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The crystal structure of room-temperature synthesised orthorhombic $TlCu_4Se_3$ from direct methods on X-ray powder data

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Abstract

An orthorhombic modification of $TlCu_4Se_3$ was synthesised at room temperature by oxidative copper extraction from $TlCu_5Se_3$. It crystallises in a new structure type, space group *Pnnm*, with the cell parameters $a = 12.4306(2)$ Å, $b = 12.7997(2)$ Å, $c = 3.93516(6)$ Å. The structure is closely related to the tetragonal structure of the parent compound. For the structure solution direct methods were used on single-phase Guinier-Hägg X-ray powder film data. In the refining stage, the Rietveld method was applied on powder diffractometer data. After being heated above 670 K, this orthorhombic form completely transforms to the tetragonal modification. Both are metallic conductors.

Keywords: X-ray powder data; Metallic conductors; Transformation mechanisms

1. Introduction

During a recent study of the Tl–Cu–Se system [1] both conventional high-temperature and soft-chemistry synthesis routes were used. Especially the latter approach proved very useful for obtaining new phases, also implemented to the Tl–Cu–S system in which $TlCu_2S_2$ could be obtained at room temperature where previous high-temperature methods had failed [2]. It was at first thought that the method *per se* implied metastability, but since later electrochemical studies have shown that the reactions of the couples $TlCu_3Se_2$/$TlCu_2Se_2$ [3] and $TlCu_3S_2$/$TlCu_2S_2$ [4] are completely reversible, this view must be altered.

Copper extraction from $TlCu_5Se_3$ yielded a new orthorhombic phase, the composition of which was not known with certainty at first [1]. Later chemical analyses [5] indicated that its composition should be $TlCu_4Se_3$. Another modification with tetragonal symmetry was then already known [6], having a cell volume only 1/4 of that of the new form. Since the tetragonal form (t-$TlCu_4Se_3$) has a cell with $Z = 1$ the new form (o-$TlCu_4Se_3$) must have $Z = 4$.

In the original paper [1], a close structure relation was anticipated between $TlCu_5Se_3$ and o-$TlCu_4Se_3$, based on the similarities in cell dimensions between parent and daughter phase. However, the structure of $TlCu_5Se_3$ was not known at that time, but a model was put forward [5] that it was related to the structure of $TlCu_7Se_4$. Since that is isostructural with $NH_4Cu_7S_4$, described in $I\bar{4}$ [7], the structures of $TlCu_5Se_3$ and o-$TlCu_4Se_3$ were tentatively assigned the space-groups $P\bar{4}n2$ and $Pnn2$, respectively. However, later work not only confirmed the hypothesis concerning the structure of $TlCu_5Se_3$ but also revised its space-group assignment to $P4_2/mnm$ [8], finally implying and proving $I4/m$ for $TlCu_7Se_4$ [9]. With the same chain of thought, i.e. a mirror plane being present, a probable new assignment for o-$TlCu_4Se_3$ would be *Pnnm*.

This was the starting point for a refinement attempt where the structure was guessed (RB) from the assumption that, on extraction, the tetrahedral copper clusters of $TlCu_5Se_3$ would disappear. In that Rietveld refinement R-values of only 16%–17% were attained and it was assumed [10] that the hypothesis was of too little credence. With the development of direct methods also for powders (since no single crystals could ever be obtained from the room-temperature synthesis), the idea now arose to take up the problem again. The successful structure solution and refinement are described in this paper.

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2. Experimental details

2.1. Synthesis

After synthesis of $TlCu_5Se_3$ at 670 K from TlSe, copper and selenium [1], the sample was also found to contain a trace of berzelianite, Cu_2Se. Swirling of the powder in ammonia solution (magnetic stirrer) for a couple of hours effectuated the air oxidation to o-$TlCu_4Se_3$. The copper ammine solution was decanted and the powder washed by water and finally by acetone. Previous studies had shown that copper also leaves berzelianite by such a procedure, umangite (Cu_3Se_2) being formed, but no trace was found of any binary copper selenide after this extraction. Either the most copper-poor selenide being formed was microcrystalline or it was effectively separated from the thallium compound by decanting owing to differences in grain size and density.

