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HIGH RESOLUTION STUDY OF THE CHALCOCITE (Cu<sub>2</sub>S)-DJURLEITE (Cu<sub>1.97</sub>S)  
TRANSFORMATION IN Cu<sub>2-x</sub>S THIN FILMS

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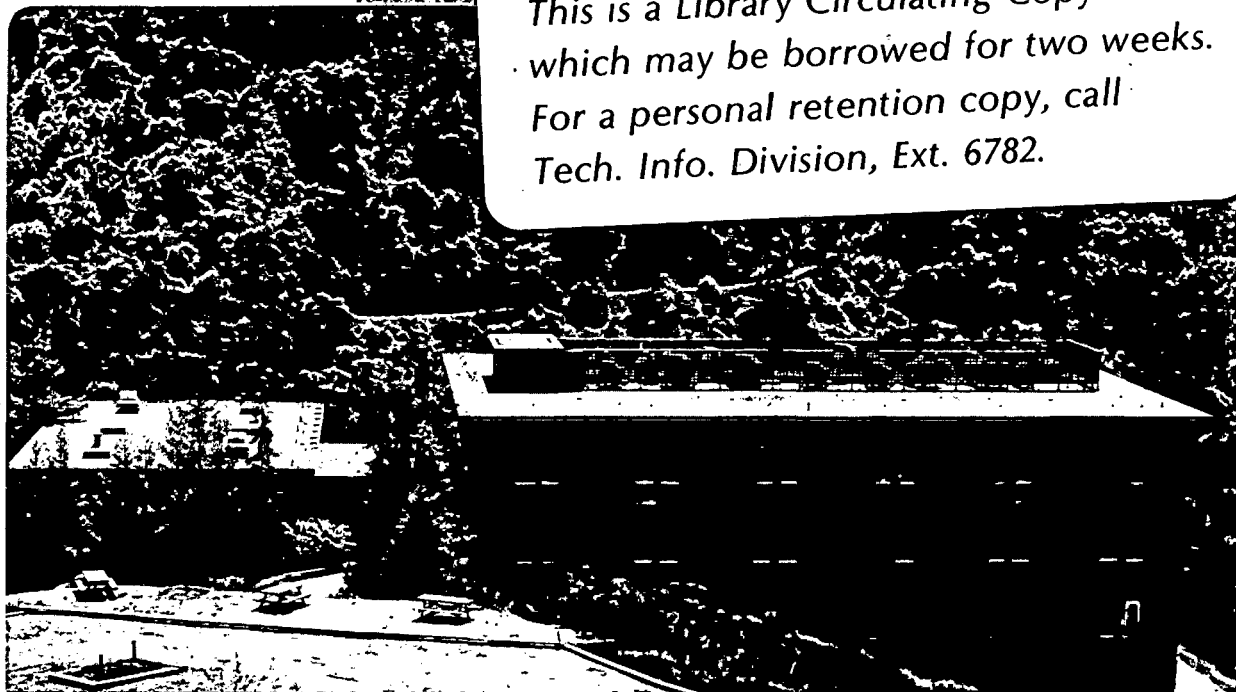
HIGH RESOLUTION STUDY OF THE CHALCOCITE ( $\text{Cu}_2\text{S}$ )-DJURLEITE  
( $\text{Cu}_{1.97}\text{S}$ ) TRANSFORMATION IN  $\text{Cu}_{2-x}\text{S}$  THIN FILMS

T.D. Sands, R. Gronsky, and J. Washburn

September 1982

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High Resolution Study of the Chalcocite ( $\text{Cu}_2\text{S}$ )-Djurleite ( $\text{Cu}_{1.97}\text{S}$ )

Transformation in  $\text{Cu}_{2-x}\text{S}$  Thin Films\*

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HIGH RESOLUTION STUDY OF THE CHALCOCITE ( $\text{Cu}_2\text{S}$ )-DJURLEITE  
( $\text{Cu}_{1.97}\text{S}$ ) TRANSFORMATION IN  $\text{Cu}_{2-x}\text{S}$  THIN FILMS

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ABSTRACT

High resolution transmission electron microscopy (HREM) has been applied to the study of the microstructural evolution of copper sulfide thin films. Both separated and supported  $\text{Cu}_{2-x}\text{S}$  thin films were prepared by the wet process on the (0001) and (000 $\bar{1}$ ) faces of CdS single crystals. HREM of as-plated films show that they are entirely low chalcocite with heavy faulting on (040). Degradation to djurleite-digenite mixtures occurs over a period of several days at 20°C for separated films. An atomic model of this transformation is presented and the effect of interfacial strain on the stability of copper sulfide layers is discussed.

INTRODUCTION

Solar cells utilizing copper sulfide as the absorber-emitter depend upon the presence of the chalcocite ( $\text{Cu}_2\text{S}$ ) phase for efficient operation (1,2).

Unfortunately, the compositional proximity and structural similarity of the djurleite ( $\text{Cu}_{1.97-1.94}\text{S}$ ) phase has led to copper sulfide films of limited reproducibility and stability (1). This study addresses the problem of determining the microscopic mechanism of the chalcocite-djurleite transformation and the dominant factors influencing the transformation so that methods to produce more stable layers or device configurations may be systematically explored.

### Background

Equilibrium electrochemical measurements by Potter (3) have established that the djurleite single phase region extends from approximately  $\text{Cu}_{1.965}\text{S}$  to  $\text{Cu}_{1.935}\text{S}$  while the low chalcocite single phase region includes compositions only slightly deficient in copper from  $\text{Cu}_2\text{S}$ . The x-ray work of Evans (4,5), another fundamental study, has resulted in nearly complete structure determinations for low chalcocite and djurleite ( $\text{Cu}_{1.938}\text{S}$ ).

The relationships between low chalcocite ( $<104^\circ\text{C}$ ), djurleite, and the high temperature disordered phase have been investigated by Putnis (6,7). Utilizing transmission electron diffraction, Putnis found that low chalcocite and djurleite form with nearly equal probability during repeated beam heating and cooling of copper sulfide crystallites. The implication is that low chalcocite and djurleite can exist at the same composition in thin film geometries (see discussion).

Previous work on the microstructural details of the low chalcocite-djurleite transformation is limited to recent papers by Echigoya and Edington (8) and Sands, Washburn and Gronsky (9). Echigoya and Edington found that unsupported thin

films of chalcocite rapidly degrade to djurleite in air at 20°C. Whereas, films of chalcocite in contact with CdS retain some low chalcocite, even after 1400 hours. In the latter work, HREM results are combined with the data of Evans to formulate a structural model of the transformation. In the following paragraphs, this model is summarized and extended to include observations of the microstructural evolution of copper sulfide thin films.

