An X-Ray Study on the System Ag-Cu-S

SEVED DJURLE

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The phase relations in the ternary system Ag-Cu-S have been investigated by X-ray diffraction methods. Ternary phases of the following approximate compositions were found to exist:

$\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ (α), corresponding to the mineral jalpaite

$\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ (β) and

$\text{Ag}_{0.93}\text{Cu}_{1.07}\text{S}$ (γ), corresponding to the mineral stromeyerite.

At room temperature the α phase is tetragonal and its body-centred unit cell has the dimensions:

$a = 8.673 \text{ \AA}$, $c = 11.756 \text{ \AA}$.

It transforms at 112°C into a body-centred cubic lattice, which transforms at about 300°C into a face-centred cubic lattice.

The β phase has two transition temperatures, the lower one at about 97°C and the upper one at about 130°C . Attempts to index its powder pattern have not been successful. At room temperature the γ phase is orthorhombic but transforms at 90°C into a hexagonal lattice. A second transition occurs at about 180°C .

Present evidence indicates that the modifications above the highest transition temperatures all belong to a face-centred cubic phase $(\text{Ag,Cu})_2\text{S}$.

Previous investigators of the ternary system Ag-Cu-S have restricted themselves to the study of the "quasi-binary" system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$.

Schwartz¹ examined the relations of chalcocite (Cu_2S)-stromeyerite (AgCuS)-argentite (Ag_2S), using both microscopic and X-ray techniques. He found the ternary compound AgCuS , which had a transition at a temperature of 93°C . He also stated that there was "considerable solubility of Ag_2S in Cu_2S and of Cu_2S in Ag_2S ". The melting points of samples of various proportions of Ag_2S and Cu_2S followed a smooth curve, indicating complete solid solubility at high temperatures.

Suhr², contrary to Schwartz, could not find any extensive solid solution regions at room temperature. He found, in addition to Ag_2S , the compound AgCuS , the compound jalpaite, Ag_3CuS_2 , and two unknown compounds, one silver-rich, which he thought was off the $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ join, and the other copper-rich, which was not Cu_2S .

Using a natural crystal of stromeyerite, AgCuS , Suhr found the unit cell to be orthorhombic with the cell dimensions:

$$a = 4.06, \quad b = 6.66, \quad c = 7.99 \text{ \AA}.$$

A crystal structure determination of stromeyerite has been made by Frueh³.

EXPERIMENTAL

The preparative methods and the X-ray technique used in this study were the same as in a preceding paper on copper sulphides⁴.

As the third component of the system finely powdered Ag ("Finsilver", Grave, Stockholm) of better than 99.9 % purity was used.

The sintering temperature was 320, 470 or 500°C.

Selected samples were chemically analyzed. After the sample had been dissolved in fuming HNO_3 and the solution evaporated to dryness, the sample was dissolved in dilute HNO_3 and Ag was determined potentiometrically by titration with 0.1 M NaCl. The AgCl precipitate was filtered off and SO_4 and Cu were then determined as previously described⁴.

The composition, calculated from the weighed amounts of the elements, was in good agreement with the chemical analysis. The maximum deviation for each element was ± 0.5 atomic per cent.

RESULTS

The present study has revealed the existence of ternary phases at the approximate compositions

$\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S} = \alpha$ phase (composition corresponding to the mineral jalpaite)

$\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S} = \beta$ phase

$\text{Ag}_{0.93}\text{Cu}_{1.07}\text{S} = \gamma$ phase (composition corresponding to the mineral stromeyerite)

which all contain $33 \frac{1}{3}$ atomic per cent sulphur *i. e.* lie on the "quasi-binary" line $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ of the ternary diagram. At each of these three compositions three different modifications appear when the temperature is raised from room temperature. These modifications are denoted by Roman numerals (I for the one existing above the highest transition temperature observed). All phases of the general formula $\text{Ag}_{2-x}\text{Cu}_x\text{S}$ ($0 \leq x \leq 2$) are listed in Table 1.

Diffraction lines of the high temperature modifications of the ternary phases were only observed at elevated temperatures in the heating camera. Quenched specimens only showed lines of the III modifications at room temperature, which shows that the high temperature modifications transform too rapidly to be preserved by quenching. Data from powder photographs of the different phases are collected in Table 2.

