

## STEPHANITE MORPHOLOGY

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### ABSTRACT

The space-group of stephanite,  $\text{Ag}_5\text{SbS}_4$ , left in doubt by Salvia's  $x$ -ray work (1932), is found to be  $Cmc2$  by the morphological method. This result is confirmed by Weissenberg photographs.

### INTRODUCTION

Stephanite has the formula  $\text{Ag}_5\text{SbS}_4$ . It crystallizes in the orthorhombic system and is generally described as short prismatic or thick tabular in habit. This mineral affords an interesting example of the way in which Donnay's method (1938*a*) for the determination of space-groups may clear up doubtful points arising from incomplete  $x$ -ray results.

The cell dimensions and space-group of stephanite have been determined by Salvia (1932),<sup>1</sup> who used rotation about [001] and oscillation about [100] with copper radiation. He obtained the following results:

$$a_0 = 7.85 \pm 0.02, b_0 = 12.48, c_0 = 8.58 \text{ \AA} \\ a_0 : b_0 : c_0 = 0.629 : 1 : 0.687$$

Space-group  $D_{2h}^{17}$  (dipyramidal class) or  $D_2^5$  (disphenoidal class), from the observed conditions,  $hkl$  present only with  $(h+k)$  even,  $00l$  present only with  $l$  even. Actually these conditions, if complete, admit only  $D_2^5$ . From Salvia's tables it can be seen that there is no further condition in  $0kl$  or  $hk0$ ; diffractions  $h0l$  are not mentioned.  $D_{2h}^{17}$  requires the condition  $h0l$  present only with  $h$  even and  $l$  even; this condition would admit also  $C_{2v}^{12}$  and  $C_{2v}^{16}$  (pyramidal class).

The choice left by Salvia's results is between  $D_{2h}^{17}-Cmcm$ ,  $C_{2v}^{12}-Cmc2$ ,  $C_{2v}^{16}-C2cm$ , on the one hand and  $D_2^5-C222_1$ , on the other hand.

In view of the wealth of crystal forms reported on stephanite, a morphological study of this species was undertaken in order to establish its space-group. Crystals from the Ungemach Collection, bequeathed to Professor J. D. H. Donnay, were placed at my disposal, together with Ungemach's own measurements. They were from the following localities: Přibram; Zacatecas and Guanajuato, Mexico; Ste-Croix aux Mines, Alsace. Crystals from the O'Brien Mine, Ontario, lent by Professor A. L. Parsons, were also studied. The goniometric measurements obtained, although largely sufficient to identify the forms and recognize twinning on (130) and (110), were not of noteworthy quality. Goldschmidt's *Atlas* was mostly relied on for the complete form system.

The space-group, determined by the morphological method, was then checked by Weissenberg photographs.

<sup>1</sup> As reviewed in *Strukturbericht*, 2, 348 (1937); the original paper was not available.

## MORPHOLOGICAL DATA

The one hundred and four crystal drawings of stephanite figured in Goldschmidt's *Atlas der Kristallformen* (1920), were studied in order to determine the relative form importance: (1) for each zone of the mineral and (2) for the species as a whole. The method employed is the same as that used in a previous paper, on columbite (Taylor, 1940). Some figures showing complex twinning or illegible form letters are omitted. There are one hundred and thirty-three forms listed for stephanite in the *Atlas*; a great many are doubtful. About eighty-eight forms are figured on the crystal drawings. It is clearly unnecessary to consider every form reported in a zone in order to establish the zonal character. Most of the rare or doubtful forms are disregarded in the presentation of the observation data.

In the various zones the faces can be listed as follows, in the order of observed decreasing importance (based on frequency and size):

( <i>hhl</i> )	<i>P h m r l p N</i>
( <i>lkl</i> )	<i>P w γ A (212) R</i>
( <i>hkk</i> )	<i>P f ζ K Σ H</i>
( <i>okl</i> )	<i>d k e t κ j E</i>
( <i>h0l</i> )	<i>β g G (102)</i>
( <i>hkl0</i> )	<i>o π λ U I</i>

The pinakoids rank as follows: *c b a*.

## GNOMONIC PROJECTION

These forms, together with all others whose indices are sufficiently small, are plotted on a gnomonic projection (Fig. 1). The forms not found on the figured crystals are also shown as points but their importance cannot be estimated and they cannot be considered as anything more than morphological curiosities.

