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The phase transition of djurleite thin films

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Thin films of djurleite have been examined by TED in order to study the phase transition at 86° C. The samples were heated during observation in the electron microscope. Under these conditions no intermediate phase was found, but we have found two different orientations of the djurleite supercell with respect to the high chalcocite cell. The transformation matrix was determined.

1. Introduction

Thin films of cuprous sulphide have been studied in relation to their application in photovoltaic solar cells of the $Cu_{2-x}S$/CdS type where they have the active role of the heterojunction. It is well known [1, 2] that the stable phases in the range of composition $1.93 \leqq x \leqq 1.965$ at room temperature are djurleite and at temperatures higher than 93° C digenite and high chalcocite. The transformation of djurleite to high chalcocite is matter of disagreement, and has been studied by transmission electron diffraction (TED) by Putnis [3, 4] and Conde [5], heating the samples with the electron beam. These workers have found an intermediate phase between djurleite and high chalcocite, but Potter [1], Potter and Evans [6], Evans [7] and Roseboom [2] have not reported any intermediate phase.

In this work we have examined the phase transformation of djurleite by transmission electron diffraction. The electron diffraction patterns were interpreted by means of data published in [8, 9].

2. Experimental procedure

Thin films were prepared by vacuum evaporation of djurleite [8–10] obtained by synthesis in our laboratory using "specpur" Johnson and Mathey copper and tridistilled sulphur.

The evaporation was carried out in a vacuum of less than 10^{-5} torr using a Tungsten basket. The speed of deposition was about 5 nm min^{-1} [8, 9]. The film was grown on an amorphous butyl acetate cellulose substrate, near to room temperature placed at about 8 cm from the source. Thin film thickness ranged from 50 to 100 nm as measured with a surface profile measuring system (Talystep).

After dissolving the substrate, thin film specimens were examined by transmission electron diffraction (TED) in a Philips EM 301 electron microscope at 100 kV. The samples were heated in the hot stage of the electron microscope, the temperatures at the sample holder were measured with a cromel-alumel thermocouple, and ranged from 20 to 450° C. The observations were performed at the minimum beam intensity compatible with the visibility of the diffraction rings, in order to minimize heating by the electron beam.

3. Results

The TED showed the films to be in the "as-grown" conditions, polycrystalline and they contained a mixture of sulphides mainly digenite and djurleite (Fig. 1). By heating up these films at 86° C in the electron microscope we observed a change in the electron diffraction pattern of Fig. 1 to the diagram of Fig. 2. This pattern corresponded to a mixture of high chalcocite and high digenite. Heating the sample to 400° C for 2 min at a pressure of $\cong 10^{-5}$ torr, a recrystallization was produced as shown in the electron diffraction patterns taken at room temperature (Figs 3 and 4) corresponding to a single crystal of djurleite,

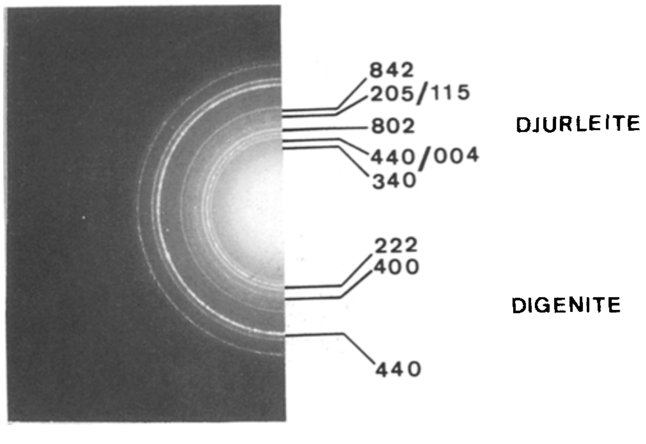

Figure 1 Electron diffraction (ED) pattern of a cuprous sulphide film "as-grown" corresponding to djurleite and digenite.

