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A reinterpretation of the $NH_4Cu_7S_4$ structure

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Abstract

The structure of $NH_4Cu_{7-x}S_4$ has been investigated using X-ray single crystal diffraction at varying temperatures. The room temperature structure is best described as a tetragonal crystalline framework with channels incorporating some of the copper atoms in a disordered, almost amorphous, manner. The crystallographic description based primarily on the framework renders the space group $I4/m$ and a unit cell with $a=10.2695(5)$ Å and $c=3.8094(3)$ Å. Upon cooling below 270 K, the copper atoms in the channels start to order. To begin with, the compound adopts the $CsAg_7S_4$ structure type with the unit-cell parameters $a=10.289(1)$ Å and $c=7.704(1)$ Å. Upon further cooling, incommensurate orderings occur, in accordance with the fact that a copper deficient sample was used in the investigation ($x\approx0.16$).

Keywords: Ammonium thiocuprate; Phase transformations; Single-crystal X-ray diffraction; Stoichiometry

1. Introduction

The $NH_4Cu_7S_4$ structure was first characterised by Gattow [1]. He chose the space group $I4$ and described it as $NH_4S_4Cu_4(Cu_{3/4})_4$ with one of the two copper sites partially occupied. In more recent studies, several other compounds have been found that adopt the same structure type. The first of these were $TlCu_7Se_4$ [2,3] and $TlCu_7S_4$ [4] although no refinement of the positional parameters was performed. For the latter, all atoms were confined to two planes, in fact conforming to the space group $I4/m$. Structural refinement on single-crystal and powder data confirmed this space group choice for $TlCu_7Se_4$ [5].

When the compounds KCu_7S_4 [6] and $RbCu_7S_4$ [7] were reported, they were described in the original space group $I4$ together with $TlCu_7S_4$. This conclusion was based on X-ray powder diffraction data treated by the Rietveld method [8]. However, the only deviation from the $I4/m$ description concerned the copper on the partially occupied site. Another investigation using the Rietveld technique, now on neutron powder diffraction data for better elucidating the copper positions, showed that the data were equally well refined in either of the two space group models. The description with the highest symmetry was therefore favoured [9], bringing $TlCu_7S_4$ to the same space group as the selenium counterpart.

Ohtani et al. [7] noted that KCu_7S_4, $RbCu_7S_4$ and $TlCu_7S_4$ go through several phase changes upon cooling. By using electron diffraction, they were able to monitor the structural changes. The first transition was indicated by a commensurate wave vector of $q=\frac{1}{2}c^*$. This was found for all compounds at a temperature of around 250 K. Upon further cooling, KCu_7S_4 showed a wave vector with $q=\frac{1}{3}(a^*+b^*)+\frac{2}{3}c^*$, indicating a further phase transformation below 180 K while the thallium compound was stable down to 85 K where a wave vector of $q=\frac{1}{2}(a^*+2b^*)+\frac{1}{3}c^*$ was found. The rubidium compound, on the other hand, showed no further phase transformations. A low temperature neutron powder diffraction study of stoichiometric $TlCu_7S_4$ [9] disclosed that it transforms to the $CsAg_7S_4$ type structure [10]. The phase transition occurs at 255 K. No further ordering was found for the stoichiometric sample even upon cooling to 10 K. The other phase transformations found by Ohtani et al. [7] are likely to depend on the composition of the sample. In a neutron diffraction study of $TlCu_{7-x}S_4$ ($0\leq x\leq0.55$) it was noted that only the already partially occupied site is affected when copper is removed from the compound [11]. The structural changes observed [6,7,9] are related to the amount and arrangement of those copper atoms.

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In their discussion of the proper space group choice of $TlCu_7S_4$, Berger and Norén [9] stressed the importance of the partially occupied copper site. One striking feature is the unusually large thermal displacement factor found for this copper position [7,9]. It is more than four times as large as the one found for the fully occupied copper site while in $TlCu_7Se_4$, the thermal displacement factors for copper are of the same order [5]. This indicates either that the copper atom in the partially occupied site behaves differently, or that the large thermal displacement factor found in the sulphide is an artefact. It could, for instance, be an inadequate description of static disorder occurring on this site [9].

It was shown by Ohtani et al. [7] that $TlCu_7S_4$ forms a complete solid solution with KCu_7S_4 while only a limited solid solubility was found in the pseudo-binary system $TlCu_7S_4$–$TlCu_7Se_4$. This suggested that the sulphides in some respects differ from the selenides. Contrary to the situation for $TlCu_7S_4$, a low temperature diffraction study of $TlCu_7Se_4$ [12] showed no indication of the $CsAg_7S_4$-type structure even upon cooling down to 10 K. In view of these variances as well as the space group ambiguity, we decided to take a new look at the parent compound, $NH_4Cu_7S_4$. At the end of our study, we came across very recent publications on $NH_4Cu_7S_4$ [13] as well as KCu_7S_4 [14–16]. For the latter, of particular interest was the non-stoichiometry and its connection to phase transformations. Since no details on $NH_4Cu_7S_4$ were given by Boller and Sing [13], we choose to present our independent results here on the room-temperature situation, including data on the phase transformations that occur on cooling.

2. Experimental details and results

2.1. Synthesis and phase analysis

The ammonium compound was synthesised by the method proposed by Gattow [1]. A concentrated aqueous solution of ammonia was saturated with hydrogen sulphide excluding air. Cuttings of copper were placed into this solution in a stream of argon. The pressure over the solution was reduced to about 2500 Pa. Black needle-like crystals grew within 3 months on the copper. Some of these crystals were collected and used in a preliminary study. However, the remainder was left to stand in solution until the investigation of $NH_4Cu_7S_4$ was resumed, some 3 years later. A few well developed crystals were collected and sealed into glass capillaries under argon atmosphere while the remaining product was cleaned and stored in air. The product was characterised using X-ray powder diffraction (Guinier–Hägg camera technique) and was found to contain $NH_4Cu_7S_4$ and a new phase, $NH_4Cu_4S_3$. The latter compound was at the same time independently characterised by Boller and Sing [13] and by Purdy [17].

