An X-Ray Study on the System Cu-S

SEVED DJURLE

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The phase relations in the system Cu-S have been investigated by X-ray diffraction methods. Phases of the following (approximate) compositions were found to exist:

Cu_2S , $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.8}\text{S}$ and CuS .

All of these phases except CuS undergo one or more transitions at higher temperatures. Each ultimately transforms into a face-centred cubic phase which probably exists at least over the composition range Cu_2S to $\text{Cu}_{1.8}\text{S}$.

The previously unknown sulphide $\text{Cu}_{1.96}\text{S}$ seems to be low-symmetric at room temperature. A high-temperature modification of this sulphide is tetragonal and can be preserved as a metastable phase at room temperature, where its body-centred unit cell has the dimensions:

$$a = 4.008 \text{ \AA}, \quad c = 11.268 \text{ \AA}.$$

The low-temperature modification of $\text{Cu}_{1.8}\text{S}$ is the only phase with a homogeneity range. The range seems to extend at least from the composition $\text{Cu}_{1.80}\text{S}$ to $\text{Cu}_{1.73}\text{S}$.

The following sulphides of copper are known as minerals: Cu_2S (chalcocite), $\text{Cu}_{1.8}\text{S}$ (digenite), CuS (covellite).

The binary system Cu-S has been the object of several studies. References to the earlier investigations are found in the bibliography of Haughton and Prince¹. Different controversial opinions about the system have been put forward.

Buerger^{2,3} studied the system Cu_2S - CuS with a controlled-temperature camera and found the compound $\text{Cu}_{1.8}\text{S}$, in addition to the earlier known Cu_2S and CuS . According to Buerger, $\text{Cu}_{1.8}\text{S}$ below approximately 78°C should have the ideal composition Cu_9S_5 , and above 78°C have a range of homogeneity with both sulphur excess and sulphur deficit. Concerning Cu_2S , Buerger states that above 105°C it has a hexagonal basic structure and below 105°C an orthorhombic superstructure. The relations between the unit cells of the modifications and their probable space groups are given. According to Buerger the superstructure phase is capable of dissolving sulphur up to eight atomic per cent CuS , while the basic structure dissolves only up to two atomic per cent CuS .

Rühl⁴ has also studied the system Cu_2S — CuS with a high-temperature camera. Contrary to Buerger, he found that $\text{Cu}_{1.8}\text{S}$ at room temperature has the homogeneity range $\text{Cu}_{1.81}\text{S}$ — $\text{Cu}_{1.77}\text{S}$, and that at higher temperatures, the solid solution region is very much broadened, but only towards the copper side. He observed that the diffraction pattern of $\text{Cu}_{1.8}\text{S}$ at room temperature and up to about 75°C had superstructure lines. The phase in equilibrium with $\text{Cu}_{1.8}\text{S}$ was not Cu_2S , but a phase whose diffraction pattern had the strongest lines in places similar to Cu_2S . He thought it probable that Cu_2S had a small range of homogeneity (up to two atomic per cent CuS).

Jensen⁵ has studied Cu_2S by differential thermal analysis and found a maximum melting temperature of 1129°C for the composition $\text{Cu}_{1.989}\text{S}$. He could not observe the limits of solubility of sulphur in Cu_2S , nor any transformations in the solid state between 404°C and the melting points in the composition range 77.00 to 82.00 weight per cent copper.

Hirahara⁶ has determined several physical properties of Cu_2S as a function of temperature and found two transition points, the lower one at about 110°C and the upper one at about 470°C .

X-Ray and thermal studies on the phase transitions of Cu_2S , performed by Ueda⁷, gave results in good agreement with those of Hirahara. For the modification of Cu_2S above 470°C , Ueda could observe only two diffraction lines. He pointed out the similarity of the places of the lines with the strongest ones of high-temperature $\text{Cu}_{1.8}\text{S}$.

Further contributions to the knowledge of the electrical conductivity of the copper sulphides, together with X-ray work, has been given by Kamai-gaichi⁸.

