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An Electron-Diffraction Study of Chalcopyrite Film grown upon Enargite

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A natural chalcopyrite film coated on (001) of enargite has been studied using electron diffraction. Chalcopyrite is so orientated that its (112), $(1\bar{1}0)$ and $(11\bar{4})$ are respectively parallel or nearly parallel to (001), (010) and (100) of enargite.

Enargite (Cu_3AsS_4) crystals have been found with (001) plated with a film of chalcopyrite ($CuFeS_2$). That the coating of crystal faces has taken place selectively suggests a possible relation in orientation between the film and the substrate. Electron diffraction is suited to the study of such a problem (Thomson & Cochrane, 1939, p. 162).

Apparatus

An all-metal horizontal-type electron camera installed in our Laboratory has been employed in the experiments. The electron beam from a hot cathode is collimated by two slits, each with a pinhole of 0·2 mm. in diameter, 7 cm. apart. The specimen–plate distance is 50 cm. The vacuum system consists of two two-stage oil diffusion pumps in series and an auxiliary rotary pump. The high-tension unit is a full-wave type with a transformer (60 kV.), two Kenotrons and a condenser (0·05 μF.). Special devices are incorporated in the camera so that focusing may be effected from outside without disturbing the vacuum and with the current on. These, combined with a fluorescent screen and a holder carrying six plates at a time, enable the beam to be adjusted quickly and the setting of specimens to be examined and photographs to be taken in rapid succession, while conditions across the camera are maintained as steady as possible.

Material

The enargite was from the Teiné mine, Hokkaido, Japan. It occurs lining druses in massive aggregates of enargite and luzonite. Dark grey prismatic crystals up to 1 cm. in length have faces (110), (320), (100), (310), (130) and (120). Usually only (001) and occasionally (100), too, are coated by a film and present a yellowish colour with a metallic lustre characteristic of chalcopyrite (Ito & Sakurai, 1947, vol. 1, p. 135). Chalcopyrite and enargite crystals, which we have examined for comparison, came respectively from the Ani mine, Akita, Japan, and from the Kinkwaseki mine, Formosa.

Experiments

We show in Figs. 1 and 2 the reflexion patterns of the film taken with the incident beam parallel to [100] and [010] respectively of the underlying enargite. Since these gave the spacing normal to the surface to be 3·0 A. compared with the known spacing of 3·1 A. for (112) of chalcopyrite, as calculated from the known dimensions, $a=5{\cdot}24$, $b=10{\cdot}30$ A. (Pauling & Brockway, 1932), we examined the latter mineral by electron diffraction using a natural (112) face and obtained patterns almost identical with those of the film (Figs. 3 and 4). The beam directions were respectively $[11\bar{1}]$ and $[1\bar{1}0]$, which happen in chalcopyrite to be at right angles. From these we may infer that in coating enargite the film of chalcopyrite is so orientated that its (112) and $[11\bar{1}]$ and $[1\bar{1}0]$ are respectively parallel to (001), [100] and [010] of enargite.

Since chalcopyrite has a tetragonal but pseudocubic symmetry the directions that coincide with [100] and [010] of enargite might possibly be other than those specified above. For example, [010] of enargite might be parallel to either $[0\bar{2}1]$ or $[\bar{2}01]$ instead of to $[1\bar{1}0]$ (Fig. 7). We have, however, eliminated such possibilities by superimposing upon the initial diffraction pattern its counterpart taken after rotating the film 180° about the normal to its surface. Were $[0\bar{2}1]$ or $[\bar{2}01]$, and not $[1\bar{1}0]$, the beam direction, the two patterns would not overlap as perfectly as was actually observed, for in chalcopyrite $[0\bar{2}1]$ and $[\bar{2}01]$ are at 89° 10′ with [221], whereas $[1\bar{1}0]$ is just at 90° to it. Further, we have taken (001) reflexion patterns of enargite, the beam direction being the same as with the film, namely, [100] and [010] (Figs. 5 and 6).

Throughout these experiments we used 45 kV.-electrons with the voltage fluctuation

$$\pm 400 \text{ V. } (\lambda = 0{\cdot}0567 \pm 0{\cdot}0003 \text{ A.})$$

Structural discussion

Using the reciprocal nets we have assigned indices to all the spots of the diffraction patterns obtained. Since in chalcopyrite $(1\bar{1}0)\wedge(112)=90°$, $(1\bar{1}0)\wedge(11\bar{4})=90°$ and $(112)\wedge(11\bar{4})=89°\ 31'$, the orientation of chalcopyrite grown on enargite may be also defined thus: $(1\bar{1}0)$ and (112) of the former are parallel to (010) and (001) of the latter respectively, while $(11\bar{4})$ is nearly parallel (0° 29′)

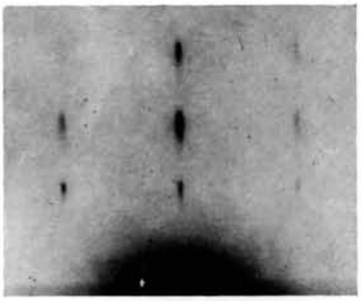

Fig. 1. Chalcopyrite film on (001) of enargite. Electrons incident along [100] of enargite.

Fig. 2. Chalcopyrite film on (001) of enargite. Electrons incident along [010] of enargite.

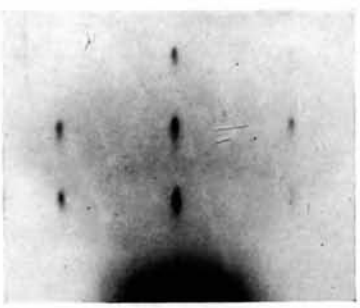

Fig. 3. Chalcopyrite. Electrons incident on (112) along [11$\bar{1}$]. Natural face.