This projection illustrates beautifully Mallard's theorem (1879), which states that the gnomonic projection is a representation of the reciprocal lattice. The main net, with a diamond mesh extending far out from the center of the projection is the first reciprocal lattice layer in true magnitude; a second net similar to the first one but on half the scale, shows the second layer; even the third and fourth layers are unmistakably evident in a third and fourth net, one-third and one-fourth of the original scale, respectively, which are restricted to the immediate vicinity of the center of projection. Note that the gnomonic poles located on the axial zones must be disregarded, inasmuch as they may be affected by glide planes; only (*hkl*) faces are governed by the lattice mode alone.

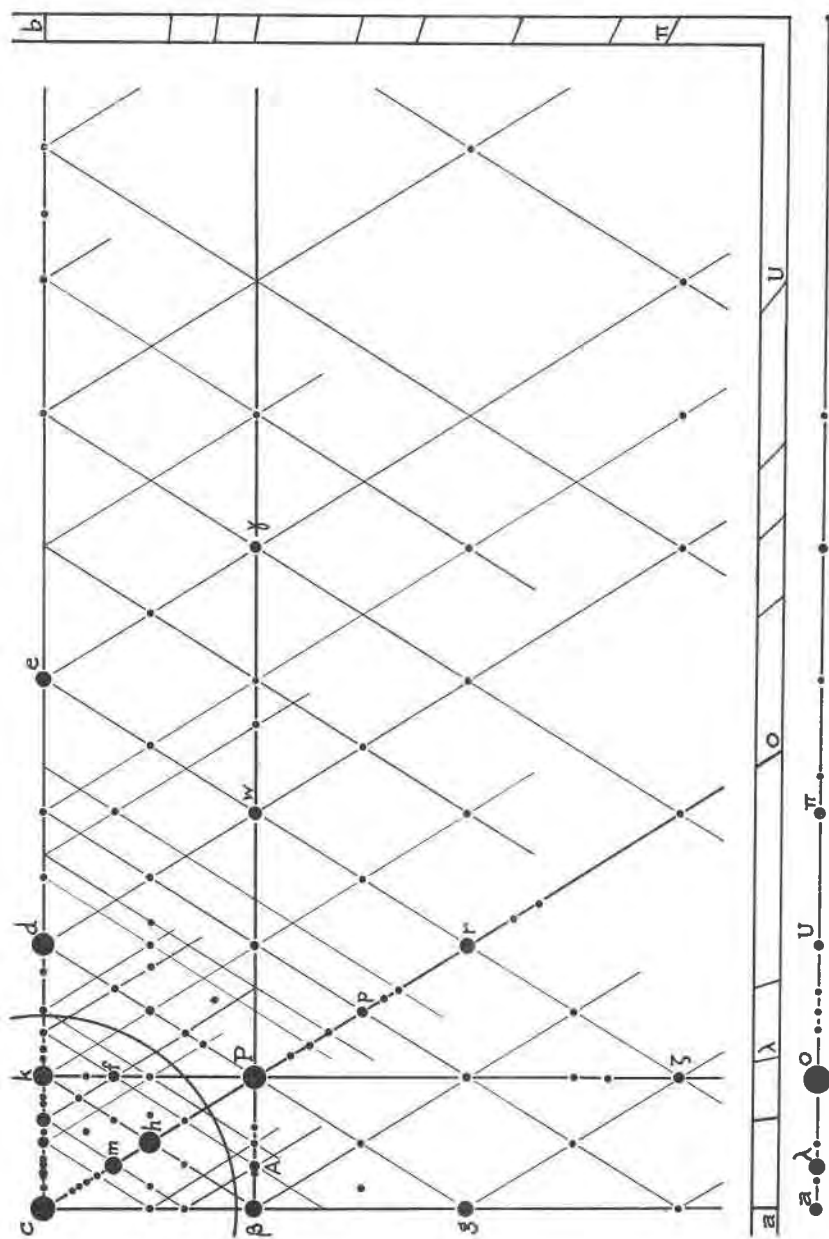


FIG. 1. Gnomonic projection of stephanite.



Figure 2 illustrates the reciprocal lattice layers from zero to five. All the observed forms which fall on each of these layers are shown by black dots. Following Peacock's nomenclature, these are the *real* nodes. The open circles represent the *virtual* nodes or those multiples of the *real* nodes which are necessary to complete the lattice net but have no morphological significance. In *x*-ray work the *real* node represents the first order of reflection actually observed; the *virtual* nodes, the other orders observed.