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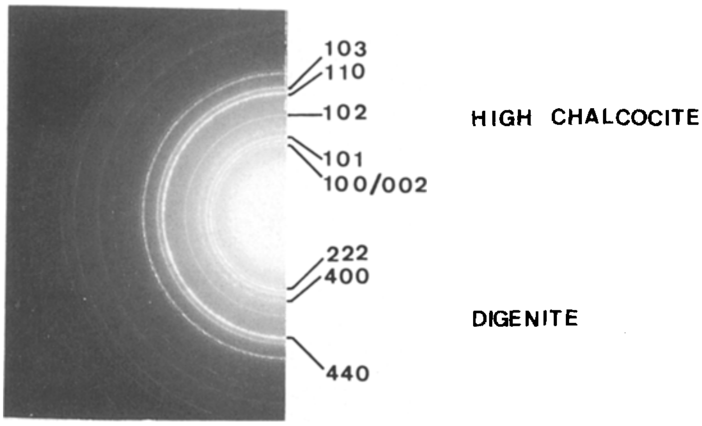

Figure 2 ED pattern of the same film as Fig. 1, but at $T > 83°$ C, corresponding to digenite and high chalcocite.

monoclinic phase with lattice constants $a = 2.6897$ nm, $b = 1.5745$ nm, $c = 1.3565$ nm and $b = 90.13°$, the diagrams show a pseudo-orthorhombic symmetry. By heating to 86° C the single crystal of djurleite changed to a single crystal of high chalcocite (Figs 5 and 6). In this first thermal cycle ($T_{\max} \cong 400°$ C) a non-reversible phase transition was produced from digenite and djurleite to the sulphide rich copper djurleite, which can be attributed to a loss of sulphur. It is well known that djurleite Cu_xS is stable only in the range of composition $1.942 \leqq x \leqq 1.988$. Then we started the next thermal cycles, for a sample of djurleite with a known range of composition.

After this first thermal cycle no preferential orientation of djurleite single crystal was found in the sample, by tilting the films in a definite position of the tilting stage we found diffraction patterns of djurleite single crystal as is shown in the Figs 3 and 7. These diagrams had the same main diffraction spots. When we heated the sample above 86° C we obtained only the same electron diffraction pattern of the high chalcocite single crystal, corresponding to the ⟨1 1 1⟩ zone. Cooling down we could obtain again the electron diffraction patterns of Fig. 3 and 7, corresponding to one or several of the three orientation variants (twinned or untwinned) of djurleite for the same high chalcocite orientation (⟨1 1 1⟩ zone).

By tilting the samples from the former position we found an electron diffraction pattern corresponding to djurleite ⟨1 0 0⟩ zone (Fig. 4). Heating above 86° C we observed the electron diffraction diagram of the ⟨0 0 1⟩ zone of high chalcocite (Fig. 6).

In many samples we have found an electron diffraction pattern (Fig. 8) corresponding to the ⟨0 1 4⟩ zone of djurleite. Heating these samples cause the electron diffraction pattern to turn to diagram Fig. 9, corresponding to the ⟨1 1 2⟩ zone of high chalcocite.

The phase transformation was reversible with a temperature hysteresis of about 13° C, the transition occurred between 73 and 86° C.

4. Discussion

The djurleite high chalcocite transformation occurs without any intermediate phase, we did not observe any isochemical transition between djurleite and low chalcocite. This agrees with the results of Potter and Evans [6] and Evans [7], but is in disagreement with those of Putnis [3, 4]. This worker observed an intermediate phase between djurleite and high chalcocite and a transition between djurleite and low chalcocite by electron diffraction, varying the temperature of a selected area by changing the electron beam intensity. Working in this way produces temperature gradients in the samples and then the copper ions can diffuse inward or outward of the selected observation area. Our observations were made, however, with a homogeneous temperature in the sample, at the minimum electron beam intensity compatible with the observation.