Attempts to solve the structure of hexagonal Cu_2S have been made by Ueda⁷, using powder data, and also by Belov and Butuzov⁹. The last two used the single crystal data given by Buerger and Buerger¹⁰. It seems to the present author that none of them has come to any quite satisfactory agreement between observed and calculated intensities, and hence the structure determination cannot be regarded as settled. For CuS , the structure has been determined by Oftedal¹¹, and later confirmed by Berry¹².

EXPERIMENTAL

Finely powdered Cu (electrolytically precipitated, E. Merck, Darmstadt) and S (sublimated sulphur, T. Schuchardt, Goerlitz) of better than 99.9 % purity were used as starting materials.

Samples were prepared by carefully mixing weighed amounts of the elements, pressing the mixtures to pellets at a pressure of up to 16 ton/cm^2 and sintering in evacuated Supremax or silica tubes at a temperature of 320 or 470°C . The heating time varied between 1 and 7 days. The samples were either quenched in cold water from the sintering temperature or allowed to cool slowly, within 24 h, in the furnace.

Visual examination or X-ray analysis indicated that some samples were heterogeneous after this treatment. They were then finely powdered, pressed into pellets and annealed in evacuated tubes for times up to 1 month.

No signs of contamination of the samples from the Supremax or silica tubes were detected.

In order to see if the preparation technique was satisfactory, selected samples were chemically analyzed. The sample was dissolved in fuming HNO_3 and the solution was evaporated to dryness on a steam bath. HNO_3 was removed by repeated evaporations

with HCl, and then the sample was diluted to 100 ml. SO_4 and Cu were determined in aliquote parts, the former gravimetrically as BaSO_4 and the latter by titration with 0.01 M EDTA with murexide as an indicator. The composition, calculated from the weighed amounts of the elements, was in good agreement with the chemical analysis. The deviation amounted to 0.5 weight per cent for copper and 0.2 weight per cent for sulphur.

The samples were investigated by taking X-ray powder photographs in Guinier type focusing cameras with quartzmonochromatized Cu- $K\alpha$ radiation (sometimes with Cr- $K\alpha$ radiation). KCl or CaF_2 were used as internal standards. The following constants of wavelengths and standards were used:

$$\begin{array}{ll} \text{Cu}K\alpha = 1.5418 \text{ \AA} & a_{\text{KCl}21^\circ} = 6.29215 \text{ \AA} \\ \text{Cr}K\alpha = 2.2909 \text{ \AA} & a_{\text{CaF}_2,21^\circ} = 5.46300 \text{ \AA} \end{array}$$

In order to investigate samples at higher temperatures in most cases from room temperature up to 500°C , X-ray measurements were made with an one-sided Debye-Scherrer heating camera of 4.55 cm film radius, registering reflexions between $2\theta = 26.456^\circ$ and $2\theta = 157.15^\circ$. The radiation used was Cu- $K\alpha$ filtered with a Ni-foil. The camera and the X-ray technique used has been described by Fischmeister¹³. The thermocouple of the camera was calibrated against known melting points¹⁴.

The temperature fluctuation limits were:

$$\begin{array}{ll} \pm 2^\circ\text{C below} & 300^\circ\text{C} \\ \pm 3^\circ\text{C between} & 300^\circ\text{C and } 400^\circ\text{C} \\ \pm 4^\circ\text{C above} & 400^\circ\text{C} \end{array}$$

The samples, in the form of very fine powder, were mounted in thin-walled capillary tubes. The tubes used were of Pyrex glass, had an outside diameter of about 0.3 mm and walls about 0.01 mm thick. The capillaries were either sealed after evacuation to prevent decomposition of the samples when heated, or continually evacuated through the camera. In order to be sure that no abnormal changes took place during heating, room temperature powder patterns before and after the heat treatment were included in each run.

RESULTS

The present study has revealed the existence of several previously unknown phases in the system Cu—S. Table 1 summarizes the result of the analysis with the high-temperature camera. The modifications have been labelled with Roman numerals (I for the one which exists above the highest transition temperature). As will be shown later, all the I-modifications probably belong to the same high-temperature phase.

The approximate composition of the phases which could be preserved at room temperature was determined by means of Guinier photographs. The X-ray analyses showed that many of the samples were not in equilibrium. In spite of different heat treatment, this could often not be completely remedied. The result of the phase analysis of two groups of samples, one annealed at 400°C and the other at 75°C during one month is summarized in Table 2, in which the denomination of the phases is the one arrived at after the high-temperature studies had been made.

