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Characterization of $TlCu_7S_4$, a Crookesite Analogue

Short Communication

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Previous claims of a compound $TlCu_9S_5$ are rejected. The true composition is $TlCu_7S_4$, the compound being isostructural with $NH_4Cu_7S_4$ and $TlCu_7Se_4$ (crookesite). The body-centred tetragonal cell (a = 10.1797 Å and c = 3.8585 Å) contains two formula units.

(Keywords: Thallium copper sulphide; Crystal structure)

Beschreibung von $TlCu_7S_4$, *einer dem Crookesit analogen Verbindung*
(Kurze Mitteilung)

Frühere Feststellungen, daß im pseudobinären System Tl_2S—Cu_2S eine Verbindung $TlCu_9S_5$ existiert, erwiesen sich als unzutreffend. Die korrekte Formel muß $TlCu_7S_4$ lauten. $TlCu_7S_4$ besitzt eine raumzentrierte tetragonale Elementarzelle (a = 10.1797 Å, c = 3.8585 Å; Z = 2) und ist isostrukturell mit $NH_4Cu_7S_4$ und $TlCu_7Se_4$ (Crookesit).

The system Tl—Cu—S has been investigated both from the point of view of crystallographically characterizing the phases and of finding their relationships. A phase diagram of the section Tl_2S—Cu_2S was proposed by *Mamedov* et al. [1] based on DTA, room-temperature magnetic susceptibilities and X-ray powder diffraction. Two intermediate phases were proposed, $Tl_2Cu_8S_5$ and TlCuS, both melting congruently. These phases were not properly characterized, and the published line diffraction patterns are at variance with the phase diagram.

A revision of the pseudo-binary phase diagram was proposed by *Abishov* et al. [2]. These workers confirmed that TlCuS melts congruently (689 K) but found two incongruently melting phases, $TlCu_3S_2$ (693 K) and $TlCu_9S_5$ (706 K).

A new attempt to clarify the situation along Tl_2S—Cu_2S tie-line was presented by *Sobott* [3]. His results, based on DTA and X-ray diffraction, agree in principle with those of *Abishov* et al. [2] but differ with respect to the incongruent melting temperatures of $TlCu_3S_2$ (683 K) and $TlCu_9S_5$ (734 K).

Further data on the ternary system were furnished by *Babanly* et al. [4–6], who also verified the phases TlCuS, $TlCu_3S_2$ and $TlCu_9S_5$. Unit-cell data were previously presented for TlCuS [7] and $TlCu_3S_2$ [8].

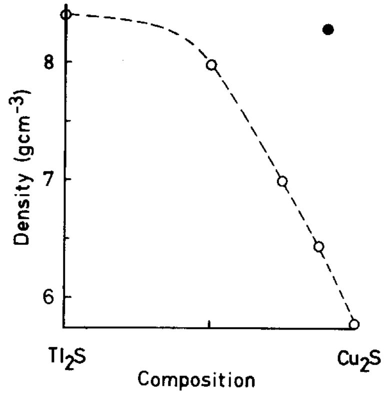

Fig. 1. The X-ray density as a function of the molar ratio along the Tl_2S—Cu_2S tie-line. The curve is a guide to the eye. The filled circle corresponds with the erroneously given cubic cell of $TlCu_9S_5$ in Ref. [3]

However, *Sobott* [3], when interpreting his powder patterns, insufficiently considered the crystallographic data already available. Two of his published line diagrams are explained by the cells provided previously for TlCuS [7] and $TlCu_3S_2$ [8]. His third pattern, rather similar to that presented by *Mamedov* et al. [1] for $Tl_2Cu_8S_5$, was attributed to a cubic cell (a = 7.207 Å) containing two formula units of $TlCu_9S_5$. The theoretical density for this composition and cell choice (8.30 g/cm^3) is much greater than expected considering the other phases along this tie-line, as illustrated in Fig. 1. Consequently, this cell or this composition had to be erroneous.