2.2. X-ray diffraction

A Guinier-Hägg subtraction-geometry focusing camera was used for determining the cell parameters accurately (Table 1) with silicon as calibrant ($a = 5.431028$ Å at 22.5 °C [11]). The line positions and raw intensities were obtained from an LS18 microdensitometer scan [12] (see Ref. [9] for details). After scanning of the film, the background was removed by applying a spline-function with points manually chosen interactively on the computer screen. These net intensity data were corrected for Lorentz and polarisation effects taking the monochromatisation into account [13] and were subsequently used for the structure solution.

For the final Rietveld refinements, data sets were used that had been collected on STOE STADI/P powder diffractometers with the sample in a symmetric transmission mode (See Ref. [9] for further details).

2.3. Structure solution and refinement procedures

In the first stage of the structure solution, data from an old single-phase material Guinier film were used in order to test whether the DIRECT METHODS program (SIRPOW.92 [14]) would work at all. This program package eventually yielded a structure proposal carrying much of the previously guessed features in it. It was possible to constructively edit the proposal (to get the proper stoichiometry) by considering expected crystal chemistry (coordination and interatomic distances). At that stage, the *R*-value was of the order of 21%. The proposal differed from the previous attempt [10] only regarding one copper site.

We then retrieved the 1990 diffractometer data set (Data set 1) [10] where $TlCu_2Se_2$ was also present and made a Rietveld refinement of the two phases using

Table 1

X-ray powder data of o-$TlCu_4Se_3$, space-group *Pnnm* ($Z = 4$). For a sample also containing t-$TlCu_4Se_3$, the refined cell was $a = 12.4306(2)$ Å, $b = 12.7997(2)$ Å, $c = 3.93516(6)$ Å. Line positions from a silicon calibrated Guinier-Hägg film (listed up to $\theta = 30°$ for Cu $K\alpha_1$ radiation) and the corresponding refined values are given as $Q \equiv d^{-2}$ in units of $Å^{-2}$. The intensities were taken from the structure refinement (first six reflections omitted) of diffractometer data on single-phase material (Dataset 2) and were put on a relative scale maximised to 100.0

h k l	*Q*(obs)	*Q*(calc)	*Int*(calc)	*Int*(obs)
1 1 0	0.01256	0.01258	4.4	
0 2 0		0.02442	0.2	
2 0 0		0.02589	0.5	
1 2 0	0.03085	0.03089	1.5	
2 1 0	0.03203	0.03199	1.5	
2 2 0		0.05030	0.4	
1 3 0	0.06140	0.06141	6.2	6.2
3 1 0		0.06435	0.1	0.1
0 1 1	0.07067	0.07068	15.9	15.7
1 0 1		0.07105	0.2	0.2
1 1 1	0.07714	0.07715	4.6	4.5
2 3 0	0.08084	0.08082	9.5	9.3
3 2 0	0.08265	0.08266	10.4	10.4
1 2 1		0.09546	0.0	0.0
2 1 1	0.09657	0.09657	26.5	26.4
0 4 0	0.09763	0.09766	42.5	42.8
4 0 0	0.10356	0.10355	47.8	48.9
1 4 0		0.10413	0.4	0.4
4 1 0	0.10962	0.10965	8.7	8.8
3 3 0		0.11318	1.4	1.4
2 2 1	0.11487	0.11488	100.0	99.8
0 3 1	0.11949	0.11951	21.7	20.9
3 0 1	0.12279	0.12282	19.6	19.3
2 4 0		0.12355	1.2	1.2
1 3 1	0.12600	0.12598	17.9	17.3
4 2 0		0.12796	0.3	0.3
3 1 1	0.12889	0.12892	45.9	44.4
2 3 1	0.14540	0.14540	1.9	1.8
3 2 1	0.14720	0.14724	0.9	0.9
3 4 0		0.15591	0.0	0.0
4 3 0		0.15848	1.8	1.8
1 5 0	0.15905	0.15907	5.4	5.5
5 1 0	0.16791	0.16790	5.1	5.3
1 4 1	0.16861	0.16871	21.2	20.8
4 1 1	0.17421	0.17423	7.6	7.5
3 3 1	0.17781	0.17776	7.8	8.1
2 5 0	0.17859	0.17848	12.9	13.6
5 2 0		0.18621	0.0	0.0
2 4 1		0.18812	0.2	0.2
4 2 1	0.19249	0.19254	11.7	11.8
4 4 0	0.20119	0.20121	10.4	10.5
3 5 0		0.21084	0.1	0.1
5 3 0		0.21673	1.2	1.2
0 5 1	0.21705	0.21717	3.0	2.9
0 6 0		0.21974	0.1	0.1
3 4 1	0.22050	0.22048	10.1	10.1
4 3 1		0.22306	6.0	6.0
1 5 1	0.22351	0.22364	11.6	11.6
1 6 0		0.22621	1.6	1.5
5 0 1	0.22632	0.22637	12.1	11.5
5 1 1		0.23247	0.0	0.0
6 0 0	0.23296	0.23298	2.5	2.6
6 1 0	0.23903	0.23908	2.2	2.4

