# The Crystal Structure of TlCu$_5$Se$_3$

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The crystal structure of copper-deficient TlCu$_5$Se$_3$ has been refined from single-crystal X-ray diffraction data. The previously suggested new structure type was confirmed with agreement factors $R_F$ = 0.033 and $R_{wF}$ = 0.035. The symmetry is tetragonal, space group $P4_2/mnm$ (136). For the investigated composition, TlCu$_{4.8}$Se$_3$, the cell dimensions are $a$ = 12.900 and $c$ = 3.968 Å ($Z$ = 4). The structure has features common to other thallium copper chalcogenides such as TlCu$_3$Se$_2$ and TlCu$_7$Se$_4$. Similarities to some multinary alkali metal oxide structures are emphasized.   © 1990 Academic Press, Inc.

## Introduction

In the Tl–Cu–Se system, quite a few ternary phases have been synthesized, some possibly being metastable owing to special synthesis conditions (*1*). Most of the phases have isostructural counterparts in the Tl–Cu–S system, a fact which has been of help for their characterization. However, the te-

tragonal TlCu$_5$Se$_3$ seems to be the only representative of its type so far.

In a systematization study (*2*) of the various ternary copper chalcogenides the idea of "crystal chemistry conservation" led to structural hypotheses for a few of the phases previously (*1*) characterized only with regard to chemical composition and cell dimensions. Single-crystal X-ray diffraction on TlCu$_6$S$_4$ (*3*) and Tl$_5$Cu$_{14}$Se$_{10}$ (*4*) corroborated these views, and results are presented in this paper on TlCu$_5$Se$_3$, showing that the proposal was essentially correct in this case as well, although solely based

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on intuition coupled with structure systematics.

## Preparation and Structure Determination

$TlCu_5Se_3$ may be synthesized from appropriate amounts of TlSe, copper, and selenium by silica-tube synthesis at 670 K for some weeks (1). However, the single crystal used for the intensity data collection was found in a phase mixture also containing $Cu_7Se_4$ and $TlCu_4Se_3$. Previous research showed that the $TlCu_5Se_3$ phase is then slightly copper deficient with the length of the c-axis as a sensitive indicator hereof.

Details of the data collection and other experimental procedures in connection with the data reduction and computer calculations are gathered in Table I.

We already had a structure model based on chemical intuition (2). The outcome of a Patterson synthesis supported this view, except that the tentative space group as-

## TABLE I

DETAILS OF THE DATA COLLECTION AND
STRUCTURE REFINEMENT

| | |
|---|---|
| Diffractometer: | CAD 4 |
| Radiation: | MoKα |
| Monochromator: | Graphite |
| Data collection | |
| Scan mode: | ω |
| Angular range (Θ°): | 1–35 |
| Index limits: | $0 \leq h, k \leq 18$ |
| | $0 \leq l \leq 5$ |
| Total number of reflections: | 702 |
| Number of test reflections: | 3 |
| Structure refinement on F | |
| Number of reflections: | 330 ($I \geq 3\sigma_I$) |
| Limits reciprocal space (sin Θ/λ): | 0.1–0.74 |
| Number of parameters: | 35 |
| Extinction coefficient (g): | $2.61(5) \cdot 10^{-7}$ |
| Final indices of agreement: | $R_F = 0.033$ |
| | $R_{wF} = 0.035$ |

Note. Mass absorption coefficients and scattering factors, including dispersion effects, were taken from Ref. (8). Computer programs are found in Ref. (9).
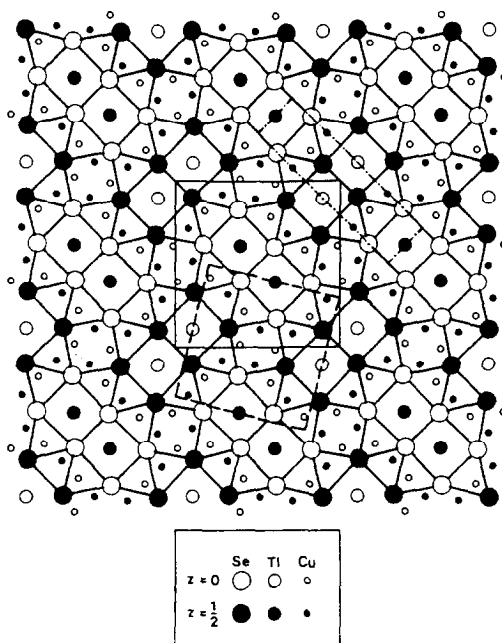


