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CRYSTALLOGRAPHIC RELATIONS BETWEEN CUBANITE SEGREGATION PLATES, CHALCOPYRITE MATRIX, AND SECONDARY CHALCOPYRITE TWINS

N. W. BUERGER AND M. J. BUERGER,
Massachusetts Institute of Technology, Cambridge, Mass.

ABSTRACT

The orientation of cubanite plates unmixed from chalcopyrite have been said to parallel $\{111\}$ of the chalcopyrite matrix, but the best method hitherto used to determine this does not lead to a unique solution. In this paper, the orientations of the cubanite plates as well as certain twin lamellae, occurring in the coarse grained chalcopyrite from Corinth, Vermont, are uniquely determined by a study of the traces of these features on two polished surfaces.

The general method of determining the pole of a plane making traces on two datum planes is discussed with the aid of the stereographic projection. The method is then applied to the cubanite and twin lamellae traces, resulting in a composite stereographic projection of these features. The orientation of the chalcopyrite crystal containing these is determined from the symmetry of this composite projection. This, in turn, permits the poles to be easily indexed. Cubanite plates are found to be parallel to $\{111\}$, as previously surmised. Two new twin lamellae are discovered, the first, parallel to $\{110\}$, called *grid twins*, the second parallel to $\{101\}$, called *echelon twins*, the names being descriptive of the habit of the lamellae. Both groups of lamellae are secondary, resulting from plastic deformation. The possible causes of this include external forces, unmixing stresses, and possible inversion stresses.

INTRODUCTION

Cubanite-chalcopyrite intergrowths have been shown by Schwartz¹ to arise by unmixing of an originally homogeneous phase. In chalcopyrite-rich intergrowths, the cubanite segregate occurs in the form of plates whose intersections with the plane of a polished section have lath-like outlines. It has been surmised that these plates have the orientation of $\{111\}$ planes in the chalcopyrite matrix. Twinning of the chalcopyrite accompanies this intergrowth; the

¹ Schwartz, G. M., Intergrowths of chalcopyrite and cubanite: experimental proof of the origin of the intergrowths and their bearing on the geological thermometer; *Ec. Geol.*, vol. 22, pp. 44-61, 1927.

nature of the twins is unknown except that some of the lamellae have been surmised to follow $\{111\}$. In order for these data to be useful in crystal structural interpretations, it is very desirable for them to be accurately established by a systematic investigation. In the present paper, both the orientation of the cubanite plates in chalcopyrite and the nature of the chalcopyrite twinning is unequivocally established.

LITERATURE

Cubanite orientation. The recorded evidence for the orientation of the cubanite segregation plates in chalcopyrite leaves much to be desired. The best evidence was offered early by Kalb and Bendig, when cubanite still went under the name of chalmersite and the origin of the intergrowth was not yet established. They said:²

In the collection of the Mineralogical Institute, a piece of massive chalcopyrite from Tunaberg, Sweden, appeared to us remarkable because of outstanding parting parallel to the faces of the unit sphenoid.

	(111):(1 $\bar{1}$ 1)	(111):(11 $\bar{1}$)
measured	70°14' ± 15'	71°8' ± 30'
calculated	70°7'	71°20'

On each parting surface, there were to be observed parallel to the traces of the three others, dark, tarnished, stripes [cubanite].

This evidence is not quoted by Schwartz, who independently deduced the orientation of the cubanite plates on the following basis:³

. . . the laths at any one place are either parallel or in parallel sets which make angles approximately 60° with one another. The last fact suggests to the writer that the blades or laths are parallel to the parting planes which may be conspicuously developed in chalcopyrite found with cubanite as at Parry Sound.

and again, (p. 57)

As a rule, however, the cubanite as long laths is oriented along the (111) planes in the chalcopyrite. . . . It is obvious that the cubanite is oriented along the sphenoid (111) planes in the chalcopyrite, and the writer has shown that chalcopyrite may show well developed parting along the same planes.

Ramdohr,⁴ Schneiderhöhn,⁵ and Schneiderhöhn and Ramdohr⁶

² Kalb, Georg, and Bendig, Maximiliane, Chalmersit von Tunaberg in Schweden: *Centralblatt für Mineralogie, etc.*, 1923, p. 643.