(*continued*)

Table 1 (*continued*)

h k l	*Q*(obs)	*Q*(calc)	*Int*(calc)	*Int*(obs)
2 5 1	0.24309	0.24306	3.2	3.2
2 6 0		0.24562	0.1	0.1
5 2 1		0.25078	0.0	0.0
4 5 0	0.25612	0.25614	16.3	17.8
6 2 0		0.25740	0.1	0.1
0 0 2	0.25830	0.25831	45.3	49.0
5 4 0		0.25945	0.5	0.5
4 4 1		0.26578	0.1	0.1
1 1 2		0.27088	0.2	0.2
3 5 1		0.27542	0.1	0.1
3 6 0		0.27798	0.1	0.1
5 3 1	0.28131	0.28130	1.9	2.0
0 2 2		0.28272	0.0	0.0
2 0 2		0.28419	0.0	0.0
6 3 0		0.28791	0.0	0.0
1 2 2		0.28919	0.1	0.1
2 1 2		0.29030	0.2	0.2
1 6 1	0.29079	0.29079	1.0	1.1
6 1 1	0.30361	0.30366	12.6	12.5
1 7 0		0.30556	0.3	0.3
2 2 2		0.30861	0.0	0.0
2 6 1	0.31023	0.31020	32.2	32.6
5 5 0	0.31435	0.31439	9.0	9.4
1 3 2	0.31981	0.31971	0.9	0.9
4 5 1		0.32072	0.0	0.0
6 2 1	0.32193	0.32197	11.9	12.2
3 1 2		0.32266	0.0	0.0
7 1 0		0.32322	0.5	0.5
4 6 0		0.32328	0.3	0.3
5 4 1		0.32403	0.3	0.3
2 7 0	0.32484	0.32497	0.6	0.6
6 4 0		0.33064	0.0	0.0
2 3 2	0.33910	0.32913	1.9	2.0
3 2 2	0.34112	0.34097	1.9	2.0
7 2 0		0.34153	0.6	0.7
3 6 1		0.34256	0.6	0.6
6 3 1	0.35248	0.35249	4.0	4.4
0 4 2	0.35605	0.35597	11.3	11.4
3 7 0		0.35733	0.0	0.0
4 0 2	0.36184	0.36185	12.7	12.0
1 4 2		0.36244	0.1	0.1
0 7 1	0.36356	0.36366	3.4	3.3
4 1 2	0.36800	0.36796	2.6	2.7
1 7 1	0.37023	0.37014	2.7	2.7
3 3 2		0.37149	0.3	0.3
7 3 0		0.37205	0.0	0.0
5 5 1		0.37896	0.0	0.0
5 6 0	0.38158	0.38153	0.5	0.5
7 0 1		0.38169	0.0	0.0
2 4 2		0.38185	0.3	0.3
6 5 0	0.38553	0.38558	4.3	4.1
4 2 2		0.38627	0.1	0.1
7 1 1	0.38779	0.38779	6.0	5.9
4 6 1		0.38786	1.4	1.3
2 7 1		0.38955	0.2	0.2
0 8 0	0.39070	0.39064	1.3	1.3
6 4 1		0.39522	0.0	0.0
1 8 0		0.39712	0.2	0.2
4 7 0		0.40263	0.0	0.0
7 2 1		0.40610	0.1	0.1
8 0 0		0.41419	0.0	0.0
2 8 0		0.41653	0.2	0.2
4 3 2		0.41679	0.7	0.7
1 5 2	0.41721	0.41737	1.9	1.8
8 1 0	0.42055	0.42029	0.4	0.4

the LHPM1 program [15]. Both phases refined very well (Table 2), but a trace of a third unknown phase was also found. Therefore, a second diffractometer data set (Data set 2) was collected from a new synthesis (*vide supra*) of $TlCu_5Se_3$ that eventually yielded o-$TlCu_4Se_3$ as a single-phase product.