### EXPERIMENTAL METHODS

All  $\text{Cu}_{2-x}\text{S}$  specimens prepared for this study were formed by the wet process (10) in basally oriented single crystals of CdS (Eagle-Picher). After mechanical polishing and a 15 second etch in 37% HCl, the CdS crystals were lowered into an aqueous ion exchange bath (6g/l 99.999%CuCl, 2g/l NaCl) which was purged and agitated with argon.

Separated thin films for HREM were made by first heat treating the as-prepared  $\text{Cu}_{2-x}\text{S}/\text{CdS}$  heterojunctions in air at 150°C for 20 minutes to homogenize the  $\text{Cu}_{2-x}\text{S}$  layer. Separation of the CdS layers was accomplished by a 10 second dip in 37% HCl which preferentially attacked the CdS at the interface (11). The layers were then floated onto the surface of a distilled water bath and lifted onto transmission electron microscopy (TEM) grids.

Supported specimens were prepared by ion milling basal slices of CdS (3-4 kV, 20-40 $\mu\text{A}$ , 15° tilt) to electron transparency and then converting the surface layers to  $\text{Cu}_{2-x}\text{S}$  by the wet process. The thinnest portions of the specimens were completely converted to copper sulfide.

HREM images were obtained on a Siemens 102 electron microscope operated at 100keV.

## RESULTS

Separated films were formed with dip times varying from 15 seconds to one minute. The low magnification TEM micrographs in Fig. 1 (from specimens converted at 99°C for 15 seconds) show that these films consist of a thin basal skin connecting thicker islands of  $\text{Cu}_{2-x}\text{S}$ . Fig. 1a reveals the crystallographic cracks characteristic of copper sulfide formation on the etched cadmium face of the CdS basal plane. The morphology of layers formed on the etched sulfur face is presented in Fig. 1b (Fig. 1a and b are from the same CdS crystal). Note the diffraction spot splittings due to the retained CdS particles usually present in sulfur face films. The films imaged in Fig. 1 were initially 100% chalcocite. However, degradation to djurleite-digenite mixtures occurred within two weeks in air at 20°C.

Fig. 2a is a HREM image of a typical Cd-face separated chalcocite film before degradation. Note the heavy faulting frequently observed in both separated and supported films. The significance of this faulting will be discussed below.

A nucleus of djurleite in a matrix of chalcocite is imaged in Fig. 3. The djurleite was nucleated at the edge of the supported film and grew to the size indicated in Fig. 3 after four days in air at room temperature. Note the appearance of both flat and rough interfaces.



A HREM sequence is pictured in Fig. 4. The as-plated microstructure represented in Fig. 4a is a mixture of chalcocite and djurleite in nearly equal proportions (conversion at 95°C for 30 seconds). After a 15 minute heat treatment in air at 180°C, the same area becomes predominantly chalcocite (Fig. 4b). Fig. 4c shows the microstructure after four days in air (shielded from light) at 20°C. All of the chalcocite and one orientational variant of djurleite have reordered into a fairly uniform region of djurleite. A map of the sequence described above is provided in Fig. 5.

## DISCUSSION

### Unit Cells

The basal projections of the unit cells of low chalcocite and djurleite and their variants are outlined in Fig. 6. Both unit cells are most accurately described as monoclinic with  $Z = 48\text{Cu}_2\text{S}$  and  $Z = 128\text{Cu}_{2-x}\text{S}$  for low chalcocite and djurleite, respectively (4,5). For simplicity, the translation vectors (indicated by primes) in the following description are given in terms of pseudo-orthorhombic unit cells which can be directly related to the unit cell of the hexagonal high temperature phase:

$$\text{low chalcocite} \quad a' = 3 \cdot a_{\text{hex}}$$

$$b' = 4\sqrt{3} \cdot a_{\text{hex}}$$

$$c' = 2 \cdot c_{\text{hex}}$$

djurleite

$$a' = 4 \cdot a_{\text{hex}}$$

$$b' = 2\sqrt{3} \cdot a_{\text{hex}}$$

$$c' = 4 \cdot c_{\text{hex}}$$

where  $a_{\text{hex}} = 0.395$  nm and  $c_{\text{hex}} = 0.675$  nm (6).

#### The Transformation on an Atomic Scale

The x-ray results of Evans (4,5) show that both low chalcocite and djurleite are based upon distorted hexagonal-close-packed sulfur substructures. The dimensions of the unit cells are determined by the complex ordering of copper among various interstitial sites in the sulfur substructures.

A study of Evans' data (9) reveals that chalcocite can be described as an assemblage of  $\text{Cu}_{12}\text{S}_6$  groups such as those pictured in Fig. 7. The faulting evident in Fig. 2a is a common structural perturbation in chalcocite. In fact, the model diagrammed in Fig. 2b suggests that this faulting may be responsible for deviations from stoichiometry in chalcocite (9), thus providing a possible explanation for the results of Putnis (see Introduction).

Although djurleite contains no simple building unit, the local ordering of copper is very similar to the ordering in chalcocite. The unit cell of djurleite ( $\text{Cu}_{1.938}\text{S}$ ) does, however, contain two  $\text{Cu}_{20}\text{S}_{12}$  units, each of which resembles two  $\text{Cu}_{12}\text{S}_6$  units placed base-to-base. This interesting feature is best interpreted as a four-Cu vacancy cluster. (All of the vacancies in djurleite appear to be localized in  $\text{Cu}_{20}\text{S}_{12}$  groups.) In other words, the djurleite structure can be derived from the low chalcocite structure by the clustering of Cu vacancies into  $\text{Cu}_{20}\text{S}_{12}$  groups which simultaneously order into the periodic framework of djurleite (Fig. 7). The high mobility of Cu ions (12) allows the rearrangement to occur in a reasonable time at temperatures as low as 20°C.

#### The Transformation on an Intermediate Scale

The loss of copper due to oxidation, electrochemical degradation, or Cu diffusion into CdS eventually results in the heterogeneous nucleation of djurleite. The nuclei may be oriented in either of two ways with respect to the chalcocite matrix. In a thin basal film the observed interfaces are generally vertical to minimize interfacial energy. Fig. 8 illustrates the strain associated with vertical interfaces of both variants. Note that a strain minimum exists for interfaces containing  $[010]_{\text{CH}}$  and with the angle between  $[100]_{\text{CH}}$  and  $[100]_{\text{DJ}}$  equal to approximately 60°. Accordingly, these lowest strain interfaces are the most frequently observed (see Figs. 3, 5b and 5c). Interfaces with strain greater than ~0.7% tend to be rough and short. The strain associated with the variant with  $[100]_{\text{CH}} \parallel [100]_{\text{DJ}}$  is intermediate in magnitude and nearly independent of orientation. Correspondingly, such nuclei appear to have no strongly preferred interface orientation (see Fig. 5b).