#### STUDY OF ZONAL CHARACTER

##### "Central" zones

Three central zones are found to have a common dominant *P*, which must therefore be noted (111).

In the zone of the (*hhl*) faces, the order *P h m r l p N* indicates a simple zone (Donnay, 1938*b*) and the indices are: *P* (111), *h* (112), *m* (113), *r* (221), *l* (223), *p* (332), and *N* (331).

The (*lkl*) faces, in the observed order of importance, are symbolized: *P* (111), *w* (131), *γ* (151), *A* (313),  $-(424)$ , and *R* (242). This is a double zone.

In the zone of the (*hkk*) faces, the indices must be written: *P* (111), *f* (133), *ζ* (311), *K* (155),  $\Sigma$  (422), and *H* (244). This is also a double zone.

The characters of the central zones, one simple and two double, establish the lattice as *C*-centered; the simple zone, that of the (*hhl*) faces, leading to the centered pinakoid.

##### "Axial" zones

In the zone of the (*0kl*) faces, the dominant is clearly *d* and the order is *d k e t κ j E*. The form *d* is (021); therefore *k* becomes (022), *e* (041), *t* (023), *κ* (043), *j* (064) and *E* (061). This zone exhibits a "shift" of the dominant, from unit position toward the *b* pinakoid, which is the normal condition for the *C* lattice.

In the zone of the (*h0l*) faces, the order is:  $\beta$  *g G* (102). The zone is simple, with  $\beta$  dominant and in unit position. The dominant, normally shifted away from the centered pinakoid, is here shifted back towards it by the action of a *c* glide plane;  $\beta$  must be written (202). The other forms are then indexed: *g* (402), *G* (602) and  $-(204)$ .

The zone of the (*hk0*) faces is double, with *o* dominant. The forms *o π λ U I* must have the indices *o* (110),  $\pi$  (130),  $\lambda$  (310), *U* (240), and *I* (150). Evidence for the zonal character follows:

$\pi$  (130) is much more important than *U* (240), occurring twenty-two times in the crystals figured, against eight times for *U*;  $\lambda$  (310) is more



TABLE 2. DEVELOPMENT OF DOUBLE ZONES

Distances from pole				Zone of the $(hkl)$ faces				Zone of the $(hkk)$ faces			
I	II	III	IV	I	II	III	IV	I	II	III	IV
$1/7$				-510				K 155			
$1/5$				$\lambda$ 310				$f$ 133			
$1/3$	$2/8$	$3/7$			L 420				H 244		
	$2/4$	$3/5$	$4/6$								
1			$6/4$	$o$ 110				P 111			
	$4/2$	$5/3$			U 240	II 350	O 460				
3		$7/3$		$\pi$ 130				$w$ 131	R 242		$\Sigma$ 422
	$8/2$	$11/3$									
5				I 150	-280			$\gamma$ 151	D 282		
7	$12/2$				-2.12.0						
9				I70							
11				-190							
13				$i$ 1.11.0							
15				I.13.0							
				-1.15.0							
Also reported in <i>Atlas</i> :				C 161 = 2.12.2 Artini (1891); Nejd (1895).				-522 = 10.4.4 Nejd (1895).			
-340 = 680 Slavik (1901-2)				-727 = 14.4.14 Vrba (1886).				-833 = 16.6.6 Slavik (1901-2).			
-3.10.0 = 6.20.0 Slavik (1901-2); also				M818 = 16.2.16 Artini (1891); Nejd (1895).				21 13.4.4 = 26.8.8 Artini (1891); Nejd (1895).			
in Ungemach's notebooks (twice).								22 18.5.5 = 36.10.10 Artini (1891); Nejd (1895).			

important than  $L$  (420), occurring on eleven figures whereas  $L$  is found only once. This zone abides by the normal condition for a  $C$  lattice.

Lists of tautozonal faces were prepared (Tables 1 and 2) to illustrate the morphological development of the central and axial zones of stephanite. These tables should be compared with those given by Donnay (1938*b*), in which the theoretical development of various types of zones is demonstrated. Table 1 deals with the simple zones. The first column shows the distances<sup>2</sup> from the gnomonic pole, while each subsequent column gives the corresponding forms in the zone considered. Forms anomalously absent have their symbols italicized. Table 2 presents similar data for the double zones.