The section of the phase diagram at 20°C which is given in Fig. 1 is based on Guinier powder photographs taken at room temperature of a great number of samples. All triangles of the diagram are three-phase regions except the one with the corners γ , $\text{Cu}_{1.80}\text{S}$ and $\text{Cu}_{1.73}\text{S}$, which represents a two-phase region. In his work on the system Cu—S the author⁴ has found that the phase denoted as $\text{Cu}_{1.8}\text{S}$ has a homogeneity range at least existing between the compositions $\text{Cu}_{1.80}\text{S}$ and $\text{Cu}_{1.73}\text{S}$.

Fig. 1. The phase diagram of Ag-Cu-S. Isothermal section at 20°C.

The α phases

The two transition temperatures observed are: the lower one 112°C, and the upper one 290–310°C.

α III

This modification is tetragonal and has a body-centred unit cell with the dimensions, at room temperature:

$$a = 8.673 \pm 0.004 \text{ \AA} \quad c = 11.756 \pm 0.006 \text{ \AA} \quad c/a = 1.355$$

Table 1. The sulphides of the general formula $\text{Ag}_{2-x}\text{Cu}_x\text{S}$ ($0 \leq x \leq 2$).

Compound	Composition (At.-%)			Approximate range of existence *	Crystal system
	Ag	Cu	S		
Ag_2S III Ag_2S II Ag_2S I	66.2/3	0	33.1/3	$< 177^\circ\text{C}$ 177–600 > 600	Monoclinic Cubic B.C. Cubic F.C.
α III α II α I	51.2/3	15	33.1/3	< 112 112–300 > 300	Tetragonal Cubic B.C. Cubic F.C.
β III β II β I	40	26.2/3	33.1/3	< 97 97–130 > 130	(Low-symmetric) Cubic F.C.
γ III γ II γ I	31	35.2/3	33.1/3	< 90 90–180 > 180	Orthorhombic Hexagonal Cubic F.C.
Cu_2S III Cu_2S II Cu_2S I	0	66.2/3	33.1/3	< 110 110–470 > 470	Orthorhombic Hexagonal Cubic F.C.

* Range of investigation 20–500°C, except for Ag_2S .

A Debye-Scherrer photograph taken at 105°C gave the values

$$a = 8.725 \pm 0.009 \text{ \AA} \quad \text{and} \quad c = 11.74 \pm 0.01 \text{ \AA}.$$

The fact that the a -axis expands and the c -axis contracts on heating, allows an unequivocal indexing.

The density, calculated from the cell constants, assuming 16 $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ per unit cell, is 6.8 g/cm^3 . Measuring of the density gave 6.9 g/cm^3 .

α II

The diffraction pattern of this modification has been indexed as body-centred cubic. The cell constant measured at different temperatures is,

$$\begin{array}{l} \text{at } 116^\circ\text{C} \quad a = 4.825 \\ \quad 152^\circ\text{C} \quad a = 4.836 \\ \quad 300^\circ\text{C} \quad a = 4.870 \end{array} \left. \vphantom{\begin{array}{l} 116^\circ\text{C} \\ 152^\circ\text{C} \\ 300^\circ\text{C} \end{array}} \right\} \pm 0.005 \text{ \AA}$$

The cell volume is $1/8$ of that of modification III, indicating 2 $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ as the cell contents.

α I

Due to the high background blackening, only two lines of the pattern of this modification could be discerned.

As will be shown below, the highest temperature modifications between Ag_2S I and Cu_2S I can all be indexed on the basis of a face-centred cubic cell, giving a straight line relationship between cell edge and composition.

The two lines of α I have therefore been given indices consistent with a face-centred cubic lattice.

The cube edge at three different temperatures is as follows:

$$\begin{array}{l} 300^\circ\text{C} \quad a = 6.110 \\ 400^\circ\text{C} \quad a = 6.123 \\ 500^\circ\text{C} \quad a = 6.140 \end{array} \left. \vphantom{\begin{array}{l} 300^\circ\text{C} \\ 400^\circ\text{C} \\ 500^\circ\text{C} \end{array}} \right\} \pm 0.006 \text{ \AA}$$

A cell content of 4 $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ is consistent with the cell constants.

The β phases

Two transition temperatures have been observed, The lower one occurs at 95 to 99°C and the upper one at 120 to 143°C. No satisfactory indexing of the diffraction patterns of the modifications β III and β II has been found.