³ Reference 1, p. 47.

⁴ Ramdohr, Paul, Neue mikroskopische Beobachtungen am Cubanit (Chalmersit) und Überlegungen über seine lagerslätten kundliche Stellung; *Zeit. prakt. Geol.*, 1928, p. 170.

also assert that the cubanite plates are oriented parallel to $\{111\}$ of the chalcopyrite matrix, but without giving specific authority or reasons.

None of the evidence offered actually established the orientation of the cubanite plates. Schwartz's observations establish practically nothing, and Kalb and Bendig's evidence does not lead to a unique solution; for example, the pseudocubic combination of plates along the basal pinacoid and second order prism is not eliminated. The planes of this combination are quasi-equivalent in low-temperature chalcopyrite and are probably rigorously equivalent in high-chalcopyrite. (See footnote 13.)

Twinning lamellae. Schneiderhöhn and Ramdohr⁷ recognize two kinds of twin lamellae in chalcopyrite. The first, a coarse banding, is said to run parallel to $\{111\}$. This is sometimes a primary growth twinning, sometimes a secondary pressure twinning, as indicated by relation to cracks and other cataclastic features. Recorded artificial production of this is still lacking. Schwartz⁸ suggests that the parting observed in the Parry Sound chalcopyrite may be due to a twinning on $\{111\}$.

The second type of twinning is manifest in finer lamellae, and its significance is unknown. Schneiderhöhn and Ramdohr suggest that this is inversion twinning (as in the cases of leucite, boracite, cristobalite, etc.) from which it might be tentatively inferred that there is an isometric, high temperature form of chalcopyrite. (Footnote 13.)

Finally, it should be noted that Dana-Ford⁹ records the following twin-laws for chalcopyrite:

- (1) Twin plane, $p(111)$
- (2) Twin plane, $e(101)$
- (3) Twin plane, $m(110)$

⁵ Schneiderhöhn, H., The mineralogy, spectrography and genesis of the platinum-bearing nickel pyrrhotite ores of the Bushveld igneous complex; (Included in Percy A. Wagner, The platinum deposits and mines of South Africa, 1929), p. 229.

⁶ Schneiderhöhn, Hans and Ramdohr, Paul, Lehrbuch der Erzmikroskopie, II, 1931, pp. 349 and 361.

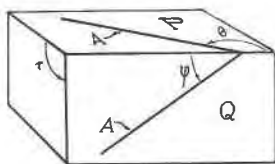
⁷ Reference 6, p. 348.

⁸ Schwartz, G. M., Primary relationships and unusual chalcopyrite in copper deposits at Parry Sound, Ontario: *Ec. Geol.*, vol. 19, p. 211, 1924.

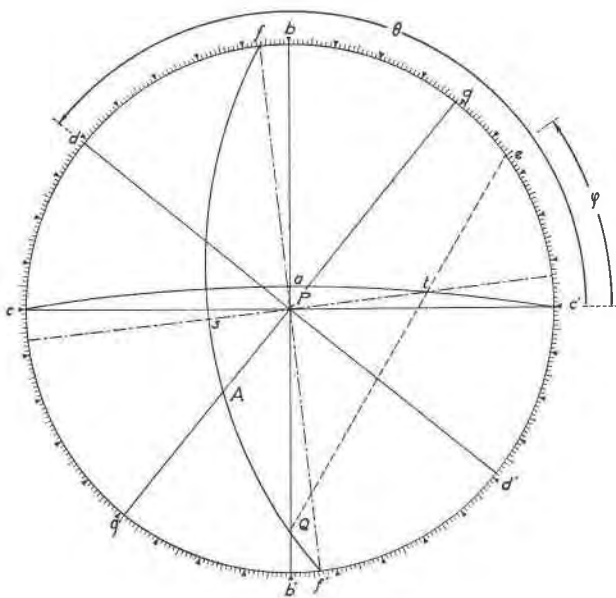
⁹ Dana, Edward Salisbury, and Ford, William E., A textbook of mineralogy, 4th edition, 1932, p. 431.