Note that the  $60^\circ$  variant of djurleite present above the crack in Fig. 5b has apparently swept across the specimen during room temperature degradation, consuming the  $0^\circ$  variant along the way (Fig. 5c). This observation, along with observations such as that in Fig. 3, suggest that the oxidation-driven degradation of chalcocite basal films proceeds by the growth of the  $60^\circ$  variant of djurleite. The djurleite is nucleated heterogeneously at cracks (Figs. 3 and 4) and possibly at sublattice grain boundaries.

### The Transformation on a Macroscopic Scale

In the absence of a driving force encouraging copper depletion, there is no evidence that a nearly stoichiometric chalcocite layer will degrade to djurleite. However, once such a driving force exists, the results above, in conjunction with the work of Echigoya and Edington, suggest that the strains present within the  $\text{Cu}_{2-x}\text{S}$  film and near the interface with CdS are critical factors in determining the rate of structural degradation.

Specifically, the cracks resulting from the lattice mismatch between copper sulfide and cadmium sulfide (Fig. 1) provide ideal sites for the formation of djurleite nuclei. Reduction of the mismatch by addition of ZnS to the CdS layer should reduce the density of nucleation sites and thus improve the stability of the  $\text{Cu}_{2-x}\text{S}$  layer. However, this beneficial effect of reducing the mismatch may be counteracted by the greatly enhanced stability of  $\text{Cu}_{2-x}\text{S}$  layers when in contact with CdS (8). It remains to be determined whether this enhanced stability is due to the tension in the chalcocite sublattice near the  $\text{Cu}_{2-x}\text{S}$ -CdS interface (the

djurleite sublattice is slightly smaller than the chalcocite sublattice) or to the compensation of Cu vacancies by diffused cadmium.

### SUMMARY

The principle conclusions of this study are summarized below:

- 1)  $\text{Cu}_{2-x}\text{S}$  films formed on the Cd face show crystallographic cracking. Films formed on the S face show evidence of retained CdS particles.
- 2) Low chalcocite can be visualized as an assemblage of  $\text{Cu}_{12}\text{S}_6$  units.
- 3) Nonstoichiometry in chalcocite may be accommodated by the common stacking faults on  $(040)_{\text{CH}}$ .
- 4) Djurleite is formed from chalcocite by the ordering of Cu vacancies into a periodic framework of  $\text{Cu}_{20}\text{S}_{12}$  four-vacancy clusters.
- 5) Chalcocite-djurleite interfaces are abrupt and coherent.
- 6) Interfacial strain appears to dictate the shape and growth of djurleite nuclei in chalcocite.

### ACKNOWLEDGEMENT

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Fig. 1. (a) TEM micrograph of a copper sulfide separated film formed by the wet process ( $99^{\circ}\text{C}$  for 15 seconds) on the Cd face of a basally oriented CdS single crystal. (b) Copper sulfide film formed simultaneously on the S face of the same crystal. Diffraction patterns indicate the presence of low chalcocite in  $[001]$  ' zone axis orientation.

Fig. 2. (a) HREM micrograph of a faulted chalcocite separated film. These faults on  $(040)_{\text{CH}}$  are responsible for the streaks in the diffraction pattern. (b) A schematic diagram of the fault model discussed in ref. 9. This model predicts a Cu:S ratio of 1.96 for the fault density in (a).

Fig. 3. A djurleite nucleus in a supported chalcocite film ( $[001]$  ' zone axis orientation). Note the flat low-strain interface on the right.

Fig. 4. A HREM sequence of the same area of a supported copper sulfide film in  $[001]$  ' zone axis orientation. (a) The as-plated condition ( $95^{\circ}\text{C}$  for 30 seconds). (b) After 15 minutes in air at  $180^{\circ}\text{C}$ . (c) After four days in air at  $20^{\circ}\text{C}$ .

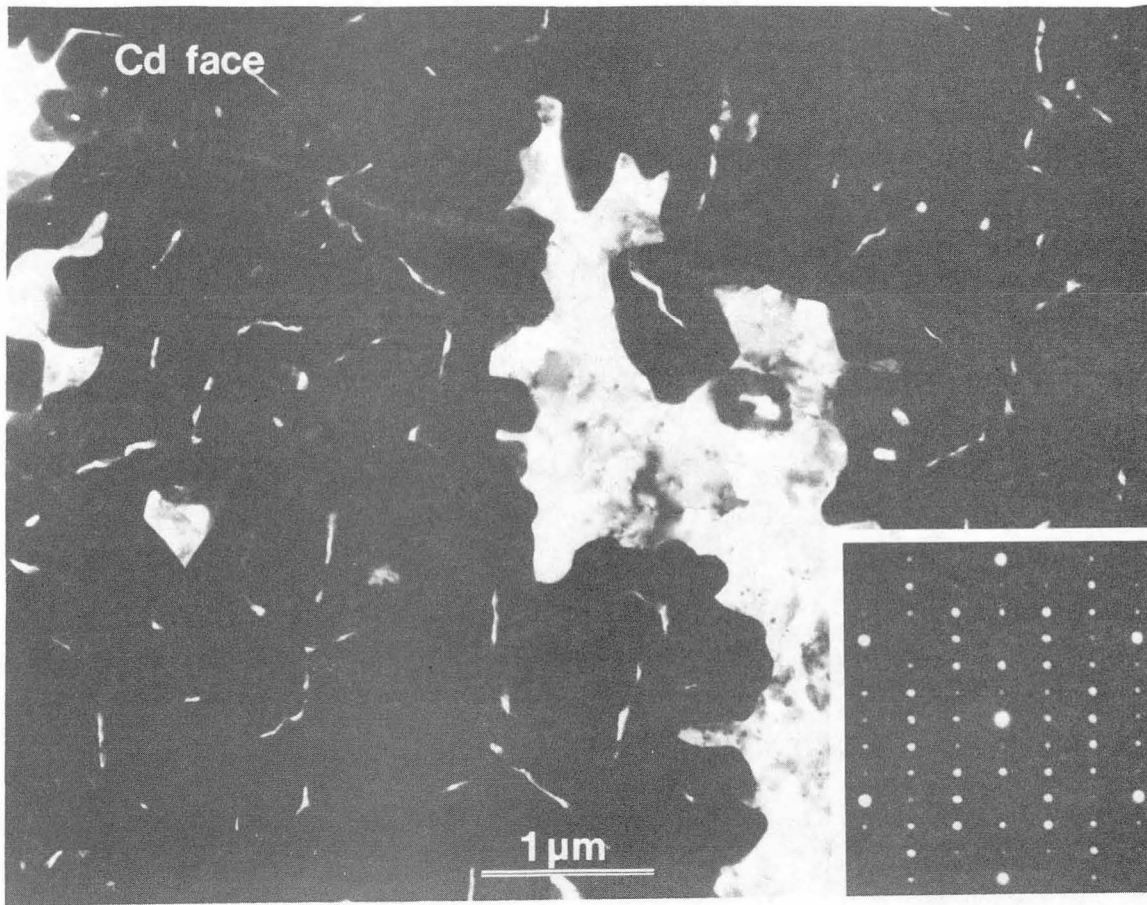
Fig. 5. A map of the sequence in Fig. 4. Darker fringes represent low chalcocite. Lighter fringes represent djurleite. The  $[100]$  ' direction in either phase is normal to the fringes.