Data from powder photographs of the different phases are collected in Table 3. The crystallographic results are discussed in the following.

Table 1. The sulphides of copper.

Compound	Approximate range of existence *	Crystal system
Cu ₂ S III	<110°C	Orthorhombic
Cu ₂ S II	110°C—470°C	Hexagonal
Cu ₂ S I	>470°C	Cubic F.C.
Cu _{1.96} S III	<100°C	"Low-symmetric"
Cu _{1.96} S II	Metastable?	Tetragonal
Cu _{1.96} S I	>100°C	Cubic F.C.
Cu _{1.8} S II	<78°C	
Cu _{1.8} S I	>78°C	Cubic F.C.
CuS	<500°C	Hexagonal

* Range of investigation 20—500°C.

Table 2. Results of the phase analysis of two groups of copper sulphide samples.

Composition of the samples	Temperature of annealing before quenching	
	400°C	75°C
	Phases observed *	Phases observed *
Cu _{1.96} S	CuS	
1.50	» + Cu _{1.8} SII	
1.63	Cu _{1.8} SII + (CuS)	
1.70	»	
1.74	»	
1.78	»	Cu _{1.8} SII
1.80	»	»
1.82	» + (Cu _{1.96} SIII)	»
1.84	» + (Cu _{1.96} SII) + (Cu _{1.96} SIII)	» + (Cu _{1.96} SIII)
1.86	» + (») + ((»))	» + (»)
1.88	Cu _{1.96} SII + Cu _{1.8} SII + ((»))	Cu _{1.96} SIII + Cu _{1.8} SII
1.90	» + » + ((»))	» + (») + ((Cu _{1.96} SII))
1.92	» + (») + (»)	» + (») + ((»))
1.94	» + (Cu _{1.96} SIII) + ((Cu _{1.8} SII))	» + (») + ((»))
1.95	» + (») + ((»))	
1.96	» + (»)	Cu _{1.96} SIII + ((Cu _{1.96} SII))
1.97	» + (») + ((Cu ₂ SIII))	
1.98	Cu ₂ SIII + (Cu _{1.96} SII) + ((Cu _{1.96} SIII))	Cu ₂ SIII + (Cu _{1.96} SIII) + ((CuSII _{1.96}))
1.99	» + (»)	» + (») + ((»))
2.00	»	»
2.03	»	
2.13	» + (Cu)	

* No parenthesis = large amount, one parenthesis = small amount, two parentheses = trace amount.

The phases occurring at the composition Cu_2S

The high temperature X-ray analysis has revealed two transitions. The lower one takes place gradually at about 110°C in agreement with data published earlier ^{3,6}, and the upper one occurs at 465 to 475°C , in agreement with the temperature reported by Hirahara ⁶.

 Cu_2S III

Minerals of chalcocite (gratefully received from the Institute of Mineralogy and Geology in Uppsala) were examined by means of powder photographs, and a single crystal was selected from a sample giving the same diffraction lines as synthetic samples. The Weissenberg photographs gave an A-centred orthorhombic cell, and after indexing the powder photograph the cell dimensions were determined as:

$$\begin{aligned} a &= 11.881 \pm 0.004 \text{ \AA}, & b &= 27.323 \pm 0.008 \text{ \AA}, \\ c &= 13.491 \pm 0.004 \text{ \AA}. \end{aligned}$$

The result is in good agreement with the works of Ueda ⁷, Buerger and Buerger ¹⁰ and Oftedal ¹¹. Buerger and Buerger give the lattice parameters:

$$a = 11.90 \text{ \AA}, \quad b = 27.28 \text{ \AA}, \quad c = 13.41 \text{ \AA}$$

with an accuracy of about 1 %.

The method of Ueda to determine the c -axis from rotation photographs and the a - and b -axis from the reflexions $|6.0.0|$ and $|3.4.6|$ is unsatisfactory, since with Cu-radiation the reflexion $|6.0.0|$ cannot be separated from $|3.12.0|$ and $|3.4.6|$ is inseparable from $|0.8.6|$.

