

Phase transitions in cuprous sulphide evaporated thin films

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The films of Cu_xS ($1 \leq x \leq 2$), prepared by evaporation in vacuum and condensation of stoichiometric sulphides of copper, change their phases by heat treatment in vacuum. Cu_2S chalcocite appears as the most stable phase in the range 270 to 450°C and the other sulphur rich phases transform into chalcocite presumably by a loss of sulphur. By electron diffraction we have confirmed the low temperature monoclinic chalcocite phase, the high temperature hexagonal chalcocite phase, the monoclinic djurleite phase, the cubic digenite low and high temperature forms and the hexagonal covellite phase. The low temperature digenite phase presents a superstructure which is similar to that observed by Kazinets *et al.* on digenite prepared by evaporation in vacuum on a single crystal substrate of NaCl at temperatures of 350 to 400°C. Electron diffraction data of chalcocite (Cu_2S), djurleite ($\text{Cu}_{\sim 1.93}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$) are presented.

1. Introduction

The study of thin films of cuprous sulphide Cu_xS in the range $1 \leq x \leq 2$ is of interest for their applications, particularly the compound Cu_2S chalcocite. The main application of chalcocite at present is in thin film solar cells of the Cu_2S -CdS type where it is used as the active part of the heterojunction. By increasing the knowledge of structures and behaviours of cuprous sulphide thin films obtained by evaporation in high vacuum the improvement of the cell characteristics may be stimulated.

Electron diffraction work on Cu_xS films obtained by vacuum evaporation have been done by Rastogi *et al.* [1] and Kazinets *et al.* [2], using glass or NaCl single crystals as substrates. The first authors studied the effect of the glass substrate temperature on the film phase composition observing Cu-rich phases for lower temperatures. At

room temperature they found the orthorhombic and hexagonal phase of chalcocite and metallic copper at 300 K of substrate temperature, while hexagonal chalcocite and djurleite at 400 K and djurleite and $\text{Cu}_{1.93}\text{S}$ at 475 K, respectively. Our present results observed on specimens prepared on amorphous soluble substrates at room temperature do not agree with the analogous ones of these authors.

Kazinets *et al.* [2] have used single crystals of NaCl at 350 to 400°C as substrates and have evaporated $\text{Cu}_{1.8}\text{S}$. They observed an epitaxial relation and a new structure phase of digenite, stable at room temperature, that we have also observed with amorphous substrates.

2. Experimental conditions

The films studied have been obtained by evaporation of chalcocite, djurleite and anilite synthesized

TABLE I Deposition conditions and "as-grown" phase

Material evaporation	Sample	Thickness (nm)	Deposition rate (nm min ⁻¹)	"As-grown" phase
Chalcocite	EC-1	105.0	10.0	Chalcocite
	EC-2	45.0	10.0	Chalcocite
	EC-3	20.0	5.0	Chalcocite
	EC-4	40.0	2.0	Digenite 2a
Djurleite	ED-1	115.0	10.0	Chalcocite + Djurleite
	ED-2	85.0	5.0	Chalcocite
	ED-3	50.0	2.0	Djurleite + Digenite 2a
Anilite	EA-1	155.0	10.0	Chalcocite + unknown phases
	EA-2	70.0	5.0	Digenite 2a + djurleite
	EA-3	55.0	2.0	Covellite + digenite

in the laboratory after identification of the phases by powder X-ray diffraction. The evaporation has been carried out in a vacuum of 10^{-5} torr with the substrate at room temperature, the distance to the tungsten crucible being less than 14 cm and the deposition rate ranging from 2.0 to 10.0 nm min⁻¹.

The substrate used in all cases was acetate butyl cellulose that was later dissolved in methyl acetate. Sulphides with compositions in the range $1 \leq x \leq 2$ have been obtained.