In a later stage of the investigation new crystals were synthesised by the above method. These were found to be of a higher copper content and were used to complement the original batch. Since the composition of the samples used is of importance, the unit-cell of each batch was determined with X-ray powder diffraction (Guinier–Hägg camera technique) using silicon ($a=5.4310280$ Å at 22.5°C [18]) as an internal standard. The length of the c-axis of $NH_4Cu_7S_4$ is very sensitive to copper content (Table 1).

Table 1
The unit cell parameters in ångström (Å) for $NH_4Cu_{7-x}S_4$, refined from calibrated powder data[a]

Sample	a-axis	c-axis	x
I	10.270(1)	3.8071(6)	
II	10.2674(4)	3.8163(3)	
III	10.2695(5)[b]	3.8094(3)[b]	0.16[b]
IV	10.2595(5)	3.8534(3)	0.1[b]

[a] The value of the c-axis is proportional to the copper content

[b] Data obtained by single crystal refinement.

2.2. Thermal analysis

The compound was analysed by Differential Scanning Calorimetry (Mettler TA 4000) in cooling and heating cycles with a rate of 5 K min^{-1} in a nitrogen atmosphere in the interval 123–343 K. The DSC-curves (Fig. 1) show that $NH_4Cu_{7-x}S_4$ has a second order phase transition at 270 K. This is most pronounced for the compound (IV) which has the largest c-axis, i.e. the highest copper content. For both compound (II and IV) there is a clear peak at 185 K indicating a new phase transition most

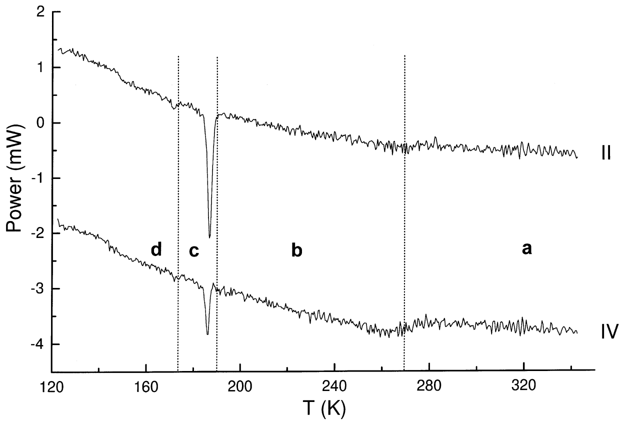

Fig. 1. DSC-curves for two samples of $NH_4Cu_{7-x}S_4$ both weighing 29.7 mg and heated with 5 degrees per minute. The top curve is from a copper-poor sample (sample II in Table 1) and shows a more pronounced phase transition at 185 K compared to the second, less copper deficient compound (sample IV in Table 1). The top curve also display a clearer phase transformation at 173 K than the curve for (IV). Both samples show a second order phase transition at 270 K which is more prominent for the copper-rich sample. Dashed lines divide the temperature range into four parts (**a**–**d**) commented on in the text.

clearly seen for the compound (II) which also shows a third phase transition at 173 K.

The thermal dependence of the d.c. resistivity was investigated (Oxford MagLab System 2000) on a single crystal of sample (II) with the dimensions 0.2×0.2×5 mm, fixed to a sapphire plate and contacted with thin copper wires using silver glue in a standard four-point configuration with the current along the crystallographic *c*-axis. For strict stoichiometry semiconducting behaviour as that of $TlCu_7S_4$ [9] is expected, with a smooth decrease of resistance vs. temperature. As seen in Fig. 2 this is not the case for the sample investigated, where several anomalies can be noted. However, these results are in agreement with measurements done on copper deficient samples of ACu_7S_4 (A=K, Rb, Tl) [7,9,14–16] and indicate that the sample investigated is copper deficient and better referred to as $NH_4Cu_{7-x}S_4$.

2.3. Single-crystal diffraction

In a preliminary investigation, a crystal of $NH_4Cu_7S_4$ was placed on a Rigaku diffractometer equipped with a rotating anode and a R-AXIS II imaging plate system to ensure a better view of reciprocal space. The area detector system contains two image plates which are exposed in cycles. The crystal (sample I in Table 1) was centred with the ϕ-axis parallel to the *c*-axis of the crystal and made to oscillate ±91°. The diffractometer also included a cryostat (Oxford Cryo system), enabling us to record diffraction data at varying temperatures down to 100 K. The crystal was slowly cooled to 120 K at a rate of 20° per hour while a new plate was exposed every 30 min to monitor any structural changes.

This preliminary investigation showed at least two phase transformations. The room temperature pattern showed the expected Bragg-reflections but also streaks of diffuse scattering, located roughly halfway between the {*hk*0} and {*hk*1}-lines (Fig. 3(a)). The first detected phase transformation was noted at 180 K and involved a doubling of the *c*-axis and an increase of Bragg reflection originating from the *ab*-planes, while many features of the room temperature modification still remained (Fig. 3(b)). This indicated that $NH_4Cu_7S_4$ might transform to the $CsAg_7S_4$ structure type at lower temperature, in line with the findings for the thallium analogue [9]. A second phase change at 160 K looked much more complicated. It appeared that the diffraction pattern from 180 K still remained but with an overlaying pattern which could not clearly be derived from the first. The Bragg reflections seemed to condense from lines of diffuse scattering found at approximately $\pm\frac{1}{3}$ from the newly formed {*hk*1}-lines (Fig. 3(c)). For elucidating the transformations a more detailed study was commenced.