Fig. 6. Chalcocite and djurleite unit cells in the basal plane of the sulfur sublattice. Note that three rotational variants (about  $[001]$  ' ) of each phase can coexist in the same sulfur sublattice.

Fig. 7. An exploded schematic illustration of the basic rearrangement of Cu required for the transformation.

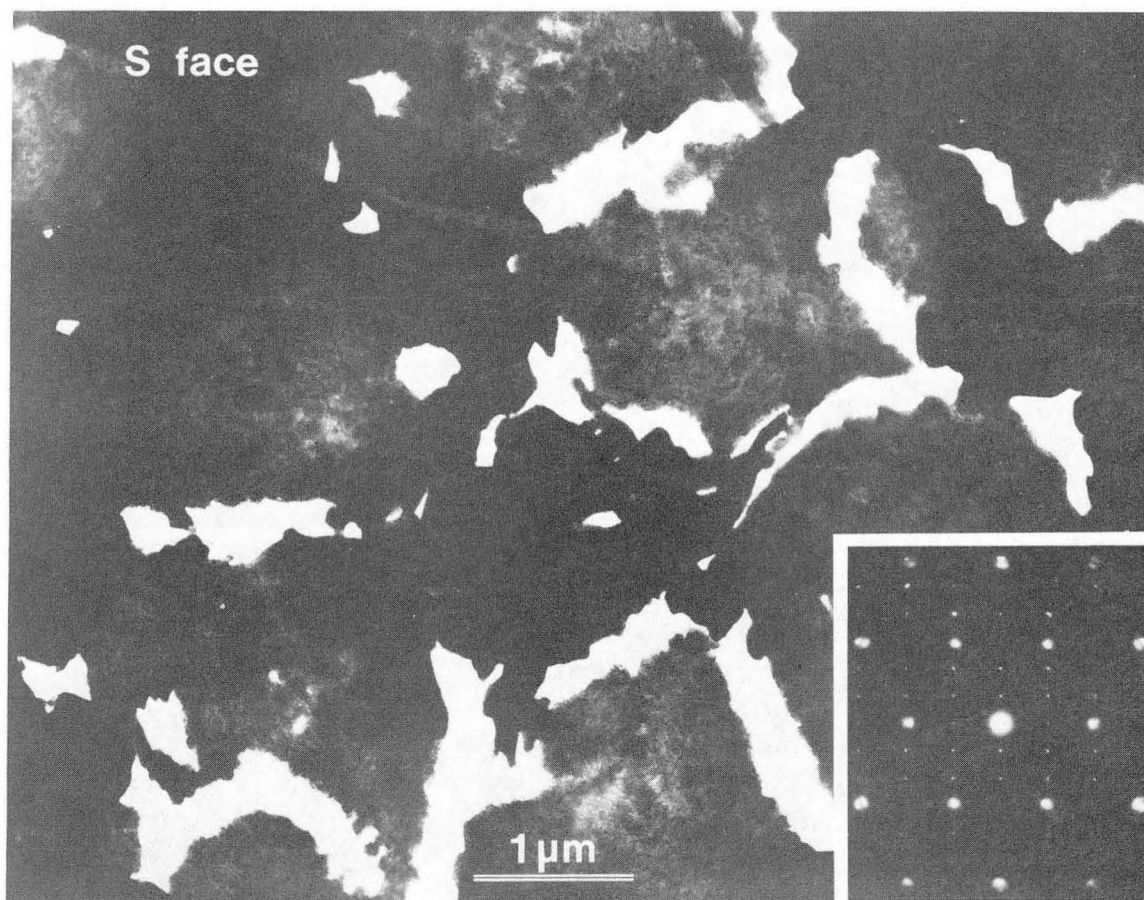
Fig. 8. Interfacial strain diagrams for the two relative orientations of chalcocite and djurleite in thin basal films. The numbers are the percent strain in the basal plane for vertical interfaces (from the lattice parameter measurements of Evans (4,5) for  $\text{Cu}_2\text{S}$  and  $\text{Cu}_{1.938}\text{S}$ ).





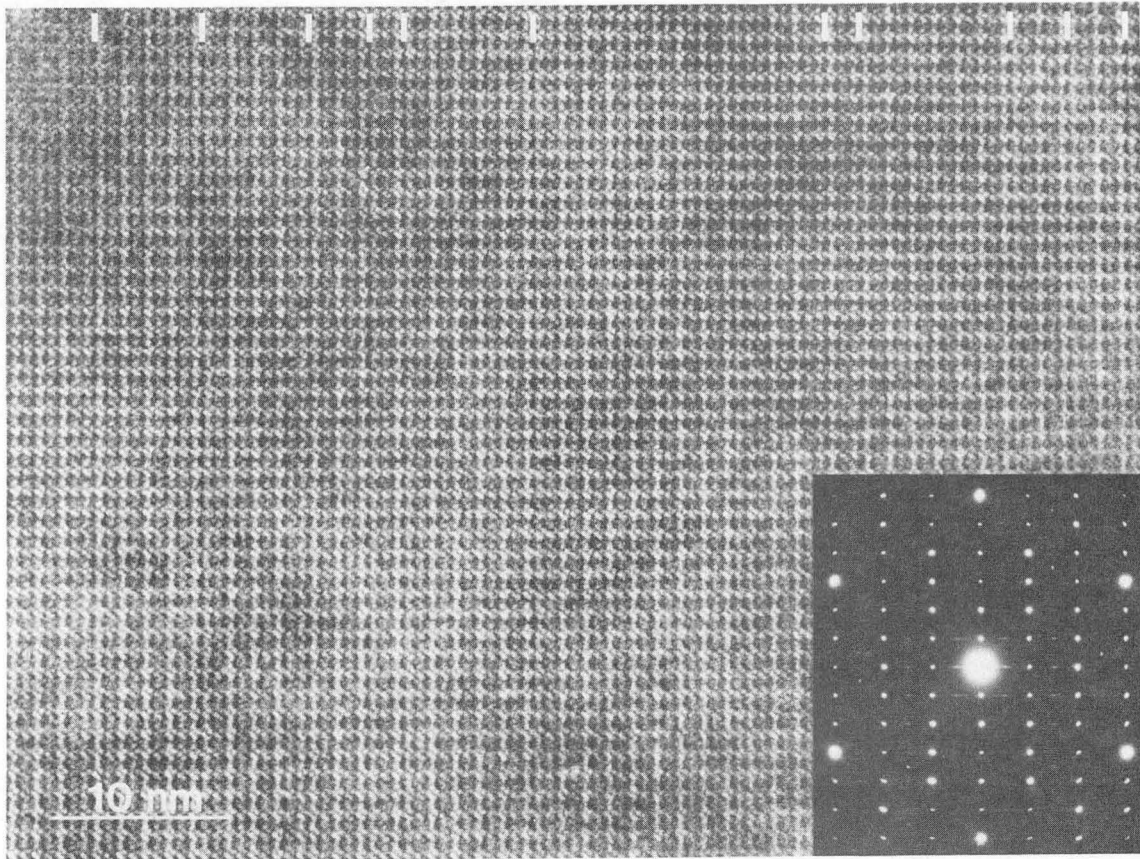
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Fig. 1a