GEOMETRICAL METHOD

The cubanite plates are visible as strip-like traces on polished surfaces of a chalcopyrite crystal. The same is true of the chalcopyrite twin lamellae. Given the traces of a plane on each of two



A



B

FIG. 1.

located polished surfaces, the orientation of the plane is completely fixed. This problem is conveniently handled graphically with the aid of the stereographic projection, as follows:

Figure 1A is a block diagram showing the traces of the desired plane, *A*, on the located surfaces, *P* and *Q*, which intersect at an

internal angle, τ . The plane A gives rise to a trace on the plane P which makes an angle θ with the intersection of P and Q , arbitrarily measured counterclockwise. The trace of A on Q makes an angle ϕ with the intersection of P and Q , arbitrarily measured counterclockwise.

Figure 1B is a stereographic projection of this case. The direction of intersection of the two located planes, P and Q is arbitrarily placed left and right; the poles of this intersection then appear in the projection on the fundamental circle at points c and c' . The locus of planes which can intersect in the edge PQ is the great circle bb' . For convenience one of the planes, P , is placed horizontally, so that its projection appears at point P (the north pole). The supplement of the intersection angle, τ , is then laid off in the zone bPb' , which locates the pole of plane Q in the projection.

The direction of trace of the desired plane A with plane P appears in the stereographic projection as the line dd' . All planes capable of intersecting the plane P at this angle θ must lie along a zone at right angles to the line dd' , namely along gg' .

A similar construction can now be carried out for the possible planes, A , which give rise to the trace on the plane Q at an angle ϕ , but in this case the construction becomes more general. The intersection of the plane Q with the sphere is first located by drawing the great circle cac' . The locus of all possible intersection directions, ϕ , is this great circle. The projection of the intersection at any particular angle ϕ is found by stereographically laying off the angle ϕ from the fundamental circle along this great circle cac' . The angle ϕ thus appears on the projection as the distance $c't$, locating the desired trace direction at t . This last operation is conveniently accomplished by laying off $c'e$ equal to the angle ϕ , and at e drawing line eQ , Q being the angle point of zone cac' . The poles of all planes capable of intersecting Q to give a trace t lie at 90 degrees from t ; i.e., along the great circle fsf' .

Since all planes capable of intersecting plane P in angle θ lie along the zone gPg' , any plane A which simultaneously gives rise to both of these traces must have a pole restricted by both of these loci. The pole of the plane sought is therefore at the intersection of these two zones fsf' and gPg' , namely point A .

MATERIAL

The investigation here presented was carried out on coarse chalcopyrite ore from the Pike Hill Mine, Corinth, Vermont. The

intergrowth in this ore is substantially duplicated in the ores of the Ely Mine and the Elizabeth Mine, which together constitute the three chief deposits of the Orange County district. The mineralogy of these ores will be more fully described in a subsequent publication.

CUBANITE PLATES

The maximum number of distinct non-parallel cubanite plate traces visible on a polished section surface in a single grain (resolved by etching, as indicated beyond, and checked by reflected polarized light) was found to be four. A block of rectangular parallelepiped shape, .6×.6×.8 inches was therefore cut and polished from a region of a polished section showing this maximum number of traces, and the entire investigation carried out on a single crystal occupying a corner of this block, and which, thus truncated, constituted the major bulk of the volume of the block itself.

Cubanite is visible against chalcopyrite without artificial aid, but is rendered very distinct by etching with the following solution:

12 cc. concentrated $K_2Cr_2O_7$
100 cc. water
3 cc. concentrated H_2SO_4 , specific gravity 1.84.

By suspending the specimen so that the entire corner or edge under observation is immersed in this solution, a 10-minute etch brings the cubanite out as a dark blue against the normal yellow chalcopyrite background.