 Cu_2S II

The powder photographs of Cu_2S II could be indexed with a hexagonal unit cell. The dimensions at different temperatures are:

$$\begin{array}{lcl} 152^\circ & a = 3.961 \\ 300^\circ & a = 3.981 \\ 460^\circ & a = 4.005 \end{array} \left. \vphantom{\begin{array}{l} 152^\circ \\ 300^\circ \\ 460^\circ \end{array}} \right\} \pm 0.004 \text{ \AA} \quad \begin{array}{l} c = 6.722 \\ c = 6.761 \\ c = 6.806 \end{array} \left. \vphantom{\begin{array}{l} c = 6.722 \\ c = 6.761 \\ c = 6.806 \end{array}} \right\} \pm 0.007 \text{ \AA} \quad \begin{array}{l} c/c = 1.697 \\ c/a = 1.698 \\ c/a = 1.699 \end{array}$$

This is in fairly good agreement with the value of B. and B.¹⁰, $a = 3.89 \text{ \AA}$, $c = 6.68 \text{ \AA}$, $c/a = 1.717$ at 112°C (accuracy 1 %) and the diagram of Ueda ⁷ (his Fig. 4).

 Cu_2S I

The powder photograph of this modification has been indexed as the pattern of a face-centred cubic lattice with the cell edge at

$$\begin{array}{l} 465^\circ\text{C} \quad a = 5.725 \\ 500^\circ\text{C} \quad a = 5.735 \end{array} \left. \vphantom{\begin{array}{l} 465^\circ\text{C} \\ 500^\circ\text{C} \end{array}} \right\} \pm 0.010 \text{ \AA}$$

A cell content of 4 Cu_2S is consistent with the cube edge.

The phases occurring around the composition $\text{Cu}_{1.96}\text{S}$

The photographs of samples of this composition have revealed that three modifications exist.

$\text{Cu}_{1.96}\text{S}$ III is stable up to at least 75°C and $\text{Cu}_{1.96}\text{S}$ II is a high temperature modification, metastable at room temperature. When heating pure $\text{Cu}_{1.96}\text{S}$ III in the high temperature camera it begins at about 100°C to transform slowly into $\text{Cu}_{1.96}\text{S}$ I. The transition from $\text{Cu}_{1.96}\text{S}$ III to $\text{Cu}_{1.96}\text{S}$ II has not been observed.

$\text{Cu}_{1.96}\text{S}$ II is formed together with $\text{Cu}_{1.96}\text{S}$ III when quenching samples of the right composition from above a temperature of at least 320°C . From Table 2 it seems that $\text{Cu}_{1.96}\text{S}$ II is metastable at room temperature and up to at least 75°C . In the high-temperature camera, its powder pattern can only be observed below 150°C . Owing to the sluggish transitions, the patterns taken in the high temperature camera probably do not correspond to equilibrium.

$\text{Cu}_{1.96}\text{S}$ III

The diffraction pattern of this phase has not been indexed. Its complexity indicates a low symmetry.

$\text{Cu}_{1.96}\text{S}$ II

The Guinier photograph, taken at room temperature corresponds to a primitive tetragonal lattice with a cell content of 4 $\text{Cu}_{1.96}\text{S}$ and with the dimensions:

$$\begin{aligned} a &= 4.008 \pm 0.002 \text{ \AA} \\ c &= 11.268 \pm 0.006 \text{ \AA} \end{aligned}$$

$\text{Cu}_{1.96}\text{S}$ I

This modification is cubic, and has a face-centred unit lattice with the cube edge $a = 5.707 \pm 0.006 \text{ \AA}$ at 500°C and a cell content of 4 $\text{Cu}_{1.96}\text{S}$. The unit cells of $\text{Cu}_{1.96}\text{S}$ II and $\text{Cu}_{1.96}\text{S}$ I have the following relations:

$$a_{\text{II}} \approx 1/\sqrt{2} \times a_{\text{I}}; \quad c_{\text{II}} \approx 2 \times a_{\text{I}}$$

The phases occurring around the composition $\text{Cu}_{1.8}\text{S}$

The high temperature investigation has established a transition at 78°C in agreement with the work of Rühl⁴.