A key to the solution of this problem was found when the Tl—Cu—S and Tl—Cu—Se systems [9] were compared. Isostructural phases exist, such as (X = S, Se) $TlCuX$, $TlCuX_2$, $TlCu_3X_2$ and $TlCu_4X_3$. The tie-line Tl_2Se—Cu_2Se contains TlCuSe, $TlCu_3Se_2$, $TlCu_5Se_3$ and $TlCu_7Se_4$. The latter is tetragonal, but the axial ratio of the unit cell is such ($a/c \approx \sqrt{7}$) that many lines overlap, giving the pattern a cubic appearance,

Table 1. *Crystallographic data of* $TlCu_7S_4$. The least-squares refined cell parameters are a = 10.1797 (2) Å, c = 3.8585 (1) Å. The reflexions are presented as $Q = d^{-2}$ Å^{-2}. For the very weakest reflexions and those situated close to strong ones no accurate values could be determined. The indices *hkl* include non-equivalent *khl*-reflexions, and only their summed intensities could be measured. The individual intensity data were calculated with the Lazy Pulverix program using the positional parameters of $NH_4Cu_7S_4$

hkl	I(Obs)	I(Calc)	Q(Obs)	Q(Calc)	hkl	I(Obs)	I(Calc)	Q(Obs)	Q(Calc)
			x 10^5	($Å^{-2}$)				x 10^5	($Å^{-2}$)
110	1	1	1928	1930	631	21	17	50149	50143
200	17	13	3861	3860	640		3		50180
101	60	35	7680	7682	512	3	5	51958	51960
220		25	7716	7720	701	2	3	54006	54003
310	69	71	9649	9650	730	1	1		55970
211	60	49	11545	11542	442	0	0		57750
301	100	89	15404	15402	721	1	2		57863
400		29		15440	532	22	21	59679	59680
330	33	24	17365	17370	103	2	3		61421
321	58	57	19263	19262	602	3	4	61657	61610
420		2		19300	800	4	2		61760
411	34	29	23117	23122	213	6	6	65278	65281
510	5	4	25089	25090	622		13		65470
002	32	22	26862	26869	651	26	13	65576	65583
112	4	6	28818	28799	820		12		65620
202		9		30729	303	8	9	69144	69141
501	62	25	30841	30843	811	10	8	69454	69443
431		26			741		5		
440		0		30880	660		3		69481
530	31	34	32807	32810	750	4	5	71412	71411
222		2		34589	323	8	12	73004	73001
521	23	20	34708	34703	712	4	2	75130	75120
600		3		34740	552		4		
312	27	23	36516	36519	413	-	0		76861
620	15	12	38601	38600	642		5		77050
402	33	8	42327	42309	831	19	15	77165	77163
611		18	42422	42423	840		3		77201
332	18	16	44240	44239	910	1	1	79105	79131
422	6	4	46179	46169	732	1	1	82832	82840
541	7	5	46277	46283	503	11	10	84554	84581
710	5	4	48240	48250	433		4		
550		1			901	6	8	84899	84883

the more so for the mineral analogue crookesite [10] than for the stoichiometric synthetic product. The mineral has previously [11] even been given the composition $TlCu_9Se_5$ analogously to the sulphide. Thus, the same tetragonal model might be applicable.

Syntheses of the compositions "$TlCu_7S_4$" and "$TlCu_9S_5$" were performed (620 K, 7 w.) followed by a renewed anneal (670 K, 4 w.). A film technique (*Guinier-Hägg*) was now utilized instead of the powder diffractometry of the original work that presented "$TlCu_9S_5$" [3]. It was confirmed that at that composition two phases are present, since very weak extra lines were detected on the powder film. These, belonging to Cu_2S (djurleite), were hardly discernible from the background noise on a diffractometer recording from the same sample. Moreover, the main pattern was accurately indexed on a tetragonal cell similar to that of $TlCu_7Se_4$. At "$TlCu_7S_4$", the same pattern was found together with very weak lines of the neighbouring phases $TlCu_3S_2$ and Cu_2S.