This etch is only incidentally used for bringing out the contrast between cubanite and chalcopyrite. It was primarily designed to bring out twinning and grain structure in chalcopyrite. For this purpose it is unexcelled, but the effectiveness of the etch is variable with chalcopyrite from different localities. Evidently this is due to variability in the composition of chalcopyrite from various sources. It is possible that incompletely unmixed chalcopyrite etches well, due to greater free energy, while that nearer to equilibrium, poorly. In favorable instances a 10–30 minute immersion brings out orientation differences due to grain boundaries and twinning, in brilliant colors. Even in unfavorable cases, the anisotropic effect of the chalcopyrite, seen in reflected, polarized light, is intensified by a short-time etch.

Before etching, the interior angle τ between the two planes P

and Q was measured on a single circle goniometer and found to be 93° . The specimen was subsequently fixed in a square wooden mounting so that each surface P and Q could be brought at right angles to the microscope axis by the mere process of laying the mount on the appropriate surface. This obviated the necessity of remounting when it was desired to change the surface under examination; this aided in maintaining the cleanness of the etched surfaces. Before mounting, the specimen was immersed in the etch solution for the required period, washed, and allowed to dry. Following this it was mounted, and fixed to the rotating stage of a polarizing metallographical microscope, with the edge, PQ , parallel to one of the translation screws of the mechanical stage accessory.

TABLE I
TABULATED AVERAGE DATA USED IN FIXING THE ORIENTATIONS OF THE CUBANITE PLATES IN THE CHALCOPYRITE MATRIX

	Angles made by various traces				
	with edge PQ		with edge QR		with edge PR
	face P	face Q	face Q	face R	face R
Cubanite band A	99.2°	36°	129.6°	74.4°	171.1°
Cubanite band B	71.6°	133°	58°		161.6°
Cubanite band C	31.4°	61.6°			
Cubanite band D	139.3°	109.2°			

Solid angle $PQ=93^\circ$
 Solid angle $PR=88^\circ$
 Solid angle $QR=90\frac{3}{4}^\circ$

The four cubanite plate possibilities have been designated as A , B , C , and D . The angles of the traces of each of these with the edge of the polished surfaces, PQ , were measured as follows: First the translation screws of the mechanical stage were manipulated to bring the apex of the angle formed by the trace, A , and the edge, PQ , to the center of the cross-hairs and translation readings taken. When the second surface was subsequently studied, the translation reading was, of course, identical for this same plate, and the reading thus served to identify the individual cubanite plate under observation. This correlation was later checked by actual perspective observation of the edge, with the aid of a binocular microscope.

The difference between the stage settings when first the edge of the block (a constant for the mounting) and then the trace of the cubanite plate, coincide with a cross-hair, with the rotation taken in a counter-clockwise direction, gave the angles θ and ϕ for each cubanite plate. The averaged values of these data appear in Table I.

For each of the four pairs of averaged values of θ and ϕ , a stereographic projection has been prepared according to the method outlined under *Geometrical Method*. Each solution indicates the orientation of one cubanite plate in the chalcopyrite matrix crystal. Each of these four planes has been transferred to the composite projection of figure 4. The interpretation of this will be deferred until after a discussion of the twin lamellae.

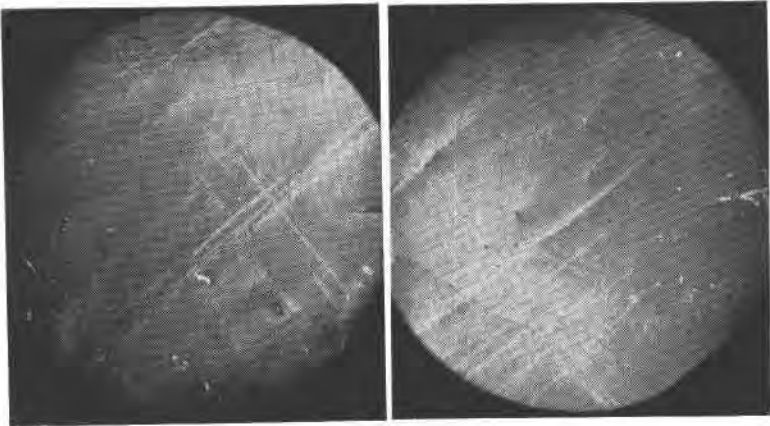


FIG. 2. *Grid twin* lamellae on polished (001) surface of chalcopyrite, brought out by etching 3 minutes with etchant. Crossed nicols, $\times 28$. A belt of cubanite bands runs parallel to one lamellae direction in each photograph.