β I

The pattern of β I was indexed as derived from a face-centred cubic lattice. The edge of the unit cube was found to be,

$$\begin{array}{lcl} \text{at } 151^{\circ}\text{C} & a = 5.999 & \\ 300^{\circ}\text{C} & a = 6.015 & \\ 500^{\circ}\text{C} & a = 6.042 & \end{array} \left. \vphantom{\begin{array}{l} \\ \\ \end{array}} \right\} \pm 0.006 \text{ \AA}$$

This is consistent with a cell content of $4 \text{ Ag}_{1.2}\text{Cu}_{0.8}\text{S}$.

The γ phases

The examination has revealed two transition temperatures, the lower one at 90°C and the upper one at about 180°C .

The value of the lower transition temperature is in good agreement with the value 93°C given by Schwartz ¹.

γ III

The Guinier photograph taken at room temperature gives an orthorhombic cell with the cell constants:

$$\begin{array}{l} a = 4.066 \pm 0.002 \text{ \AA} \\ b = 6.628 \pm 0.003 \text{ \AA} \\ c = 7.972 \pm 0.004 \text{ \AA} \end{array}$$

as compared with the values reported by Suhr ²

$$a = 4.06 \quad b = 6.66 \quad c = 7.99 \text{ \AA}$$

γ II

This modification has been indexed hexagonally, giving a unit cell with a cell content of $2 \text{ Ag}_{0.93}\text{Cu}_{1.07}\text{S}$ and the dimensions

$$\begin{array}{lcl} \text{at } 100^{\circ}\text{C} & \begin{array}{l} a = 4.138 \pm 0.004 \text{ \AA} \\ c = 7.105 \pm 0.007 \text{ \AA} \end{array} & \left. \vphantom{\begin{array}{l} \\ \end{array}} \right\} c/a = 1.983 \end{array}$$

and at

$$\begin{array}{lcl} 152^{\circ}\text{C} & \begin{array}{l} a = 4.158 \pm 0.004 \text{ \AA} \\ c = 7.068 \pm 0.007 \text{ \AA} \end{array} & \left. \vphantom{\begin{array}{l} \\ \end{array}} \right\} c/a = 1.963 \end{array}$$

γ I

With the indexing chosen, the unit cell is face-centred cubic, has a cell content of $4 \text{ Ag}_{0.93}\text{Cu}_{1.07}\text{S}$ and the following cell constant,

$$\begin{array}{lcl} \text{at } 196^{\circ}\text{C} & a = 5.961 & \\ 300^{\circ}\text{C} & a = 5.973 & \\ 500^{\circ}\text{C} & a = 5.993 & \end{array} \left. \vphantom{\begin{array}{l} \\ \\ \end{array}} \right\} \pm 0.009 \text{ \AA}$$

The phases occurring at the composition Ag_2S

The transition temperatures as found in the present study are in complete agreement with the work of Kracek ⁵. He states that there exist three modifications, the lower transition from Ag_2S III to Ag_2S II occurring between

176 and 178°C, the upper transition from Ag₂S II to Ag₂S I at a temperature of $586 \pm 3^\circ\text{C}$ in the presence of excess silver, and of $622 \pm 3^\circ\text{C}$ when sulphur is in excess.

Ag₂S III

The indexed Guinier photograph at room temperature gives a monoclinic unit cell with the following lattice parameters:

$$\left. \begin{array}{l} a = 9.531 \\ b = 6.925 \\ c = 8.278 \end{array} \right\} \pm 0.005 \text{ \AA}$$

$$\beta = 123.85 \pm 0.10^\circ$$

in fair agreement with the values of Ramsdell ⁶

$$a = 9.47 \text{ \AA}, \quad b = 6.92 \text{ \AA}, \quad c = 8.28 \text{ \AA}, \quad \beta = 124^\circ$$

Ag₂S II

Powder photographs of Ag₂S II were taken with the high-temperature camera, and the patterns have been indexed as belonging to a body-centred cube in accord with the work of Rahlfs ⁷. Only the three strongest lines of the patterns have been used for evaluating the cell edge. This is,

$$\left. \begin{array}{ll} \text{at } 189^\circ\text{C} & a = 4.870 \\ 300^\circ\text{C} & a = 4.890 \\ 500^\circ\text{C} & a = 4.926 \end{array} \right\} \pm 0.008 \text{ \AA}$$

The cell dimensions are in good agreement with the value 4.88 Å at 250°C given by Rahlfs.