FIG. 1. The structure of $TlCu_5Se_3$ projected on (001). The tetragonal cell is indicated by solid lines. The cell encompassed by dashed lines contains the structure motif of $TlCu_7Se_4$ (although here without appropriately lower copper occupancies) while that bounded by dot–dashed lines illustrates the composition $TlCu_2Se_2$ almost as in the true tetragonal structure. The analogous relationships may be deduced between the structures of $RbLiZn_2O_3$, $RbLiZn_3O_4$, and $RbLiZnO_2$, as discussed in the text.

signment was changed from $P\bar{4}n2$ to the less liberal $P4_2/mnm$. In addition to the constraints, the origin is moved according to convention.

The structure model derived from the $TlCu_7Se_4$, as sketched in Fig. 1, supplied the starting parameters for a series of least-squares refinements. In the first step, 345 averaged observations were used for refining one scale factor, nine positional parameters, and six isotropic temperature factors. The $R_F$ value of 11.7% indicated that our model was sound but that probably absorption effects were important. Trials to correct for these with the Gaussian grid method were not particularly successful;

TABLE II

STRUCTURAL PARAMETERS OF $TlCu_{5-\delta}Se_3$ FROM THE LEAST-SQUARES REFINEMENT ASSUMING SPACE GROUP $P4_2/mnm$

| Atom | Site | Occupancy | $x$ | $y$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $B_{eq}/\text{Å}^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Tl | $4f$ | 1 | $0.10749_6$ | $x$ | $0.0298_3$ | $U_{11}$ | $0.0266_5$ | $-0.0024_5$ | $2.27_2$ |
| $Cu_1$ | $4g$ | $0.931_7$ | $0.8196_2$ | $1-x$ | $0.038_1$ | $U_{11}$ | $0.013_2$ | $0.008_2$ | $2.34_7$ |
| $Cu_2$ | $8i$ | $0.940_6$ | $0.2137_2$ | $0.4183_2$ | $0.013_1$ | $0.042_2$ | $0.034_2$ | $0.006_1$ | $2.34_7$ |
| $Cu_3$ | $8i$ | $0.973_5$ | $0.0159_2$ | $0.3935_2$ | $0.014_1$ | $0.027_1$ | $0.022_1$ | $0.002_1$ | $1.66_5$ |
| $Se_1$ | $4f$ | 1 | $0.3979_1$ | $x$ | $0.0111_5$ | $U_{11}$ | $0.018_1$ | $0.0009_9$ | $1.06_4$ |
| $Se_2$ | $8i$ | 1 | $0.6160_1$ | $0.1714_1$ | $0.0126_6$ | $0.0129_6$ | $0.0143_6$ | $0.0003_3$ | $1.08_3$ |

*Note.* Cell parameters: $a = 12.900(3)$ Å, $c = 3.968(2)$ Å (single-crystal diffractometer, 25 reflections), respectively; $a = 12.9034(4)$ Å, $c = 3.9776(2)$ Å (powder diffraction, 76 reflections (*1*)). All atoms are situated at $z = 0$. $U_{13} = U_{23} = 0$. $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$. The subscripts to the measured values are the estimated standard deviations to the last figure given.

a very high absorption coefficient ($\mu = 567$ cm$^{-1}$) and large crystal dimensions (roughly $0.36 \times 0.08 \times 0.03$ mm) made such attempts difficult. Instead we tried the DIFABS program with an approach recommended by Walker and Stuart (*9b*).