$\text{Cu}_{1.8}\text{S}$ II

The Guinier powder photographs of four samples with the composition $\text{Cu}_{1.82}\text{S}$, $\text{Cu}_{1.78}\text{S}$, $\text{Cu}_{1.74}\text{S}$ and $\text{Cu}_{1.70}\text{S}$ are listed in Table 3. It appears that line displacements occur for variation in the composition. As the displacements are regular and the lines, except for some very weak ones, can be followed through the series of samples, it seems that the most probable interpretation

Fig. 1. Cube edge of Cu_{2-x}S at 500°C as a function of x .

of the data implies the existence of a single phase, called $\text{Cu}_{1.8}\text{S}$ II, having a homogeneity range. The range extends surely from $\text{Cu}_{1.80}\text{S}$ to $\text{Cu}_{1.73}\text{S}$, and possibly from $\text{Cu}_{1.82}\text{S}$ to $\text{Cu}_{1.70}\text{S}$. The uncertainty is due to possible errors in the measurements.

Attempts to find a common indexing of the four photographs of $\text{Cu}_{1.8}\text{S}$ II have not been successful. However, most of the strongest lines of the photographs seem to correspond to a face-centred cubic basic lattice. The basic cube edge for the various compositions are:

$\text{Cu}_{1.82}\text{S}$	$\text{Cu}_{1.78}\text{S}$	$\text{Cu}_{1.74}\text{S}$	$\text{Cu}_{1.70}\text{S}$
$a = 5.570$	$a = 5.564$	$a = 5.556$	$a = 5.551 \pm 0.003 \text{ \AA}$

The displacements of most of the other lines when the composition is varied shows, however, that the real lattice cannot be cubic.

$\text{Cu}_{1.8}\text{S}$ I

The unit cell of this modification is face-centred cubic and is evidently closely related to the basic cell of $\text{Cu}_{1.8}\text{S}$ II. At the composition $\text{Cu}_{1.82}\text{S}$, it has the following cell constants,

at	80°C	$a = 5.577$	$\left. \begin{array}{l} a = 5.577 \\ a = 5.593 \\ a = 5.610 \\ a = 5.639 \end{array} \right\} \pm 0.006 \text{ \AA}$
	152°C	$a = 5.593$	
	300°C	$a = 5.610$	
	500°C	$a = 5.639$	

A cell content of 4 $\text{Cu}_{1.8}\text{S}$ is compatible with the cube edge.

Table 3. X-Ray diffraction data of the phases Cu_2S , $\text{Cu}_{1.98}\text{S}$ and $\text{Cu}_{1.8}\text{S}$. Cu_2S III 20°C Cr- $K\alpha$

