutral metal

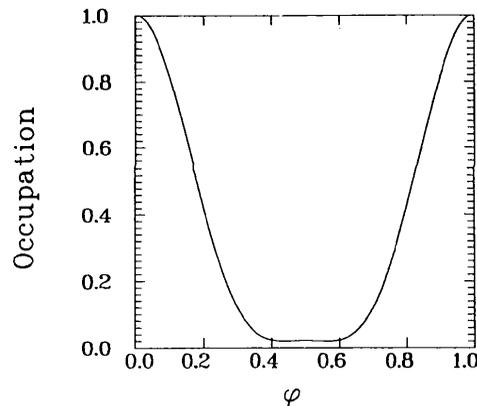


Fig. 3. Occupation P of the Ni^{II} site as a function of φ (note that P is an average over the Ni^{II} sites along *b*).

(pointing to only a small charge transfer). The metal atoms fit well into the octahedral holes of the anion lattice. Comparable Te—Te distances are found in FeTe (3.80 Å, NiAs type), FeTe₂ (3.85 Å, marcasite type) and TiTe₂ (3.76 Å, CdI₂ type).

The temperature factors for all atoms are nearly isotropic and the differences between the temperature factors of different types of atoms is very small (Table 4). A structure refinement with one overall isotropic temperature factor gave an only slightly higher $R_{F^2} = 0.050$ with $B^{\text{overall}} = 0.819$ (7) [versus 0.045 for anisotropic and 0.046 for isotropic refinement with $B^{\text{Ni}^{\text{I}}} = 0.93$ (1), $B^{\text{Ni}^{\text{II}}} = 0.92$ (2), $B^{\text{Te}} = 0.789$ (7); the factor for the isotropic thermal vibrations is $\exp(-B^{\mu}\sin^2\theta/\lambda^2)$]. The structure can thus be represented as a close packing of spheres, without strong anisotropic interactions.

Colaitis, Delavignette *et al.* (1979) describe the structure of Ni_{3±x}Te₂ in terms of a model with partial ordering of Ni^{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 a periodic removal or insertion of a filled Ni^{II} layer in one of the commensurate end phases, $q_x = \frac{1}{2}$ and $q_x = \frac{1}{3}$ (van Dyck *et al.*, 1979). In order to be in accordance with compositional requirements, excess Ni must be accommodated in a random fashion over the empty Ni^{II} sites. The superstructure of approach (I) which explains the incommensurate satellites corresponding to $\mathbf{q} = 0.385\mathbf{a}^*$, is that having the stacking sequence (3.5²)² (notation Colaitis, Delavignette *et al.*, 1979). The ordering in this superstructure is not very different from the ordering in the modulated structure which we deduced from our structure refinement. With the second approach also, with (3².7)² and $\mathbf{q} = 0.385\mathbf{a}^*$, the Ni^{II} ordering can be approximated. We must realize that our refinement is an approximation, too, in the sense that we used first- and second-order harmonics only (as we could only measure first- and second-order satellites).

Let us discuss the origin of the incommensurate phase. In metallic compounds as for example K_{0.3}MoO₃ (Schutte & de Boer, 1993b), the modulation is well understood as being due to an instability of the Fermi surface. For calaverite (AuTe₂) (Schutte & de Boer, 1988) the interplay of valence fluctuations on the metal atom with the polarizability of the Te lattice is taken to be responsible for the incommensurate distortion. In the present case we propose a mechanism similar to that in calaverite, with the role of valence fluctuations of Au replaced by the ordering on the Ni^{II} sites. The origin of the incommensurate structure can be based on the existence of two independent transformation modes which have energy-lowering interactions (Heine & McConnell,

1981). The main transformation mode describes the ordering of the Ni^{II} atoms, while the second transformation mode is related to displacements of the atoms. The Ni^{II}—Ni^{II} correlations are strongest in the *ab* plane, and by ordering on the Ni^{II} sites the high-temperature tetragonal phase transforms into the orthorhombic phase. Twinning is often encountered, because the system can choose between an ordering along *a* or along *b*.

Concluding remarks

The structure of the orthorhombic phase Ni_{3±x}Te₂ is a close packing of Te spheres in which partially occupied Ni^{II} sites are ordered in the *a* direction. The occupation of sites along the *b* axis is random and there is no antiphase ordering along *c*. From the Te—Te distances we conclude that there is only a small charge transfer from Ni to Te, the formal valency of Te being slightly negative. This is reflected in the modulation, as the Te atoms are hardly displaced. Displacements of the Ni^I atoms in the tetrahedral holes are such that they move in the direction of the empty Ni^{II} sites.

The complex ordering of the Ni^{II} sites along *a* (Fig. 2) is described by the modulation wave $\mathbf{q} = 0.378\mathbf{a}^*$, incommensurate with the basic lattice. The ordering is described with harmonics of up to second order; higher-order harmonics should be used for a more precise description.

The incommensurate modulation can be represented approximately by a shear structure model and is the result of two competing interactions, the ordering on the Ni^{II} sites and the displacements of the atoms.

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Determination of the Incommensurately Modulated Structure of Cu_{3-x}Te₂

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Abstract

The incommensurately modulated structure of copper telluride Cu_{3-x}Te₂ (Cu_{2.91}Te₂) 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, $V = 97.1$ Å³, $Z = 2$, $\mu = 304$ cm⁻¹ ($\lambda = 0.7107$ Å), $M_r = 440.1$. The symmetry of the structure is given by the superspace group $C_{2v}^{Pmn} \Gamma_{11}$. The final R_F factor is 0.045. The modulated structure is related to the structure of Ni_{3±x}Te₂ [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_{3-x}Te₂ for which a tetragonal structure of the defective Cu₂Sb 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_{3-x}Te₂ ($x \approx 0.2$) 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^I atoms in tetrahedral sites and Cu^{II} 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

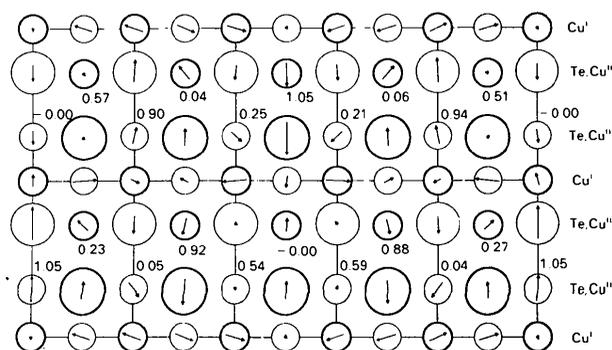


Fig. 1. Modulated structure of Cu_{3-x}Te₂ ($5a \times 2c$). Small circles are Cu atoms, larger ones are Te atoms. Bold circles are at $y = 0$, other circles are at $y = \frac{1}{2}$. Occupation numbers of the Cu^{II} sites are indicated. Modulation displacements are represented, in direction and (factor 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_{3±x}Te₂, as given in Fig. 1 of Schutte & de Boer (1993).