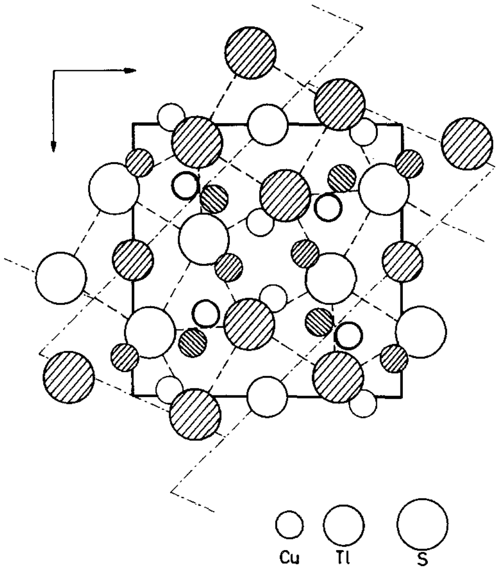

Fig. 2. The crystal structure of $TlCu_7S_4$ projected onto (001). Unfilled circles denote atoms at $z = 1/4$ and hatched ones atoms at $z = 3/4$ (ideally). Deviations from this occur for one of the copper sites (slightly different notation in the figure for the copper site where the occupancy is only 75% even for strict stoichiometry). In addition to the markings of the tetragonal cell (————) and the coordination polyhedra (– – – – –), the motif of the monoclinic cell of $TlCu_3S_2$ has been accentuated (– · – · – · –)

While microprobe analyses on single crystals of $TlCu_7Se_4$ and crookesite [9, 10] yielded very good results, the analysis data on the corresponding almost single-phase sulphide were less satisfactory. The reproducibility was very low and the values were unreasonable. One plausible explanation is that the phases are heavily intergrown in the from of lamellae with a separation smaller than the area probed by the electron beam [12]. Even if a single-phase area may be found at the sample surface, other phases interfere underneath.

The powder data are given in Table 1. Indications of a slight homogeneity range were found; the cell of a sample heated at 620 K is slightly smaller than that from the 670 K anneal. The effect is more pronounced for the *c*-axis which may be due to less copper, as found in the selenide [9, 10]. The density based on the new data is 6.46 g/cm^3, now quite in line with expectations (Fig. 1). Moreover, the identity is established by intensity calculations based on the positional parameters of the isostructural $NH_4Cu_7S_4$ [13]. A conventional *R*-value of 13% was obtained, calculated on the summed powder intensities.

The structure is given in Fig. 2. Tl^+ (r = 1.47 Å) replaces NH_4^+ in a tetragonal pseudo-cubic prism of sulphur atoms. The interatomic distances Tl—S are about 3.4 Å. This regular arrangement and high coordination number is rather different from the situation found in the binary thallium sulphides [14]. However, a similar "cubic" coordination occurs in other ternary thallium copper chalcogenides, such as $TlCu_2Se_2$ [15] and $TlCu_4S_3$ [16]. $TlCu_2S_2$ has not been prepared, but phases of composition $TlFe_xS_2$ ($1.3 < x < 1.8$) exist of the same structure type or with vacancy ordered superstructures [17, 18]. The Tl—S distances are 3.34 Å and 3.38 Å (distorted polyhedron) in $TlFe_{1.5}S_2$ [18] and 3.35 in $TlCu_4S_3$ [16]. The coordination number of eight for thallium proves it to be monovalent rather than trivalent. For the latter situation, a tetrahedral coordination, as it occurs for one of the thallium sites in Tl_4S_3 [19], would be expected. As in many other sulphides, copper coordinates either four (tetrahedron) or three (triangle, distorted tetrahedron), but is monovalent in both arrangements [20].

In the original determination [13], the copper atoms of the tetrahedral holes deviate from the ideal position of $z = 1/4$. This site is filled only to 75% to give the appropriate stoichiometry.

If the structure is idealized with atoms only at $z = 1/4 \pm 1/2$, one may discern similarities with other structures. For instance, the linking of the thallium-centred chalcogen cubes by help of tetrahedrally coordinated copper atoms is the same in $TlCu_2Se_2$ [15]. Areas with the same crystal chemistry as in $TlCu_3S_2$ [8] may also be found. The motif is accentuated in Fig. 2 in the form of $TlCu_3S_2$ "unit cells". However, the monoclinic *b*-axis has been reversed.

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