The refinement encompassed the zero-point, a scale factor, three half-width parameters, six background parameters, one peak-shape parameter (pseudo-Voigt profile description) and three cell parameters in addition to the structural and thermal parameters, in total 38 variables in the final run, also including a small correction for preferred orientation (along ⟨002⟩).

Some minor difficulties were encountered when trying to describe the background owing to amorphous contributions from the backing material (specimen on tape). To circumvent this, the first part, containing six weak reflections, was not included in the refinement.

3. Results and discussion

The results of the cell parameter determination (Guinier-Hägg film data) are collected in Table 1. The indices are consistent with the space-group *Pnnm* used for the structure solution.

The refinement from Dataset 2 carried a higher precision than that from Dataset 1 (Table 2). Moreover, the serial correlation indicated by the Durbin-Watson *d* statistics [16] is less. Still, the standard deviations are underestimated. In the following, we thus present and discuss the result mainly from Dataset 2 with occasional comparison with Dataset 1. The structural parameters are found in Table 3 and the interatomic distances in Table 4. Fig. 1 shows the fit obtained between the observed and calculated STADI/P patterns. The (002) reflection is observed slightly stronger than calculated, probably owing to texture, not efficiently taken care of in the refinement.

Table 2
Some details of the refinements. Dataset 1 consisted of three-phase and Dataset 2 of single-phase diffractometer data

		Dataset 1	Dataset 2
Halfwidth parameters:	u:	0.099(15)	0.127(8)
	v:	−0.004(12)	−0.060(7)
	w:	0.005(2)	0.024(1)
Profile fitting:	R_P:	0.042	0.043
	R_{wP}:	0.062	0.056
Goodness-of-fit:	χ^2:	1.34	0.94
Durbin-Watson index	(d):	0.30	0.47
Structure model-fitting:			
o-$TlCu_4Se_3$:	R_I:	0.087 (301 refl.)	0.027 (340 refl.)
$TlCu_2Se_2$:	R_I:	0.17 (39 refl.):	

Table 3

Structural parameters of o-$TlCu_4Se_3$. First line, dataset 1; second line, dataset 2; for each atomic site (all atoms in 4*g* with *z*-parameter zero) in space-group *Pnnm*. The occupancy (*G*) was refined only for Cu(4), keeping all temperature factors for copper equal. Values within parentheses are the estimated standard deviations from the least-squares treatment

Atom	*x*	*y*	*B* (Å²)	*G* (%)
Tl(1)	0.1041(3)	0.1272(3)		
	0.1048(2)	0.1273(2)	4.48(6)	
Cu(1)	0.1940(9)	0.8276(8)		
	0.1940(4)	0.8292(4)	4.21(7)	
Cu(2)	0.1849(8)	0.4184(8)		
	0.1843(4)	0.4193(4)	4.21(7)	
Cu(3)	0.4180(9)	0.2304(8)		
	0.4129(5)	0.2316(4)	4.21(7)	
Cu(4)	0.3953(12)	0.0369(9)		
	0.4042(6)	0.0412(4)	4.21(7)	92.1(8)
Se(1)	0.3792(7)	0.4129(7)		
	0.3799(3)	0.4105(3)	3.45(12)	
Se(2)	0.5952(8)	0.1462(8)		
	0.5948(4)	0.1444(4)	3.04(10)	
Se(3)	0.1820(6)	0.6351(7)		
	0.1799(3)	0.6322(4)	3.46(10)	

Table 4

Interatomic distances (Å units) up to 3.8 Å in o-$TlCu_4Se_3$. Estimated standard deviations within parentheses. Structural parameters from dataset 2