The samples so obtained have been examined by electron diffraction in a Philips EM 301 electron microscope with hot stage, using the minimum electron beam intensity compatible with the observation. Some selected samples had a 20 nm thick evaporated aluminium film that was used for calibration purposes taking into account the variation of the lattice constant [3]. When the aluminium film was used, heating temperatures were limited to 150°C in order to avoid its diffusion into the sulphide.

3. Results

Four samples of films obtained by evaporation of chalcocite were observed having 20 to 105 nm thickness. Table I indicates deposition conditions and as-grown phases.

All the samples give diffraction diagrams of polycrystalline fine grained films at room temperature prior to heating. Fig. 1 shows one of these diagrams corresponding to the monoclinic chalcocite phase. By heating the samples of the monoclinic chalcocite the transformation to

hexagonal chalcocite is found to occur in the range 63 to 83°C [4] and is reversible on cooling.

When cooling down, the transformation to monoclinic chalcocite is observed and the diffraction diagram shows numerous sharper rings (Fig. 2). This diffraction pattern has allowed us to measure the room temperature interplanar distances and visual intensities of electron diffraction which are summarized in Table II.

In Table III similar data are given for the high temperature hexagonal phase of chalcocite obtained in this work that agree with the X-ray data of Djurle [6].

Fig. 3 is obtained on the EC-4 sample which presents the crystallographic plane distances summarized in Table IV. This phase corresponds to the

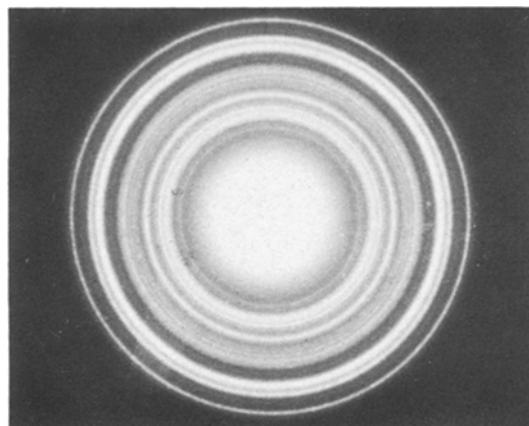


Figure 1 Electron diffraction diagram of sample EC-2, corresponding to the low temperature chalcocite phase.

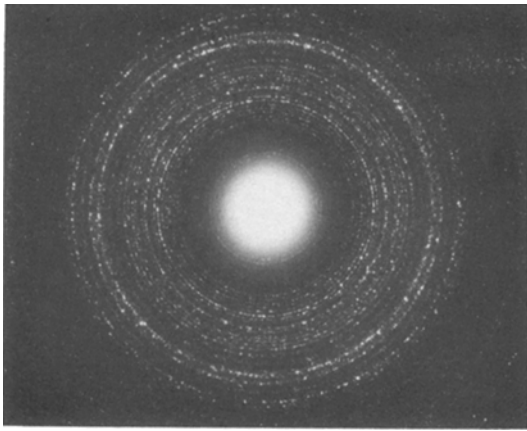


Figure 2 Electron diffraction diagram of sample EC-2 after heat treatment of the low temperature chalcocite phase.

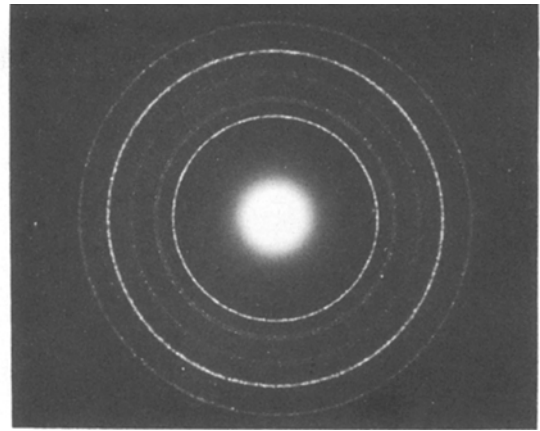


Figure 3 Electron diffraction diagram of sample EC-4 corresponding to the low temperature digenite phase.