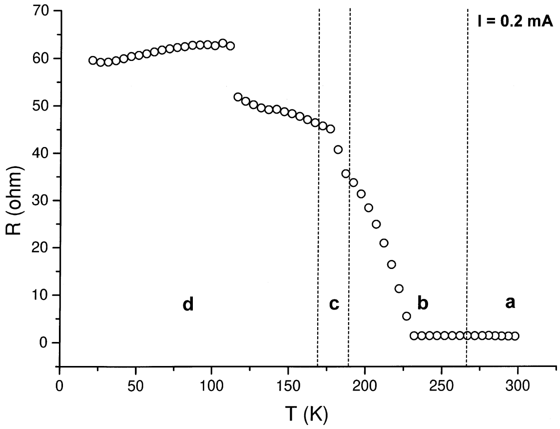

Fig. 2. Resistance vs. temperature measured with a four-point d.c. method on a single crystal of $NH_4Cu_{7-x}S_4$ (*c*-axis=3.8 149(3) Å) while cooling. Dashed lines refers to four temperature ranges (**a**–**d**) and are commented on in the text.

A crystal, previously stored in an argon atmosphere, was selected (sample III in Table 1). The study was conducted on a STOE diffractometer equipped with an image plate and a cryostat (Oxford Cryo system). Details on the data collection and refinement are given in Table 2.

Thermal analysis of stoichiometric $TlCu_7S_4$ shows a phase transition at 255 K [9] but the temperature for this phase transition appears to be lowered with almost 50 degrees if the compound is made copper deficient. Recent studies of KCu_7S_4 show a similar behaviour of composition vs. temperature [14–16]. The exact copper content of our crystal was not known, but we assumed that $NH_4Cu_7S_4$ would behave similarly to the potassium and thallium analogues. Therefore we collected diffraction patterns at various temperatures. Only diffraction patterns recorded at 293 and 200 K are discussed in detail. The data collected below the phase transition seen at 185 K indicate transformations to incommensurable structures and will be reported on later [19].

The detector distance was chosen to be 70 mm and the radiation used was Mo Kα. Each frame was exposed for 10 min during which a rotation of 1° in ϕ was carried out. A total of 200 frames were collected at each temperature. These data were corrected for Lorentz and polarisation effects, and a semiempirical absorption correction was also applied using the programs X-RED and X-SHAPE supplied with the diffractometer [20]. The structures were refined using the program SHELX [21] and JANA96 [22]. Fourier maps were used for elucidating the copper ordering schemes.

2.4. Structure analysis: room temperature structure

The corrected diffraction data were tested against the two models used in the description of the $NH_4Cu_7S_4$ structure type [1,5]. Both the space groups *I*4/*m* and *I*4 were tested, using the positional parameters for $TlCu_7S_4$ [9] as input. The main difference between the two models are that in the *I*4/*m* setting, all atoms are located on mirror planes and $\frac{1}{2}c$ apart. In the *I*4 space group no such

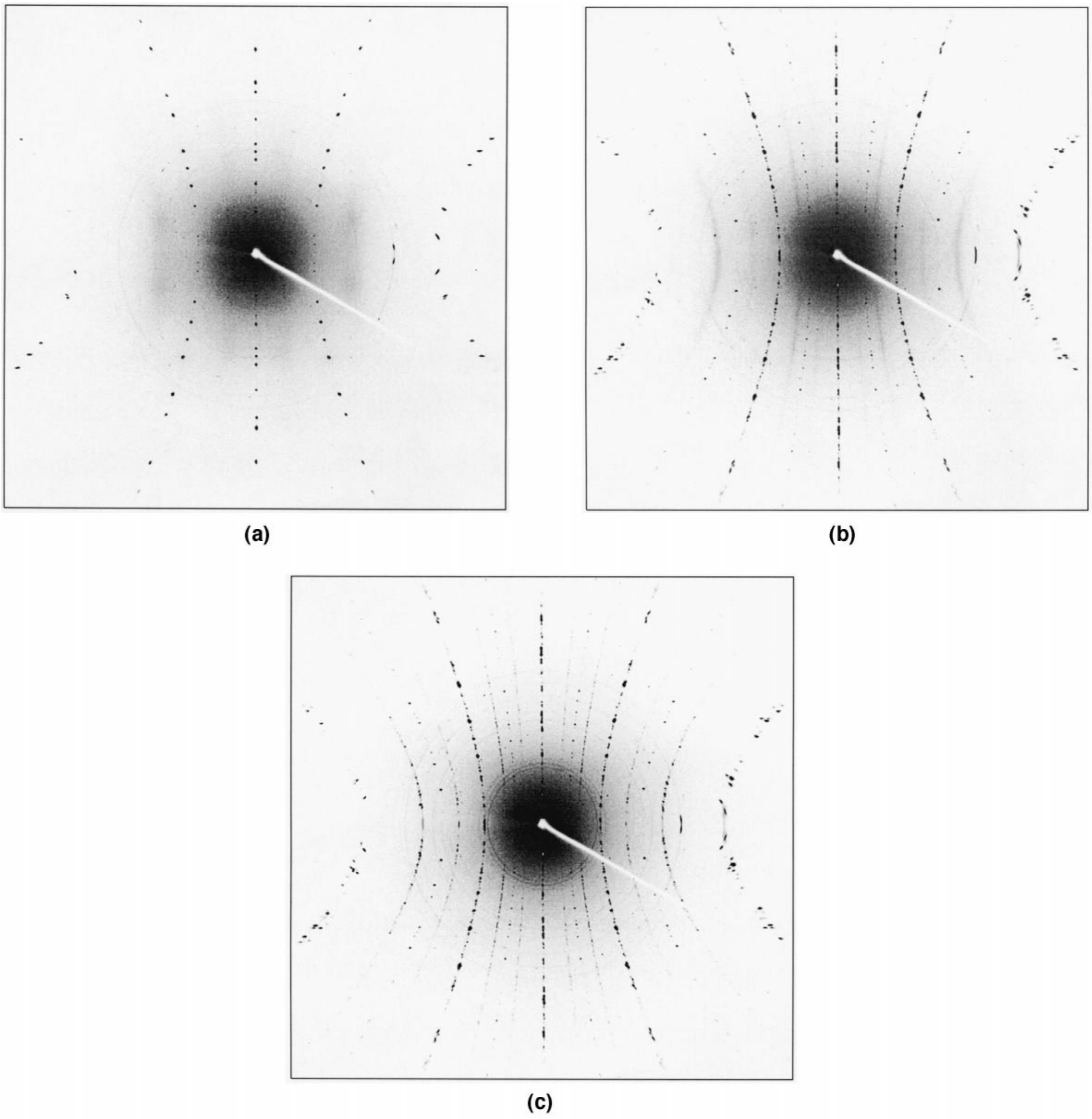
(a) (b) (c)