Refinement of the copper occupancies gave a minor reduction of $R_F$ (11.5%), but with an extinction parameter ($g$) included the $R$ value decreased to 8.0%. A test on the whole reflection material gave an $R$ value of 9.4% using these parameter values. Encouraged by this we applied the absorption correction procedure by DIFABS and arrived at $R_F = 5.9\%$ for 655 observations and 20 variables. After averaging the material, including only those where $I \geq 3\sigma_I$, 382 observations rendered $R_F = 5.8\%$. The $R$ value indicating the internal consistency of the averaging process was $R_I = 2.8\%$. At this stage we introduced anisotropic temperature factors and arrived at $R_F = 4.0\%$ for 35 variables. Finally, a modification of the weights was applied according to $w^{-1}(F^2) = \sigma^2(I) + (0.03F_0^2)^2$. With the (550) rejected on the basis of asymmetric background and the dataset cut at $I \geq 3\sigma_I$ the following $R$ values were obtained: $R_F = 0.033$ and $R_{wF} = 0.035$. An "observation of unit weight" had an estimated standard de-

viation of 1.12 which indicates that the weighting scheme is appropriate.

The structure is depicted in Fig. 1 and the structural parameters presented in Table II. The corresponding interatomic distances are given in Table III.

Interestingly, within statistical errors the same result for the positional parameters

TABLE III

INTERATOMIC DISTANCES IN $TlCu_{4.8}Se_3$ UP TO 3.95 Å

| | | | |
|---|---|---|---|
| $Se_1$– $Se_1$ | $3.727_2$ | $Cu_2$– $Se_1$ | $2.389_2$ |
| | | – $Cu_3$ | $2.571_3$ |
| $Se_2$– $Se_2$ | $3.877_3$ | – $Se_2$ | $2.610_3$ |
| | | $-2Se_2$ | $2.620_2$ |
| Tl–$4Se_1$ | $3.355_2$ | $-2Cu_1$ | $2.724_2$ |
| $-4Se_2$ | $3.475_1$ | $-2Cu_3$ | $2.728_2$ |
| $-2Cu_1$ | $3.831_1$ | – Tl | $3.900_2$ |
| $-2Cu_3$ | $3.874_2$ | | |
| $-4Cu_2$ | $3.900_2$ | $Cu_3$– $Se_2$ | $2.421_3$ |
| – Tl | $3.922_1$ | $-2Se_2$ | $2.511_2$ |
| | | – $Cu_2$ | $2.571_3$ |
| $Cu_1$–$2Se_1$ | $2.444_1$ | $-2Cu_2$ | $2.728_2$ |
| $-2Se_2$ | $2.629_3$ | – $Cu_3$ | $2.778_4$ |
| $-4Cu_2$ | $2.724_2$ | $-4Cu_3$ | $2.792_2$ |
| $-2Cu_3$ | $3.739_2$ | – $Cu_1$ | $3.739_3$ |
| $-2Tl$ | $3.831_1$ | – Tl | $3.874_2$ |

*Note.* The subscripts to the measured values denote the estimated standard deviations.

*and* the equivalent isotropic temperature factors was arrived at in a refinement including anisotropic thermal parameters on the averaged reflections *without* any absorption correction. The $U_{33}$ values are systematically higher and $U_{11}/U_{22}$, lower than in the correct refinement indicating that the crystal morphology (the crystal was longer along the *c*-axis) played some part. The outcome of $R_F = 0.035$ and $R_{wF} = 0.040$ (with the same weighting scheme) indicates that the data are insensitive to the size of the crystal with regard to its volume. The very strong absorption in this case may rather yield surface contributions so that equivalent reflections may attain reasonable values.

## Discussion of Crystal Chemistry and Properties

The structure comprises features that are common to many copper-rich ternary phases in the Tl–Cu–Se system, namely a roughly cubical coordination of selenium about thallium and either a tetrahedral or a triangular environment about copper. The latter situation occurs in a structural configuration where the copper atoms lie slightly off the faces of selenium tetrahedra, the copper atoms themselves therefore forming tetrahedral "clusters" (although without Cu–Cu bonds). In TlCu$_5$Se$_3$ these four atoms are equivalent, having $\bar{4}$ symmetry (Cu$_3$ in Table II). Corresponding clusters, in some cases of lower symmetry, occur in TlCu$_3$Se$_2$, Tl$_5$Cu$_{14}$Se$_{10}$, TlCu$_7$Se$_4$, and probably in *o*-TlCu$_4$Se$_3$ (2). Tetrahedrally coordinating copper is found in all these phases but also in TlCuSe, TlCuSe$_2$, TlCu$_2$Se$_2$, and *t*-TlCu$_4$Se$_3$. Here, two modifications of TlCu$_4$Se$_3$ are distinguished by a prefix denoting orthorhombic (*o*) or tetragonal (*t*) symmetry. The structure of *o*-TlCu$_4$Se$_3$ is still unknown but is most probably related closely to that of TlCu$_5$Se$_3$, from which this

phase is obtained on mild oxidation in ammoniacal medium (*1, 2*).

