SYNTHESIS AND CHARACTERIZATION OF THE LAYERED METAL TlCu$_2$S$_2$

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Summary

The compound TlCu$_2$S$_2$ was synthesized at room temperature by chemical treatment of TlCu$_3$S$_2$ made at 670 K. It is tetragonal with cell parameters a = 3.7771(1) Å and c = 13.3791(9) Å; it is metastable and decomposes on heating at 390(5) K into a three-phase mixture of TlCuS, TlCuS$_2$ and TlCu$_4$S$_3$. According to electrical transport measurements (resistivity, Seebeck and Hall effects) it is metallic owing to the presence of one valence-band hole per formula unit. The Fermi energy of 2.1(1) $\times$ 10^{-19} J and the hole effective mass of 1.3m_0 are similar to the data previously obtained for isostructural TlCu$_2$Se$_2$.

1. Introduction

A comparison between the Tl–Cu–Se and Tl–Cu–S systems indicates that many isostructural phases occur, such as TlCuX$_2$ [1], TlCuX [2, 3], TlCu$_3$X$_2$ [4, 5], TlCu$_4$X$_3$ [6] and TlCu$_7$X$_4$ [5, 7] (X $\equiv$ S, Se). Counterparts to TlCu$_2$Se$_2$ [8], TlCu$_5$Se$_3$ [5] and TlCu$_6$S$_4$ [9] have not been found although a mineral TlCu$_6$Se$_4$ has been claimed [10]. However, this phase lacks a proper characterization and may in fact be TlCu$_4$Se$_3$ [9].

Since the quaternary TlCu$_{1.5}$Fe$_{0.5}$X$_2$ compounds exist as the minerals thalcusite (X $\equiv$ S) [11] and bukovite (X $\equiv$ Se) [12] and full solid solubility has been established in the system TlCu$_{1.5}$Fe$_{0.5}$Se$_2$–TlCu$_2$Se$_2$ [13], it seems very likely that the terminal phase TlCu$_2$S$_2$ may exist. However, previous attempts to prepare this compound from the elements or from simple binary compounds have failed [2, 6, 14]. At 670 K a three-phase mixture (TlCuS, TlCuS$_2$ and TlCu$_4$S$_3$) is obtained at this composition. In order to succeed, the synthesis must be performed in another manner.

Experience from the Tl–Cu–Se system suggests an alternative route of synthesis [5]. Several ternary selenides are affected by an aerated ammonia solution so that copper is leached out. In this manner the homogeneity ranges of TlCu$_7$Se$_4$ and TlCu$_5$Se$_3$ have been established and new phases have been created. On treating TlCu$_3$Se$_2$ with ammonia, TlCu$_2$Se$_2$ is obtained.

Therefore, a natural step is to treat isostructural $TlCu_3S_2$ in a similar manner. This paper describes the successful synthesis of $TlCu_2S_2$ and provides data on measurements of various physical properties.

It has been shown that $TlCu_2Se_2$ is metallic owing to the presence of a valence-band (VB) hole — one electron per formula unit [15]. It is thus anticipated that a similar situation may occur in the isostructural sulphide.

2. Experimental details

2.1. Synthesis

The synthesis of $TlCu_2S_2$ was carried out in three steps. Thallium was etched by sulphuric acid and was then melted under vacuum in a Pyrex glass tube so that the melt could be transferred (by tilting the tube) to the reaction compartment leaving the oxide dross behind on the glass wall. The appropriate amount of sulphur was added to give Tl_4S_3; this synthesis was performed at 470 K after evacuation and sealing. The first product was single-phase β-Tl_4S_3 according to its diffraction pattern [16]. In the next step, copper powder and sulphur were added to give $TlCu_3S_2$ which was synthesized at 670 K. In the final stage, single-phase $TlCu_3S_2$ powder was immersed in concentrated ammonia with 30% hydrogen peroxide added dropwise.

2.2. X-ray diffraction

The end product and the intermediate reaction products were all investigated using a Guinier–Hägg focusing camera. A Guinier–Simon camera was used for checking the thermal stability. Further details are reported in ref. 15.

2.3. Electrical transport measurements

The equipment used for measuring the Hall effect and the thermovoltage has been described previously [13, 15]. However, some alterations were made for the Hall effect measurements. The Hall voltage was detected by a lock-in amplifier from an 83 Hz a.c. source and a d.c. magnetic field. The signal was sampled while the field modulus was raised from zero in discrete steps in the range −3 T to +3 T. Any zero-point drift was compensated for by changing the field polarity.