<i>hkl</i>	<i>I</i> rel	$\sin^2 O$ Obs.	$\sin^2 O$ Calc.	<i>hkl</i>	<i>I</i> rel	$\sin^2 O$ Obs.	$\sin^2 O$ Calc.
111	vw	0.0181	0.0183	373			0.2347
131	w	0.0319	0.0323	235	w	0.2337	0.2332
231	w	0.0604	0.0602	155			0.2335
151			0.0604	471			0.2420
240	vw	0.0648	0.0653	2.10.2	m	0.2419	0.2418
013	vw	0.0675	0.0666	480	m	0.2611	0.2612
222	w	0.0728	0.0730	502			0.2612
251	w	0.0882	0.0883	255			0.2613
133	vw	0.0899	0.0900	404	vw	0.2639	0.2641
062	w	0.0920	0.0921	315	vw	0.2667	0.2656
242	m	0.0940	0.0941	075			0.2664
162	m	0.1013	0.1014	026			0.2666
053	vw	0.1082	0.1088	522	m	0.2690	0.2682
080	vw	0.1123	0.1125	106			0.2688
233	w	0.1179	0.1179	126			0.2759
153			0.1181	1.11.3	w	0.2758	0.2868
322	m	0.1193	0.1195	046	vw	0.2874	0.2877
024	m	0.1223	0.1224	444	w	0.2924	0.2922
262	m	0.1292	0.1293	533	vw	0.3133	0.3131
351	vw	0.1347	0.1348	2.12.2	w	0.3192	0.3191
342	m	0.1404	0.1406	562	w	0.3247	0.3245
280	w	0.1496	0.1497	246			0.3248
400			0.1487	464	w	0.3274	0.3273
182	m	0.1505	0.1506	415	vw	0.3308	0.3307
204	m	0.1526	0.1525	195	vw	0.3322	0.3319
144			0.1528	166			0.3321
411	m	0.1576	0.1577	600	m	0.3346	0.3346
173	w	0.1597	0.1603	3.12.0	st	0.3368	0.3367
224			0.1596	553	vw	0.3415	0.3412
333	w	0.1645	0.1644	580	m	0.3447	0.3448
431	m	0.1716	0.1717	435			0.3447
362	m	0.1757	0.1758	306			0.3432
440	m	0.1768	0.1768	631	vw	0.3571	0.3576
244	w	0.1803	0.1806	493			0.3560
422	m	0.1847	0.1846	266	w	0.3598	0.3600
291	w	0.1879	0.1868	3.12.2	w	0.3653	0.3656
164			0.1879	117			0.3643
115			0.1913	346	st	0.3714	0.3713
353	m	0.1912	0.1925	086			0.3720
451			0.1999	582	w	0.3734	0.3737
0.10.2	m	0.2046	0.2046	455			0.3729
442	m	0.2055	0.2057	137	vw	0.3783	0.3784
135			0.2053	651	vw	0.3858	0.3858
1.10.2	m	0.2139	0.2139	366	w	0.4060	0.4065
413	m	0.2154	0.2154	237			0.4062
193			0.2165	157			0.4065
215	w	0.2194	0.2192	2.12.4	w	0.4106	0.4056
344	st	0.2272	0.2271	2.14.2			0.4105
084	st	0.2280	0.2278	564	w	0.4140	0.4110
433	w	0.2293	0.2294	633			0.4153
				475			0.4151
				515			0.4144

Cu₃S III 20°C Cr-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² θ Obs.	sin ² θ Calc.
4.11.3	w	0.4263	0.4263
257	vw	0.4340	0.4344
0.10.6			0.4353
593			0.4396
4.10.4	w	0.4396	0.4398
317			0.4387
077			0.4394
653	vw	0.4438	0.4434
3.13.3	vw	0.4447	0.4456
177	w	0.4497	0.4487
604			0.4499
3.12.4			0.4521
624	vw	0.4565	0.4570
555			0.4565
584			0.4602
008	w	0.4612	0.4614
1.15.3	w	0.4690	0.4696
1.14.4			0.4691
028			0.4684
466	w	0.4756	0.4715
682			0.4759
0.16.2			0.4788
277	w	0.4786	0.4765
128			0.4777
722			0.4913
048	w	0.4903	0.4895

Cu_{1.96}S II 20°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² θ Obs.	sin ² θ Calc.
101	w	0.0419	0.0417
003			0.0421
102			0.0557
110	w	0.0741	0.0740
004	vw	0.0750	0.0749
103	st	0.0789	0.0791
111			0.0789
194			0.1119
113	w	0.1161	0.1161
200	m	0.1486	0.1480
114			0.1489
201			0.1527
202	w	0.1666	0.1667
203	w	0.1900	0.1901
211			0.1898
212			0.2037
106	vw	0.2055	0.2055
213	w	0.2273	0.2271
214	vw	0.2598	0.2599
107	w	0.2664	0.2663
215	m	0.3014	0.3020
221			0.3007
108			0.3365
301	w	0.3368	0.3377
223			0.3381
312			0.3887
217	w	0.4143	0.4143

Cu_{1.96}S III 20°C Cu-K α

sin ² θ Obs.	<i>I</i> _{rel}	sin ² θ Obs.	<i>I</i> _{rel}
0.0323	w	0.0906	w
0.0392	w	0.0936	w
0.0422	m	0.0968	w
0.0462	w	0.1017	w
0.0519	m	0.1040	st
0.0553	w	0.1106	w
0.0583	w	0.1131	w
0.0617	w	0.1157	w
0.0644	w	0.1292	w
0.0655	w	0.1336	w
0.0676	w	0.1385	w
0.0687	w	0.1416	w
0.0710	w	0.1539	m
0.0714	w	0.1550	m
0.0723	w	0.1697	st
0.0740	w	0.1771	w
0.0750	w	0.2077	m
0.0765	w	0.2102	w
0.0821	w	0.2591	w
0.0843	w	0.3659	m
0.0878	w	0.4732	w