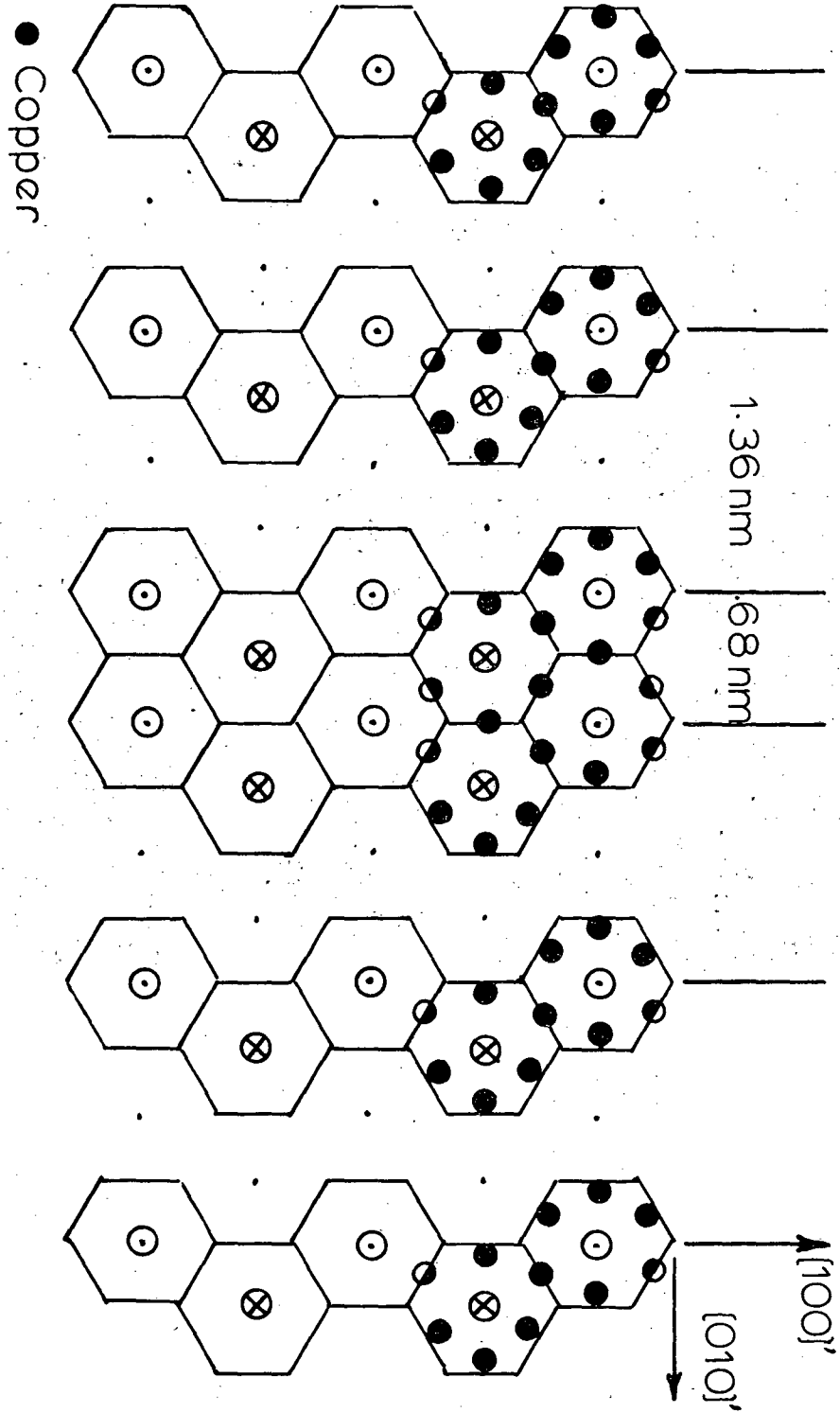
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Fig. 1b



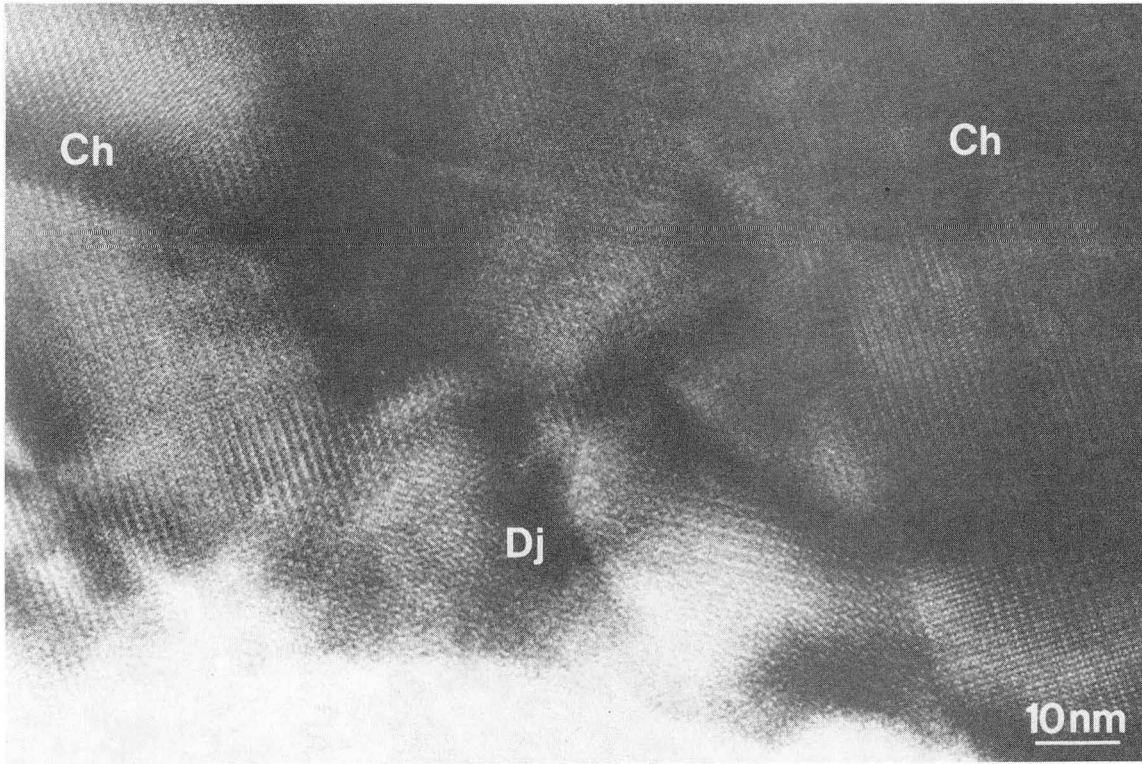
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Fig. 2a