The Hall coefficient R was calculated from the slope of the Hall voltage V_{xy} vs. internal induction B_z plot. Since the Hall voltage was very small (approximately 10^{-7} V), R was calculated as an average from a number of isothermal field scans. The formulae used were $\bar{R} = \Sigma_i^n w_i R_i / \Sigma_i^n w_i$ and $s(\bar{R}) = 1/(\Sigma w_i)^{1/2}$ with $w_i = 1/s_i^2$ (the s_i values were calculated from the least-squares refinement of the V_{xy} vs. B_z slope for each scan (containing at least six V_{xy}–B_z data pairs)). Ten to twenty terms (n) were needed in the sums, giving relative standard deviations of about 2%. Scans with $s_i/R_i > 15\%$ (owing to spurious signals) were discarded.

The resistivity was measured in a similar cryostat as used for the Seebeck coefficient measurements. An 83 Hz a.c. source was used in a four-point method; the voltage drop was detected by a lock-in amplifier. Data were automatically collected in a microprocessor monitored scan from 4 K up to 425 K with at least two readings per temperature.

3. Results

3.1. Chemical characterization

While treatment of $TlCu_3Se_2$ with ammonia solution yielded $TlCu_2Se_2$ as end product owing to oxidation by air [5], the same procedure applied to $TlCu_3S_2$ only results in a slight copper deficiency as indicated by the change in unit cell volume found by X-ray diffraction. Addition of H_2O_2 seems necessary for obtaining a new phase. The diffraction pattern of the end product can be indexed on a body-centred tetragonal cell with parameters similar to those of $TlCu_2Se_2$. Chemical analysis of the copper content in the ammonia solution by atomic absorption spectrometry indicates that one copper per formula unit of $TlCu_3S_2$ has been extracted [17]. Moreover, calculation of the powder intensities (LAZY PULVERIX [18]) using the positional parameters of $TlCu_2Se_2$ [8, 14] proves the isostructurality. Powder X-ray diffraction data of $TlCu_2S_2$ and the intermediate products are presented in Table 1 and the structure ($ThCr_2Si_2$-type) is depicted in Fig. 1.

According to X-ray diffraction at elevated temperatures, $TlCu_2S_2$ decomposes irreversibly at about 390 K into a three-phase mixture of $TlCuS$, $TlCuS_2$ and $TlCu_4S_3$, the same phases as obtained by direct synthesis at high temperature. This indicates that $TlCu_2S_2$ is a metastable phase of the Tl–Cu–S system.

3.2. Physical property measurements

As seen from Fig. 2, the resistivity varies linearly with temperature up to 390 K where a jump occurs. This correlates well with the high-temperature diffraction data, indicative of the decomposition of $TlCu_2S_2$. Unfortunately, no values could be taken above 405 K because of overload and broken contacts owing to strain in the compact as a result of the phase change. A separate run on the three-phase product obtained showed overall metallic conductivity owing to $TlCu_4S_3$, with an increase in resistivity by a factor of 5–10.

Evidence for metallic $TlCu_2S_2$ is also obtained from the results of the measurements of the Seebeck (Fig. 3) and Hall (Fig. 4) coefficients. Both effects show the presence of p-type carriers. The magnitude of the Seebeck coefficient indicates rather light carriers. Using broad-band formalism, as carried out for isostructural $TlCu_2Se_2$ [15], a similar value of the Fermi energy is obtained from the thermoelectrical data above 80 K (E_F = 2.1(1) $\times$ 10^{-19} J) and at an effective mass $m^* = 1.3\ m_0$.

The Hall coefficient is constant above 80 K (4.87(4) $\times 10^{-10}$ m^3 C^{-1}). This value can be translated into p = 1.28(1) $\times 10^{28}$ m^{-3} in single-carrier

TABLE 1

X-ray diffraction data of $TlCu_2S_2$ (ThCr$_2$Si$_2$ type; space group, $I4/mmm$)