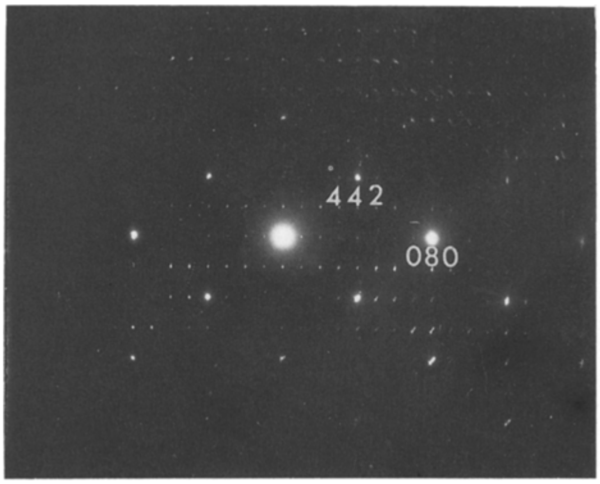

Figure 3 ED pattern of zone ⟨1 0 2⟩ djurleite film.

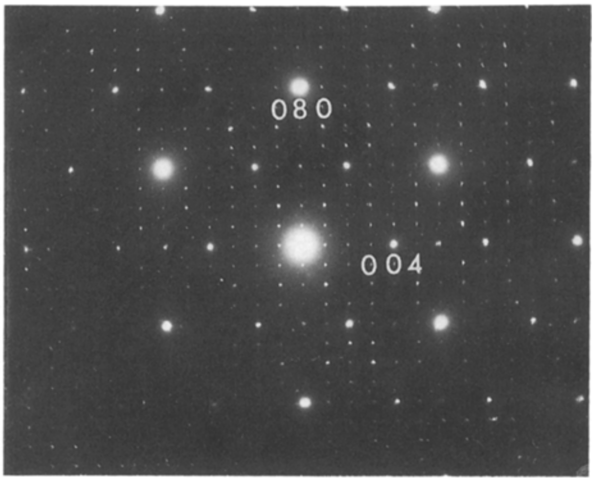

Figure 4 ED pattern of djurleite corresponding to ⟨1 0 0⟩ zone.

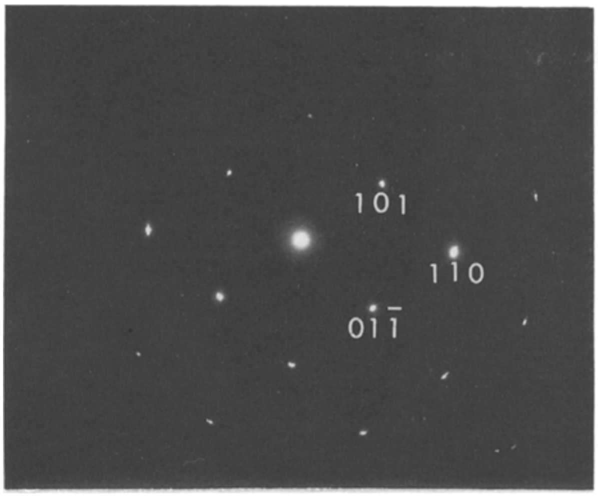

Figure 5 ED pattern of same film as Fig. 3 but at $T > 83°$ C corresponding to $\langle 1\,1\,1\rangle$ zone of high chalcocite.

Figure 7 ED pattern of a mixture of djurleite variants, $\langle 1\,0\,2\rangle$ and $\langle 2\,3\,2\rangle$ zones.

of djurleite to high chalcocite occurs between 73 and 86° C, lower than the transition temperature in the bulk 90–93° C for Cu_xS ($1.942 \leqslant x \leqslant 1.988$) [1]. This fact also occurs in low chalcocite thin films [8, 9].

In the following paragraphs the structural relation between high chalcocite and djurleite are analysed.

Comparing the electron diffraction patterns of Figs 3 and 4 with those of the Figs 5 and 7, respectively, we deduce three relations for the transformation matrix

$$\begin{aligned}(1\,1\,0)\,\tau_{\mathrm{DI}} &= (0\,8\,0)\\(1\,0\,1)\,\tau_{\mathrm{DI}} &= (4\,4\,2)\\(1\,\bar{1}\,0)\,\tau_{\mathrm{DI}} &= (0\,0\,4)\end{aligned}$$