TABLE II Diffraction data of the monoclinic chalcocite phase ($a = 1.5235$ nm, $b = 1.1885$ nm, $c = 1.3496$ nm and $\beta = 116.26^\circ$ [5])

I	Electron diffraction	
	d_{obs} (nm)	(hkl)
vw	1.391	(100)
vw	1.185	(010)
vw	0.901	(110)
vw	0.857	{(011)}
		{(11 $\bar{1}$)}
vw	0.642	{(21 $\bar{1}$)}
		{(111)}
w	0.594	{(020)}
		{(210)}
vw	0.537	(21 $\bar{2}$)
		{(220)}
vw	0.447	{(31 $\bar{2}$)}
		{(22 $\bar{2}$)}
vw	0.424	{(022)}
		{(32 $\bar{2}$)}
w	0.374	{(122)}
		{(41 $\bar{2}$)}
w	0.360	{(212)}
		{(230)}
2	0.342	{(400)}
		{(10 $\bar{4}$)}
w	0.328	{(30 $\bar{4}$)}
		{(42 $\bar{2}$)}
w	0.320	{(222)}
		{(11 $\bar{4}$)}
vw	0.316	{(31 $\bar{4}$)}
		{(33 $\bar{2}$)}
M	0.3051	{(132)}
		{(51 $\bar{2}$)}
w	0.2955	{(312)}
		{(14 $\bar{1}$)}
w	0.2876	{(041)}

TABLE I Continued

I	Electron diffraction	
	d_{obs} (nm)	(hkl)
m	0.2725	(240)
		{(24 $\bar{2}$)}
vw	0.2662	{(042)}
		{(402)}
w	0.2531	{(60 $\bar{2}$)}
		{(60 $\bar{2}$)}
w	0.2479	{(412)}
m	0.2405	(204)
		{(422)}
w	0.2331	{(62 $\bar{2}$)}
		{(440)}
w	0.2235	{(15 $\bar{2}$)}
vw	0.2210	{(31 $\bar{6}$)}
		{(44 $\bar{4}$)}
vw	0.2122	{(044)}
		{(243)}
vw	0.2092	{(54 $\bar{3}$)}
vw	0.2026	
vw	0.1995	
S	0.1975	{(630)}
vw	0.1949	{(060)}
vw	0.1904	
M	0.1879	{(13 $\bar{6}$)}
		{(53 $\bar{6}$)}
		{(10 $\bar{6}$)}
		{(70 $\bar{6}$)}
vw	0.1804	
vw	0.1787	
vw	0.1746	
vw	0.1727	
M	0.1706	

TABLE III Diffraction data of the hexagonal chalcocite phase* ($a = 0.395$ nm, and $c = 0.678$ nm)

I	Electron diffraction*	
	d_{obs} (nm)	(hkl)
m	0.3424	{(002) (100)
S	0.3055	(101)
m	0.2392	(102)
S	0.1975	(110)
M	0.1887	(103)
M	0.1698	{(200) (112) (004)
M	0.1659	(201)
vw	0.1516	{(104) (202)
w	0.1361	(203)
w	0.1287	{(210) (114)
vw	0.1275	(211)
w	0.1264	(105)
vw	0.1138	{(300) (301)
w	0.1120	(213)

*at 120°C.

†at 460°C.

low temperature digenite phase of cubic structure having a superstructure ($a = 1.114$ nm) that has been obtained by Kazinets *et al.* [2] evaporating a synthesized compound of $\text{Cu}_{1.8}\text{S}$ composition in vacuum on the (100) face of a NaCl single crystal at temperature of 350 to 400°C [2]. For comparison the data of these authors are also indicated in Table IV.