The TlSe$_8$ pseudo-cubes which run in single columns in TlCu$_7$Se$_4$ and Tl$_5$Cu$_{14}$Se$_{10}$ occur condensed to double columns in TlCu$_5$Se$_3$ and to whole sheets in TlCu$_2$Se$_2$ and *t*-TlCu$_4$Se$_3$. Condensed sheets arranged in a zigzag fashion may be recognized in Cs$_2$Cu$_5$Se$_4$ (*5*).

The interatomic distances (Table III) are similar to those found in other phases of the system. The shortest Se–Se distance of 3.73 Å hardly implies any bonding between these chalcogen atoms but is rather a geometrical effect. The TlSe$_8$ polyhedron is slightly less symmetrical (*mm* symmetry) than the pseudo-cube found in Tl$_5$Cu$_{14}$Se$_{10}$ (2/*m* symmetry) (*4*) with edges (Å units) 4.09 × 3.76 × 3.96. Taking the average between the parallel Se$_1$–Se$_1$ and Se$_2$–Se$_2$ one obtains, correspondingly, 4.08 × 3.80 × 3.97 for TlCu$_{4.8}$Se$_3$, and the volumes of the pseudo-cubes in TlCu$_{4.8}$Se$_3$ and Tl$_5$Cu$_{14}$Se$_{10}$ differ by only 1%. Comparison with TlCu$_2$Se$_2$ and *t*-TlCu$_4$Se$_3$, which have TlSe$_8$ pseudo-cubes with 4/*m* symmetry, is less valid, since there the Se–Se distances in the tetragonal {001} planes are reduced owing to interactive attraction by valence-band holes (*6*).

The average Tl–Se distance of 3.42 Å is very similar to that found in Tl$_5$Cu$_{14}$Se$_{10}$ for the pseudo-cubic configuration (3.41 Å) and must be taken as "normal" for CN = 8 of monovalent thallium toward divalent selenium.

In Tl$_5$Cu$_{14}$Se$_{10}$ short Cu–Cu distances occur between atoms with different coordination number (2.53 and 2.54 Å). The Cu$_2$–Cu$_3$ distance of 2.57 Å occurs in a similar configuration in TlCu$_{4.8}$Se$_3$. The other Cu–Cu distances are all at least 2.7 Å, including those within the tetrahedral "clusters." As in the other copper-rich thallium selenides, copper occurs in layers, where each copper has four like neighbors. Only when such

layers cross, a higher coordination number may be achieved. Within the layers the copper atoms form a more or less perfect quadratic lattice. Taking the chalcogen atoms into consideration, this situation is reminiscent of the ordering in the fluorite-type structure.

Although copper occurs with two coordination numbers it must be considered monovalent. The bonding is certainly far from ionic, but formal charges are still applicable, leading to $Tl^+Cu_5^+Se_3^{-2}$ suggestive of semiconducting properties. However, a slight copper deficiency (without any change in copper valence) may inject holes in the valence band. From thermoelectric measurements on a more stoichiometric sample of TlCu₅Se₃, as judged from the cell parameters (1), a positive Seebeck coefficient ($\alpha$) was obtained, indicating positive charge carriers. Its temperature ($T$) dependence is reminiscent of metallic behavior in the sense that, above 80 K, the slope of $\alpha$ vs $T$ is constant (Fig. 2). The Fermi energy calculated from this slope—260 · $10^{-9}$ $VK^{-2}$—is of the correct order expected for an essentially broad band (Se 4p) rather than for a $d$-band (for copper mixed-valence) and is quite compatible with the

results obtained for the nearly semiconducting solid–solutions in the system TlCu₂Se₂–TlFe₂Se₂ (7) with a low concentration of valence-band holes.