Fig. 3. Rotation diffractograms recorded for a single crystal of $NH_4Cu_{7-x}S_4$ (Cu Kα radiation, $U=45$ kV, $I=150$ mA). Exposure time is 30 min and temperatures are 260 K (a), 180 K (b) and 150 K (c), respectively. The unit-cell parameters for the compound determined with X-ray powder diffraction (sample I in Table 1). The diffraction rings found at the lowest temperature are due to the formation of ice.

constraints are imposed. The ammonium ion could not be accurately described by the least-squares programs used in the refinements. An attempt to introduce hydrogen atoms gave no significant improvement of the *R*-values, and as a consequence only nitrogen was used in the refinements. The occupancies of the copper sites were also included in the refinements. It was found that the Cu_1 site was fully occupied while the Cu_2 site had an occupancy of less than 75%. The compound was thus copper deficient, a fact also supported by the outcome of the resistivity measurements (Fig. 2).

Both models refined to an *R*-value of around 10%. Similar to $TlCu_7S_4$ [9], no significant deviations from the mirror plane confinement were seen for the ammonium ion, the sulphur and the Cu_1 atom in the $I\bar{4}$ setting when compared with the $I4/m$ description. The partially occupied copper site is significantly removed from $z=0$ in $I\bar{4}$, but the thermal displacement factors for this site are in both models very high and anisotropic. This indicates that the description of this copper position is inadequate in either setting while the rest of the structural framework is best described in $I4/m$. However, the *R*-value is lower for the refinement made in $I\bar{4}$, since that space group model allows for some of the anomalies to be accommodated.

When the Fourier maps were inspected, it was clear that a large electron concentration was not accounted for. Thus, another copper site (Cu_3) was introduced which lowered the final *R*-value to below 3% for both models (Table 3). This gave a better fit to the diffraction data but led to far too short Cu–Cu distances in the average structure.

Table 2
Details of the data collection and structure refinement

Diffractometer:	STOE-IPDS	
Radiation:	Mo Kα	
Monochromator:	Graphite	
	Data collection	
Temperature:	293 K	200 K
Scan mode:	1° in ϕ/plate	1° in ϕ/plate
Number of plates:	200	200
Index limits:	$-12\leq h\leq 12$	$-12\leq h\leq 12$
	$-12\leq k\leq 12$	$-12\leq k\leq 12$
	$-4\leq l\leq 4$	$-8\leq l\leq 8$
Total number of reflections:	1609	6075
Unique reflections:	217	738
Observed reflections ($F_o>2\sigma$):	201	605
Suppressed reflections:	1	1
Absorption coefficient (μ):	18.83 mm^{-1}	18.84 mm^{-4}
Min. and max. transmission:	0.2265, 0.4129	
	Structure refinement on F^2	
Number of parameters:	30	69
Weighting factors [21]:	$a=4.1778$	$a=3.1771$
	$b=0.0327$	$b=0.0800$
Extinction coefficient:	0.004(1)	0.0000(7)
Final indices of agreement:		
(Based on $F_0>2\sigma$)	$R_{F\mathrm{obs}}=0.0255$	$R_{F\mathrm{obs}}=0.0399$
(Based on the whole material)	$R_F=0.0268$	$R_F=0.0470$
	$R_{wF^2}=0.0759$	$R_{WF^2}=0.1124$

The final refinement was chosen to be in the space group $I4/m$ where the atom coordinates, scale factor and thermal parameters were allowed to vary. Sulphur and nitrogen were not found to be significantly better described with anisotropic thermal displacement parameters. Hence, those were only introduced to the copper atoms. The occupancy of Cu_2 and Cu_3 atoms were also refined. Effects of primary extinction was compensated for, making it a total

Table 3
Data from X-ray single crystal refinement of $NH_4Cu_7S_4$ recorded at 293 K using the space groups $I4/m$ (bold) and $I\bar{4}$, respectively, an additional copper site (Cu_3) has been included to accommodate some of the static disorder found in the structure and in both refinements, N has been used instead of NH_4^+

Unit cell:	$a=10.2970(10)$ Å,	$c=3.8470(10)$ Å				
	$R_{F\mathrm{obs}}=0.0255$	**30 parameters**				
	$R_{F\mathrm{obs}}=0.0251$	36 parameters				
Atom	Site	*x*	*y*	*z*	*B* (Å^2)	Occ
N	**2a**	**0**	**0**	**0**	**1.3(2)**	**1**
	2a	0	0	0	1.3(2)	1
S_1	**8h**	**0.2352(1)**	**0.4334(1)**	**0**	**0.99(3)**	**1**
	8g	0.2353(1)	0.4333(1)	−0.000(1)	0.98(2)	1
Cu_1	**8h**	**0.0238(1)**	**0.3600(1)**	**0**	**1.86(3)**[a]	**1**
	8g	0.0238(1)	0.3600(1)	0.000(1)	1.86(2)[a]	1
Cu_2	**8h**	**0.3108(11)**	**0.2250(4)**	**0**	**3.9(2)**[a]	**0.53(2)**
	8g	0.3120(6)	0.2274(5)	0.0239(30)	3.9(2)[a]	0.45(2)
Cu_3	**16i**	**0.2322(15)**	**0.2598(11)**	**0.3168(64)**	**1.3(8)**[a]	**0.09(1)**
	8g	0.2275(36)	0.2607(23)	0.3285(127)	10.5(20)[a]	0.28(3)