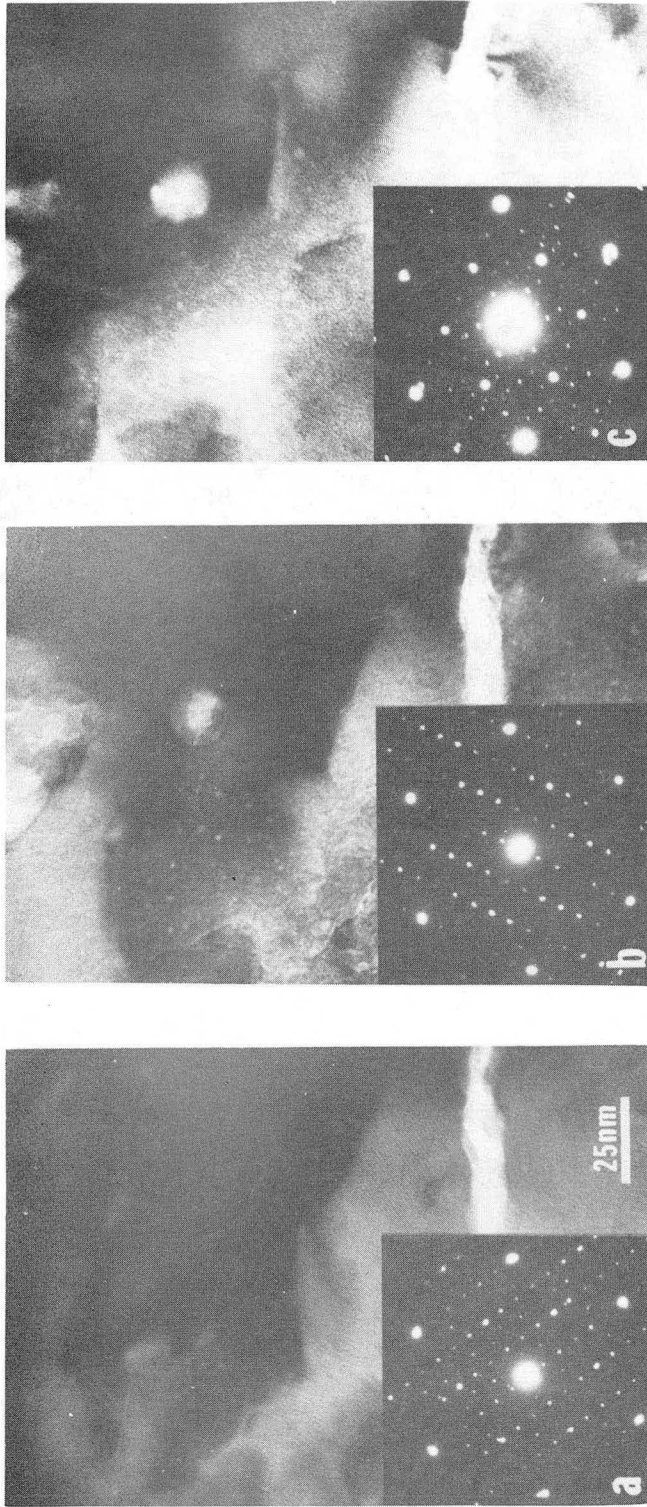
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Fig. 2b