h k l	Intensity		$Q \times 10^5$ (Å^{-2})	
	Obs.	Calc.	Obs.	Calc.
0 0 2	4	6	2236	2235
1 0 1	63	61	7573	7568
0 0 4	22	37	8940	8939
1 0 3	74	100	12029	12037
1 1 0	19	11	14012	14019
1 1 2	91	97	16259	16253
0 0 6	2	2	20114	20112
1 0 5	25	33	20977	20976
1 1 4	—	<1	22975	22957
2 0 0	60	34	28036	28037
2 0 2	2	2	30262	30271
1 1 6 ⎫	38	43	34133	34130
1 0 7 ⎭		6	34373	34384
2 1 1 ⎫	30	16	35615	35605
0 0 8 ⎭		11	35745	35754
2 0 4	25	21	36972	36976
2 1 3	44	35	40078	40075
2 0 6	3	3	48152	48149
2 1 5	19	20	49011	49013
1 1 8	4	4	49772	49773
1 0 9	9	8	52261	52261
0 0 10	—	<1	—	55866
2 2 0	25	12	56071	56074
2 2 2	1	1	58269	58309
2 1 7	5	6	62406	62421
3 0 1 ⎫	24	4	o	63642
2 0 8 ⎭		19	63776	63791
2 2 4	11	10	65016	65013
3 0 3	12	10	68115	68112
1 1 10 ⎫	11	10	69883	69885
3 1 0 ⎭		4	70082	70093
3 1 2	33	25	72320	72328
1 0 11	7	9	74605	74607
2 2 6	2	2	76186	76186
3 0 5	7	7	77059	77050
3 1 4	—	1	—	79032
2 1 9 ⎫	10	12	80308	80298
0 0 12 ⎭		3	o	80447
2 0 10	—	<1	—	83903

The intensities were recorded with a microdensitometer and were calculated on the basis of a sulphur z parameter of 0.36. The observed Q values were transformed from Guinier–Hägg film line readings and the calculated values were obtained from a weighted least-squares refinement of the cell parameters, yielding $a = 3.7771(1)$ Å and $c = 13.3791(9)$ Å. The cell parameters of the intermediate synthesis products were: β-Tl_4S_3, $a = 7.7373(4)$ Å, $b = 13.0120(7)$ Å, $c = 7.9500(3)$ Å and $\beta = 103.502(4)°$; $TlCu_3S_2$, $a = 14.6088(9)$ Å, $b = 3.8623(2)$ Å, $c = 8.2921(5)$ Å and $\beta = 111.683(5)°$.
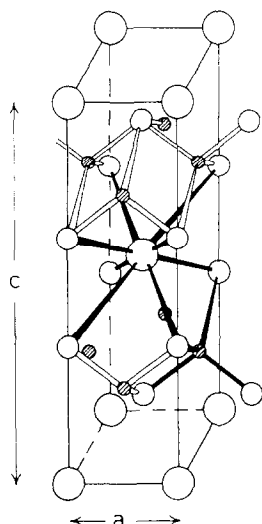
Fig. 1. The structure of TlCu₂S₂. The sulphur coordinations of thallium and copper are especially emphasized: Tl, ○; S, ○; Cu, ⊘.
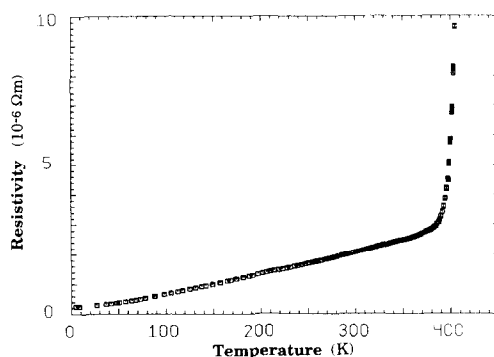
Fig. 2. The temperature dependence of the resistivity of a powder compact of TlCu₂S₂ heated to 425 K. Decomposition at 390 K is accompanied by a steep resistivity increase (beyond the range of measurement used).
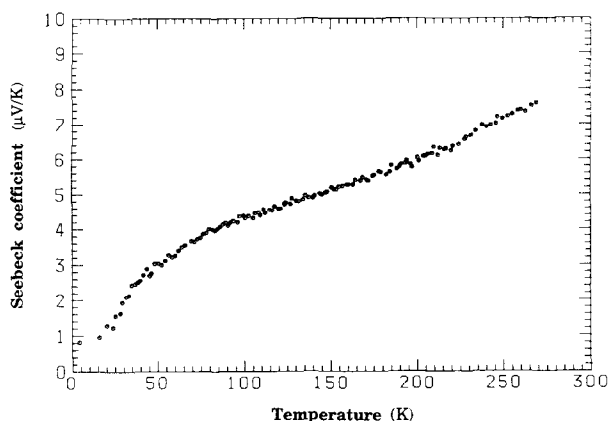

Fig. 3. The temperature dependence of the Seebeck coefficient.