The indexes on the right corresponding to djurleite. The matrix is

$$\mathrm{DI} = \begin{bmatrix} 0 & 4 & 2\\ 0 & 4 & -2\\ 4 & 0 & 0\end{bmatrix}$$

The hexagonal plane $(0\,0\,1)$ transforms into the plane $(4\,0\,0)$ monoclinic (pseudorthorhombic). We can find a relation between the djurleite and high chalcocite cell parameter. The inverse matrix should satisfy the relation

$$\begin{aligned}(0\,8\,0)\,\tau_{\mathrm{DI}}^{-1} &= (1\,1\,0)\\(0\,0\,4)\,\tau_{\mathrm{DI}}^{-1} &= (1\,\bar{1}\,0)\\(8\,0\,0)\,\tau_{\mathrm{DI}}^{-1} &= (0\,0\,2)\end{aligned}$$

solving the above equations we deduce the following relations

$$\begin{aligned}a_{\mathrm{DI}} &\cong 4c_{\mathrm{H}}\\b_{\mathrm{DI}} &\cong 4a_{\mathrm{H}}\\c_{\mathrm{DI}} &\cong 2\sqrt{3}\,a_{\mathrm{H}} \cong 2b_{\mathrm{H}}\end{aligned}$$

the subscripts DI and H corresponding to djurleite and high chalcocite, respectively. The relative orientation between the hexagonal and monoclinic cells is shown in Fig. 10. This relative orientation has also been proposed by Evans [7] in the bulk material.

Finally the electron diffraction pattern of Figs 8 and 9 are analysed. These patterns imply a different relative orientation between the hexagonal chalcocite and the monoclinic djurleite cells.

Considering Figs 8 and 9 the transformation matrix

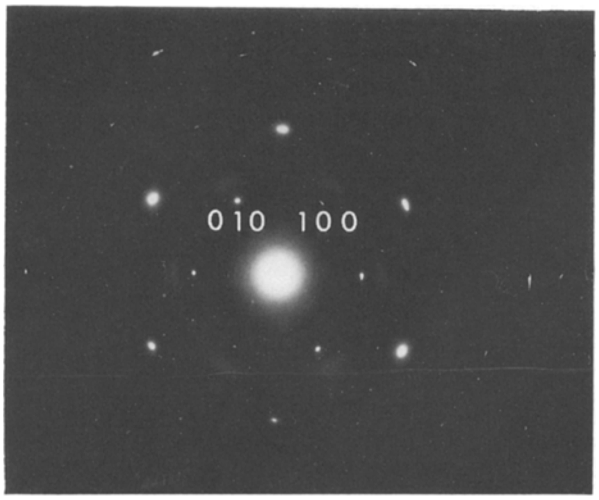

Figure 6 ED pattern of high chalcocite film taken at $T > 83°$ C, corresponding to $\langle 0\,0\,1\rangle$ zone.

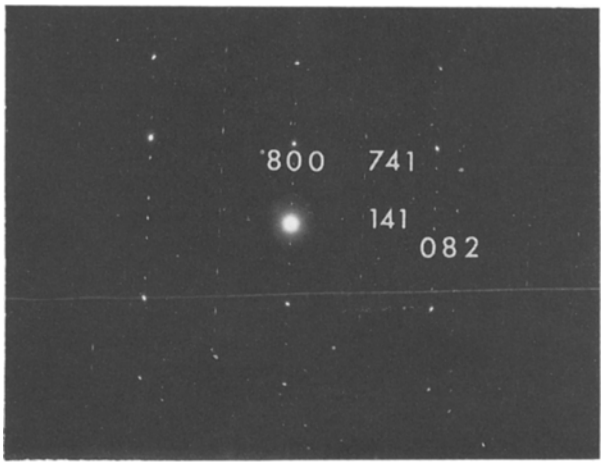

Figure 8 ED diagram of zone $\langle 0\,1\,4\rangle$ djurleite film.