CHALCOPYRITE TWIN LAMELLAE

Two types of twin lamellae occur in the Pike Hill chalcopyrite. These have been designated by the writers as the *grid twins* and the *echelon twins*.

The grid twinning occurs on the faces P and Q of the specimen as a series of bands parallel to the intersection edge PQ . On an auxiliary face, R (which subsequently proved to be almost exactly (001)), ground and polished at right angles to both P and Q , this twinning occurs as a grid of intersecting bands. Grid twinning is illustrated in figure 2.

There is a maximum of two sets of *echelon* groups present on any face. The word group as here used refers to a strip of disturbed chalcopyrite bounded by approximately parallel lines. This strip, in the simplest and most common occurrence, is crossed obliquely by a single set of polysynthetic twin bands, figure 3. The entire group, therefore, has the appearance of short twin bands placed accurately *en echelon*. Each individual twin band is bounded by lines parallel to two directions: (1) the common edge of the strip, and (2) the long direction of the individual bands. This gives the individual band the appearance of a distorted lozenge. For any polished surface on which this twinning is visible, there are therefore two measurable angles to be derived from each group, namely

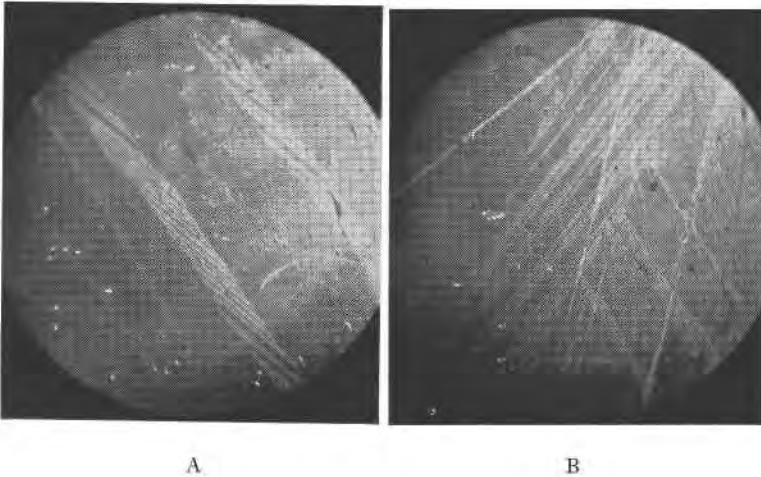


FIG. 3. *Echelon twin* lamellae, on surface of chalcopyrite polished parallel to *c* axis, and brought out by etching 3 minutes with etchant. Crossed nicols, $\times 28$. Figure 3A shows a set of two wide and one narrow group of *echelon twins*, with a cubanite band almost parallel to these. The faint, dark, broad bands running across the field, transverse to the *echelon twins* are the *grid twins* as seen on this surface. Figure 3B shows two different group directions in the *echelon twins*, and also shows the interchangeability of individual direction within an *echelon* group. This photograph also illustrates the intersection of cubanite bands and *echelon twins*.

the azimuth of the group as a whole (thus the short edge of the individual twin), and the long direction of the individual twin. These two angles are characteristic of the group, and in general, are different from either of the angles in the second possible group on that surface.

The grid twinning and the echelon twinning represent two types which seem to be distinct from one another and not crystallographically equivalent. On the other hand, it may be safely assumed that the two individual directions composing the grid are crystallographically equivalent, and also that the two groups of echelon twins are crystallographically equivalent, on the grounds of similarity.