formalism or, taking the unit-cell volume into account, 1.2 holes per formula unit (f.u.). The deviation from the expected 1 hole (f.u.)$^{-1}$ is not too serious, considering the systematic errors which may occur. Firstly, the sample was in the form of a cold-pressed powder compact with a density of less than the theoretical. Moreover, since the material was obtained by chemical decomposition in the solid state at room temperature, it most probably had a high dislocation density (also affecting the residual resistivity) and contained traces of other phases. Lastly, the formula relating the Hall coefficient to the carrier density is not necessarily strictly valid.
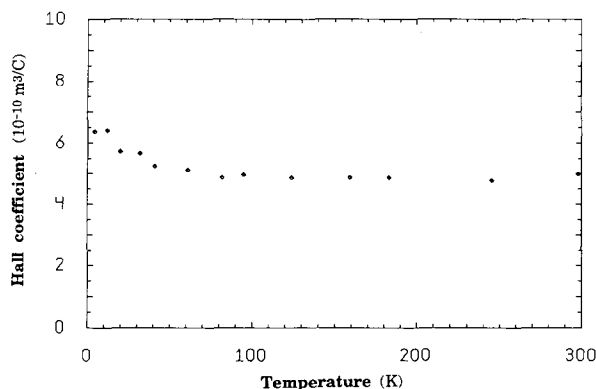
Fig. 4. The temperature dependence of the Hall coefficient. The sizes of the symbols are of the same order as the standard deviations.

The relative change (statistically significant) in the Hall coefficient at temperatures below 80 K is indicative of an effective decrease in hole concentration. This interpretation is supported to some extent by the temperature dependence of the Seebeck coefficient on lowering the temperature. Partial hole condensation may thus occur. However, no definite conclusions can be drawn from these data.

4. Discussion and conclusions

$TlCu_2S_2$ was studied in the metastable state. Its crystal structure (Fig. 1) has a definite two-dimensional character with sulphur layers interleaved by layers of alternating thallium or copper. There is only one crystallographic site per type of atom and a mixed valence is unlikely. As argued previously from investigations of isostructural $TlCu_2Se_2$ [15] and its solid solution with iron [13], both thallium and copper are monovalent, which is also indicated by their coordination numbers. Preliminary X-ray photoelectron spectroscopy (XPS) measurements [19] support this idea. The copper core 3p spectra show no satellite peaks [20] typical of divalency. Altogether this adds up to a charge formalism with a lowered valency of sulphur, $Tl^+Cu_2^+S_2^{3/2-}$, as suggested for the selenide [15]. Since the S–S distances are greater (3.78 Å, 3.97 Å, 3.75 Å, calculated from $z = 0.36$) than the diameter of sulphur, this electron deficit, compared with the usual $3p^6$ configuration, is delocalized and manifests itself as one valence-band (VB) hole per formula unit as indicated by the transport measurements and confirmed by the valence spectrum obtained using XPS [19].

Since the top of the VB carries a large S 3p character and therefore contains antibonding S–S states, the presence of VB holes induces an attraction between the sulphur atoms, effective within each layer, and leads to a distortion of the CuS_4 tetrahedra. This phenomenon was investigated and discussed in more detail in the study of the system $TlCu_{2-x}Fe_xSe_2$, where iron substitution reduces the VB hole concentration giving an increase in the

a parameter (filling of antibonding selenium states) and a decrease in *c* (more regular tetrahedra) [13].

The existence of VB holes thus leads to a smaller cell volume than otherwise expected. This is further verified by comparing the densities of the compounds on the tie-line $TlS-Cu_2S$ [21]. For the ternary compounds, which according to the formulae are all likely to contain VB holes, the densities all lie above a line through the values for the binary end members; the deviation is the largest for $TlCu_2S_2$, the compound with the largest VB hole concentration. The *a* axes of the tetragonal cells of the ternary compounds $TlCu_2S_2$, $TlCu_4S_3$ and $TlCu_6S_4$ all reflect the intralayer S–S distance; these distances are 3.78 Å (1 hole/2S), 3.91 Å (1 hole/3S) and 3.95 Å (1 hole/4S) respectively. According to the same trend, the next member of the same structural series would have an *a* parameter of 3.97 Å if it existed.

Acknowledgments

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Note added in proof

According to Xia and Stroud [22], a polycrystalline sample of a quasi-two-dimensional metal would yield a reduction in the measured Hall coefficient $R_H = \frac{4}{5} R_H^\circ$, where R_H° is the theoretical value from the single-carrier formalism. This model seems valid in the present case and explains very well the observed deviation from the expected value.

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