Ag₂S I

A powder photograph of this modification was taken at 600°C. Due to the very high background blackening, only one line of the pattern could be seen. With regard to the suspected isomorphism of the highest temperature modifications, discussed below, and the fact that all the I modifications have /220/ as their strongest diffraction line, this line has been indexed as /220/ of a face-centred cubic lattice, with the cube edge $a = 6.269 \pm 0.020 \text{ \AA}$.

The I-modifications

As has been mentioned above, and as can be seen from Tables 1 and 2 all the I-modifications of the sulphides on the "quasi-binary" line Ag₂S—Cu₂S give X-ray diffraction patterns which can be indexed with a face-centred cubic

Table 2. X-Ray diffraction data of the phases Ag₂S, α , β and γ . α III 20° Cu-K α Ag₂S III 20°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² Θ Obs.	sin ² Θ Calc.
101	w	0.0124	0.0122
200	m	0.0318	0.0316
211	w	0.0440	0.0438
103	w	0.0467	0.0466
202	w	0.0490	0.0488
301	st	0.0755	0.0754
213	st	0.0783	0.0782
312	m	0.0963	0.0962
204	st	0.1004	0.1004
321	st	0.1072	0.1070
303	w	0.1098	0.1098
105	w	0.1153	0.1154
400	w	0.1266	0.1264
224	m	0.1319	0.1320
215	w	0.1467	0.1470
332	vw	0.1593	0.1594
116	vw	0.1706	0.1706
404	w	0.1952	0.1952
501	vw	0.2020	0.2018
334	vw	0.2109	0.2110
503	vw	0.2357	0.2362
415	vw	0.2417	0.2418
523	w	0.2677	0.2678
514	vw	0.2743	0.2742
532	w	0.2854	0.2858
611	w	0.2968	0.2966
336			0.2970
435	w	0.3049	0.3050
327	vw	0.3134	0.3134
534	w	0.3370	0.3374
525			0.3366
631	vw	0.3598	0.3598
516			0.3602
512	vw	0.4205	0.4201
329	vw	0.4515	0.4510

Ag₂S II 300°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² Θ Obs.	sin ² Θ Calc.
200	st	0.0992	0.0994
211	m	0.1491	0.1491
220	w	0.1989	0.1988

Ag₂S I 600°C Cu-K α

<i>hkl</i>	sin ² Θ Obs.
220	0.1210

<i>hkl</i>	<i>I</i> _{rel}	sin ² Θ Obs.	sin ² Θ Calc.
10 $\bar{2}$	vw	0.0355	0.0355
200	w	0.0379	0.0380
111	vw	0.0466	0.0466
002	m	0.0503	0.0503
210			
212	w	0.0519	0.0520
012	m	0.0627	0.0627
31 $\bar{1}$	m	0.0738	0.0738
121	m	0.0838	0.0838
220	st	0.0875	0.0875
222	m	0.0891	0.0891
11 $\bar{3}$	w	0.0986	0.0986
022	m	0.0999	0.0999
31 $\bar{3}$	w	0.1014	0.1014
40 $\bar{2}$	m	0.1047	0.1047
13 $\bar{1}$	w	0.1214	0.1214
123	vw	0.1355	0.1357
202	m	0.1370	0.1369
323	vw	0.1387	0.1386
204	w	0.1418	0.1418
212	w	0.1494	0.1493
230			0.1495
214	w	0.1542	0.1542
032	vw	0.1621	0.1618
410	w	0.1643	0.1642
414	w	0.1708	0.1707
040	vw	0.1982	0.1983
51 $\bar{1}$	w	0.2014	0.2012
420			0.2014
14 $\bar{1}$	vw	0.2082	0.2082
240	vw	0.2363	0.2362
332	vw	0.2459	0.2460
024	vw	0.2509	0.2508
34 $\bar{1}$	vw	0.2597	0.2597
133	vw	0.2706	0.2707
115	vw	0.2754	0.2754
553	vw	0.2794	0.2793
143	vw	0.2846	0.2844
511	vw	0.3235	0.3230
335	vw	0.3288	0.3287
242	vw	0.3354	0.3352
600	vw	0.3420	0.3415
214	vw	0.3490	0.3489
422			0.3490

α II 152°C Cu- $K\alpha$

hkl	I_{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
200	m	0.1016	0.1016
211	st	0.1524	0.1525
220	w	0.2033	0.2033
400	vw	0.4067	0.4066