Tl(1)–2Se(3)	3.322(3)	Average Tl–Se:	3.43
Tl(1)–2Se(1)	3.407(4)		
Tl(1)–2Se(1)	3.453(4)		
Tl(1)–2Se(2)	3.525(4)		
Tl(1)–2Cu(3)	3.581(5)		
Tl(1)–1Cu(1)	3.756(6)		
Cu(1)–2Se(1)	2.408(4)	Average Cu(1)–Se:	2.50
Cu(1)–1Se(3)	2.527(7)		
Cu(1)–1Se(2)	2.647(7)		
Cu(1)–2Cu(3)	2.683(5)		
Cu(1)–2Cu(2)	2.737(5)		
Cu(1)–1Tl(1)	3.756(6)		
Cu(1)–1Cu(4)	3.767(8)		
Cu(2)–2Se(2)	2.402(4)	Average Cu(2)–Se:	2.49
Cu(2)–1Se(1)	2.434(6)		
Cu(2)–1Se(3)	2.726(7)		
Cu(2)–2Cu(1)	2.737(5)		
Cu(2)–2Cu(4)	2.741(5)		
Cu(2)–1Cu(3)	3.721(8)		
Cu(3)–1Se(1)	2.326(7)	Average Cu(3)–Se:	2.52
Cu(3)–1Cu(4)	2.440(7)		
Cu(3)–1Se(2)	2.522(8)		
Cu(3)–2Se(3)	2.612(5)		
Cu(3)–2Cu(1)	2.683(5)		
Cu(3)–2Tl(1)	3.581(5)		
Cu(3)–1Cu(2)	3.721(8)		
Cu(4)–1Se(2)	2.375(7)	Average Cu(4)–Se:	2.53
Cu(4)–1Cu(3)	2.440(7)		
Cu(4)–2Se(3)	2.514(5)		
Cu(4)–1Cu(4)	2.605(13)		
Cu(4)–1Se(2)	2.713(8)		
Cu(4)–2Cu(2)	2.741(5)		
Cu(4)–1Cu(1)	3.767(8)		
Se(1)–Se(1)	3.763(8)		
Se(1)–Se(3)	3.773(6)		

On refining the individual temperature factors, the value for Cu(4) was found to come out considerably higher than for the other sites. One interpretation of this observation is that the thermal movement of copper is in fact anisotropic and cannot be refined properly on an isotropic model. Another, which we chose, is that the copper extraction may proceed still further than corresponding to the ideal stoichiometry. A support for that view was that the cell volume was found to vary somewhat, but significantly so. We therefore put all copper temperature factors equal and tried to refine the occupancies. Out of this treatment, a deficiency on Cu(4) was the only physically reasonable result, the deviation from ideal stoichiometry being statistically significant. The absolute values of the thermal parameters are probably in error owing to absorption effects. A rough estimation shows that values similar to those of $TlCu_5Se_3$ [8] are obtained when assuming the very realistic sample thickness of 30 μm.

The structure of o-$TlCu_4Se_3$ is depicted in Fig. 2 together with the parent phase, $TlCu_5Se_3$ [8], of which many features are retained. The main differences occur for the original eightfold sites of $TlCu_5Se_3$ where its Cu_2 8*i*-site corresponds to a division into two fourfold sites, while Cu_3 (8*i*) is transformed only to one fourfold position to account for the change in stoichiometry. (The former unsuccessful refinement differs only in the choice concerning what half of the original 8*i* copper atoms to be discarded when the 4_2 symmetry operation is removed.) The triangular coordination of selenium by copper found in $TlCu_5Se_3$ then disappears, and all copper is found in a tetrahedral environment in o-$TlCu_4Se_3$, although with some irregularities concerning the distances (Table 4). The change in coordination number seems to be connected to the stoichiometry, implying a borderline between the 4:3 and 3:2 Cu/Se ratios, copper clustering (in a Cu_4Se_4 conformation) occurring only for the higher ratios.