[a] Anisotropic thermal displacement factors.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu_1	**0.022(1)**	**0.024(1)**	**0.024(1)**	**−0.009(1)**	**0**	**0**
Cu_2	0.022(1)	0.024(1)	0.025(1)	−0.009(1)	0.003(2)	0.002(1)
Cu_2	**0.063(4)**	**0.016(1)**	**0.068(5)**	**0.018(2)**	**0**	**0**
Cu_2	0.070(2)	0.018(1)	0.059(4)	0.017(2)	−0.014(4)	0.015(3)
Cu_3	**0.018(10)**	**0.000(4)**	**0.031(26)**	**0.016(4)**	**0.004(6)**	**−0.005(6)**
Cu_3	0.122(26)	0.044(9)	0.234(48)	−0.052(13)	−0.139(33)	0.089(18)

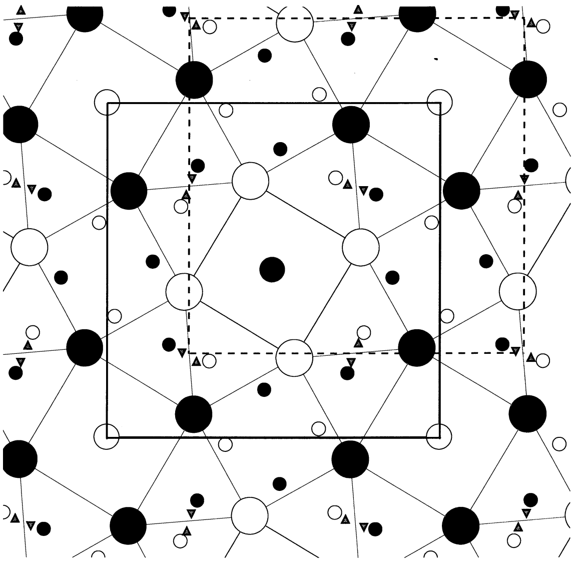

Fig. 4. The structure of $NH_4Cu_7S_4$ at room-temperature projected on (001). Large circles depict sulphur, medium circles ammonium and small circles copper. White is used for atoms at $z=0$ and black for atoms at $z=\frac{1}{2}$. Triangles are used for the intermediate Cu_3 (see Table 3). Dashed lines show a unit cell for an alternative choice of origin emphasising the similarities to the low temperature form as found in Fig. 5.

of 29 parameters refined. The composition of the crystal was thus determined to $NH_4Cu_{6.84}S_4$, and the resulting structure is depicted in Fig. 4.

2.5. 200 K structure

The compound $TlCu_7S_4$ adopts the $CsAg_7S_4$ structure-type at lower temperature [9]. We refined the data collected at 200 K accordingly. However, the refinement was rather poor, with very large anisotropic temperature factors for Cu_2 and Cu_2' (Table 4). Again, a difference Fourier map showed that a large electron concentration remained. It was located close to the Cu_2 atoms, and an extra copper atom (Cu_3) was introduced in this position. This led to a much lower *R*-value but, just as in the room temperature study, to unacceptably short Cu–Cu distances. The *R*-factor is higher for this refinement than for the room temperature data set. Since the data were collected from a copper deficient sample at a temperature close to that of the first incommensurate phase transition this is to be expected. It is apparent from the difference Fourier maps that the largest disagreement concerns the description of the copper atoms that made up the partially occupied site in the room temperature structure. A better fit to the diffraction data

Table 4

Data from X-ray single crystal refinement of $NH_4Cu_7S_4$ recorded at 200 K (bold), the room-temperature structure (*I*4/*m*) with an alternative choice of origin and where the *c*-axis has been doubled, is used as comparison and an additional copper site (Cu_3) has been included to accommodate some of the static disorder found in the structure[a]

Space group:	*P*4/*n* (No. 85)	$Z=4$				
Unit cell:	$a=10.2890(14)$ Å	$c=7.7038(1)$ Å				
Atom	Site	*x*	*y*	*z*	*B* (Å^2)	Occ
N_1	**2c**	**$\frac{1}{4}$**	**$\frac{1}{4}$**	**0.374(1)**	**0.71(16)**	**1**
		$\frac{1}{4}$	$\frac{1}{4}$	0.375		
N_1'	**2c**	**$\frac{1}{4}$**	**$\frac{1}{4}$**	**0.878(1)**	**0.88(16)**	**1**
		$\frac{1}{4}$	$\frac{1}{4}$	0.875		
S_1	**8g**	**0.0135(2)**	**0.6843(2)**	**0.3736(2)**	**0.66(4)**[b]	**1**
		0.015	0.683	0.375		
S_1'	**8g**	**0.0155(2)**	**0.6855(2)**	**0.8703(2)**	**0.74(4)**[b]	**1**
		0.015	0.683	0.875		
Cu_1	**8g**	**0.1132(1)**	**0.7693(1)**	**0.1222(1)**	**1.23(3)**[b]	**1**
		0.110	0.774	0.125		
Cu_1'	**8g**	**0.1082(1)**	**0.7784(1)**	**0.6199(1)**	**1.22(3)**[b]	**1**
		0.110	0.774	0.625		
Cu_2	**4d**	**0**	**0**	**0**	**2.68(16)**[b]	**0.647(11)**
Cu_3		0.01	0.018	−0.067		
Cu_2'	**8g**	**0.9425(1)**	**0.4766(1)**	**0.3514(2)**	**2.50(4)**[b]	**0.865(6)**
		0.938	0.475	0.375		
Cu_3	**8g**	**−0.0269(5)**	**0.0544(8)**	**0.1228(13)**	**4.26(24)**[b]	**0.219(8)**
Cu_2		0.975	0.062	0.125		
[b]Anisotropic thermal displacement factors.						
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S_1	**0.0046(8)**	**0.0071(8)**	**0.0132(11)**	**0.0006(5)**	**−0.0007(5)**	**−0.0005(5)**
S_1	**0.0059(8)**	**0.0081(8)**	**0.0143(11)**	**0.0014(5)**	**−0.0008(5)**	**−0.0005(5)**
Cu_1	**0.0143(5)**	**0.0134(6)**	**0.0191(7)**	**−0.0054(3)**	**0.0013(3)**	**0.0000(3)**
Cu_1'	**0.0151(6)**	**0.0107(6)**	**0.0204(7)**	**−0.0058(3)**	**0.0007(3)**	**−0.0012(3)**
Cu_2	**0.0142(12)**	**0.043(2)**	**0.045(3)**	**−0.098(11)**	**−0.0167(13)**	**0.029(2)**
Cu_2'	**0.0419(8)**	**0.0111(6)**	**0.0420(9)**	**−0.0066(5)**	**−0.0037(5)**	**−0.0061(4)**
Cu_3	**0.010(3)**	**0.076(5)**	**0.077(7)**	**0.0006(3)**	**0.002(2)**	**−0.0009(4)**

[a] The Cu_2 and Cu_3 sites are reversed compared to the room-temperature structure.