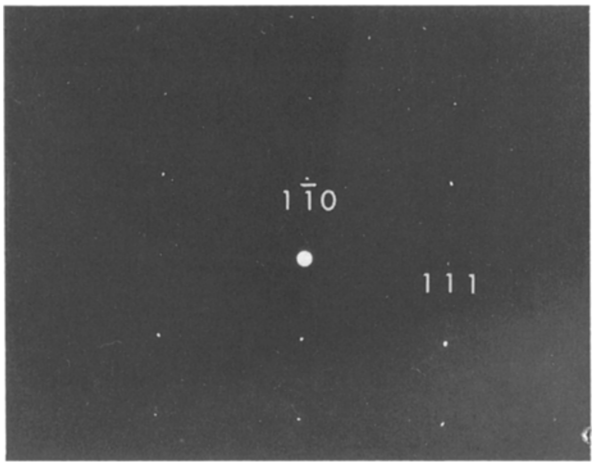

Figure 9 ED diagram of same area as Fig. 8 at $T > 83°$ C, corresponding to $\langle 1\,1\,2\rangle$ zone of high chalcocite.

should satisfy

$$(1\,1\,0)\,\tau_{\mathrm{D_{II}}} = (8\,0\,0)$$

the indexes on the left corresponding to high chalcocite. This implies

$$d_{800}^{\mathrm{D_{II}}} = d_{1\bar{1}0}^{\mathrm{H}}$$

where D_{II} refers to this type of djurleite and H to the hexagonal chalcocite. It is easy to see

$$d_{800}^{\mathrm{D_{II}}} = a_{\mathrm{D_{II}}}/8$$

and

$$d_{1\bar{1}0}^{\mathrm{H}} = (3/2)a_{\mathrm{H}}$$

then

$$\mathrm{a_{D_{II}}} \cong 4\sqrt{3}\,a_{\mathrm{H}} = 4b_{\mathrm{H}}$$

This is a logical result since in the high chalcocite (hexagonal symmetry) $C_{\mathrm{H}} \simeq b_{\mathrm{H}}$. Therefore this type of djurleite should have the same parameters as djurleite, but the orientation with respect to high chalcocite must be different, as follows:

$$a_{\mathrm{D_{II}}} \cong 4\sqrt{3}\,a_{\mathrm{H}} = 4b_{\mathrm{H}}$$
$$b_{\mathrm{D_{II}}} \cong 4a_{\mathrm{H}}$$
$$c_{\mathrm{D_{II}}} \cong 2C_{\mathrm{H}}$$

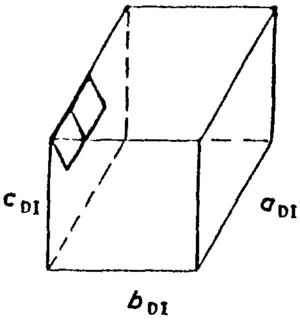

Figure 10 Relative orientation between hexagonal cell (high chalcocite) and monoclinic cell (djurleite DjI).

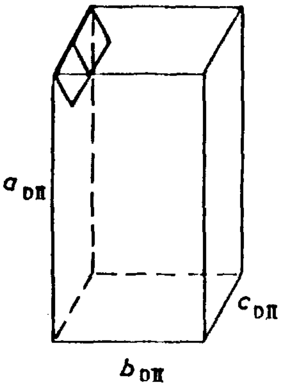

Figure 11 Relative orientation between hexagonal cell and monoclinic cell (modificated djurleite DjII).

then D_{II} should have the parameter $\mathrm{C_{D_{II}}}$ parallel to the C_{H} parameter of high chalcocite. The relative orientation between high and low temperature phases are shown in Fig. 11 the same kind of phenomenon for low chalcocite crystals has been reported by Mulder [11], but for djurleite the phenomenon has not been reported before.

5. Conclusions

The monoclinic djurleite to hexagonal chalcocite transformation in thin films of 50 to 100 nm thickness takes place with a topotactic relation by which the low-temperature phase takes a superstructure based on the high-temperature hexagonal lattice. During the transformation the reflections corresponding to the hexagonal phase keep their positions. We have found two different orientations of the djurleite supercell with respect to the hexagonal cell. One of which has not been reported before. The transformation matrix was determined. It remains to be determined if it is the displacements of the atoms that cause the change of structure, presumably the copper atoms could explain the formation of the superstructure.

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