TABLE II
TABULATED AVERAGE DATA USED IN DETERMINING THE TWIN PLANES IN CHALCOPYRITE

	Angles made by various traces with edge PQ		Angles made by various traces with edge PR	
	plane P	plane Q	plane P	plane R
ECHOLON TWINS				
First group				
Group direction	114.5°	131.8°		148.3°
Individual direction	126.2°	65°	38.3°	12.2°
Second group				
Group direction	54.5°	48°		
Individual direction	45°	113°		
GRID TWINS				
First pair	0°	0°	90°	163°
Second pair	0°	0°	90°	77°

Solid angle $PQ = 93^\circ$

Solid angle $PR = 88^\circ$

Solid angle $QR = 90\frac{3}{4}^\circ$

Both directions of the grid twinning on faces P and Q happen by pure chance to be mutually parallel to the edge PQ . The solution of the planes giving rise to these parallel traces is therefore indeterminate. On face R , however, the grid twinning shows in a well developed grid-work.

Each of the four twin directions contained in the echelon groups on face P have been accurately correlated with their corresponding directions contained in the echelon groups on face Q .

There are thus six distinctly different composition planes, two grids and four echelons. The angles necessary for the stereographic projection of these planes have been measured and averaged values are given in Table II. A stereographic solution has been

carried out for an average pair of trace angles, θ and ϕ , for each of the six composition planes. The solutions of these have been transferred to the composite stereographic projection given in figure 4. The interpretation of the projection will be given in the following section.

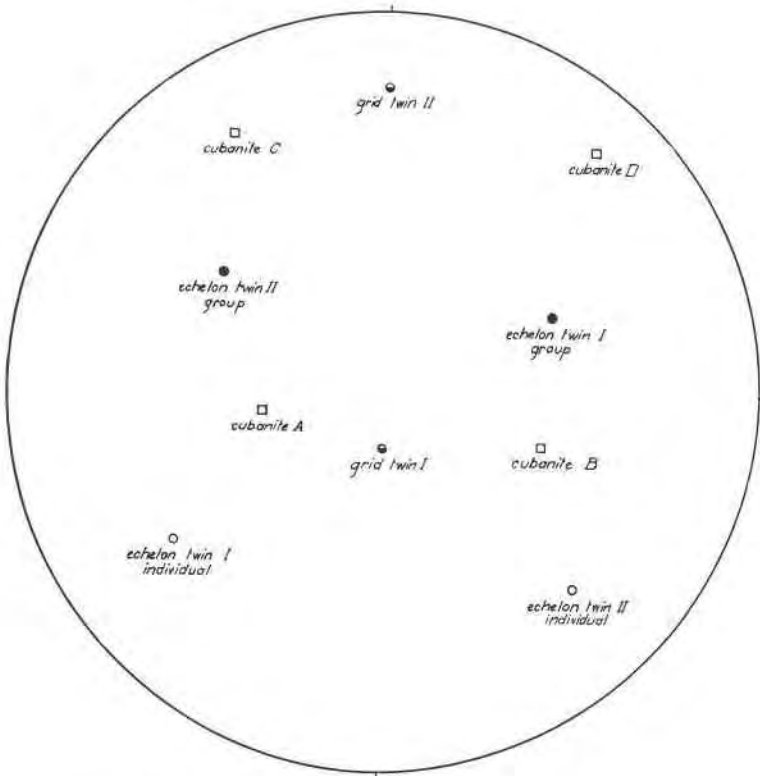


FIG. 4. Distribution of cubanite plates and chalcopyrite twin lamellae in chalcopyrite matrix crystal. Original diagram.

ORIENTATION OF THE CHALCOPYRITE CRYSTAL

The chalcopyrite matrix can now be oriented by the following considerations. The processes of gliding and exsolution are centrosymmetrical processes, so they, in themselves introduce symmetry centers into any field in which they may be regarded as entering.¹⁰

¹⁰ Buerger, M. J., Translation-gliding in crystals; *Am. Mineral.*, vol. 15, pp. 52-54, 1930.