Cu₃S II 460°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² θ Obs.	sin ² θ Calc.
102	m	0.1004	0.1007
110	st	0.1481	0.1482
103	st	0.1651	0.1649
112	w	0.1992	0.1995
201	vw	0.2109	0.2104

Cu₃S I 500°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² θ obs.	sin ² θ Calc.
111	w	0.0544	0.0542
200	w+	0.0722	0.0723
220	st	0.1445	0.1446
311	m	0.1991	0.1988

Phase $\text{Cu}_{1.9}\text{S}$ II 20°C Cu-K α

<i>hkl</i>	Composition							
	$\text{Cu}_{1.82}\text{S}$		$\text{Cu}_{1.78}\text{S}$		$\text{Cu}_{1.74}\text{S}$		$\text{Cu}_{1.70}\text{S}$	
	$\sin^2\Theta$ Obs.	<i>I</i> _{rel}	$\sin^2\Theta$ Obs.	<i>I</i> _{rel}	$\sin^2\Theta$ Obs.	<i>I</i> _{rel}	$\sin^2\Theta$ Obs.	<i>I</i> _{rel}
111	0.0512	vw	0.0515	vw			0.0516	vw
	0.0528	w	0.0527	vw	0.0528	vw	0.0526	vw
							0.0557	vw
200	0.0576	m+	0.0576	m+	0.0578	m	0.0579	m
	0.0656	m	0.0652	m	0.0647	w	0.0643	w
	0.0767	m+	0.0769	m+	0.0770	m	0.0771	m
	0.0784	vw	0.0794	vw			0.0828	vw
	0.0909	w	0.0919	vw	0.0929	vw	0.0949	vw
	0.1084	w	0.1070				0.1020	vw
							0.1172	vw
	0.1291	m	0.1284	m	0.1273	w	0.1257	w
					0.1297	vw	0.1303	vw
220					0.1358	vw	0.1368	vw
	0.1530	st	0.1536	st	0.1539	st	0.1543	st
	0.1802	vw	0.1791	vw			0.1760	vw
	0.1930	w	0.1918	w	0.1897	w	0.1876	w
							0.1914	vw
							0.2058	vw
311	0.2058	vw	0.2060	vw			0.2124	m
222	0.2109	m	0.2113	m	0.2117	m	0.2124	m
	0.2297	w	0.2301	w	0.2304	vw	0.2310	w
	0.2440	vw	0.2460	vw				
400	0.2825	w	0.2817	w	0.2812	vw	0.2799	vw
	0.3065	w	0.3071	w+	0.3081	w	0.3088	w
	0.3464	w	0.3455	w	0.3441	vw	0.3420	vw
	0.3592	vw	0.3598	vw			0.3604	vw
	0.3640	vw	0.3640	vw			0.3670	vw
	0.3716	vw	0.3721	vw			0.3730	vw
	0.3980	vw	0.3979	vw	0.3993	vw	0.4037	vw
	0.4106	vw	0.4094	vw				
	0.4352	vw	0.4348	vw			0.4347	vw
422	0.4597	m	0.4605	m	0.4623	m	0.4632	m

 $\text{Cu}_{1.8}\text{S}$ I 500°C Cu-K α

Composition $\text{Cu}_{1.82}\text{S}$			
<i>hkl</i>	<i>I</i> _{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
111	m—	0.0561	0.0561
200	m	0.0748	0.0748
220	st	0.1496	0.1495
311	w+	0.2057	0.2056
222	vw		
400	w	0.2984	0.2990
422	vw	0.4489	0.4486
511	}	0.5048	0.5046
333			