The interatomic distances are of the same order as found in other thallium selenocuprates [6,8,9,17], except for the distance between Cu(3)–Se(1) of 2.33 Å which is the shortest found so far. Since there is a very strong similarity with the mother compound, a comparison with $TlCu_5Se_3$ should be especially fruitful. One finds that, on average, the Cu–Se distances are shorter in o-$TlCu_4Se_3$. This could indicate stronger bonding. However, special care must be given to the fact that the effective radius of selenium is a function of its charge, i.e. dependent on the valence-band hole concentration. As has been argued previously – for instance when

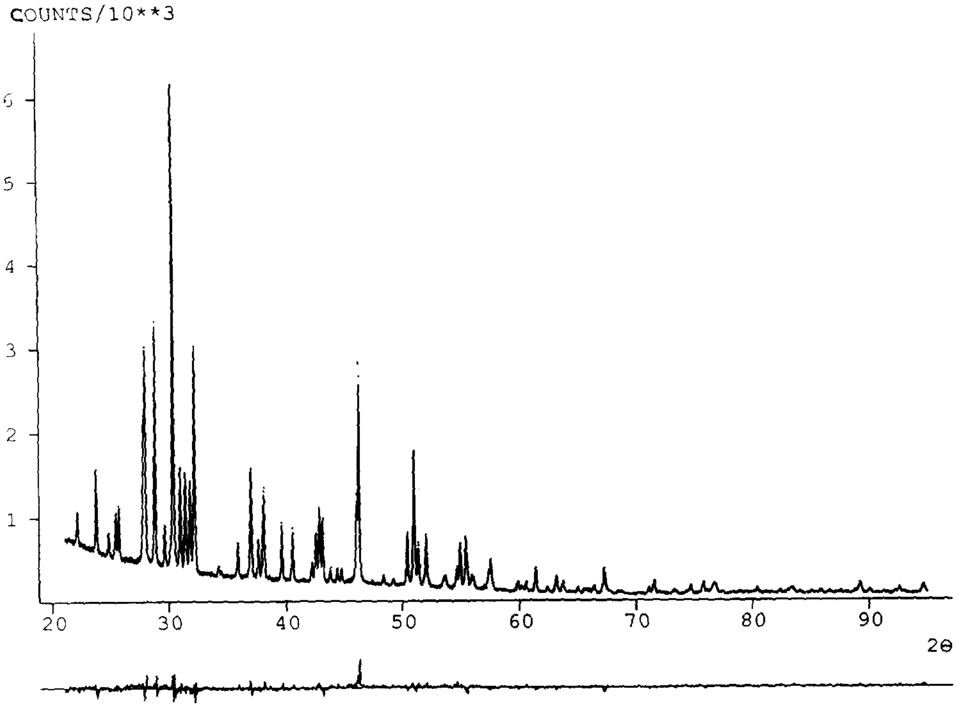

Fig. 1. The powder pattern of o-$TlCu_4Se_3$ given as observed (dots) and calculated (full line) values. The difference is given below the pattern on the same scale.