By heating up the digenite superstructure the transformation to cubic digenite ($a = 0.557$ nm) with face centred cubic symmetry is observed in the range 50 to 60°C (Fig. 4). The transformation

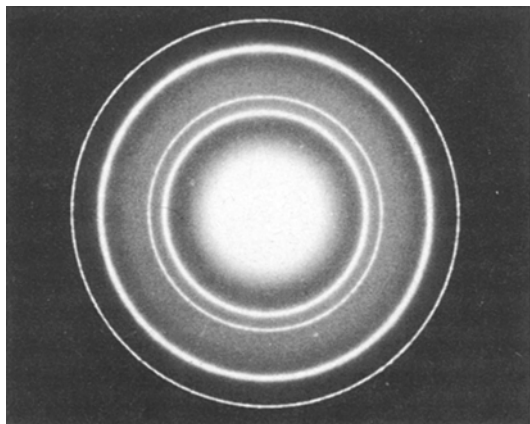


Figure 4 Electron diffraction diagram of sample EC-4 at 91°C showing temperature cubic digenite phase.

TABLE IV Electron diffraction data of the low temperature phase of digenite (cubic phase: $a = 1.114$ nm)

I	Present work	(hkl)	by Kazinets <i>et al.</i> [2]
	d_{obs} (nm)		d_{obs} (nm)
		(100)	1.121
		(200)	0.565
vw	0.377	{(221) (300)	0.374
S	0.322	(222)	0.323
		(320)	0.312
		(321)	0.300
m	0.2780	(400)	0.280
m	0.2726	{(410) (322)	0.272
		(330)	0.264
		(420)	0.251
		(332)	0.239
w	0.2295	(422)	0.229
w	0.2241	{(430) (500)	0.224
S	0.1970	(440)	0.1985
vw	0.1952	{(441) (552)	0.1950
		{(530) (433)	0.1925
vw	0.1881	{(442) (600)	0.1875
		{(540) (443)	0.1750
vw	0.1750	(621)	
m	0.1695	(533)	
M	0.1682	(622)	0.1696
		(631)	0.1650
vw	0.1612	(444)	0.1610
		{(641) (720)	0.1545
		(642)	0.1495
		{(544) (722)	0.1483
w	0.1395	(800)	0.1400
		(820)	
		(644)	0.1360
vw	0.1326	{(660) (822)	0.1320
vw	0.1278	(662)	0.1288
vw	0.1263	(840)	0.1259
vw	0.1226	(842)	0.1228
vw	0.1192	(664)	0.1193
w	0.1134	(844)	0.1147

takes place in a reversible way when the thermal cycle does not exceed 200°C. The high temperature form is similar to that observed by Morimoto and Kullerud [7] and Rhalfs [8] and is retained up to 270°C. Above this temperature this cubic phase transforms slowly into a hexagonal phase identified as chalcocite. On cooling down the hexagonal phase transforms into monoclinic chalcocite at temperatures below 63°C.

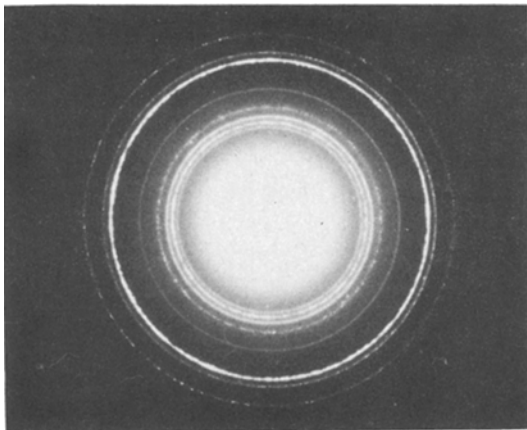


Figure 5 Electron diffraction diagram of sample ED-1 at 74°C showing the form of cubic digenite and hexagonal chalcocite.

Three films obtained by evaporating djurleite have been examined, with 115, 85 and 50 nm thickness. At room temperature in the “as-grown” condition, different phases have been found as indicated in Table I. The digenite is the low temperature superstructure mentioned above.