While preparing this manuscript we came across a recent article on $RbLiZn_2O_3$ (10), also crystallizing in $P4_2/mnm$. This oxide structure shows such large similarities to that of TlCu₅Se₃ that we can identify Tl ~ Rb (4f), Se ~ O (4f, 8i), and Cu ~ Li (4g). Owing to the difference in charge, the two Cu 8i positions only have one counterpart for Zn in the oxide, namely the tetrahedral position. Two kinds of atoms (Li, Zn) in the oxide make up for a charge of +5 that is distributed evenly over the copper sites in the selenide. Remembering that the TlCu₅Se₃ structure may be formally derived from that of TlCu₇Se₄ (synthetic crookesite) (2) we consulted the literature to see if there was any corresponding quaternary oxide where a charge of +7 is distributed over two kinds of atoms in a corresponding manner. Indeed, Hoppe et al. (11) had prepared and described $RbLiZn_3O_4$, where again site correspondence is available except for the filling of the chalcogen tetrahedra with a small cation in the $\bar{4}$ eight-fold position. $RbLiZn_3O_4$ is described on the space group $I4/m$, while the ternary structure type, that of NH₄Cu₇S₄, was determined within an $I\bar{4}$ framework (12). However, preliminary intensity calculations on TlCu₇Se₄ (13) and TlCu₇S₄ (14) showed good agreement with observations also when all atoms are situated in two layers separated by $\frac{1}{2}c$, in fact a description according to $I4/m$.

In analogy with the vector relations between the cell parameters of TlCu₅Se₃ and TlCu₇Se₄ on the basis of their structures (2) (Fig. 1), one may deduce the $a$-axis of RbLiZn₃O₄ from the parameters of RbLiZn₂O₃. The shortest distance between Rb atoms of different double columns in RbLiZn₂O₃ is 8.40 Å which should correspond to the length of the $a$-axis of
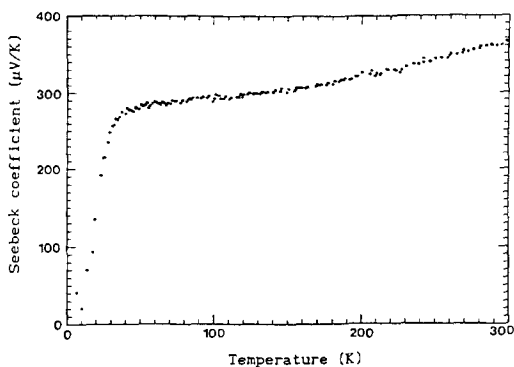


FIG. 2. The Seebeck effect as measured on a powder compact of virtually stoichiometric TlCu₅Se₃.

$RbLiZn_3O_4$. The actual value is 8.24 Å, a 2% difference only.

A slab with pseudo-tetragonal symmetry may be cut out of the $RbLiZn_2O_3$ and $TlCu_5Se_3$ structures with $a[110]$ as the $c$-axis and the chalcogen pseudo-cube edge as the $a$-axis. Such a slab (illustrated in Fig. 1) has the composition $AB_2C_2$. By applying tetragonal symmetry elements to it, this slab becomes a unit-cell of the $ThCr_2Si_2$ type, although with a shift of origin. This is an interesting fact since this type (or rather the $BaZn_2P_2$ subtype according to a suggested classification (15)) occurs for both $TlCu_2Se_2$ (16) and $RbLiZnO_2$ (10). If further analogy were valid, one should also expect $RbLi_3ZnO_3$ (if it exists with the small cations randomly over the available sites) to crystallize in the $KCu_4S_3$ type as does $TlCu_4Se_3$ (17).

The main difference between the oxide and selenide structures discussed here lies in the filling of tetrahedral chalcogen holes with tetrahedral clusters of small atoms. The same relationship between two structure types is known from alloy chemistry where the $Nb_5Cu_4Si_4$ type (18) is a "stuffed" variant of the $Ti_5Te_4$ type (19).

## Acknowledgments

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