Such tables are illuminating. They show, for instance, that, in the zone of the  $(hk0)$  faces, if we consider the section between  $o$  (110) and  $\pi$  (130),  $U$  (120) must become (240) because of the presence of  $u$  (350), which is in turn justified by the presence of (460). This eliminates any doubt as to the character of the zone. Attempting to make it a simple zone, one could account for (230) as a secondary face, between (110) and (120), the tertiary faces becoming (340) and (350). This scheme is open to the following objections:  $U$  (120) is made more important than  $\pi$  (130); (230), more important than (350); and there should be a face (340) more frequent than (350), all of which is contrary to observed facts.

Similarly the decision that  $k$  must be written (022) is borne out by the presence of the secondary face  $\kappa$  (043), and the tertiary faces  $j$  (064) and  $\iota$  (065). If  $k$  were to be considered as (011), the face  $j$  would become (032), more important than  $k$  (043), and  $\iota$  (065) could only be accounted for by inserting a face (054), which has not been reported. Again,  $s$  would become (012), hence more important than  $t$  (023); and the face (034), unreported, would be required to explain the presence of (035) and (045).

### *Pinakoids*

The axial zones, being so well established, determine the character of the pinakoids. That is,  $a$  and  $b$  must be doubled because they terminate a double zone; they are therefore written (200) and (020). Also it is necessary that  $c$  be doubled and become (002) on account of the "shift" of the dominant  $\beta$ , in the zone of the  $(h0l)$  faces, toward  $c$ . There is an anomaly to be reported in this respect: the theoretical order  $(bca)$  conflicts with the observed order  $(cba)$ . The zonal data are quite reliable and outweigh the observations on the order of the pinakoids.

<sup>2</sup> These distances are interrelated by Peacock's Harmonic-Arithmetic Rule (1937).



## MORPHOLOGICAL DETERMINATION OF THE SPACE-GROUP

Two stereographic projections are given (Figs. 3a and 3b). In these projections only the dominant form in each zone is shown. The characters of the zones and dominants are indicated: a single line represents a simple zone and a double line, a double zone; a black dot represents a form with coprime indices and an open circle, a form with doubled indices. Figure 3a represents the "initial pattern" (Donnay, 1939) of the  $C$  lattice, while Fig. 3b gives the pattern observed for stephanite.

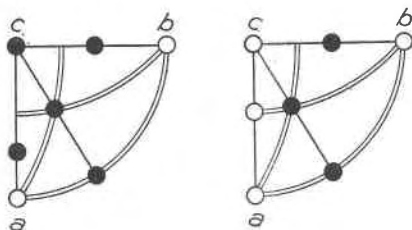


FIG. 3a. Aspect  $C^{***}$ . Fig. 3b. Aspect  $C^*c^*$ .

It is seen in the first of these that the criteria for the "initial pattern," or the aspect  $C^{***}$  are as follows: One of the central zones, that leading to the  $c$  face, is simple while the other two are double; the two axial zones that intersect in the centered pinakoid exhibit a "shift" away from unit position toward the  $b$  and  $a$  pinakoids, respectively; the zone of the  $(hk0)$  faces is double and the indices of the  $a$  and  $b$  faces are doubled. In the second projection the aspect represented is  $C^*c^*$ ; the only changes indicating a  $c$  glide plane lie in the "shift" of the dominant in the zone of the  $(h0l)$  faces and the doubling of the indices for all the faces in the zone (including  $c$ ).

The characters of the "central" zones show that the lattice is  $C$ . In the discussion of axial zones it is shown that the zone of the  $(0kl)$  faces obeys the  $C$  criterion. In the zone of the  $(h0l)$  faces, the "shift" of the dominant indicates the  $(010)$  plane to be a  $c$  glide plane. The third zone, that of the  $(hk0)$  faces, is again normal for the  $C$  lattice.<sup>3</sup> Therefore the morphological aspect is written  $C^*c^*$  and the symmetry class  $222$  is ruled out.

This aspect admits of three possible space-groups:  $Cmcm$ , in the holohedry  $(2/m\ 2/m\ 2/m)$ , and  $C2cm$  or  $Cmc2$ , in the antihemihedry  $(2mm$  or  $mm2)$ . The frequently noted twinning on  $(001)$ , established by Miers (1889), is incompatible with the holohedry, since  $(001)$  cannot be a plane

<sup>3</sup> The fact that only one axial zone violates the condition imposed by the  $C$  lattice accounts for the correct determination of the lattice made by Friedel (1904), on the strength of the classical Law of Bravais alone.

of symmetry. The fact that, in the present setting, the  $c$ -axis is a two-fold axis eliminates the possibility of  $2mm$  in the antihemihedry. Hence the class must be  $mm2$  and the space-group is uniquely determined as  $C_{2v}^{12}-Cmc2$ .