XBB 829-7601

Fig. 3



After 4 days in air  
at 20°C

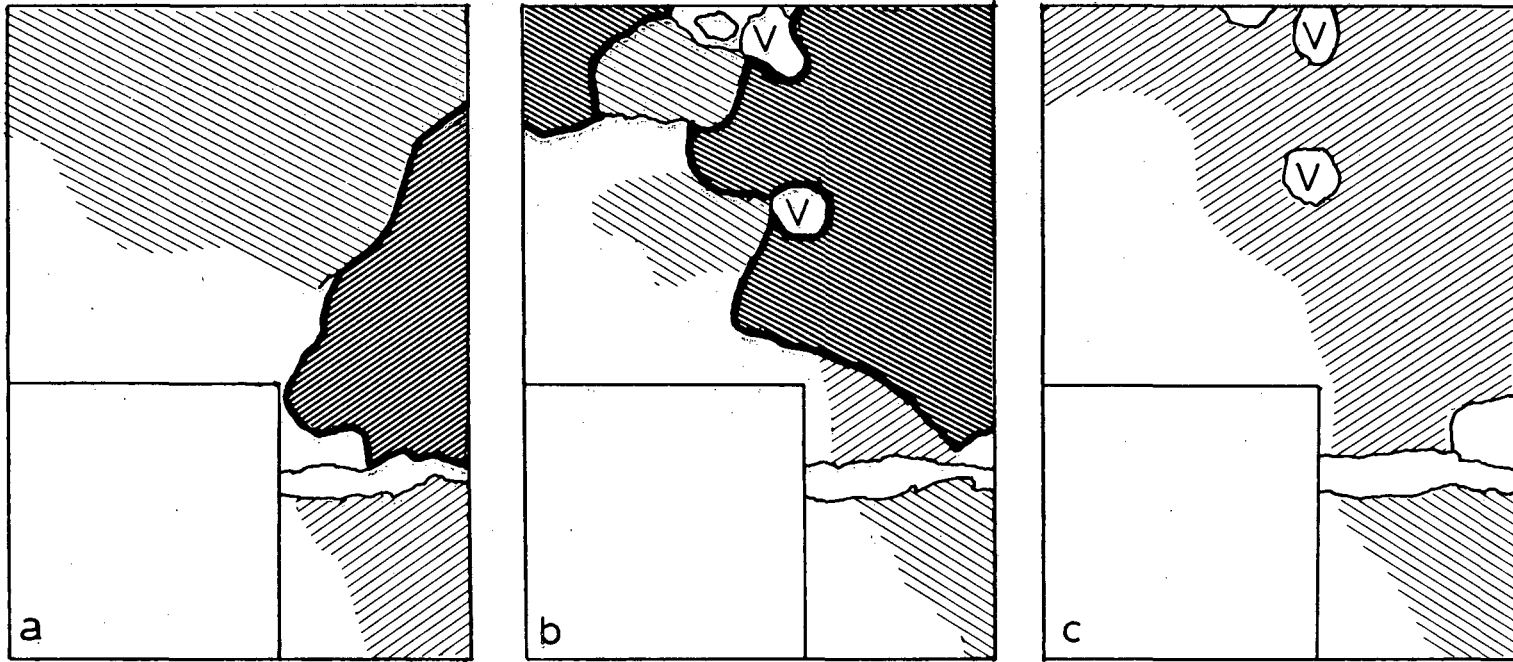
After 15 min. in air  
at 180°C

As-Plated

XBB 819-8915

Fig. 4

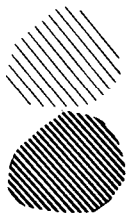
Fig. 5



As-Plated

After 15 min. in air  
at 180°C

After 4 days in air  
at 20°C

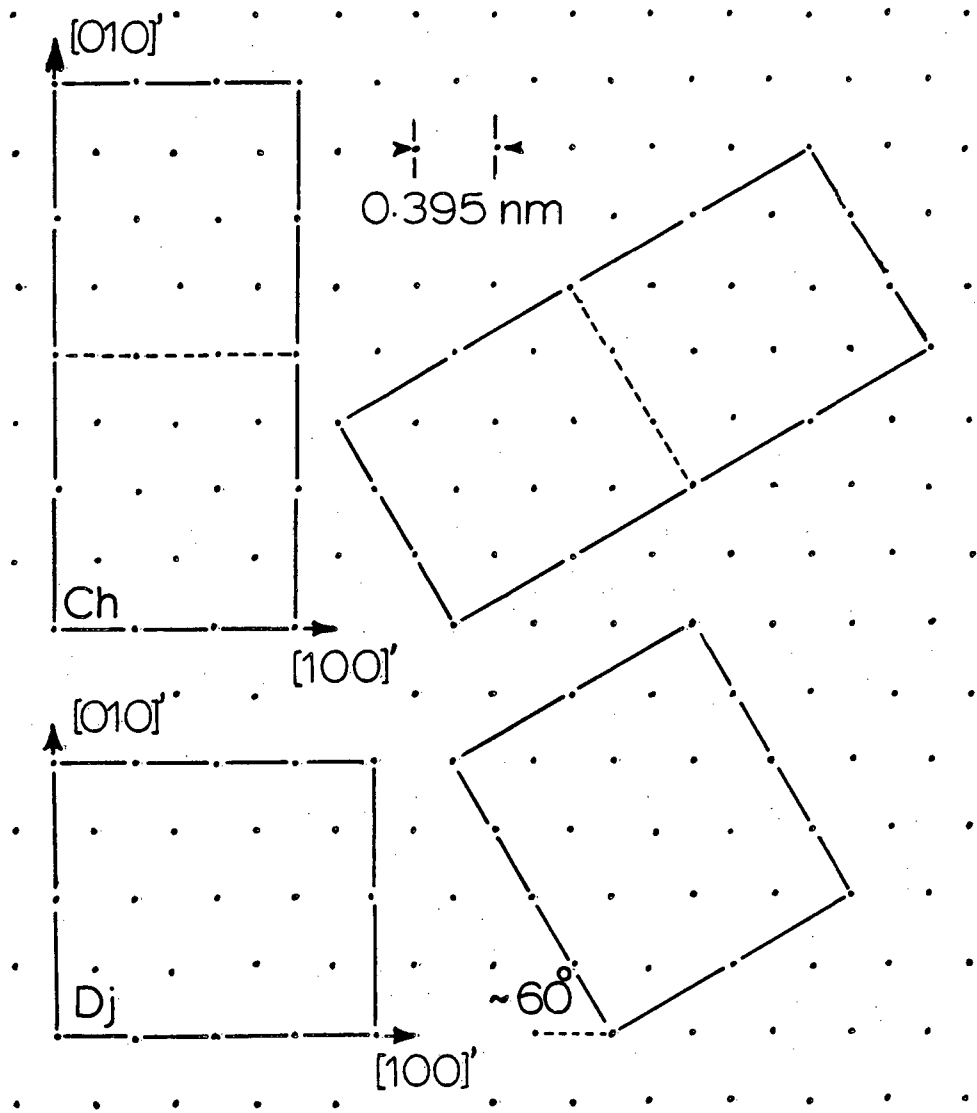


Djurleite

Chalcocite

'a' vectors of pseudo-orthorhombic  
unit cells are normal to fringes for both phases