On heating up, sample ED-1 at 70 to 90°C becomes hexagonal chalcocite with traces of cubic high temperature form of digenite up to 270°C and at this temperature the cubic digenite disappears (Figs. 5 and 6). Heating up to 360°C does not produce any change in the hexagonal chalcocite phase and on cooling down it transforms into monoclinic chalcocite below 63°C. The chalcocite film of sample ED-2 shows, on heating, a similar behaviour as that of the chalcocite films described previously. Sample ED-3 presents the diffraction

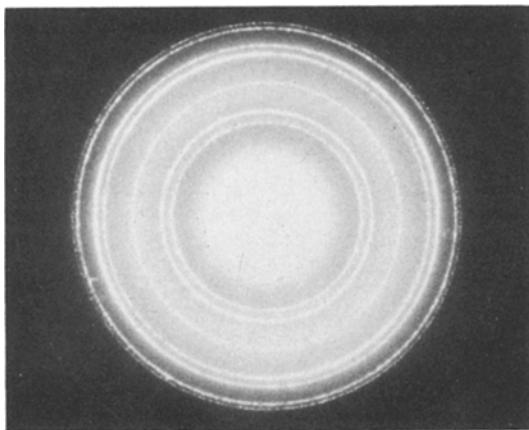


Figure 6 Electron diffraction diagram of sample ED-1 at 120°C showing chalcocite phase.

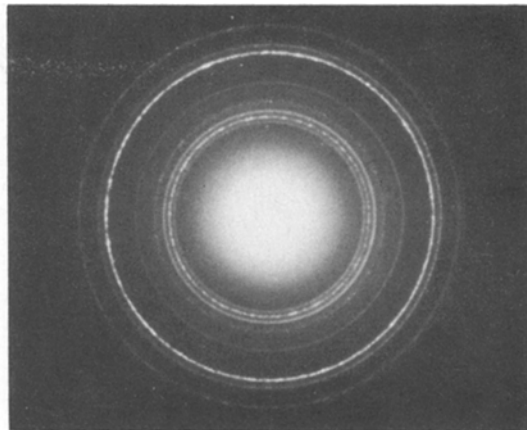


Figure 7 Electron diffraction diagram of the djurleite phase and the digenite low temperature phase.

pattern of Fig. 7 and on heating it transforms into hexagonal chalcocite and digenite at 70 to 90°C. Above 270°C the digenite phase disappears, remaining the hexagonal chalcocite only. On cooling down below 63°C the hexagonal chalcocite transforms into a mixture of phases (Fig. 8) with many spots and streaks of diffraction that we could not identify. Fig. 9 shows an electron diffraction diagram of the djurleite phase. In Table V, the lattice spacings and visual intensities for electron diffraction of the djurleite phase are summarized, showing good agreement with the data of X-ray diffraction reported by Potter and Evans [5] and Evans [9].

Three samples have been obtained from evaporated anilite. Deposition conditions and

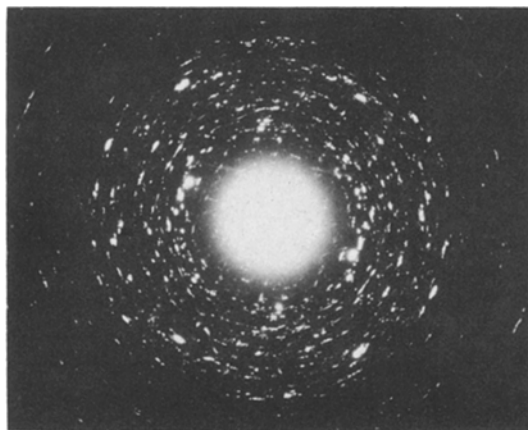


Figure 8 Electron diffraction diagram of sample ED-3 corresponding to a mixture of non identified phases after heating up to 370°C and cooling down to room temperature.