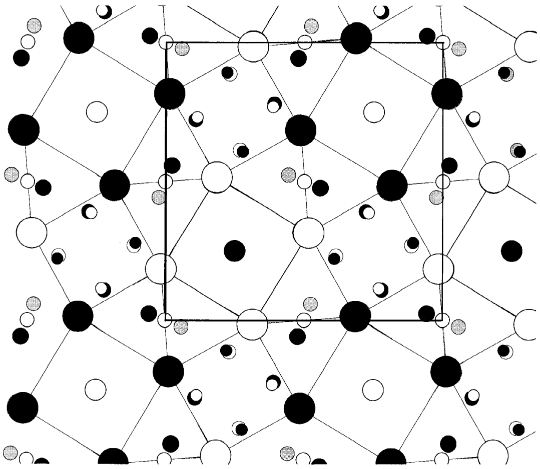

Fig. 5. The low-temperature structure of $NH_4Cu_7S_4$ viewed along the c-axis. Large circles depict sulphur, medium circles ammonium and small circles copper. The atomic parameters are found in Table 3.

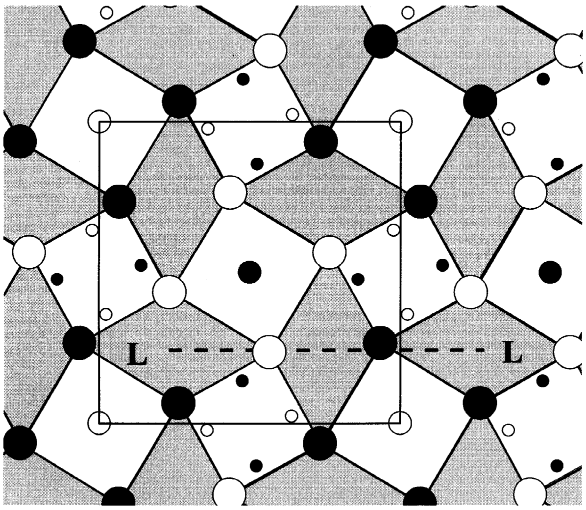

Fig. 6. The rigid partial framework of $NH_4Cu_7S_4$. Atom symbols as in Fig. 4. The shaded areas indicate the sulphur channels incorporating highly disordered copper atoms. The line ‘L’ indicates the cut along c through the structure as is illustrated in Fig. 8.

can be obtained by introducing more copper atoms in the refinement, but this improvement is not large enough to justify the introduced extra parameters. Adding extra copper sites is only an artificial means of modelling the disorder that has been introduced in the low temperature modification by the copper deficiency of the sample.

In the final model a total of 69 parameters were refined. These included thermal parameters, scale factors, atomic coordinates and primary extinction. Anisotropic thermal displacement parameters were introduced for all but the nitrogen atoms. The occupancy of the Cu_2, Cu_2' and Cu_3 atoms were also refined. In this case the total copper content would be 6.84 atoms per formula unit, in good agreement with the value found for the room-temperature measurement. The refined low-temperature structure is illustrated in Fig. 5. It is worth noting that a similar arrangement was also found in recent studies of $KCu_{6.88}S_4$ [14–16].

3. Discussion

3.1. The commensurate structures

Clearly, at least copper deficient $NH_4Cu_{7-x}S_4$ cannot easily be described by a simple crystallographic model at room temperature. One way of describing the situation is to introduce ‘extra’ copper atoms in the refinement. This leads to lower R-values but gives too short interatomic distances between the affected copper atoms.

Another modelling approach is to separate the structure into two parts. The first part is made up of NH_4^+, Cu_1, and S. At room temperature this partial structure is best described in the space group $I4/m$, with the cell parameters $a=10.2695(5)$ Å, $c=3.8094(3)$ Å (for $NH_4Cu_{6.84}S_4$). This ‘framework-structure’ of $NH_4Cu_4S_4$ is depicted in Fig. 6. The shaded regions are often described as a double column of edge-sharing sulphur tetrahedra. Another way of describing this arrangement is as a channel of sulphur atoms.

The remaining copper must reside in these channels. We can use two simplified models to describe this. In the description by Gattow (model 1) the copper is tetrahedrally coordinated to sulphur. There are two such sites per channel in a unit cell, but only 1.5 copper ions can occupy them in a stoichiometric compound. If we double the c-axis we will have three copper ions and one vacancy per ‘unit translation’ (Fig. 7(i)). Since experimentally no super-structure reflections have been found at room temperature, it follows that no long-range ordering of copper atoms and vacancies exists. This can be described as a disordered copper site with a 75% occupancy in the average unit cell, and no doubling of the c-axis is then necessary (Fig. 7(ii)). This description implies that the

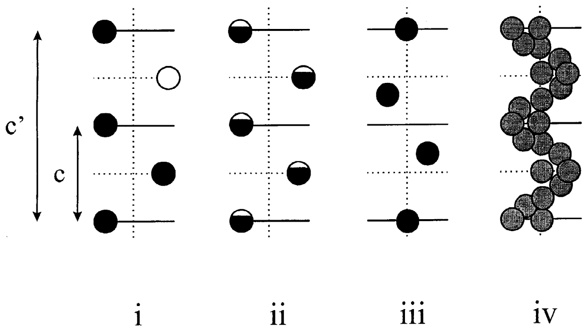

Fig. 7. (i) Arrangement of three copper atoms and a vacancy along (001). The unit translation-length for the room-temperature form is denoted (c), with $c'=2\times c$. (ii) The same sites with partial occupancy. (iii) An equidistant arrangement of three copper atoms. (iv) Combination of the two sequences to a disordered, liquid-like arrangement.

strongest interactions are between these copper atoms and the sulphur, since all these copper ions are identically coordinated to their surroundings. But this model gives, when refined, very high anisotropic thermal displacement parameters for that site, indicating an inaccurate description of these copper ions.