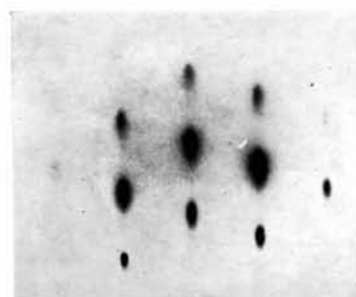

Fig. 4. Chalcopyrite. Electrons incident on (112) along [1$\bar{1}$0]. Natural face.

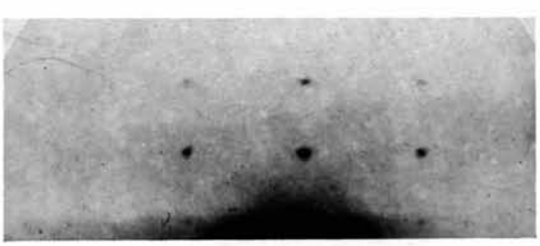

Fig. 5. Enargite. Electrons incident on (001) along [100]. Polished face.

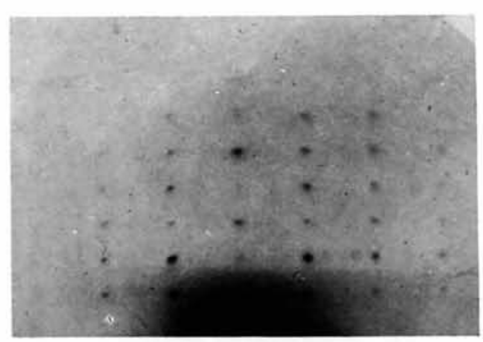

Fig. 6. Enargite. Electron incident on (001) along [010]. Polished face.

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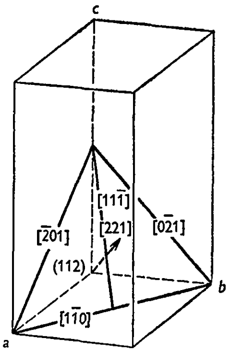

Fig. 7. (112) in chalcopyrite in relation to [$1\bar{1}0$] and other zone-axes used to define its overgrowth on enargite.

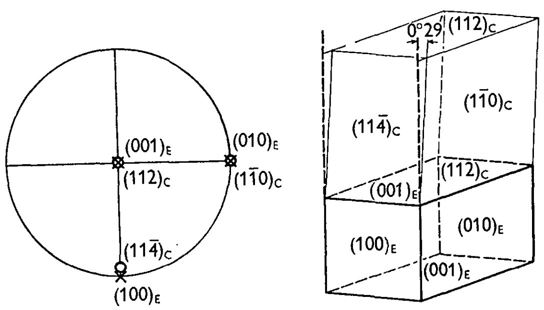

Fig. 8. The relationship in orientation between enargite and chalcopyrite in parallel growth as revealed by electron diffraction. The position of ($11\bar{4}$) of chalcopyrite is displaced slightly for clarity. In the accompanying stereographic projection crosses denote enargite and circles chalcopyrite.

to (100) (Fig. 8). These findings can be verified by inspection in the diffraction patterns indexed. We observe in them that ($2\bar{2}0$) and (112) spots of chalcopyrite occur at the same points as (040) and (002) spots of enargite respectively, while ($22\bar{8}$) spot of chalcopyrite corresponds in position approximately to (600) spot of enargite. The spacings of these planes compare thus:

Chalcopyrite		Enargite	
($1\bar{1}0$)	3·70 A.	(010)	3·72 A.
(112)	3·01 A.	(001)	3·09 A.
($11\bar{4}$)	2·12 A.	(100)	6·46 A.

In order that we may further understand the significance of the selective coating of enargite by chalcopyrite we have to take into consideration their crystal structures (Pauling & Brockway, 1932; Pauling & Weinbaum, 1934). They are very similar, one being of the zincblende type and the other of the wurtzite type. If we look at the structure of enargite in the direction normal to (001) and that of chalcopyrite in the direction normal to (112), they will present virtually the same aspects, especially in the arrangement of sulphur atoms, except for some vacant positions in enargite. A possible way in which the (001) atomic layers of enargite pass upon growing into the (112) atomic layers of chalcopyrite is illustrated in Fig. 9. We see in this that, whereas in enargite two layers alternate, in chalcopyrite the same layer repeats itself.

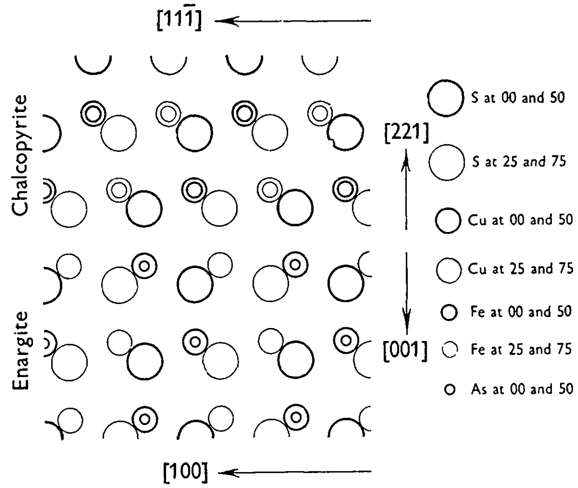

Fig. 9. Possible way in which (001) atomic layers of enargite are converted to (112) atomic layers of chalcopyrite. Enargite projected on (010) and chalcopyrite on ($1\bar{1}0$). Heights of atoms are expressed in percentage of the *b* translation of the enargite cell.

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