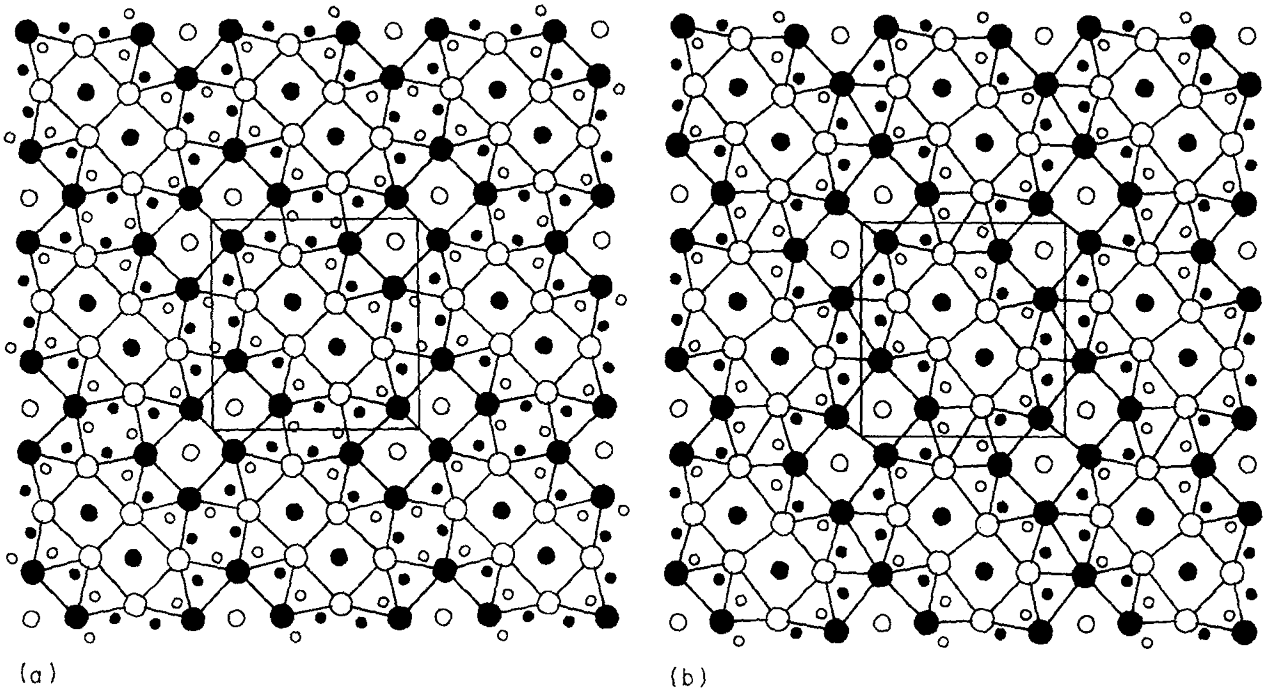

Fig. 2. The structures of $TlCu_5Se_3$ (left) and o-$TlCu_4Se_3$ (right) projected along the mirror plane normals. Large circles, selenium; medium circles, thallium; small circles, copper. Unfilled symbols denote $z=0$ and filled $z=1/2$.

discussing the crystal chemistry of this kind of phases [5] – and corroborated experimentally [2,18,19,20], copper occurs only in its monovalent state. Therefore, the stoichiometries $TlCu_4Se_3$ and $TlCu_2Se_2$ imply the presence of holes in the selenium band, i.e. holes in the valence band. In the analogous structural series $TlCu_{2n}S_{n+1}$, where members for $n=1,2,3$ are known, the a-axis (which directly probes the chalcogen–chalcogen intralayer distances) increases on increasing n which is a nice illustration of the effect of filling antibonding states at the valence-band top [21]. A similar effect was noted on doping $TlCu_2Se_2$

with iron or manganese (also with a decreasing hole concentration) [22].

As a by-product, the refinement on multiphase material (Data set 1) yielded the z(Se)-parameter of $TlCu_2Se_2$ as 0.3594(6). Previous estimations gave $z = 0.358$ [23], 0.36 [24] or 0.361 [19].

That valence-band holes are created on copper depletion from $TlCu_5Se_3$ may be supported from experimental evidence. Firstly, the temperature variation of the Seebeck coefficient of copper deficient (though not by extraction) $TlCu_5Se_3$ [8] is typical of a broad-band p-metal. Secondly, the electrical resistivity of o-$TlCu_4Se_3$ has a linear temperature dependence (at least in the range 200–300 K) as has t-$TlCu_4Se_3$ [25], into which form o-$TlCu_4Se_3$ completely transforms after heating to 670 K. The electrical properties of o-$TlCu_4Se_3$ are metallic, but the temperature dependence of the resistivity is more complicated than for the tetragonal form, probably an effect of its more one-dimensional character. Valence-band holes certainly occur in t-$TlCu_4Se_3$, as in the isostructural KCu_4S_3 [19]. Viola and Schöllhorn [26] performed reversible phase transformations by electrochemical methods for the couple KCu_5S_3/KCu_4S_3, showing that the filling of KCu_4S_3 with an extra copper atom (not yielding the $TlCu_5Se_3$ structure type, however) annihilates the holes initially present.

4. Conclusions

We have synthesised a new orthorhombic modification of $TlCu_4Se_3$ at room-temperature (295 K) by "chimie douce" from $TlCu_5Se_3$ and have been able to solve the structure by using DIRECT METHODS applied on powder diffraction data. There are strong analogies between parent and daughter structures, but the transformation is nevertheless probably of first order including nucleation. On extraction, the semiconducting properties of $TlCu_5Se_3$ change to metallic. In later work, we hope to shed further light on the transformation mechanism that begins with copper extraction in the mother phase ($TlCu_5Se_3$), experimentally by using neutron diffraction to better discern the copper occupancies, and theoretically by electronic structure calculations. This combination of experiment and theory was used successfully for elucidating details of the $TlCu_3S_2/TlCu_2S_2$ transformation mechanism [27].

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