The other extreme is to describe the copper arrangement as practically non-interacting with the rest of the structure (model 2). This means that the dominant force a copper ion would be subjected to would be the electrostatic repulsion of the other copper ions in a channel. This would lead to an ordering that favoured the largest, equidistant separation of the ions (Fig. 7(iii)). This arrangement would lead to a doubling of the *c*-axis as found in the low-temperature form of $TlCu_7S_4$, i.e. the $CsAg_7S_4$ structure type.

It seems that the 200 and 293 K situations carry elements of both these models. During the preliminary investigations of $NH_4Cu_7S_4$ we noticed bands of diffuse scattering which with decreasing temperature ‘condensed’ to Bragg reflections (Fig. 3). This diffuse scattering is located perpendicular to c^*. Our interpretation is that the diffuse scattering originates from the partially occupied copper channels and indicates that there is little or no long-range coherence between the channels in the *ab*-plane. The bands are located at $1/2c^*$ at temperatures above the first phase transition (Fig. 3(a)). This tells us that there are repeat units with a length of twice the crystallographic *c*-axis but that these units do not ‘communicate’ with each other. There is a lack of coherence and diffuse scattering is the result. We can thus interpret this as if both our simplified models are valid at the same time and overlaying each other in a disordered way. This is illustrated in Fig. 7(iv) where copper atoms have been stacked according to both models and then superposed to one unit cell.

To get a better view of the copper arrangement in these channels a small test was conducted. The refined positions for NH_4^+, Cu_1 and S were used as fixed atomic coordinates in a unit cell were the *c*-axis had been doubled. The space group *P*4 was chosen which meant that three extra atomic coordinate sets had to be introduced for each atom in order to keep the basic structural framework unchanged. This was done in order to prevent a ‘false arrangement’ of Cu_n ($n \geq 2$) atoms imposed by symmetry operations working along the *c*-axis. By drawing a Fourier map with one axis as indicated by the line ‘L’ in Fig. 6 and the other as the crystallographic *c*-axis, the behaviour of the copper ions along the *c*-axis can be observed for the two temperatures (Fig. 8). It is striking that the partially occupied site meanders through the structure at room-temperature while the fully occupied sites show a distinct periodicity (Fig. 8(a)). This ‘amorphous’ behaviour is absent from the low-temperature structure (Fig. 8(b)).

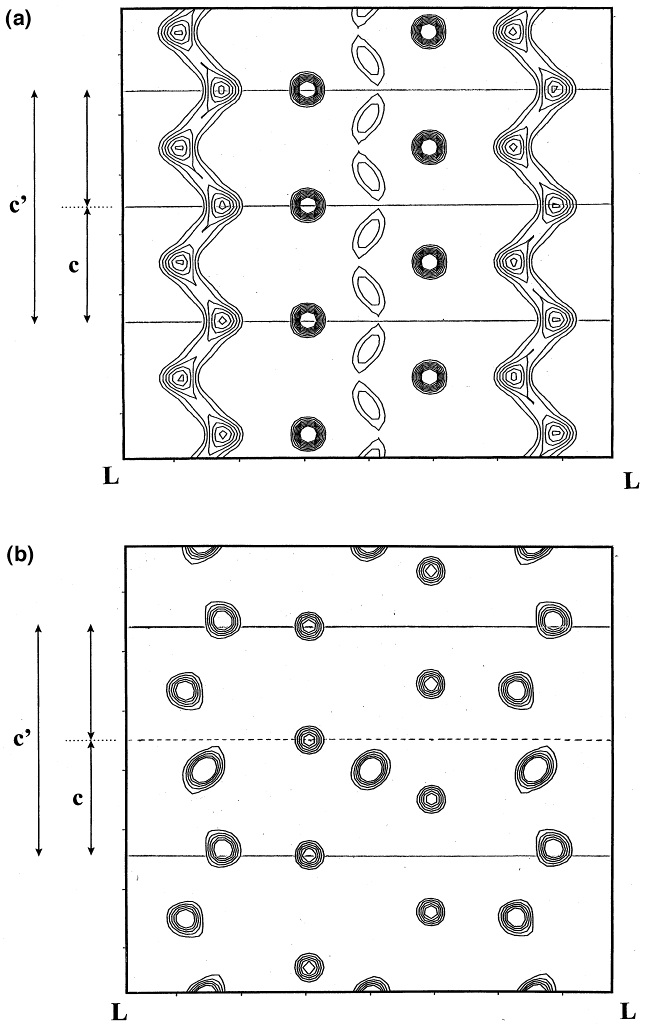

Fig. 8. Fourier maps of the 293 K structure (a) and the low-temperature modification (b) as viewed along ⟨001⟩. The *c*-axis for the room-temperature structure is denoted *c*, while that of the low-temperature model is called **c**′.

In the study of the low temperature modification of $TlCu_7S_4$ there was no need to introduce a fifth copper site in the refinement [9]. The reason for the difference is probably that the $TlCu_7S_4$ study was done on stoichiometric material while the ammonium compound used in this study was copper deficient. Since copper depletion affects the partially occupied site, the description of the copper arrangement of (and around) the Cu_2 and Cu_2' sites will be inadequate in a sub-stoichiometric sample. It should be kept in mind that the $TlCu_7S_4$ compound was investigated with powder diffraction which made a detailed analysis of the structure infeasible. However, a recent study of the isostructural compound KCu_7S_4 using X-ray powder diffraction also shows this behaviour for non-stoichiometric samples [15]. It is worth noticing that the description given for stoichiometric KCu_7S_4 in that article is close to the $CsAg_7S_4$ structure type with some extra atoms included in the ‘channel’. The cause for this is probably that the diffraction data were recorded at 295 K which is close to the phase-transition temperature (293 K) given for the compound [15]. It is our experience that even small differences in copper concentration lead to quite noticeable changes in the phase-transition temperature for compounds of this type. It is therefore possible that the potassium compound was at least partially transformed to the low temperature modification at the temperature at which the structure determination was done. We suspect that a new study, performed at temperatures selected further away from the phase transformation, would show the $NH_4Cu_7S_4$ structure type at higher temperatures and the $CsAg_7S_4$ structure type at temperatures below the phase transition.