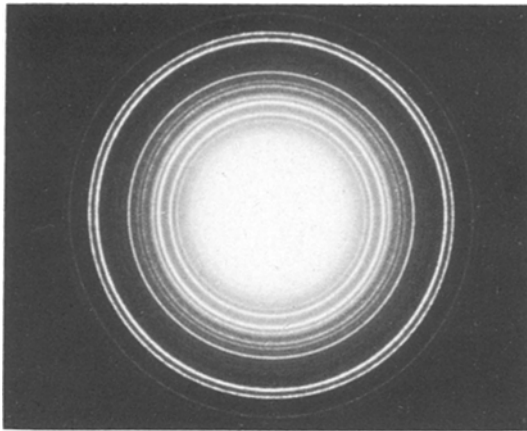


Figure 9 Electron diffraction diagram of sample ED-1 "as-grown" corresponding to the djurleite phase.

phases found by electron diffraction are given in Table I.

On heating sample EA-3 up to 320°C the mixture of covellite and digenite remains unchanged (Fig. 10) and at this temperature it transforms first into digenite and later on, in a short time interval at the same temperature, into hexagonal chalcocite. This phase is stable up to 430°C although a recrystallization into large grains is observed producing a single crystal electron diffraction diagram (Fig. 11). Decreasing the temperature, the hexagonal phase is stable down to 63°C temperature at which electron diffraction patterns showing the presence of chalcocite and djurleite appear. In a second thermal cycle the chalcocite plus djurleite mixture becomes hexagonal chalcocite at a temperature in the range 63 to 83°C, which stays

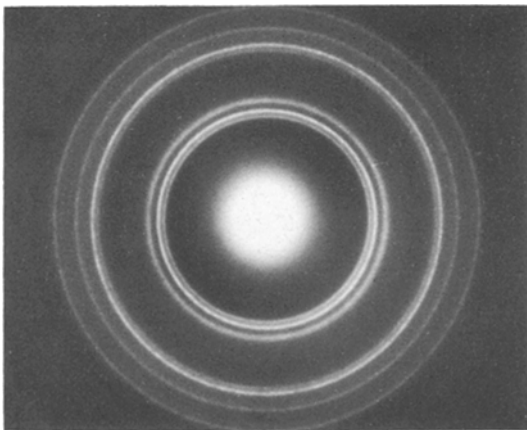


Figure 10 Electron diffraction diagram of showing the covellite and the high temperature form of digenite sample EA-3 at 50°C.

TABLE V Diffraction data of the djurleite phase (monoclinic: $a = 2.6897$ nm, $b = 1.5745$ nm, $c = 1.3565$ nm and $\beta = 90.13^\circ$ [9])

I	Electron diffraction	
	d_{obs} (nm)	(hkl)
vw	0.686	{(220) (002) (410) (130)
vw	0.476	{(421) (402)
w	0.431	{(610) (331)
w	0.360	{(711) (340)
w	0.339	{(133) (440) (004) (811) (821) (802)
M	0.3021	(901)
m	0.2919	{(542) (911)
vw	0.2863	{(424) (514) (10,00) (105) (524) (205) (115)
vw	0.2685	
w	0.2650	
vw	0.2572	
m	0.2388	(842)
vw	0.2347	
vw	0.2261	
vw	0.2191	
vw	0.2124	
vw	0.2011	
S	0.1950	(146)
M	0.1872	(12.42)
vw	0.1802	
m	0.1691	
m	0.1639	
vw	0.1518	
vw	0.1445	
w	0.1414	
w	0.1350	
w	0.1274	
w	0.1257	

unchanged up to 420°C. A thermal treatment of 20 min at this temperature produces, on cooling down, only monoclinic chalcocite below 63°C. As shown in Fig. 12 the start of the transformation shows up in the form of haloes and Fig. 13 shows the diagram at the end of the transformation. Fig. 14 shows a monocrystalline electron diffraction diagram of the djurleite phase [10, 11], obtained



Figure 11 Electron diffraction diagram of sample EA-3 after heat treatment showing monocrystalline hexagonal chalcocite (at 105°C).

after one thermal cycle of EA-2 in vacuum. Sample EA-2 behaves in a similar way as sample ED-3 on thermal cycling.