#### X-RAY DETERMINATION OF THE SPACE-GROUP

Since the space-group of stephanite, as determined by its morphology, was compatible with Salvia's work, provided  $h0l$  diffractions be present only with  $h$  and  $l$  even, it was thought desirable to check the space-group by means of Weissenberg photographs, with special attention to the diffractions  $h0l$ . This was done in the Department of Mineralogy, University of Toronto, with the assistance of Professor M. A. Peacock and Mr. L. G. Berry using a small twinned crystal from Ste-Croix aux Mines, Alsace (Ungemach Collection).

The following photographs were taken with copper radiation: rotation about  $[001]$  and Weissenberg photographs of the zero, first, and second layer lines. In view of the complication of the pattern due to twinning on  $(110)$ , and some random spots from adhering foreign material, reciprocal lattice nets were constructed to ensure correct indexing. The following results were obtained:

$$a_0 = 7.70, b_0 = 12.32, c_0 = 8.48, \text{ all } \pm 0.05 \text{ \AA}$$

$$a_0 : b_0 : c_0 = 0.625 : 1 : 0.688$$

in fair agreement with Salvia. The morphological ratios for the Ste-Croix crystal (calculated from Ungemach's one-circle measurements) are:

$$a : b : c = 0.6285 : 1 : 0.6856.$$

For the material from the O'Brien mine, my two-circle measurements yielded:

$$a : b : c = 0.6289 : 1 : 0.6847.$$

Dana gives the following values:

$$a : b : c = 0.6291 : 1 : 0.6851.$$

TABLE 3. DIFFRACTION SPOTS OBSERVED ON THE WEISSENBERG PHOTOGRAPHS

	Zero-layer	First-layer	Second-layer
$hkl$		$(h+k)$ even	$(h+k)$ even
$0kl$		021, 041, 061, 081, 0.10.1, 0.12.1, 0.14.1	022, 042, 062, 082, 0.10.2, 0.12.2, 0.14.2
$h0l$		All absent	202, 402, 602, 802
$hk0$	$(h+k)$ even		
$h00$	200, 400, 600		
$0k0$	020, 040, 060, 080, 0.10.0, 0.14.0		
$00l$		Absent	002

Table 3 lists the diffraction spots observed in the different zones. The observed diffractions conform to the condition,  $hkl$  present only with  $(h+k)$  even. No further condition is observed, except in the critical zone of the  $h0l$  planes,<sup>4</sup> where all  $h01$  are absent, all  $h02$  with  $h$  odd are also missing, while all  $h02$  within reach are present with  $h$  even.

If one relies on *absence* of diffraction spots, the aspect  $C^*c^*$  may be considered confirmed. If, on the other hand, one demands *presence* of diffraction spots to bolster his conclusion, then the space-group  $C222_1$  will still remain a possibility from the  $x$ -ray standpoint. The morphological method is here at an advantage, for the fact that the zone of the  $(h0l)$  faces is a simple zone, with  $\beta$  (202) dominant, firmly establishes the extinction criterion and the concomitant  $c$  glide plane.

The holohedral class being ruled out by the twinning data and the  $c$  axis being a symmetry axis, the space-group  $Cmc2$ , determined by morphology, is thus confirmed within the limitations of the  $x$ -ray method.

#### ACKNOWLEDGMENTS

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It is also a pleasure to record my indebtedness to Professor M. A. Peacock, University of Toronto, who kindly put at my disposal all the facilities of his laboratory and who, with Mr. L. G. Berry, assisted and instructed me in the technique of taking Weissenberg pictures.

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<sup>4</sup> The previous uncertainty in the zone  $h0l$  may be connected with the complication caused by twinning, which is common in stephanite. On the film ( $hk1$ ) a spot was noted near the position 401 for the principal individual. On careful measurement it was decided that this spot was definitely displaced beyond the limit of error in measuring on the photograph. If 401 were present, then of course the condition  $h0l$  with  $h$  even and  $l$  even would not exist.