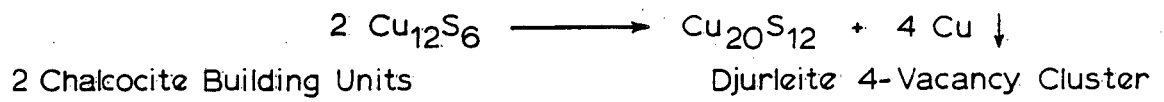
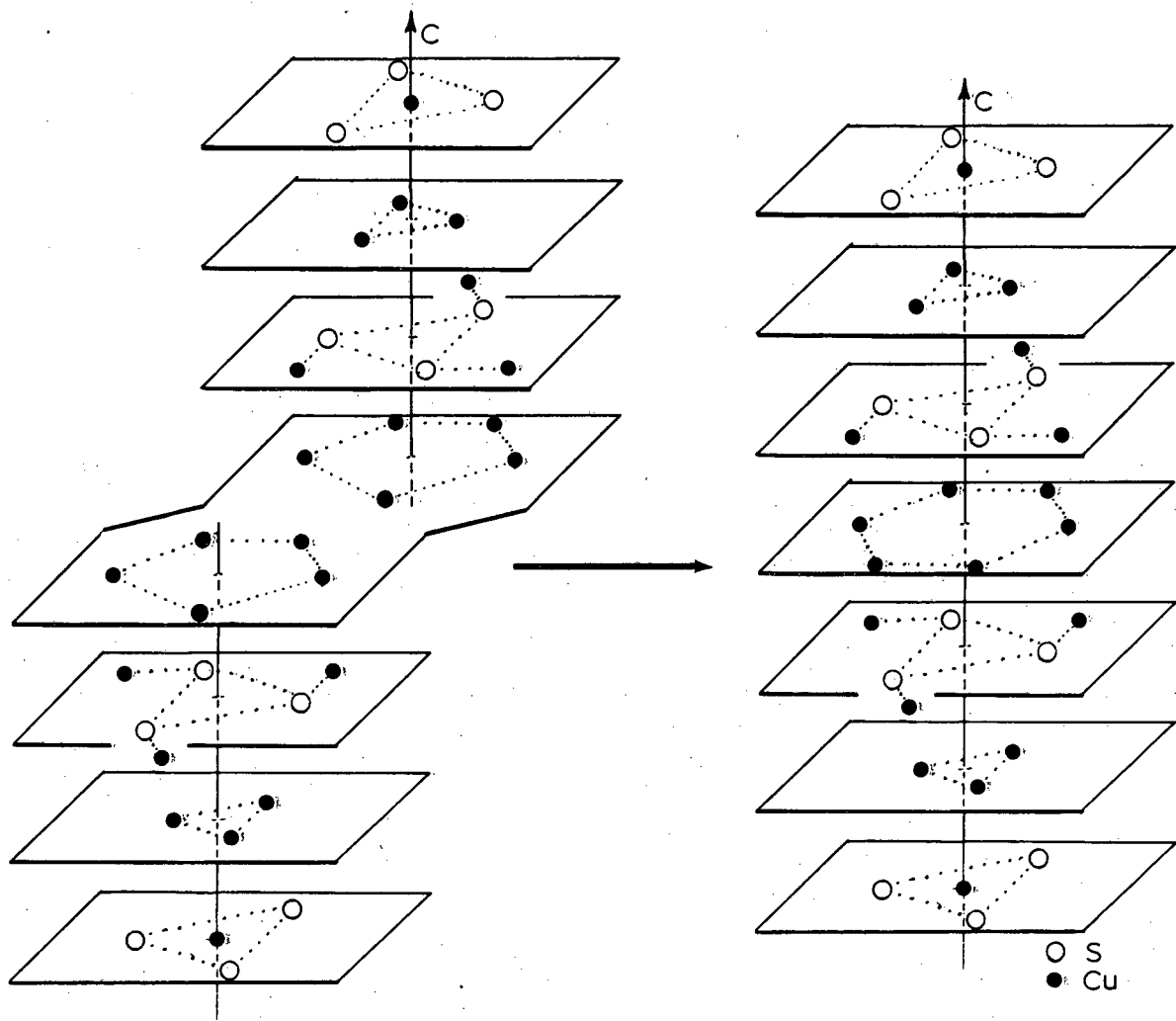
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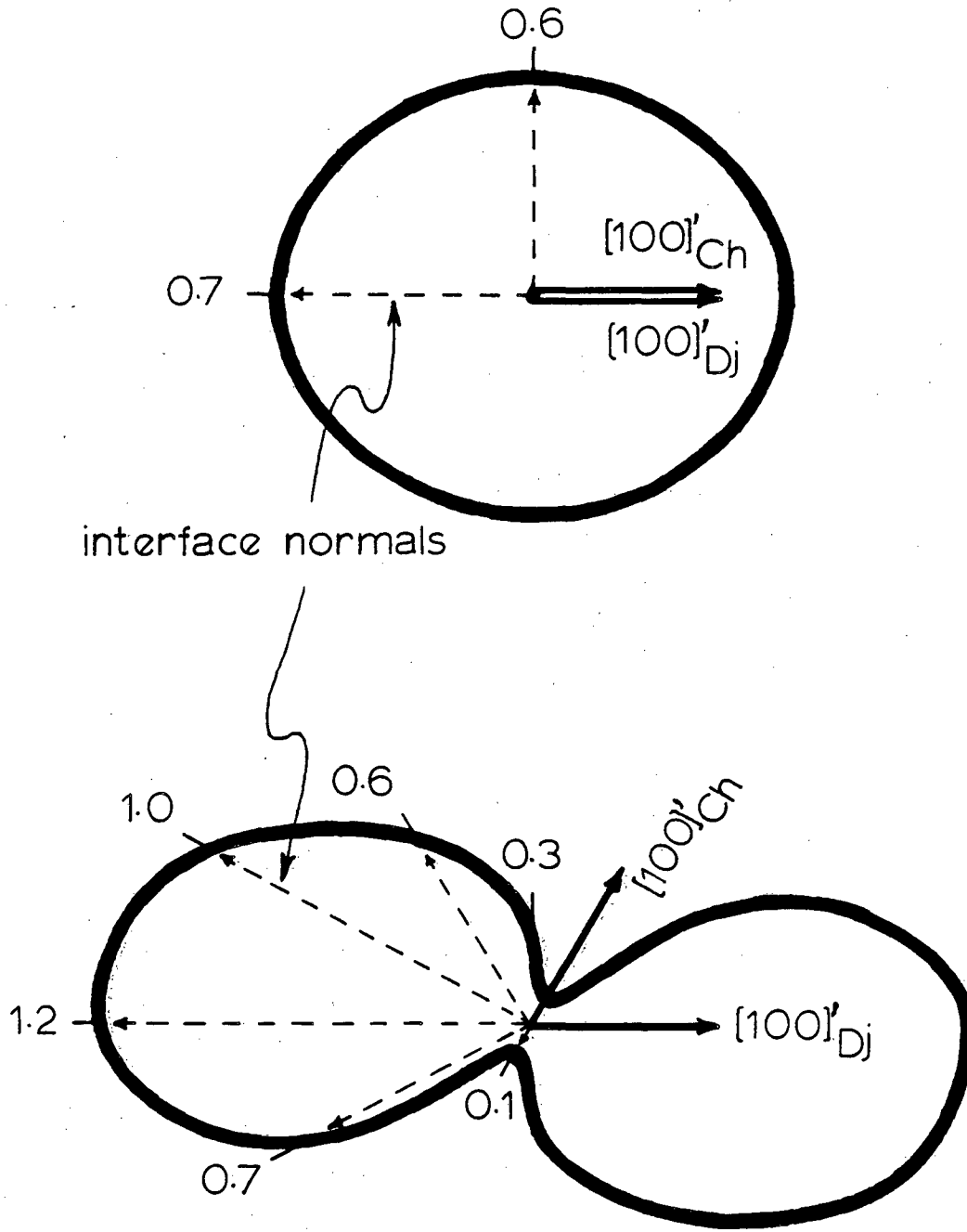
Fig. 6





XBL 829-11379

Fig. 7



XBL 829-11378

Fig. 8

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