The symmetry of chalcopyrite, V^d , must therefore be multiplied by C_i giving the point group D_4^h , as the symmetry of distribution of exsolution plates and of twin planes.¹¹ The distribution of important axes in this group is as follows. A four-fold axis (coincident with the crystallographic c axis) has two kinds of two-fold axes at

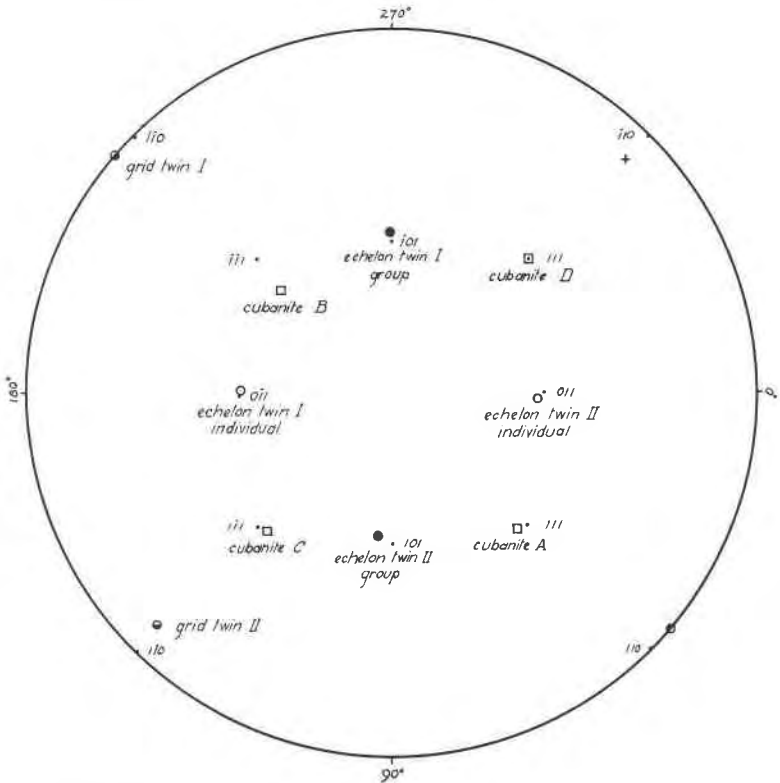


FIG. 5. The distribution of cubanite plates and chalcopyrite twin lamellae in the chalcopyrite matrix crystal, after rotating the projection to conventional crystallographic orientation. The indexed dots give the ideal positions of chalcopyrite poles.

right angles to it. Equivalent two-fold axes of a first kind are mutually at right angles and a second kind of two-fold axes bisect these right angles. The a axes coincide with one of the kinds of two-fold axes, the choice being arbitrarily exercised by the first to de-

¹¹ Reference 10, p. 53. The symbols V^d and C_4 should be transposed in this paper. They have been copied from Roger's paper cited, where the error originally occurs.

scribe the crystal species. This choice may be ascertained for the specific example in question by ascertaining which of the two alternatives gives rational indices with the axes recorded in reference works.

Identification of planes. The poles obtained by the stereographic solutions previously described have been transferred onto a Leitz model of the Wulff rotating net. The resulting composite diagram in the original unrotated position is shown in figure 4.

Considering only the poles of the four cubanite plates, there is at once evident a symmetrical arrangement of these poles about a four-fold axis of symmetry. This applies only to the poles of the cubanite planes. It is apparent that this axis is an important one, and its position gives a hint as to the rotation necessary to orient the chalcopyrite matrix.

After discovering and carrying out the correct rotation the resultant grouping of poles obtained by this rotation is as shown in the composite diagram of figure 5. It is now evident that the four-fold axis applicable to the cubanite planes alone and which now appears along the 0°-180° axis is coincident with a two-fold axis which may be applied to *all* the planes in this grouping. A second two-fold axis appears along the 90°-270° axis, two others along the 45°-225° and 135°-315° axis, and a four-fold axis appears through the north pole.

The coordinate axes having been fixed, (the *a* axis alternative being kept in mind), the planes of the cubanite segregation, and the twinning in chalcopyrite may now be identified on the stereographic projection by the usual methods. This results in the following determination of indices for the various features studied:

		Number of non-parallel equivalent planes in form
cubanite segregation planes,	sphenoid {111}	4
grid twin lamellae,	prism {110}	2
echelon twin lamellae	sphenoid {101}	4

It may be noted in passing, that the solutions of the orientations of the cubanite plates *A*, *C*, and *D* are within 3° or less of their ideal sphenoid positions. This is a satisfactory agreement for the type of measurement involved. The cubanite plate *B*, however, is some 10°

from ideal position. This is ascribable to the bent condition observed in this set of plates.