 β III 20°C Cu- $K\alpha$

$\sin^2\Theta$ Obs.	I_{rel}
0.0371	w
0.0394	w
0.0484	m
0.0636	m
0.0725	m
0.0851	w
0.0873	st
0.0903	w
0.0933	w
0.0950	vw
0.1025	m
0.1114	m
0.1240	w
0.1267	w
0.1359	w
0.1386	m
0.1471	w
0.1567	m

 α I 500°C Cu- $K\alpha$

hkl	I_{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
220	st	0.1259	0.1261
311	w	0.1736	0.1734

 β II 99°C Cu- $K\alpha$

$\sin^2\Theta$ Obs.	I_{rel}
0.0920	w
0.1311	w
0.1384	st
0.1434	w
0.1512	st
0.1611	m

 β I 151°C Cu- $K\alpha$

hkl	I_{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
200	w	0.0660	0.0660
220	st	0.1322	0.1321
311	m	0.1816	0.1816
222	vw	0.1975	0.1981

 γ II 100°C Cu- $K\alpha$

hkl	I_{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
102	st	0.0933	0.0934
110	st	0.1388	0.1388
103	st	0.1521	0.1521
200 } 112 }	w	0.1856	{ 0.1852 0.1859
004	w	0.1888	0.1883
201	w	0.1967	0.1970

 γ I 500°C Cu- $K\alpha$

hkl	I_{rel}	$\sin^2\Theta$ Obs.	$\sin^2\Theta$ Calc.
220	st	0.1319	0.1324
311	w	0.1825	0.1820

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

γ III 20°C Cu-K α

<i>hkl</i>	<i>I</i> _{rel}	sin ² θ Obs.	sin ² θ Calc.	<i>hkl</i>	<i>I</i> _{rel}	sin ² θ Obs.	sin ² θ Calc.
002	vw	0.0375	0.0374	024	w	0.2033	0.2036
101	vw	0.0451	0.0453	221	w	0.2071	0.2073
110	m	0.0496	0.0495	222	w	0.2352	0.2353
020	m	0.0542	0.0541	213}	w	0.2417	{0.2414
021	w	0.0635	0.0635	133}			{0.2418
112	st	0.0868	0.0868	233	w	0.2819	0.2820
022	m	0.0915	0.0915	204	m	0.2934	0.2932
113	vw	0.1333	0.1335	224	w	0.3476	0.3474
023	w	0.1382	0.1382	312}	w	0.3747	{0.3744
200	m	0.1438	0.1438	150}			{0.3742
004	m	0.1494	0.1494	116}	w	0.3863	{0.3857
131}	m	0.1670	{0.1671	321}			{0.3870
211}			{0.1667	026}			{0.3904
132}	m	0.1949	{0.1951	135}	w	0.3912	{0.3912
212}			{0.1947	215}			{0.3908
220	w	0.1975	0.1979	331	vw	0.4551	0.4547
114	w	0.1986	0.1989				

unit cell. They also have comparable line intensities. The values of the cube edge, extrapolated to 600°C from values at different temperatures in order to be comparable, are as follows:

<i>x</i> in Ag _{2-x} Cu _x S	<i>a</i> , Å
0	6.269 ± 0.020
0.45	6.153 ± 0.006
0.80	6.055 ± 0.006
1.07	6.000 ± 0.009
2.00	5.752 ± 0.010

The value for Cu₂S I is extrapolated from measurements reported in Ref.⁴

Fig. 2. Variation of cube edge of Ag_{2-x}Cu_xS with *x*.

The values of the cell edge are plotted against the composition in Fig. 2, and within the errors of measurement, a straight line is obtained for the variation of the cell edge with the composition.

This indication of isomorphous phases with complete solid solubility is in accord with the melting point curve determined by Schwartz¹.

From the present investigation it thus seems probable that in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ there is only one common highest temperature modification $\text{Ag}_{2-x}\text{Cu}_x\text{S}$, $0 \leq x \leq 2$.

With regard to the face-centred cubic phase Cu_{2-y}S , where y varies from 0 to at least 0.18, in the system $\text{Cu}-\text{S}^4$, there is a possibility, not investigated, that the ternary phase $\text{Ag}_{2-x}\text{Cu}_x\text{S}$ could also exist with a small deficit of copper and/or silver atoms.

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