4. Discussions and conclusions

The thermal evaporation in vacuum of cuprous sulphides produces, by condensation on a non intentionally heated amorphous substrate, copper sulphide phases that in general do not maintain the source compositions. Although the deviation of stoichiometry is not large it is sufficient to produce other phases richer in sulphur. The composition of the films obtained is sensitive to the deposition rate, the higher deposition rate keeping the stoichiometry of the source at the film.

The thermal treatments inside the electron



Figure 12 Electron diffraction diagram of the same sample as in Fig. 11, at 85°C, showing hexagonal chalcocite with some haloes.

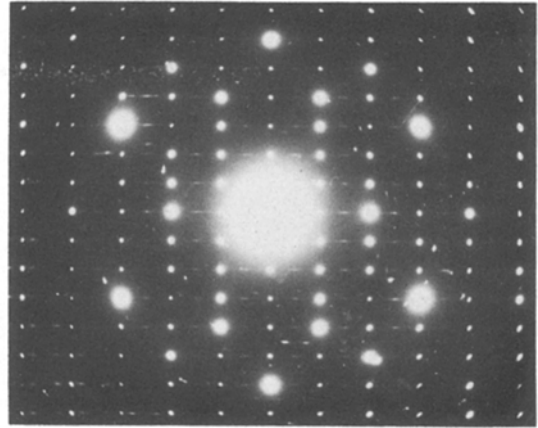


Figure 13 Electron diffraction diagram of same sample as in Fig. 12, at 30°C, showing monocrystalline monoclinic chalcocite.

microscope produce new phases in which the fraction of copper increases up to the Cu_2S composition. This might be due to the loss of sulphur by evaporation in vacuum. The thermal stability of Cu_2S is good up to 450°C, after which neither metallic copper nor copper oxides appear. All the interplanar distances of phases observed by electron diffraction in this work, i.e. the low temperature monoclinic chalcocite phase, the high temperature hexagonal chalcocite phase, the djurleite phase, are in good agreement with those of X-ray diffraction data [5, 9].

Concerning the digenite phase, we have observed a superstructural modification of type 2a at room temperature after thermal cycling. This phase is similar to an epitaxial phase found by Kazinets *et al.* [2] when evaporating digenite on single crystal NaCl substrates at temperatures 350

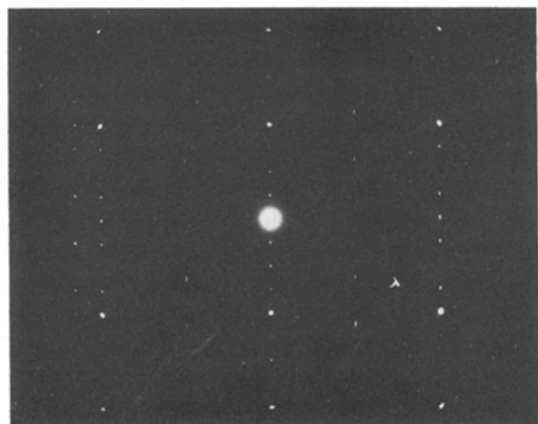


Figure 14 Electron diffraction diagram of the monocrystalline djurleite phase.

to 400°C, as is shown in Table IV. This low temperature form of digenite transforms, by heating in vacuum, into a high temperature form with a face centred cubic symmetry in the range 50 to 60°C. The superstructure of types 5a and 6a of the digenite phase at room temperature is observed in thinned single crystals by several workers and discussed in terms of twinning [7,12, 13]. We could not, however, confirm this type of superstructure on our polycrystalline evaporated thin films.

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Received 15 April

and accepted 26 April 1983