DISCUSSION

Several interesting points develop from the solutions given. In the first place, the surmises with regard to the orientation of segregated cubanite plates in chalcopyrite have been confirmed; the plates develop parallel to the unit sphenoid, $\{111\}$. In addition, two new kinds of twin lamellae have been discovered and determined in chalcopyrite, parallel to $\{110\}$ and $\{101\}$ respectively. Taken together these correspond with pseudo-dodecahedral twinning, yet their appearances are distinguishable. It should be noted that if the recognized,¹² though not very well established, $\{111\}$ lamellae are added to these, all the known twin laws of chalcopyrite are represented by lamellae.

One may inquire whether the new $\{110\}$ and $\{101\}$ lamellae are primary growth phenomena or whether they are secondary twins of some sort. The evidence points rather conclusively to the latter interpretation. If the lamellae were primary, then, since they differ from the crystal proper only in regard to orientation, the cubanite segregations would have had a chance proportional to the volumes involved of precipitating either in the lamellae or in the crystal proper. A very complete study of the cubanite segregation plates has shown that they are related to the crystal proper alone, not to any of the six possible lamellae orientations. This indicates that the appearance of the cubanite plates antedated the appearance of the twins; otherwise some of the cubanite plates would have followed one or more of the twin orientations. Other evidence pointing in the same direction is the following: The cubanite plates end abruptly at chalcopyrite grain boundaries. One deduces from this that the grain boundaries were already present when the cubanite segregated. Now, twin boundaries are simply special cases of grain boundaries. If, therefore, the twin boundaries antedate the cubanite exsolution, the cubanite plates should have the same reason to stop at twin boundaries as at grain boundaries. Actually, however, the cubanite plates cut indiscriminately through twins of both sorts, from which it may be concluded that the twins came into existence *after* the cubanite unmixed. The twinning movement, on the other hand, should disturb the cubanite plates if these were

¹² Reference 6, p. 348.

present first. In confirmation of this, the cubanite plates are frequently in a bent condition. A measure of the bending is gained by noting that the solutions of the orientations of cubanite plates are in error from some 3° average, to 10° maximum, as previously mentioned, due to curvature of the cubanite plates.

Since the cubanite segregation appeared subsequent to the formation of the crystal, this requires the lamellae to be secondary twins. They have arisen, therefore, either from external or internal forces sufficiently intense to cause plastic deformation. The latter forces may be ascribed to volume changes. Either the volume change due to the exsolution of the cubanite, or that due to a possible inversion of the chalcopyrite from a high temperature type,¹³ come up for consideration.

SUMMARY

(1) Cubanite plates segregate on the sphenoid $\{111\}$ planes of chalcopyrite.

(2) The grid twinning lamellae of chalcopyrite are along the prism $\{110\}$ planes.

(3) The polysynthetic echelon twinning lamellae of chalcopyrite are along the sphenoid $\{101\}$ planes.

(4) The grid twinning and the echelon twinning correspond to two of the three known twin laws of chalcopyrite established by crystal surface study.

(5) The grid twinning and the echelon twinning are subsequent to the segregation of the cubanite.

(6) Since the twinning is secondary, it has been caused by plastic deformation, and the twin laws stated in (2) and (3) are two new plastic deformation twin laws.

(7) The exsolution of cubanite from chalcopyrite may have been the cause of the stresses which produced the twinning.

¹³ Since writing this the writers have established the existence of two forms of chalcopyrite by a thermal and *x*-ray study. High-chalcopyrite is a disordered structure; low-chalcopyrite is an ordered structure. The onset of order with lowering temperature causes exsolution of atoms present in excess of simple, rational proportions, in the form of cubanite. Details of this study will appear shortly. The theory of the inversion, unmixing, etc., is given in M. J. Buerger, "The temperature-structure-composition behavior of certain crystals"; *Proc. Nat. Acad. Sci.*, vol. 20, July, 1934.