 $\text{Cu}_{1.96}\text{S}$ I 500°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
111	w	0.0548	0.0547
200	m	0.0729	0.0729
220	st	0.1459	0.1460
311	m	0.2005	0.2007

vw = strong
m = medium
w = weak
vw = very weak

The phase CuS

The powder photograph of this phase gave, for the hexagonal unit cell, the dimensions:

$$\begin{aligned} a &= 3.794 \pm 0.003 \text{ \AA} \\ c &= 16.332 \pm 0.010 \text{ \AA} \end{aligned}$$

in close agreement with the values of Oftedal¹¹ and Berry¹²

$$\left. \begin{aligned} a &= 3.80 \text{ \AA} \\ c &= 16.4 \text{ \AA} \end{aligned} \right\} \quad \text{and} \quad \left. \begin{aligned} a &= 3.796 \text{ \AA} \\ c &= 16.36 \text{ \AA} \end{aligned} \right\} \quad \text{respectively}$$

From the above it is evident that all the compounds, except CuS, have cubic, face-centred high-temperature modifications, whose diffraction lines show nearly the same relative intensity.

This points to a common high-temperature phase Cu_{2-x}S , where x can vary from 0 to at least 0.18 ($x > 0.18$ was not investigated). The variation of the unit cell edge of Cu_{2-x}S with the composition at 500°C, as shown in Fig. 1, supports this view.

DISCUSSION

The results of the present study are contradictory to the phase diagram reported by Buerger^{2,3}.

The fact that Buerger's results do not agree with those of the present author is not surprising because of the way Buerger's samples were prepared. According to Buerger, chalcocite and synthetic CuS powders were compacted, placed in an open glass tube and heated at a temperature of about 110°C for at least 12 h. This treatment is so much more astonishing as Buerger himself, later in his paper, states: "When chalcocite is heated in direct contact with air, it begins to convert to digenite", and "It appears, then, that oxygen can proxy for sulphur".

The data reported by Rühl⁴ are in good agreement with those of the present author. Thus he observed the diffraction pattern of Cu_2S only in the range Cu_2S — $\text{Cu}_{1.98}\text{S}$ (compare Table 2): and his Cu_2S -similar phase probably is the phase $\text{Cu}_{1.96}\text{S}$ III. The largest divergence between the work of Rühl and that of the present author concerns the homogeneity range of $\text{Cu}_{1.8}\text{S}$.

More work is needed to establish the composition-temperature phase diagram. Particular attention ought to be called to establishing the range of existence of the modifications of $\text{Cu}_{1.96}\text{S}$.

Acknowledgements. The author wishes to thank Professor G. Hägg for his encouraging interest in this investigation and Mr. H. Fischmeister and Mr. S. Rundqvist for stimulating discussions and valuable advice.

REFERENCES

1. Haugton, J. L. and Prince, A. *The constitutional diagrams of alloys: A Bibliography. Institute of Metals Monograph and Report Series No. 2*, 1956.
2. Buerger, N. W. *Am. Mineralogist* **27** (1942) 712.
3. Buerger, N. W. *Econ. Geol.* **36** (1941) 19.
4. Rühl, W. *Diplomarbeit. Röntgenuntersuchung des Phasendiagramms Cu_2S — CuS* , Physikal.-Inst. d. Univ. Erlangen 1952. *Private communication.*

5. Jensen, E. Avh. *Norske Videnskabs-Akad. Oslo I Math.-Nat. Kl.* No. 6 (1947).
6. Hirahara, E. *J. Phys. Soc. Japan* 6 (1951) 422.
7. Ueda, R. *J. Phys. Soc. Japan* 4 (1949) 287.
8. Kamaigaichi, T. *J. Sci. Hiroshima Univ. A* 16 (1952) 325.
9. Belov, N. V. and Butuzov, V. P. *C. R. Acad. Sci. USSR* 54 (1946) 717.
10. Buerger, M. J. and Buerger, N. W. *Am. Mineralogist* 29 (1944) 55.
11. Oftedal, I. *Z. Krist.* 83 (1932) 9.
12. Berry, L. G. *Am. Mineralogist* 39 (1954) 504.
13. Fischmeister, H. F. *J. Inorg. & Nuclear. Chem.* 3 (1956) 182.
14. Fischmeister, H. F. *Acta Cryst.* 9 (1956) 416.

Received May 5, 1958.