3.2. Thermal behaviour

We have in our study investigated samples of $NH_4Cu_{7-x}S_4$ with different copper compositions (Table 1). It has been shown that the copper content greatly affects the properties of the sample and this has prompted us to use temperature-zones in our discussion of the thermal behaviour of the compound. The first region (**a**) is the temperature above 270 K and includes the room-temperature structure while the second (**b**) lies between 190 and 270 K and contains the $CsAg_7S_4$ structure type. The region third (**c**) is between 170 and 190 K and the fourth (**d**) continues from 170 K downwards (see also Figs. 1–3).

The phase transition of the room-temperature structure in region (**a**) to the commensurate low-temperature structure in region (**b**) is of the second order (Fig. 1) and initiates at 270 K. This can be seen as a change of the baseline alignment, and is most clearly seen for the copper-rich sample (IV). But initial diffraction experiments on the more copper deficient samples (I and II) indicated no further ordering at that temperature. In fact, the temperature had to be reduced to 200 K in order to clearly observe the expected superstructure reflections. The resistivity measurements also indicate a change in behaviour but this most clearly seen below 232 K. However, a recent diffraction experiment using the most copper rich sample (N) showed superstructure reflections appearing between 263 and 253 K.

Our interpretation is that the disordered copper atoms in $NH_4Cu_{7-x}S_4$ start to order in the same way as was found for the low-temperature form of $TlCu_7S_4$ [9]. This ordering starts at 270 K for the compositions studied and occurs in the sulphur channels. For the most copper-poor samples the correlation length of the ordering is initially rather short and only diffuse scattering can be seen with X-ray diffraction. As the temperature is lowered this correlation length increases such that at around 200 K it is long enough for Bragg reflections to occur. The most copper-rich sample (IV) shows a much stronger signal at the first phase-transition temperature than a sample with low copper content (Fig. 1). This indicates that a larger amount of the sample was transformed to the low-temperature form. This in turn implies that the superstructure reflections should be observed at higher temperature as we in fact found. This might also explain the behaviour of stoichiometric $TlCu_7S_4$ which appears to have a first order phase transition to its low-temperature form at 255 K. If the compound is stoichiometric there will be no vacancies in the $CsAg_7S_4$ structure type and all the amorphous copper atoms ‘freeze’ at the transition temperature. The whole sample adopts the low-temperature form. If copper is removed from the sample, this will not occur since the increased number of vacancies will prevent a correlated ‘freezing’ of all the copper ions at the transition temperature. This in turn, lowers the detected ‘freezing’ temperature as observed for $TlCu_7S_4$.

At 185 K the remaining disordered copper atoms ‘freeze’. The temperature for the second phase transition does not change for a copper-rich sample but the decreased peak-area indicates fewer disordered copper atoms at this temperature (Fig. 1).

In the third temperature region (**c**) the compound adopts an incommensurate structure. The diffraction patterns in Fig. 3(b) illustrate this for sample (I). This ordering is likely due to the non-stoichiometry of the sample. A low copper content leads to vacancies in the $CsAg_7S_4$ structure type and further ordering can occur. This ordering seems to occur the *ab*-plane and indicates some long-range ordering between the copper channels which is incommensurate with respect to the rest of the structure. The streaks of diffuse scattering show that some disorder still persists in the *ab*-plane. This effect is currently under investigation and will be reported [19].

The (**d**) region is yet to be studied. A third phase transition (145 K) involving a further modulation along *c*-axis (Figs. 1 and 3(c)) is apparent for the most copper deficient sample.

4. Conclusions

On the basis of single crystal X-ray refinement we describe the room temperature modification of $NH_4Cu_{7-x}S_4$ as a tetragonal $NH_4Cu_4S_4$ framework in which the remaining $(3-x)$ copper ions are located as a quasi one-dimensional ‘liquid’ within sulphur channels. Removal of copper from the compound occurs in these channels. Even in a stoichiometric compound, copper in these channels has disordered arrangement only approximately explained in the original description by Gattow [1]. At lower temperatures vacancy ordering starts, and the compound transforms to the $CsAg_7S_4$ structure type. This second order phase transition is initiated at 270 K but its completion is strongly dependent on the stoichiometry of the sample, i.e. the copper content in the channels. We believe that strict stoichiometry of $NH_4Cu_7S_4$ would yield a semi-conducting behaviour as found for $TlCu_7S_4$ [9] and low-temperature ordering to the $CsAg_7S_4$ type. On the other hand, a crystal with low copper concentration appears to retain the room-temperature structure even at 50 degrees below the transition temperature found by DSC. This is because copper in the low-temperature arrangement has insufficient correlation length to be detected with X-rays. In samples with higher copper content this low-temperature arrangement is more predominant and the super-structure reflections are detected close to 270 K.

The commensurate low-temperature arrangement, due to the copper depletion, is not stable below 185 K for $NH_4Cu_7S_4$ and further ordering occurs as the 'amorphous' parts of the crystal freeze. For slightly copper-deficient $NH_4Cu_7S_4$, the 'frozen' form is incommensurate while the primary Bragg reflections are those of the $CsAg_7S_4$ structure (Fig. 3(b)). Since the intensity of the satellite reflections are very weak, they might be overlooked in ordinary powder diffraction, and a quite satisfactory refinement may be obtained on the main structure. However, it seems that these incommensurate orderings can de indirectly detected as resistivity anomalies. For more extended copper deficiency, other ordering schemes are possible as indicated in the literature [7,14–16].

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